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# Wool Portfolio

## D.2.3.1 Report on the Properties of Wool:

## Green-Tex Portfolio of Wool Fibres

## A 2.3 Pilot 2: Testing wider application of natural fibres in textile production

## Specific objective 2: Testing Green-Tex solutions

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*"Renewable, recyclable and biodegradable, wool fits perfectly into the new circular economy. Grown on a diet of sunlight, water and grass, wool delivers a supreme sustainability message. And because wool is made of protein, it does not contribute to microplastic pollution. Wool's applications range from the personal to the industrial, and lanolin, its by-product, is a highly desirable ingredient for cosmetics. Hand knitters swear by it. Designers adore it. Much imitated, never duplicated, the power of wool continues unsurpassed."*

*Wool Notes, Issue 3, 2024*

Wool Notes is issued by The International Wool Textile Organization (IWTO), which has been responsible for standards in the wool textile industry worldwide since 1930.

IWTO is committed to a sustainable future of wool,

so, as the Green-Tex!



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# 1 Wool

The problems of soil, water and air pollution caused by large quantities of micro- and/or nanoplastics released from primary and secondary sources have recently fuelled debates on sustainability and imposed the benefits of natural materials. The interest has turned back to the natural fibres of vegetable (cotton, flax, hemp, etc.) and animal (wool and silk) origin [1,2]. Wool is a raw material that has been used for many years in the textile industry and other industrial sectors, as sheep's wool is an excellent material that can be utilised in a variety of ways [1].

According to [3] „*Sheep are economically the ideal fibre factory as provide milk, meat and wool and produce minimal waste. The development of products and technologies for processing according to the principles of sustainability has opened up new avenues for research, therefore wool, which is often unwanted waste, can be commercialised as a valuable sustainable raw material*". The complete sustainability and safety of functional textile wool blends is confirmed by the BlueSign® label, which guarantees that production is carried out in accordance with strict safety and environmental standards [4].

As wool are natural, renewable and biodegradable fibres, they are perhaps the most sustainable resource of all fibres. Sheep's wool is the first textile raw material to be used by humans for clothing purposes. It is believed that the ability to process wool into textile products was first developed in ancient Babylon (the word Babylon means land of wool). Other peoples, particularly in the Mediterranean region, were also involved in the cultivation of wool in BCE time [5]. Wool was once one of the most important and valuable sheep products and was known as "white gold" because of its importance [6]. Most of the produced high-quality wool (approx. 56%) is processed by the textile industry, and is experiencing growing interest. However, interest in processing of coarse wool (low-grade wool) which is most common in Europe and Croatia, has declined significantly as a result of strong competition from synthetic fibres [6].

Global sheep wool production remained relatively unchanged, at around 1 million tonnes of clean wool fibre in 2023, accounting for 0.9% of the global fibre market. The market share of wool produced according to the Responsible Wool Standard (RWS), ZQ, SustainaWOOL™ (GREEN and GOLD), Sustainable Cape Wool Standard (SCWS), and Climate Beneficial™ increased from around 4.2% in 2022 (82,685 tons) to 4.8% (94,037 tons) in 2023 [7]. In some apparel wool-producing countries/areas, RWS-certified wool had considerable market shares in 2023. Most significantly, in terms of both volume and market share, 43% of all wool produced in South Africa was RWS-certified. Recycled wool continued to account for around 6% of the global total wool market in 2023 [7]. While global wool production has declined over the years, the market share of wool programs is increasing.

Figure 1 shows the IWTO cycle, which links the properties of wool and the areas of application [8].



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**Figure 1:** Wool IWTO cycle - the properties and the areas of application

Wool is a natural protein fibre obtained from the fleece of various types of sheep. As a result of their structure, chemical composition, diversity and heterogeneity, wool fibres differ significantly from other natural and synthetic fibres and have some advantage over other fibres [9]. The protein from which the wool fibres are derived is called keratin and consists of various amino acids linked together to form long-chain macromolecules. It is estimated that wool contains more than 170 different proteins with different structures, not evenly distributed throughout the fibre [10]. This heterogeneous composition is responsible for the different physical and chemical properties of the various wool breeds. The proteins in wool consist of amino acids, containing basic amino ($-NH_2$) and acidic carboxyl (-COOH) groups, which are potentially active sites for the binding of various substances from the environment. The complex structure of proteins is the reason for their behaviour towards chemicals. Thanks to the presence of peptide bonds and other characteristic groups in the organic residues of amino acids, protein macromolecules can bind significant amounts of moisture and water, as well as dyes and various chemicals, which enables the finishing of textiles from protein fibres [5].

The number of breeds and species of sheep in the world is large, with a smaller number (around forty) developing spontaneously, and a fivefold greater number under human supervision. The differences between the breeds are related to the size of the sheep and the nature of the meat, production of milk, quality and quantity of their fleece (sparse or dense, curly or straight). Depending on the wool quality, sheep are classified into five groups [5]:



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- Fine wooled sheep, the main representative is merino sheep, the finest wool characterized by short fibres with a diameter of 18 to 25 μm and a length of 8 to 11 cm, from which the finest wool fabrics are made.
- Crossbred wooled sheep produce something a little lower quality wool suitable for coarser fabrics and other products such as luxury carpets.
- Medium wooled sheep is medium coarse, used to produce coarser fabrics, home textiles, furniture applications, etc.
- Long wooled sheep is quite coarse and long, suitable for handicrafts, doormats, industrial and technical applications.
- Coarse woolled sheep used for decorative, household and clothing products.

There are three main types of wool fibres on a sheep's body:

Fine fibres: soft, thin, more or less crimped, short, without medulla and easy to separate.

Transitional fibres: varying fineness, long, with or without medulla, main component of the fleece.

Axial hairs: coarse and stiff, have a medullar channel.

The classification of the wool according to their position was a time-consuming process, therefore today only the fibres with the lowest quality are separated during shearing, while a fibre mixture is made from the rest.

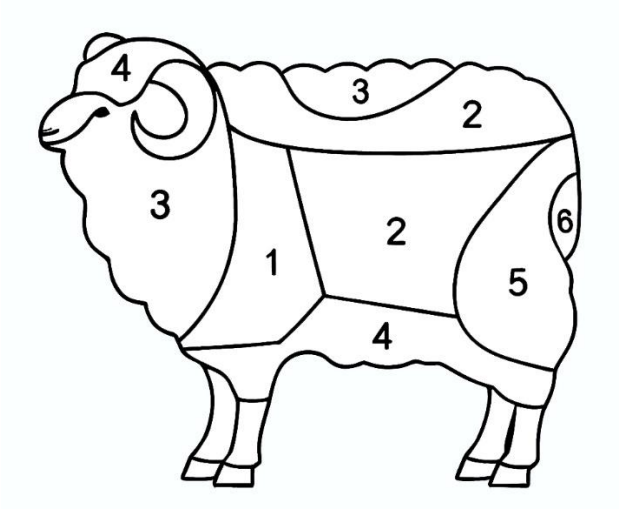



**Figure 2:** Classification of wool fibres (T. Dekanić adapted according to [5])

Classification of wool quality on the body of a sheep, the quality of the wool fibres decreases as the number increases.

Raw wool, obtained by shearing of sheep contains impurities: sweat, grease (lanolin), vegetable impurities (burdock, grass), soil, tar, signature dyes, etc. The common and usual name for all non-fibrous impurities is sierra and contribute to the compactness of the wool fleece. Depending on the breed, breeding method and climate, their proportion varies between 20% and 80% of the mass of the raw wool [11].



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To remove these impurities on industrial scale, scouring processes have been developed in devices called leviathans. The amount of pure wool obtained after removing the impurities is called wool yield (Yld) and is expressed as a percentage of the mass of the raw wool. This value indicates the content of clean wool substance in the raw wool. Depending on the type of sheep, its range is between 50 and 80% and the finer the fibre, the lower is the yield.

## 1.1 Properties

As already mentioned, wool is a natural protein fibre obtained from the fleece of various sheep species and differs in structure and chemical composition and properties.

In general, the chemical composition - the proportion of individual elements in the wool fibre - depends on the aforementioned characteristics of the breed and the climatic and agrotechnical conditions of sheep farming. Table 1 shows the average proportion of the individual elements (chemical composition) in the wool fibre [5].

**Table 1:** Elemental composition of wool

| Element | Share (%) |
|---|---|
| Carbon (C) | 50.0 - 52.0 |
| Oxygen (O) | 22.0 - 25 |
| Nitrogen (N) | 16.0 - 17.0 |
| Hydrogen (H) | 6.5 - 7.5 |
| Sulphur (S) | 3.0 - 4.0 |
| Ash | 0.5 |

A more recent method of identifying wool quality is based on its most important properties: the average fibre diameter (fineness), the colour and the content of impurities in the fleece [8].

The excellent properties of wool fibres and their good compatibility with other raw materials open up numerous areas of application [8]. However, specific properties of wool are listed below, which differ significantly from other natural and synthetic fibres.

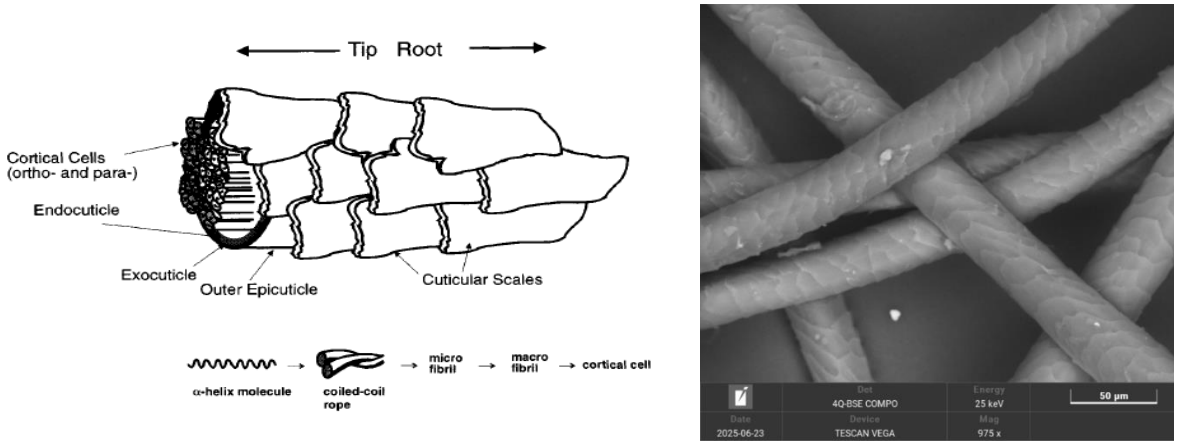
### Wool morphology

The microscopic image shows two, in some cases even three, basic parts: the cuticle (outer sheath), the cortex (the main part of the fibre) and the medulla or nucleus (a channel running through the middle of the fibre, characteristic of coarser fibres). The main feature of the cuticle are scale cells, which are characterized by overlap and direction from root to tip, Figure 3a [12]. The shape of the scales also depends on the fineness of the fibres. In finer fibres, they are ring-shaped and lie on top of each other, while one part protrudes from the fibre, which is the reason for the tendency of wool fibres to pilling. In coarser fibres, the scales are plate-shaped, overlapping and a smaller part protrudes from the fibre, which is the reason that coarser wool is less prone to pilling than fine wool.



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The scanning electron microscopy (SEM) scanning electron micrograph of scoured wool tested in the research activities of Green-Tex project is presented by Figure 3b.




a. b.

**Figure 3:** Morphology of wool fibres: a. simplified view of wool fibre; b. scanning electron microscope image of scoured wool fibres (Green-Tex portfolio)

There is a thin wax film on the outside, which makes undamaged wool fibres hydrophobic. As a result of its hygroscopicity, it absorbs water well and its surface repels droplets. This wax layer can be removed mechanically, by scouring or friction, enhancing wetting properties.

The cuticle surrounds the cortex - a ground substance consisting of spindle cells that are thicker in the middle than at the ends, Figure 4.

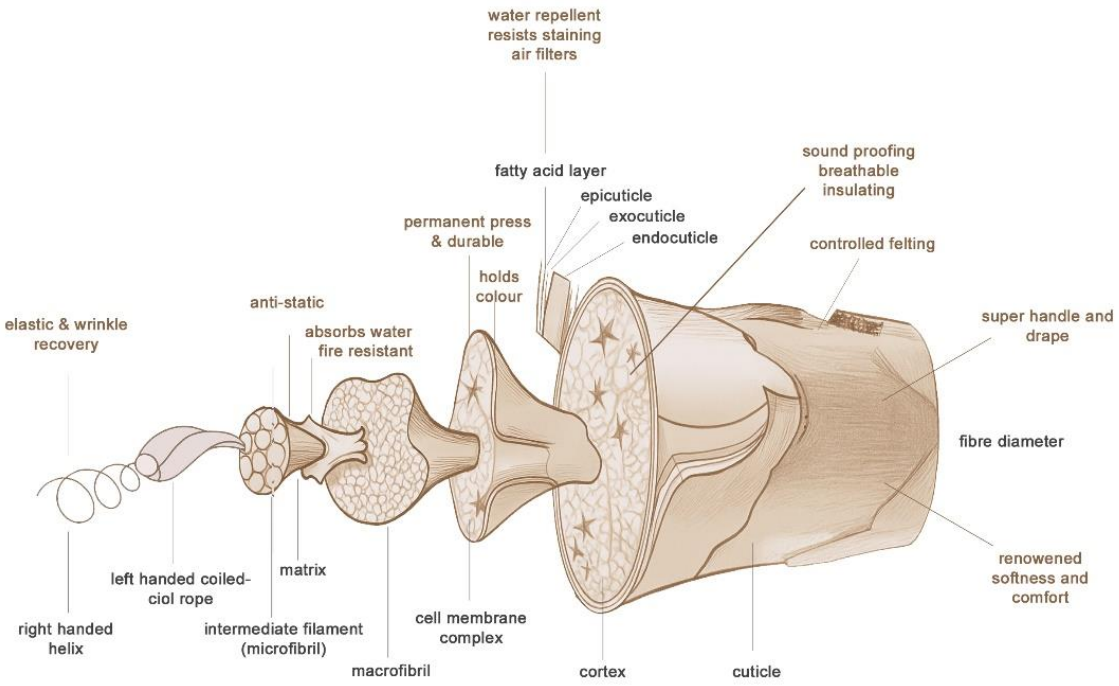



**Figure 4:** Structural analysis of wool fibres (T. Dekanić adapted according to IWTO)



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The cortex, which is formed from two types of cells (para-cortex and ortho-cortex), builds for app. 90% of the fibres. Amphoteric properties are specific for wool fibres because of chemical difference of the para-cortex (basophilic cells) and the ortho-cortex (acidophilic cells). The cortex cells consist of macrofibrils, which are composed of even finer filamentous elements, and microfibrils, which are composed of even finer protofibrils.

In coarser fibres, a wider or narrower dark stripe called the nucleus, or medulla is visible in the central part and consists of hollow cells, while finer wool fibres have no medulla.

All this underlines the fact that the properties of wool fibres depend on the breed. Their colour is pale yellowish, and some breeds produce grey, black and brown wool. Finer wool is darker, and coarser wool has a greater lustre [8].

## Length

The length of the wool fibres depends primarily on the breed of sheep, but also on the intervals between shearing dates. Coarser wool fibres are usually longer than fine fibres. Very fine wool fibres are generally short (average length 3.7 to 12.0 cm). Medium-fine wool has a length of 6.0 to 15.0 cm and coarse wool fibres up to 38 cm. Wool of shorter length is usually very curly, while long fibres are generally less curly, therefore the average number of curls in the different types of wool is between 2 and 12 curls/cm [5].

## **Fineness (**the average fibre diameter)

Fibre fineness is an important property by which fibres are distinguished and is related to length. Shorter fibres are finer, and longer fibres are coarser. Fibre fineness of wool is usually expressed in terms of diameter, and the average diameter of the fibres different breeds is from 12 to 70 μm [5]. The diameter of individual fibres in a wool sample varies greatly, and the average value is taken as the fibre fineness, along with statistical data on variability and non-uniformity (range of values, standard deviation, and coefficient of variation). The corresponding mean value is from 3 to 40 dtex.

Wool is divided into groups according to the average diameter [5,8], which are also related to the use of wool products, Table 2.

**Table 2:** Grade, diameter and usage of wool fibres [5,8]

| Grade | Diameter (μm) | Usage |
|---|---|---|
| Superfine | 15.0 – 17.0 | Cloth next to skin; shawls, babywear, gloves, underclothes |
| Fine | 18.5 – 20.5 | Apparel next to skin, high-quality fashion, soft handling wovens and knitwear |
| Medium<br>Broad | 20.6 – 22.5<br>22.6 – 25.0 | Different woven apparel cloth, knitwear, socks, blankets, rugs, industrial felts |
| Coarse | 26.0 – 32.0 | Rugs, upholstery, insulation |
| Very Coarse Wool | 32.0 – 48.0 | Carpets |



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## Crimping

The different types of wool differ both in the number and the shape of the crimps, which are determined by the bilateral structure of the cortex. The crimp facilitates spinning, increases the cohesion between the fibres and also determines the appearance of the yarn. The crimp is expressed by the number of crimps per centimetre and is 14 crimps/cm for coarser wool [5]. As a result of the tenacity of the crimp, wool garments retain their fullness throughout the wear cycle. The reason for this is that wool textiles are warm and comfortable to wear in winter.

## Strength and elasticity

Wool fibres have a lower strength than other fibres and are among the weakest natural fibres. The low strength is the reason why somewhat coarser yarns are made from wool to compensate for the necessary resistance to various stresses during use and processing. In addition, the strength also depends on the friction between the fibres in the yarn, which is high in wool fibres as a result of the scaly surface. Wool fibres can withstand severe deformation and the ability to recover elastically after stress is high. Textiles made of wool are not prone to deformation and wrinkling, and any wrinkles disappear after a certain period. However, repeated stresses lead to permanent deformation (stretched areas "knee bends", collars, sleeves) [5].

## Thermal properties

Wool fibres and textiles have a high heat storage capacity. It is a poor conductor of heat and its insulating properties are because of air, which is ten times a worse conductor of heat than fibres. Air is stored in small spaces between the fibres - the good thermal insulation properties are largely because of the crimp and the scaly surface of the fibres [5].

## Moisture and water absorption

Wool fibres are hygroscopic because of the large number of hydrophilic groups. In a standard atmosphere, they absorb about 13.5 to 16.5% moisture. The ability to absorb and retain water is also high (40 to 45%). Raw fibres cannot be soaked without the addition of wetting agents [5].

## The ability to felting

The absorption of water causes the fibres to swell, which is particularly pronounced in an alkaline medium. In washing process wool products are usually deformed because of the alkalinity of detergents. The phenomenon of felting, which is accelerated by the friction and mechanical movement of the textiles during the washing process, also contributes to this, Figure 5.

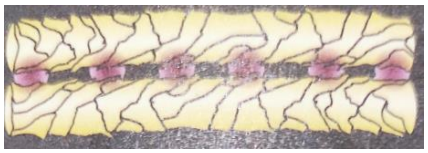


**Figure 5:** Felting caused by friction [13]

The scaly surface causes the fibres to become matted and lie close together, which leads to shrinkage and deformation of the product. Coarse wool has a lower tendency to felt compared to fine wool. The finer the fibres, the more pronounced these phenomena are.

The natural ability of wool to felting can be an advantage in the manufacture of woollen products, which can be produced with no chemicals, just in a few steps, by shaking and moisture or with a felting needle.

## Chemical properties

As already mentioned, wool possesses an amphoteric character, which is a result of the presence of cationic and anionic groups. Wool is more sensitive to the action of alkalis than to the action of acids.

Oxidizing agents destroy disulphide bonds and reducing agents can be used for bleaching and dyeing. Wool fibres are sensitive to alkaline oxidizing agents, which can be quantified by the alkali solubility (AS) value.

Wool fibres are sensitive to the effects of weathering, especially UV radiation, which damages them, resulting in increased yellowing because of the destruction of disulfide bridges. Damp wool is attacked by bacteria and mold, which leads to damage. Uncleaned wool fibres and the most expensive wool items are also attacked and permanently damaged by parasites such as moths. Female moth laying of its eggs in protein fibres can be prevented by moth repellents.

Because of wool sensitivity to alkalis and certain enzymes that hydrolyse them, wool products should be washed with special detergents [8].

## Elasticity

Because of its crimped fibre structure, wool has a natural elasticity, therefore garments made of wool can stretch and then return to their natural shape. A wool fibre can bend and twist more than 20,000 times without breaking. Wool can stretch and return up to 30% of its original length. This elastic structure gives the wool soft and resilience and makes it resistant to pressure [8].

## Drape

Drape refers to the way a fabric hangs and moves and is influenced by several factors, including the length, crimp and twist of the fibres. Wool fibres are naturally crimped, creating air pockets between the fibres which allow the fabric to drape more easily. The ability of wool to drape is also influenced by the twist of the yarn. A higher twist means that the fibres are closer together, which can reduce drape. Conversely, a lower twist means that the fibres are more loosely packed, which can increase the drape [8].

## Handle

Handle refers to the way a fabric feels when you touch it. It is a subjective assessment that is influenced by several factors, including the texture, smoothness and elasticity of the fibre. A fabric with a positive hand feels soft, smooth and comfortable against the skin. It should also drape well and retain its shape without being too stiff or limp. Wool has a distinct feel that is often described as soft, smooth and slightly bouncy [8].

## Breathability

One of the most useful natural properties of wool is its ability to breathe. Because of its hydrophilic core, wool can absorb up to 35% of its own weight in moisture, which is then released into the air as vapour. This built-in property is permanent and one of the reasons why wool is such a versatile fibre with therefore many applications. Thanks to its natural and high breathability, wool is ideal for many end uses: because of breathability, active wear products worn directly against the skin, such as underwear, socks, base layers or functional T-shirts, ensures lasting comfort during extended sports, outdoor, travel, work and everyday activities.
Sleepwear wool continuously absorbs moisture from the body and releases it into the air in the form of vapour. This keeps the sleeper dry and comfortable and improves the quality and duration of sleep.
Bedding and mattresses – the breathability of wool reduces humidity and prevents temperatures in the immediate environment from rising. This limits the opportunities for dust mites to develop and improves sleeping conditions, particularly for allergy sufferers and asthmatics [8].

## UV protection

In addition to its other natural performance properties, wool offers excellent protection against the sun's UV rays. Even when completely untreated, wool absorbs the radiation of the entire UV spectrum much more effectively than many other materials. The classification according to ultraviolet protection factor (UPF) indicates that wool garments generally have a significantly higher rating than the average UPF of 10 for a cotton T-shirt. Depending on the density of the fabric and the type of finish and/or dyeing, wool clothing usually has a UPF between 20 and 50 [8,14].

## Fire resistance

Wool is inherent fire-resistant fibre because of presence of high nitrogen and water content. Conditions must reach 570-600 °C before wool ignites, compared to cotton at 255 °C, polyester at 252-292 °C and polyamide at 160-260 °C. When wool ignites, it usually smoulders rather than ignites quickly. This slow combustion process makes it easier to extinguish and reduces the risk of the fire spreading. Unlike synthetic fibres, which melt and drip, which can lead to further damage, wool leaves a soft, ash-like residue when it burns. This inherent flame resistance makes wool an excellent choice for interior furnishings such as carpets, curtains and bedding where fire safety is critical.

Wool is also widely used in personal protective equipment (PPE) for firefighters and others professionals exposed to fire hazards [15].

## Wearability - the suitability, comfort and care of wool products

There are many reasons why using, wearing and caring for wool fibres is different from other fibres and can make a real contribution to reducing environmental impact [8]. Wool garments need to be washed less often than garments made from other fibres as airing between wears removes odour. Odour resistance results from breathability and the ability to absorb moisture. Due to the elastic nature of wool fibres, wool garments are naturally crease resistant and also naturally stain resistant due to the protective outer cuticle of the wool fibres. Airing or hanging in a steamy bathroom also eliminates odours and creases.

Wool items can be cared for in an aqueous medium and in organic solvents, depending on the structural parameters, finish and type of fabric. Professional care methods, dry cleaning and wet cleaning are recommended for maintaining the properties of wool products, with wet cleaning being promoted more than dry cleaning due to its environmental benefits. Lagoon™ is the only professional wet cleaning process approved by The Woolmark Company since 2004 [16,17].

Washing at lower temperatures means less energy consumption per wash cycle. A German study on consumer behaviour has shown that consumers wash wool at an average of 30.3 °C, while cotton is washed at an average of 41.1 °C [8].

Most woollen garments are dried naturally (line, flat, line drip, flat drip). Drying wool in a tumble dryer is not recommended as the mechanical friction can lead to changes in the surface and dimensional stability. This is a more economical option and also a benefit for the environment as dryers consume more electricity.

## Biodegradability

The biodegradation of textile fibres is a natural process in which microorganisms break down textile materials into simpler substances such as water, carbon dioxide and biomass. This process is influenced by factors such as the chemical structure of the fibre, the environment and the presence of microorganisms. Natural fibres generally degrade faster than synthetic fibres, but natural fibres can also be treated with various chemicals that can slow down degradation. As wool fibres also biodegrade in the aquatic environment, recent research in New Zealand has shown that different types of wool biodegraded by about 20% after 90 days in salt water, Figure 6 [18]. Further research efforts will focus on the biodegradation of wool under different sea level and temperature conditions.

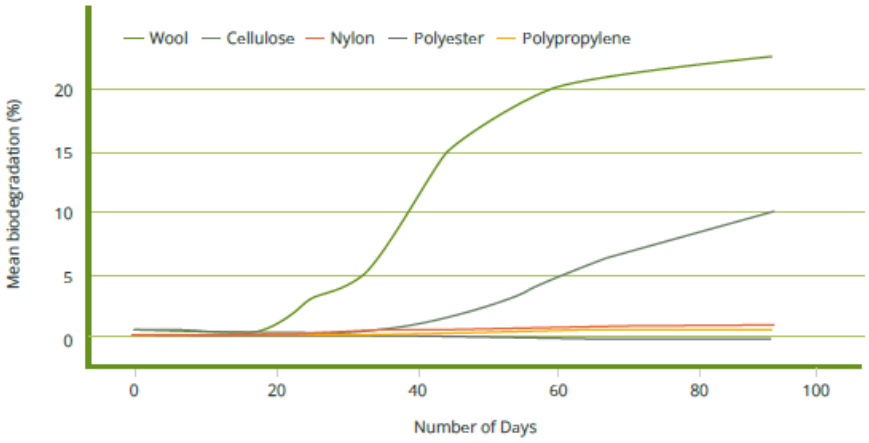



**Figure 6:** Mean biodegradation of different fibres [8]

As a result of the unique structure of wool and its water-repellent outer membrane, the wool fibres are resistant and durable when wearing and caring for a wool garment. Microorganisms in the soil or water break down and consume matter. The tests show that, under ideal conditions, wool products are almost completely degraded after six months in the soil.

In addition, research has shown that wool acts as an effective soil conditioner and fertilizer, as it slowly releases sulphur, nitrogen, phosphorus and potassium during biodegradation [19,20], Figure 7.

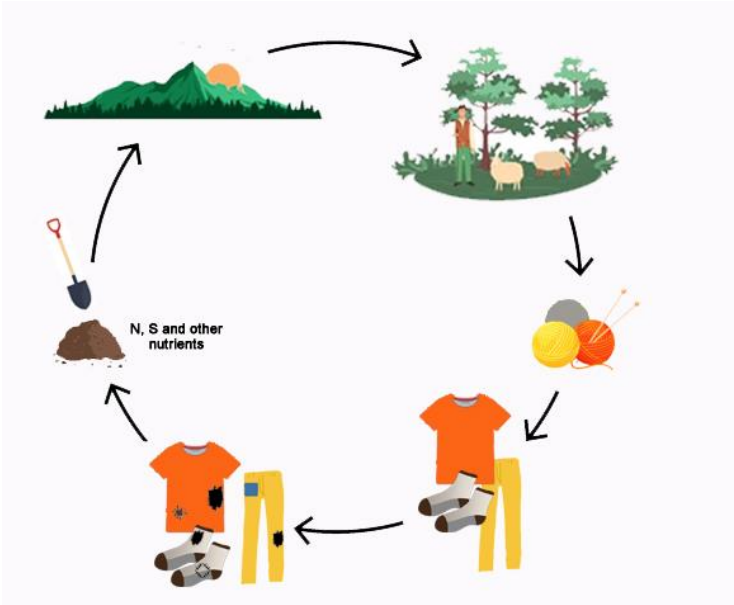



**Figure 7:** Biodegradation of woollen products (design T. Dekanić)

Previous research examining the effects of modern wool fibre processes shows that typical dyes and standard machine-washable treatments do not significantly reduce the relative rates of biodegradation of wool and synthetic fibres. Furthermore, it is known that synthetic textiles not



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only biodegrade extremely slowly but can also break down into fragments known as microplastics [21].

## Recycled wool

The growing awareness of the importance of environmental protection and the increasing demand for safe and sustainable bio-based materials are driving the search for new methods of recycling wool waste and manufacturing new products. A major challenge for the future is therefore to find economically viable, marketable and environmentally friendly solutions for low-grade wool and wool waste which directly benefit farmers and contribute to environmental protection [6].

The recycling of wool has a long history. With a share of around 6% of the global wool market, the production of recycled wool is estimated at 73 thousand tons in 2023, which is roughly the same as in 2022. The Italian district of Prato is an important producer of recycled wool and estimation for 2023 in production was around 30,000 tons of the fibre, Figure 8. Other important production centres for wool recycling are China and the Indian city of Panipat. The key standards for recycled wool are the Recycled Claim Standard (RCS), Global Recycled Standard (GRS), and Cardato Recycled for recycled wool from Prato in Italy [7].

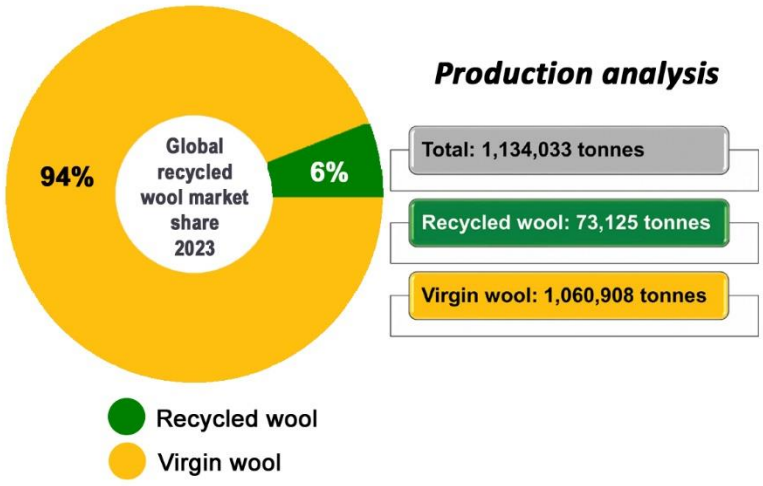



**Figure 8:** Global recycled wool market share (design by T. Dekanić according to [7])

## Wool Life Cycle Assessment, LCA - importance of use phase

The LCA for cotton fibres was published, while never it was done for synthetics or other cellulosic fibres. After seven years of dedicated work, a team of researchers from Australia, New Zealand and Norway published the first complete LCA for wool in 2020. The study analysed the lifespan of a 300 g of wool sweater produced from Australian wool, processed in China and sold in the European Union. Most LCA studies for wool have focused on a single segment of the supply chain, Figure 9.

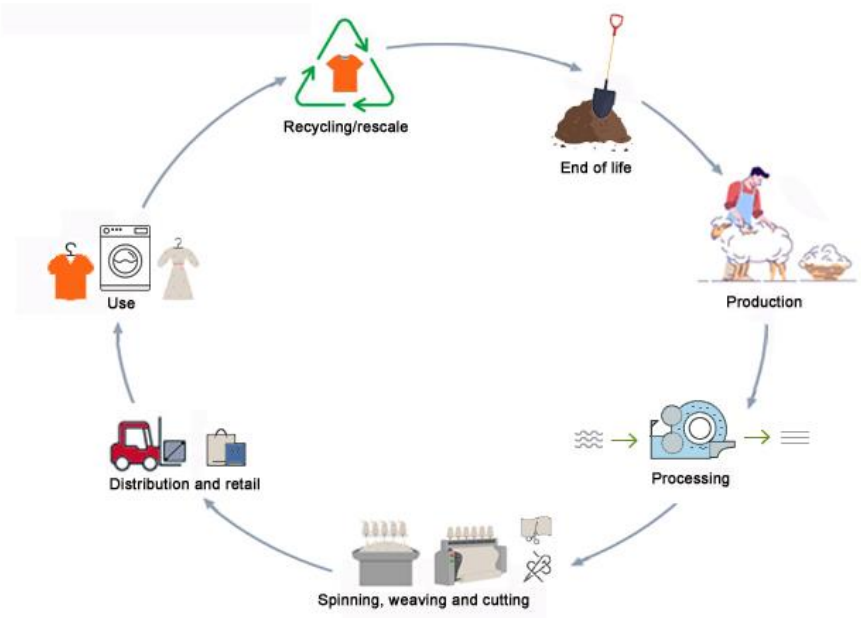



**Figure 9:** Schematic view of wool LCA (designed by T. Dekanić)

The LCA of wool has shown that the use phase is key to the sustainability of clothing, with the number of times a garment was worn being the most influential factor in determining its impact. In practice, this means that a garment that is worn more often and kept for longer will have less overall impact on the environment than a garment that is worn less often and kept for a shorter period of time. The comparison between typical use phase characteristics for cotton and wool items were given in Table 3 [8].

**Table 3:** Comparison between cotton and wool items

| Product category | Unit weight (g) | Fibre | Wearing per wash | Garment wear life | Wearing per lifetime (number) | Washings per year Per unit |
|---|---|---|---|---|---|---|
| | assumed | example | [8,22] | [8,22] | [23] | By derivation |
| Socks | 0.05<br>0.05 | Cotton<br>Wool | 1.5<br>2.5 | 3.3<br>5.5 | 52.3<br>52.3 | 10.6<br>3.8 |
| T-shirt (baselayer) | 0.2<br>0.2 | Cotton<br>Wool | 1.5<br>3 | 4.6<br>4.6 | 36.4<br>40.5 | 5.3<br>2.9 |
| Sweater (mid/outer) | 0.3<br>0.3 | Cotton<br>Wool | 5<br>10 | 5.6<br>6.0 | 81.4<br>92.4 | 2.9<br>1.5 |

The more frequently a garment is worn, the more efficiently the resources used in its production are utilized. As the number of wears increases, the cost per use decreases, and the need for



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replacement garments is reduced. This extended use means that no additional resources are required to produce a new item, making the original garment more sustainable. Despite this, only a limited number of studies have examined the full lifespan of wool garments.

## 1.2 Wool processing

Raw fleece pass through several processes before wool can be used as end product. Wool processing steps depend on end products requirements. Conventional wool processing transforms raw fleece into yarn and fabrics through a series of steps. These include shearing, scouring, sorting, carding, spinning, and weaving or knitting. Further processing like dyeing and finishing can also be involved.

When making products using the wool felting technique, processing steps are reduced. The production of non-woven fabrics requires methods to form layers of fibres into coherent fabrics without the need to spin yarns.

The conversion of wool fibres into a finished product is possible with chemical and mechanical processes through the following operations [24]:

- scouring of the raw wool
- carbonising
- carding
- combing
- spinning
- weaving, knitting or felting
- finishing.

### Scouring

Wool fleeces have various amounts of foreign impurities, grease or wax and sweat 6-68%, water 15-18%, which depend on the type of sheep and the area where it is grown. The impurities are divided into biological impurities and incidental impurities (foreign impurities) depending on their composition. Biological impurities are sweat and wax, and incidental impurities consist of various impurities (mud, dust, vegetable impurities, etc.). However, impurities, such as dirt and grease must be removed before further processing [25,26]. Impurities on wool are partly soluble in water; wool sweat and part of foreign impurities are soluble, while wool wax (lanolin), vegetable impurities and sand are insoluble. Wool grease is known and referred to as fat, lanolin, neutral wool grease, and degras, and by various other terms. Chemically, wool grease is a wax rather than a fat since it contains no ester of glycerol [27].

The complexity of the wool structure because of the different chemical groups in the polymer molecule and the large number of bonds between the molecules makes wool fibres sensitive to sunlight, heat, water and chemicals. They are particularly sensitive to alkalis, and the intensity of the changes is related to the concentration and temperature of the alkalis in the process. During

the various wet treatments, care should be taken to prevention of fibres damage during the process.

Greasy raw wool is cleaned by scouring with about 1% surface active agent in several baths, whereby grease, dirt, sand and grime are removed from the fibre [24].The IWTO defines wool scouring as a process in which wool is washed in hot water and detergent to remove the non-wool impurities (natural fats, waxes, proteins and other components as well as dirt, oil and other impurities) [28].

In the scouring process, all impurities are removed except vegetable impurities, which are removed by carbonization. The properties of the fibres, such as lustre, tensile strength, moisture, hygroscopicity, etc. should be preserved during scouring process as much as possible [24,25].

The scouring of wool can be carried out in such a way that all impurities are removed (theoretical wool yield) and a clean wool substance is obtained, or that some wool wax (1 to 2%) remains on the wool (practical wool yield). This amount is higher for coarser wool fibres than for fine wool fibres. This scouring process is preferred in factories where residual wax facilitates spinning [25].

Several scouring procedures exist:
1. Emulsion scouring
2. Scouring in organic solvents
3. Scouring in sweat
4. Ice scouring

Within the group of mentioned processes, emulsion scouring is most frequently carried out, usually in solutions of soap or surfactants in an alkaline medium using soft water. Alkalinity is achieved by adding soda to soft water, therefore acidic waxes can be emulsified more easily. Surfactants play a multifaceted role in the wool scouring process. They enhance the wetting of the greasy wool fiber surface, emulsify waxes that are resistant to saponification, and help retain these emulsified waxes along with other impurities in the bath. This prevents the redeposition of contaminants onto the fiber.

The concentrations of surfactants and sodium carbonate (soda) vary and depend on the quality of the wool to be scoured.

The scouring time depends on the processing step; duration in the first bath is up to 3 minutes; the time is gradually reduced till 90 seconds in the last bath. The specified dwell time of the wool in the individual baths is only sufficient if the temperature is above 40 °C. In the first bath it is 50 °C, in the second 42 °C to 45 °C, and in the following baths 40 °C, 30 °C, 20 °C. In the first bath, the medium is alkaline (pH 10), but because of the short dwell time and the sweat, which protects the wool by acting as a buffer, there is no risk of damaging the disulphide bonds. In the other baths, the pH value is slightly lower because the wool becomes cleaner and therefore more susceptible to damage. The last bath consists of a clean water with a pH of 8. The final step is the rinsing, as important to remove the alkali from wool fibres. Regardless of the processing details, the purpose of wool scouring is to remove impurities while preserving the physical and mechanical properties of the wool fibre as much as possible [29].

Recently, environmental guidelines and sustainability have mandated the use of enzymes and their complexes. The replacement of conventional procedures with enzymatic ones leads to decreased amount of chemicals and energy as a result of specificity of the enzyme, like Cellulases, Pectinases, Proteases, Cutinases, Lipases, and Collagenases, which are good for selective removing vegetable residue and grease from the raw wool [30]. Comparison of the chemically and enzymatically treated wool revealed a better performance of enzymes mixture as scouring agents [31].

Wool can be scoured in a slightly acidic medium with the addition of surfactants. Sustainable requirements-imposed application of biodegradable products from renewable sources. It is known that saponins are bioactive compounds produced mainly by plants, but also by some marine organisms and insects' natural surface-active substances, therefore they can clean various surfaces [32,33]. Saponins are structurally diverse class of compounds found in many plant species, characterised by a skeleton derived from the 30-carbon precursor oxidosqualene to which glycosyl residues are attached [34]. Such specialised metabolites are mainly found in the plant kingdom, although they have also been discovered in marine invertebrates [35,36]. Figure 10a shows a natural source of saponins harvested in the Botanical Garden of the Faculty of Science, University of Zagreb, Figure 10b shows soapnuts purchased in a store.



a. b.

**Figure 10:** Saponines from different natural sources: a. *Sapindus drummondii;* b. *Sapindus mukorossi*

A whole range of other activities is attributed to saponins, and the literature is full of various pharmacological properties [37].

## Wastewaters

The process of raw wool scouring can be carried out in different ways, and one of the waste streams is wastewater [38,39]. As a result of the differences between the various sheep breeds with regard to non-wool contaminants, no standardised process parameters can be applied [26]. Removal of the grease and the dirty substances demand large amounts of water and surfactants,



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therefore the scouring process generates a high contaminating wastewater, Biological oxygen demand – $BOD_5$ about 20.000-40.000 mg/ and Chemical oxygen demand - COD of 100.000 mg/L. To reduce the generation of wastes, some scouring plants recover part of the grease as a cream phase because the grease material, containing mainly the wool wax, remains in the superficial layer of the different washing tanks. Those superficial waters are centrifuged, and a cream subproduct can be sold as a source to obtain lanolin (after extraction and purification) which is a high value product in pharmaceutical applications and baby care products [40].



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# 2 Green-Tex Portfolio



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# 2.1 Analysis of raw wool

Chemically, wool is a fibrous protein fibre made of α-keratin. The elemental analysis of wool shows the content of carbon, hydrogen, oxygen, nitrogen, and sulphur. The high sulphur percentage (around 5 wt%) results from the cystine content of the fibre [24]. Calcium (7755 mg/kg), magnesium (95 mg/kg) and iron (600 mg/kg), zinc and copper can be found in wool fleece as they are required for wool growth [41]. The copper, manganese and zinc contamination levels in sheep wool is increased with its age [41]. Additionally, copper and zinc concentrations of black wool were significantly higher than of white wool. Copper and iron are responsible for photo yellowing of wool. According to some sources sheep wool can be considered as bioindicator of heavy metal pollution meaning that evaluation of contamination levels can be used for evaluation of environmental contamination in some areas [41].

**Analytical assessment of selected raw wool – "Merino Wirtemberg" breed**

"Merino Wirtemberg" sheep is one of the most respected breeds, originated in West Germany in the province of Wirtemberg. Analytical assessment of wool fleece was performed to determine the presence of elements and contamination level of wastewater from the scouring process. For that purposes, Merino Wirtemberg natural breed, grown in Majur region, was analysed.

Analysis was based on determination of:

- total chrome (Cr)
- manganese (Mn)
- iron (Fe)
- copper (Cu)
- zinc (Zn)
- cadmium (Cd)
- lead (Pb)
- nitrogen (N)
- dry matter fraction (105 °C)
- Dissolved Organic Carbon (DOC)
- Total Organic Carbon (TOC)
- phosphorus (P)
- potassium (K)
- lipophilic substances of low volatility (Total oil and grease)
- biochemical oxygen demand ($BOD_5$)
- sulphate
- ammonium
- dissolved sulphur.

In Table 4 are given all parameters, methods, technique and results of analysis.

**Table 4:** Analysis of raw wool samples – "Merino Wirtemberg"

| Analysis | Method | Technique | Unit | Result | U++ |
|---|---|---|---|---|---|
| Total chrome | HRN EN 13657:2008 | | mg/kg | < 5 | |
| Manganese (Mn) | HRN EN 13657:2008 | | mg/kg | 19 | |
| Iron (Fe) | HRN EN 13657:2008 | | mg/kg | 341 | |
| Copper (Cu) | HRN EN 13657:2008 | | mg/kg | 2.9 | |
| Zinc (Zn) | HRN EN 13657:2008 | | mg/kg | 71.0 | |
| Cadmium (Cd) | HRN EN 13657:2008 | | mg/kg | < 1.5 | |
| Lead (Pb) | HRN EN 13657:2008 | | mg/kg | < 10.0 | |
| Nitrogen (N) | HRN EN 16169:2013 | Kjeldahl method | % mass of dry matter (d.m.) | 9.52 | ± 0.76 |
| Dry matter fraction (105°C) | HRN EN 15934:2013 | Gravimetric analysis | % | 89.3 | ± 1.4 |
| Disolved Organic Carbon (DOC) | HRN EN 1484:2002 | | mg/kg d.m. | 44350 | ± 12595 |
| Total Organic Carbon (TOC) | HRN EN 15936:2022 | | % mass of d.m. | 55 | ±7 |
| Phosphorus (P) | HRN EN 15309:2008 | X-ray | % mass of d.m. | 0.025 | |
| Potassium (K) | HRN EN 15309:2008 | X-ray | % mass of d.m. | 7.87 | |
| Lypophilic substances of low volatility (Total oil and grease) | SM 24th Ed. 2023, 5520 B | | mg/kg d.m. | 647 | |
| Biochemical oxygen demand ($BPK_5$) | HRN EN 1899-1:2004; modified | Electrochemistry | mg/kg d.m. | 44690 | |
| Sulfate | ASTM D516-22 | Spectrophotometry | mg/kg d.m. | 2400 | |
| Ammonium | HRN ISO 7150-1:1998 | Spectrophotometry | mg/kg d.m. | 756.40 | |
| Dissolved sulphur | HRN ISO 10530:1998 | Spectrophotometry | mg/kg d.m. | 0.60 | |



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The content of nitrogen is 9.52 %, and it confirms applicability of fibrous materials of animal origin for cultivation of green plants, which are characterized by the highest nitrogen content demand [20,42].

The nitrogen and sulphur constitute the largest portion of sheep wool on an elemental basis with other nutrients, in descending order, including calcium (Ca), potassium (K), zinc (Zn), phosphorus (P), iron (Fe) and copper (Cu) [43]. Analysis of raw wool Merino Wirtemberg from Majur region showed different relations: iron (341 mg/kg), zinc (71 mg/kg), phosphorous (0.025%) and copper 2.9 mg/kg. Analysis proved a high level of iron, as specific for "Merino Wirtemberg" breed.

As trace metals essential for biological activity are always present in wool fibres as natural protein, in Table 5 they were compared with contaminated wool raw fibres [41].

**Table 5:** Comparison of elements found in "Merino Wirtemberg" (Green-Tex) with raw wool fibres from literature [41,44].

| Element | "Merino Wirtemberg" (Green-Tex) | Merino [41] | Ireland sheeps [44] min-max |
|---|---|---|---|
| | mg/kg | | |
| Manganese | 19.0 | 2.1 | |
| Iron | 341 | 20 | 4.8 - 42.0 |
| Copper | 2.9 | 8.6 | 3 - 10 |
| Zinc | 71.0 | 126 | 44 - 2.200 |
| Yellowness index (YI) | 38.14 | 8.3 | - |

It is difficult to compare the results obtained with literature because raw wool is natural fibre, a non-homogeneous sample, as a result of the presence of grass, soil and faeces contaminants matted into the wool [42]. The other reasons were related to keratin nature and inherent sorption properties. Therefore, sheep fleece can serve as a chemical indicator reflecting the quality of feed nutrition and environmental factors.

Sheep which produce a greater level of suint that contain higher level of boron, manganese and iron and less levels of sodium, phosphorous and zinc tend to have more yellow wool and higher yellowness index [41]. The levels of iron and manganese presented in Table 5 confirm this hypothesis. The amount of zinc (71.0 mg/kg) is less than amount in wool fleece being contaminated (126 mg/kg).

## 2.2 Scouring of raw wool – selection of sheep breeds

Samples of scoured wool form three sheep breeds, grown in Majur region were analysed as a result of comparison of their properties, Table 6.

**Table 6:** Scoured wool samples grown in Majur region - Green –Tex

| Breed | Wool label | Fleece shearing |
|---|---|---|
| „Merino Wirtemberg“ | 0 | 2024 |
| „Slovenian landras“ | 2 | 2024 |
| „Pramenka” | 4 | 2024 |

All samples of raw wool were scoured with conventional process using surfactant, Felosan RG-N (non-ionic agent – etoxylated fat alcohol) produced by CHT and soda ($Na_2CO_3$) at 50 °C according to protocol elaborated in Table 7.

**Table 7:** Scouring protocol

| Step | | Bath composition | T (°C) | t (minutes) | pH |
|---|---|---|---|---|---|
| 0 | Pre-scouring | Water | 50 | 5 | |
| 1 | Scouring | 2 g/L Felosan RG-N<br>0.5 g/L $Na_2CO_3$ | 50 | 10* | 8.8 |
| 2 | Scouring | 1 g/L Felosan RG-N<br>0.35 g/L $Na_2CO_3$ | 50 | 10* | 8.2 |
| 3 | Scouring | 0.2 g/L Felosan RG-N | 50 | 10* | 6.5 |
| 4 | Warm rinsing | Water | 50 | 5 | |
| 5 | Cold rinsing | Water | - | 5 | |
| 6 | Cold rinsing | Water | - | 5 | |

*time is prolonged from 5 to 10 minutes as a result of using of cold processing bath.

Samples were scoured in Linitest Original, Hanau in cuvettes volume of 300 mL using a bath ratio 1:20. Scoured and rinsed samples were air dried in ambient conditions.

Raw wool samples were analysed by determining the following parameters:

- length
- fineness and strength
- residual grease
- yield
- spectral values
- morphology (SEM images)
- elemental analysis (EDS analysis).



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## Length of scoured wool samples

It is known that wool fibres are weak, which is compensated by other characteristics, such as fineness, elasticity, curliness, good adhesion etc.

The length of the fibres significantly affects the quality of wool products. Therefore, the length of wool samples (wool staple) is important for selection of processing steps and the final product, Figure 11.

Length of scoured wool fibres was determined by individual measurement method, Table 8.



"Merino Wirtemberg" – Sample 0 "Slovenian landras" – Sample 2 „Pramenka" – Sample 4

**Figure 11:** Randomly isolated wool samples and prepared staples

**Table 8:** Length of wool scoured samples with statistical indicators

| Sample | Average length (mm) | Stand. deviation (mm) | Coefficient of variation (%) | Error (%) |
|---|---|---|---|---|
| "Merino Wirtemberg" – Sample 0 | 75.32 | 11.77 | 15.63 | 0.63 |
| "Slovenian landras"– Sample 2 | 83.00 | 15.7 | 18.01 | 0.86 |
| „Pramenka" – Sample 4 | 127.97 | 20.85 | 16.29 | 1.14 |

The length of the analyzed fibres varies, the longest fibres being from "Pramenka", followed by "Slovenian landras" and "Merino Wirtemberg". In accordance with the previously highlighted relationships, the wool of Pramenka breed is coarser compared to the finer fibres of the other



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analysed breeds. Standard deviations follow the same trend, the highest for “Pramenka” and the lowest for “Merino Wirtemberg”.

## Fineness and strength

Fineness and strength of scoured wool samples were measured using instrument produced by Lenzing Instruments, Austria: Vibroskop/Vibrodyn 400, serial number: 1529/1519; gauge length: 20 mm; test speed: 30 mm/min; tension weight: 1500 mg.

The results were presented in Tables 9-11 and Figures 12-14. “Merino Wirtenberg” wool shows the highest tenacity value of 16.08 cN/tex among all tested samples while its fineness is 15.38 dtex. “Pramenka” breed shows the coarsest fibres with fineness of 18.02 dtex and its tenacity was 14.19 cN/tex. “Slovenian landras” breed has the finest fibre with fineness value of 9.43 dtex while its tenacity was the lowest – 12.94 cN/tex.

**Table 9:** Fineness and strength of scoured wool fibres – Sample 0

| “Merino Wirtemberg” – Sample 0 | Titer (dtex) | Force (cN) | Elongation (%) | Tenacity (cN/tex) | YM, 1% cN/tex | Work cN*cm |
|---|---|---|---|---|---|---|
| Average | 15.38 | 24.72 | 33.99 | 16.08 | 307.42 | 12.47 |
| Std. dev. | 2.87 | 6.68 | 6.21 | 3.17 | 44.39 | 4.52 |
| CV (%) | 18.65 | 27.05 | 18.28 | 19.73 | 14.44 | 36.24 |

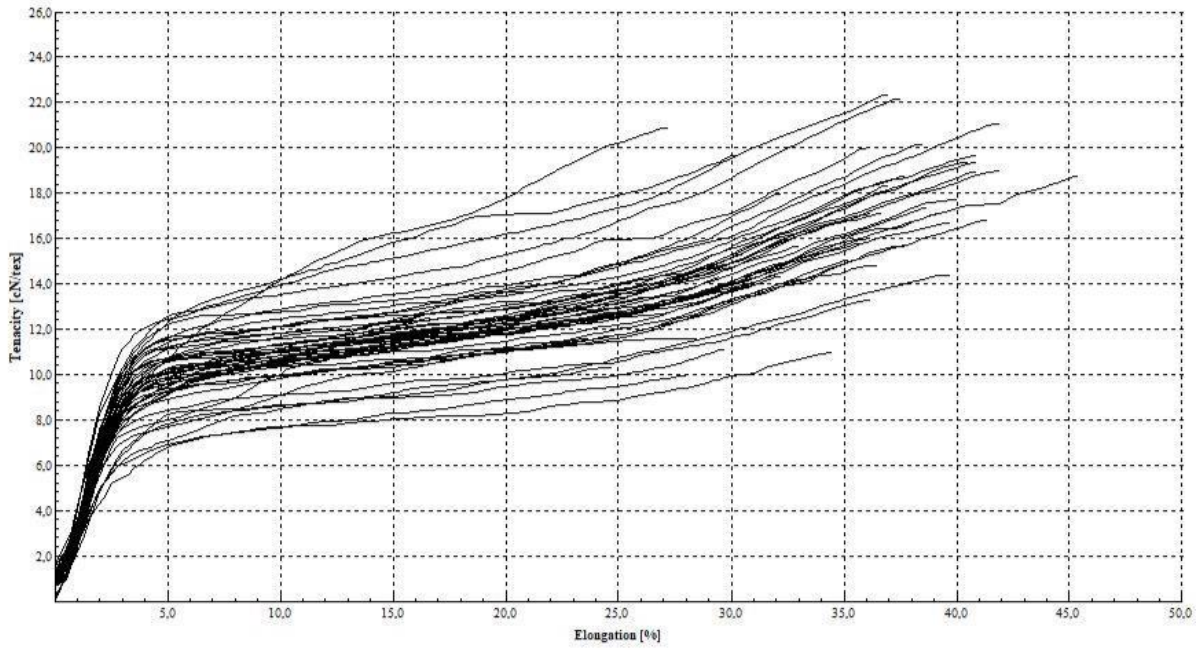



**Figure 12:** Tenacity and elongation of scoured wool fibres – Sample 0



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**Table 10:** Fineness and strength of scoured wool fibres – Sample 2

| "Slovenian landras" – Sample 2 | Titer (dtex) | Force (cN) | Elongation (%) | Tenacity (cN/tex) | YM, 1% cN/tex | Work cN*cm |
|---|---|---|---|---|---|---|
| Average | 9.43 | 12.22 | 27.51 | 12.94 | 261.46 | 5.28 |
| Std. dev. | 2.39 | 3.77 | 8.38 | 1.97 | 77.45 | 2.51 |
| CV (%) | 25.31 | 30.88 | 30.46 | 15.21 | 29.62 | 47.59 |

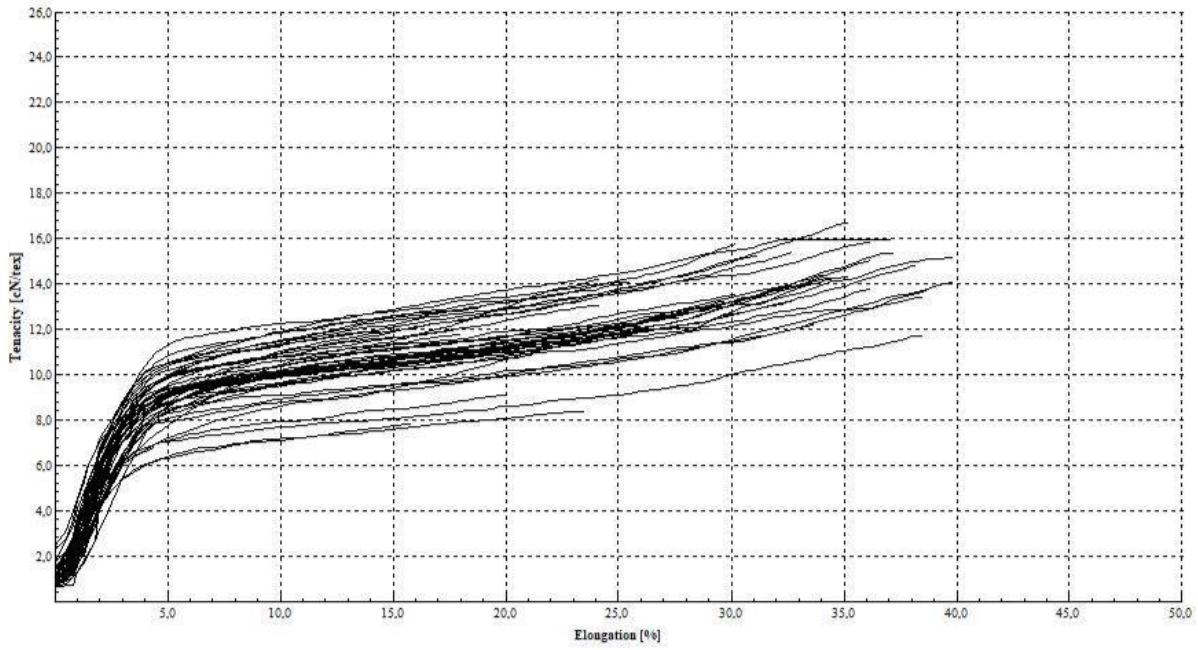



**Figure 13:** Tenacity and elongation of scoured wool – Sample 2

**Table 11:** Measurement of fineness and strength of scoured wool – Sample 4

| "Pramenka" – Sample 4 | Titer (dtex) | Force (cN) | Elongation (%) | Tenacity (cN/tex) | YM, 1% cN/tex | Work cN*cm |
|---|---|---|---|---|---|---|
| Average | 18.02 | 25.69 | 32.13 | 14.19 | 237.03 | 12.55 |
| Std. dev. | 4.48 | 8.36 | 9.19 | 2.78 | 56.63 | 5.92 |
| CV (%) | 24.88 | 32.56 | 28.59 | 19.60 | 23.89 | 47.20 |



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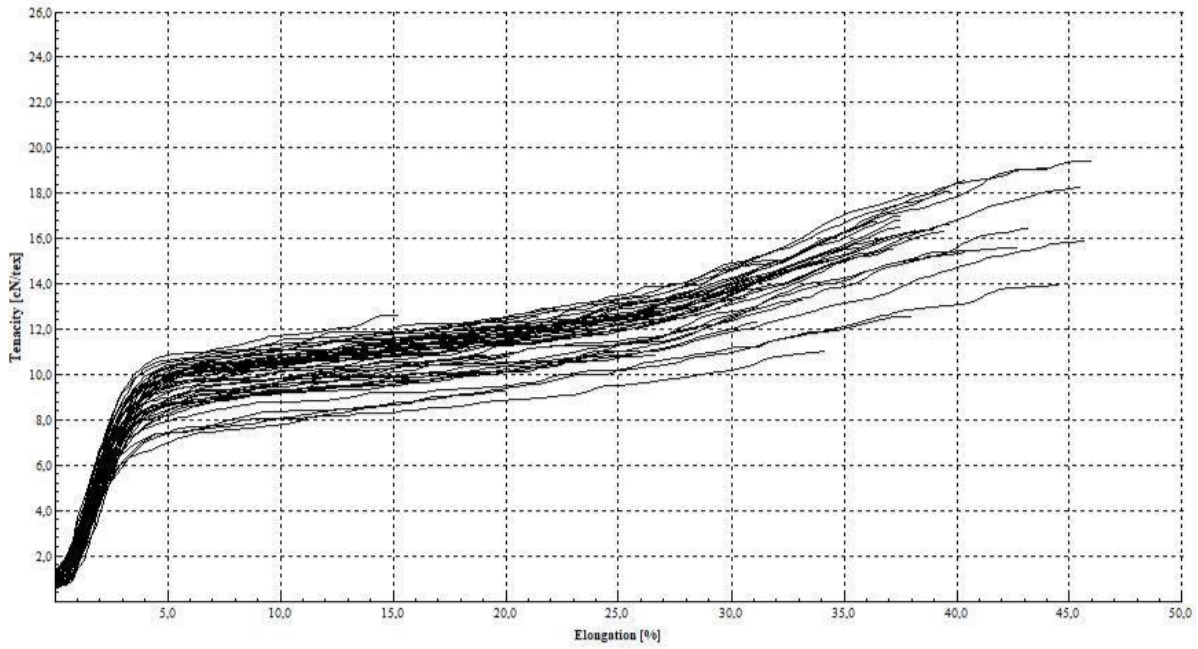



**Figure 14:** Tenacity and elongation of scoured wool – Sample 4

### Residual grease

Residual grease (RG) is the fatty matter or grease left on the fibres after scouring. Refined recovered grease becomes lanolin. The amount of RG depends on the wool type, the season, and the scouring performance. Grease content was determined following ASTM D 1574 – 87: Standard Test Method for Extractable Matter in Wool and Other Animal fibres, using ethanol as a solvent for extraction procedure. Results were presented in Table 12.

**Table 12:** Wool samples residual grease content (RG)

| Sample | RG (%) |
|---|---|
| "Merino Wirtenberg" Sample 0 | 26.3 |
| "Slovenian landras" Sample 2 | 24.9 |
| "Pramenka" Sample 4 | 25.2 |

Results showed that residual grease of 26.3 % was found in "Merino Wirtemberg" wool fibres, 24.9 % in Slovenian landras and 25.2 % in "Pramenka" breed. All analysed wool fibres have similar values since they come from the same herd and were treated by the same scouring process.

**Yield (%)**

To determine the wool yield (Yld), samples of raw wool were dried and weighed before and after scouring by procedure specified in Table 7.

**Table 13:** Wool yield values

| Sample | Yld (%) |
|---|---|
| "Merino Wirtemberg" Sample 0 | 62.2 |
| "Slovenian landras" Sample 2 | 65.4 |
| "Pramenka" Sample 4 | 63.1 |

Yield is the amount of useful fibre that can be obtained from a known weight of wool. Obtained yield values are similar and correspond to literature available values, approx. 65%.

**Spectral parameters (Yellowness Index, Reflectance Value)**

Samples of raw wool and wool scoured by the conventional method were analysed by the remission spectrophotometry on a DataColor 300, Switzerland, to determine their reflectance curves (R), and yellowness index (YI).

**Table 14:** Yellowness index of scoured wool samples

| Sample | YI |
|---|---|
| "Merino Wirtemberg" Sample 0 | 41.11 |
| "Slovenian landras" Sample 2 | 38.14 |
| "Pramenka" Sample 4 | 32.61 |

Merino Wirtemberg possesses the highest value of yellowness index in relation to other samples, while the Pramenka breed has the lowest value. All samples were scoured by the same protocol, but initial color was not the same. As yellowness depend on elemental content, as it was presented in previous sub-chapter, results showed that Merino Wirtemberg is more yellow than other wool samples.

Difference in spectral parameters of raw and scoured wool fibres are presented by reflectance curves, of raw (R) and scoured (S) wool samples in Figures 15-17.

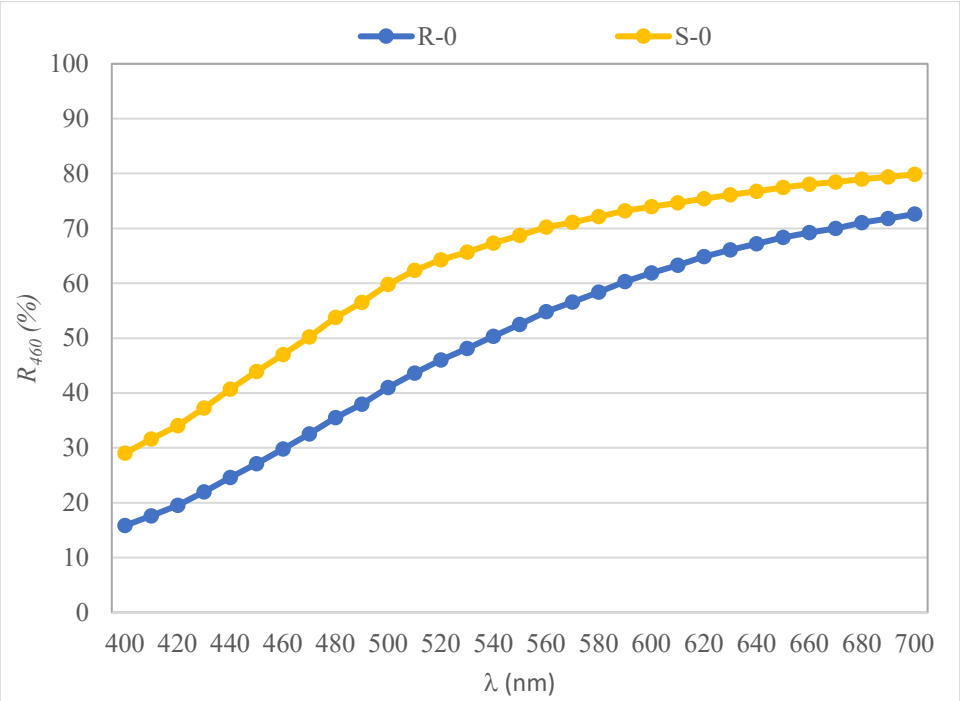



**Figure 15:** Reflectance curves of raw and scoured wool Sample 0 – "Merino Wirtemberg"

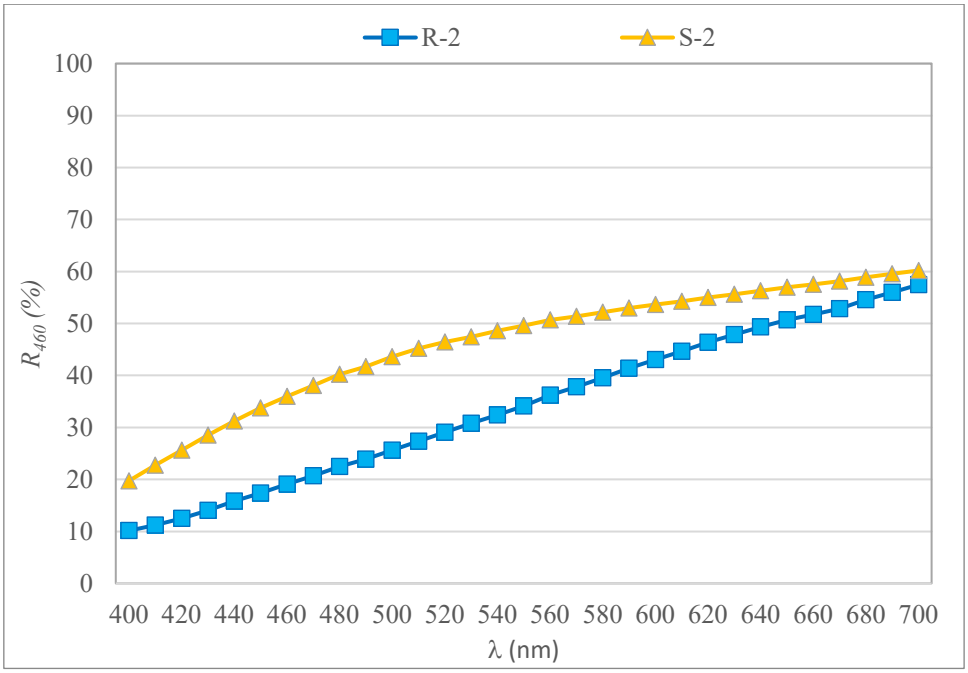



**Figure 16:** Reflectance curves of raw and scoured wool Sample 2 – "Slovenian landras"



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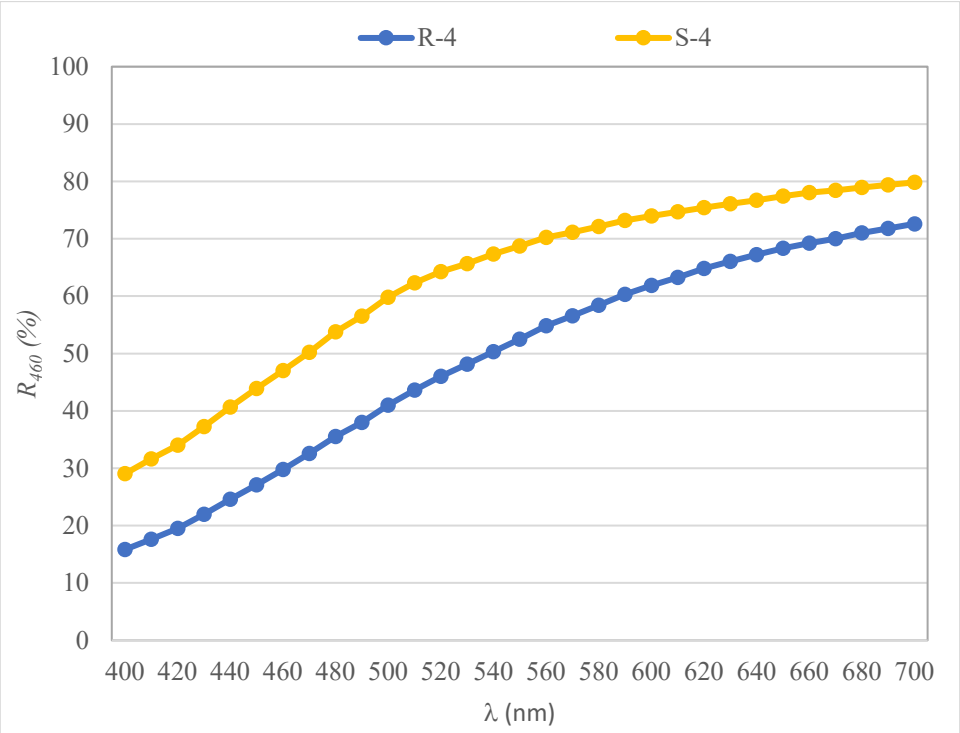



**Figure 17:** Reflectance curves of raw and scoured wool Sample 4 – "Pramenka"

The reflectance values at wavelength region from 420 to 460 nm show the scouring efficiency that can be assessed visually. It is obvious that scouring process enhance reflectance values in whole wavelength range. Some differences were observed between "Slovenian landras" in comparison to "Merino Wirtemberg" and "Pramenka".

**Morphology features**

Scoured wool fibres as part of Green-Tex portfolio were assessed using microscopic examination by the Czecz model, Tescan Vega Scanning Electron Microscope, low vacuum 25 Pa, BSE detector, HV 5 kV under magnification of 1 kx, Figures 18 - 20.

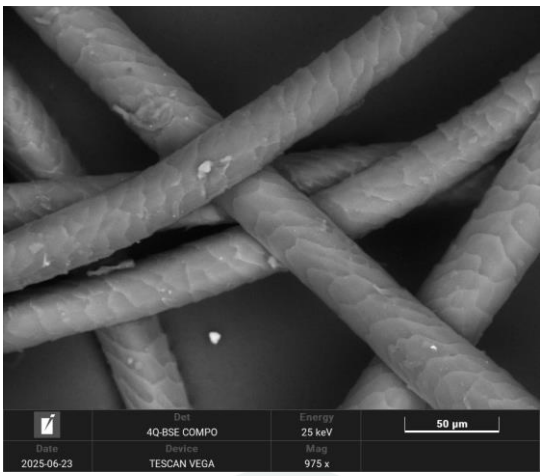



**Figure 18:** SEM image of scoured "Merino Wirtemberg" wool fibres - Sample 0



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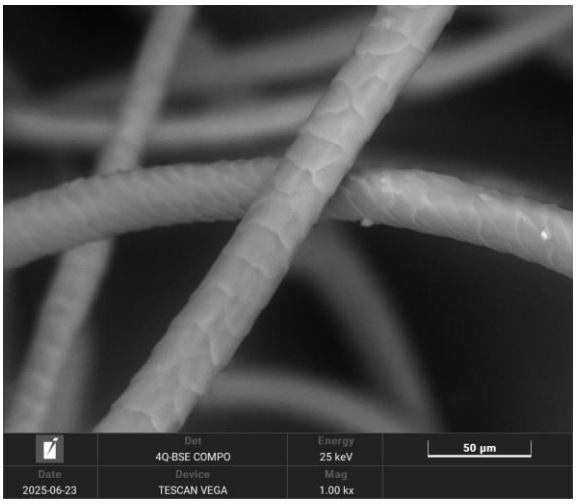



**Figure 19:** SEM image of scoured “Slovenian landras” wool fibres - Sample 2

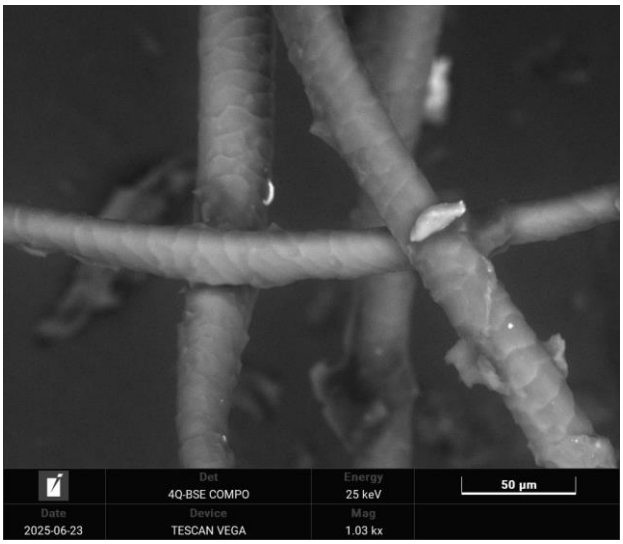



**Figure 20:** SEM image of scoured “Pramenka” wool fibres - Sample 4

SEM images of analysed wool fibres show the similarities and specificities of each type of wool fibres. The thickness, uniformity and overlap levels of scales varies, where “Merino Wirtemberg” wool fibres possess the best uniformity. Wool fibres from “Pramenka” breed have not uniform thickness. The surface of these fibres is specific by deposition of some unknown matters.



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## Elemental analysis of wool

Characterization of wool through chemical composition of the fibres on the micro scale was done by Dispersive X-ray spectroscopy (EDS), Tescan Essence, 25 kV. Results were shown in Tables 15-17 and Figures 21-23.

**Table 15:** Elemental analysis in a sample of scoured wool “Merino Wirtemberg” -wool Sample 0

| Element | Atomic% | Weight % |
|---|---|---|
| Carbon | 78.11 | 71.21 |
| Oxygen | 20.12 | 24.23 |
| Sulphur | 1.61 | 3.92 |
| Calcium | 0.10 | 0.32 |
| Aluminum | 0.06 | 0.12 |

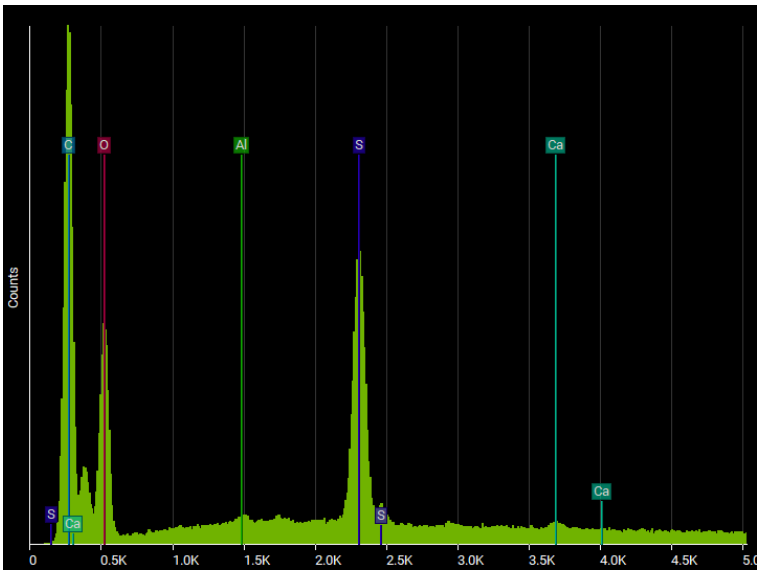



**Figure 21:** Analysis of elements in a sample of scoured wool sample “Merino Wirtenberg”

**Table 16:** Elemental analysis in a sample of scoured “Slovenian landras” fibres - Sample 2

| Element | Atomic% | Weight % |
|---|---|---|
| Carbon | 79.63 | 73.34 |
| Oxygen | 18.99 | 23.3 |
| Sulphur | 1.32 | 3.25 |
| Aluminum | 0.06 | 0.11 |



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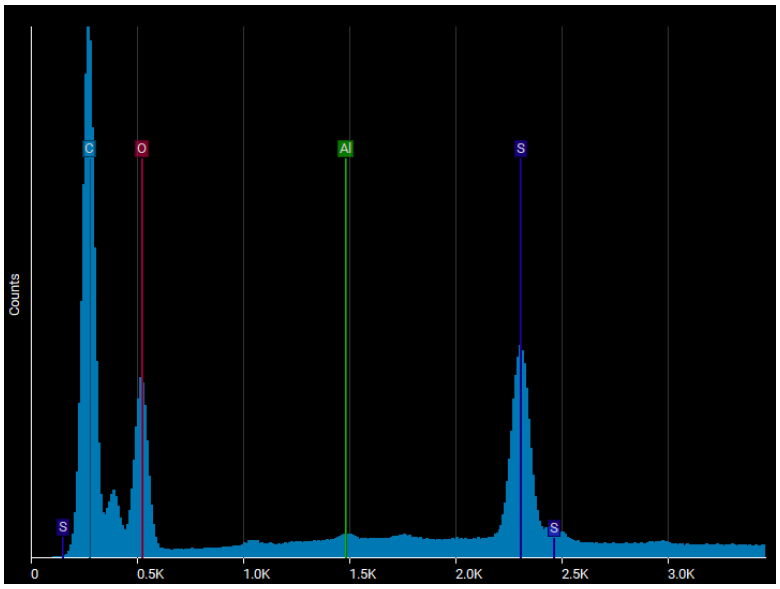



**Figure 22:** Analysis of elements in a sample of scoured wool sample – "Slovenian landras"

**Table 17:** Elemental analysis in a sample of scoured "Pramenka" wool – Sample 4

| Element | Atomic% | Weight % |
|---|---|---|
| Carbon | 79.63 | 73.34 |
| Oxygen | 18.99 | 23.3 |
| Sulphur | 1.32 | 3.25 |
| Aluminium | 0.06 | 0.11 |

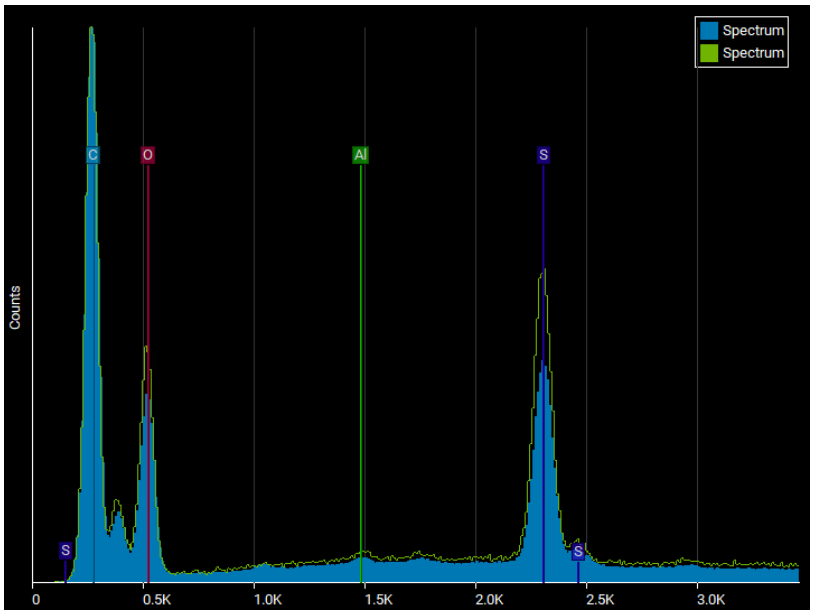



**Figure 23:** Analysis of elements in a sample of scoured wool "Pramenka"

The dominant weight in all samples belong to carbon (up to 80 %) and oxygen (app 20 %), while weight of sulphur and aluminium was significantly smaller. Calcium was identified just in "Merino



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Wirtemberg" scoured fibres. The absence of nitrogen can be explained by its removal or isolation in the scouring process.

## 2.3 Scouring of raw wool - proof of sustainable concept

The original contribution to a Green-Tex project is a research aimed to promotion of sustainable scouring of raw wool fibres with saponins isolated from chestnuts fruits as alternative - natural agents. The project tasks involved horse and sweet chestnuts as they serve as natural and green products that contain saponins, efficient degreasing and washing agents [33].

The fruits of the chestnut tree, which is widespread in rural and urban areas of Croatia, were selected as a source of saponins in this study. The horse chestnut, *Aesculus hippocastanum* L., is a deciduous plant from the *Sapindaceae* family whose fruits are not edible but are used for other purposes (source of starch, horse feed, medicinal preparations for veins, etc.). Chestnuts can be useful for washing as a source of the saponins they contain, which many consider as a natural – "green detergent". The saponins consist of four substances that make up 60% of the total mixture. Its extract consists mainly of escins and a mixture of triterpenoid saponins (α- and β-escin). Escins form a rich family of saponins (Saponosides) and are the most active components in the seeds of *Aesculum hippocastanum* [45].



a. b.

**Figure 24:** The chestnut fruits: a. *Castanea sativa* Mill – the sweet chestnut [46]; b. *Aesculus hippocastanum* L. – horse chestnut [47]

The sweet chestnut is a deciduous tree from the beech family (*Fagaceae*) [48]. They are particularly valued for their high carbohydrate content and gluten-free nature. The main component of fresh chestnuts is water and depending on the type of chestnut, the dry matter contains starch and polysaccharides (up to 25%) [49]. In contrast to horse chestnut, extracts from *Castanea sativa* Mill. can be a potential source of natural tannins with possible application in nutrition and therapy [50].

The fruits of the wild chestnut (hc) were collected in the western part of the city of Zagreb, and the fruits of the sweet chestnut (sc) in the Majur area, both in October 2024 and stored in dry and dark

conditions. A basic analytical assessment, extraction and isolation of the active ingredients from horse chestnut and sweet chestnut was performed as the first step.

The second step was focused on scouring performance of both chestnuts using domestic raw wool of the "Pramenka" sheep breed. After the scouring process, the spectral properties of the treated wool fibres and the composition of the wastewater were analysed in order to verify the concept of functionality and sustainability.

Raw wool fibres (R-WO) of the Pramenka breed from the Lika region were selected for scouring with horse chestnut and sweet chestnut suspensions.

### Preparation of chestnut fruit suspension

The suspension of horse and sweet chestnuts was prepared step by step by quartering 100 g of chestnuts and placing them in a laboratory beaker to which 2 litres of distilled water was added. The procedure for preparing the suspension was carried out on a magnetic stirrer at 400 rpm at 60 °C for 2 hours. The suspension was cooled, covered and left to stand overnight. In the morning, the peel was removed from the chestnut, the suspension was filtered, and the isolated chestnut was crushed in a blender and returned to the filtrate to obtain a suspension for the scouring process. Before scouring with the horse chestnut fruit, the wool yield was determined using an in-house procedure of conventional scouring (L) in five baths with interphase squeezing.

**Table 18:** Protocol for determination of wool yield

| Bath | Composition | Conditions |
|---|---|---|
| I | 2 g/L Felosan RG-N (CHT)*<br>0.05 g/L $Na_2CO_3$ | 50°C, 5 minutes |
| II | 1 g/L Felosan RG-N<br>0.3 g/L $Na_2CO_3$ | 50°C, 5 minutes |
| III | 0.2 g/L Felosan RG-N | 50°C, 5 minutes |
| IV | Warm distilled water | 50°C, 5 minutes |
| V | Cold distilled water | 5 minutes |

Scoured samples were dried under the constant mass was achieved.

### The process of scouring raw wool in chestnut fruit suspension

The scouring process raw wool fibres (800 g) with a suspension of horse and sweet chestnut was carried out in two stages, pre-scouring and scouring with intermediate rinsing. The pre-scouring procedure was carried out with tap water at a temperature of 30 °C for 15 minutes, followed by a rinsing cycle with cold tap water for 5 minutes. The waters from the pre-scouring and rinsing process were collected in separate containers (1-w, 2-w) to analyse their composition, Table 18.

The scouring process was continued by gently kneading the wool in a suspension of horse and sweet chestnuts (2 litres) for 15 minutes. The samples were then drained and rinsed in tap water at a temperature of 30 °C for 3 cycles, each cycle lasting 5 minutes.



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Wastewater from the pre-scouring (1-w, 2-w) and scouring process was collected in separate containers (1-hc, 2-sc) to analyse its composition (Table 19). The scoured wool samples were placed on a textiles mesh screen and allowed to air dry.

**Table 19:** Labels of wastewaters from pre-scouring and scouring of wool samples

| Wastewater label | | Wastewater composition |
|---|---|---|
| 1 | 1-w | pre-scouring of wool |
| | 1-hc | scouring with horse chestnut |
| 2 | 2-w | pre-scouring of wool |
| | 2-sc | scouring with sweet chestnut |

## Methods

In order to evaluate as objectively as possible, the effect of horse and sweet chestnut suspensions when scouring raw wool, the methods of analysis specified in Table 20 include:

(i) chestnut fruit
(ii) horse and sweet chestnut fruit suspensions
(iii) raw and scoured wool
(iv) wastewater.

**Table 20:** Analysis parameters

| Analysis parameters | | | |
|---|---|---|---|
| (i) chestnut fruit | (ii) chestnut fruit suspensions | (iii) wool | (iv) wastewater |
| Et-OH extract | pH | Wool Yield (Yld) | pH |
| Wa- isolate | | Whiteness degree (W) | Conductivity (κ) |
| | | Yellowness index (YI) | Turbidity (T) |
| | | Reflectance (R) | Chemical oxygen deman (COD) |
| | | Alkali solubility (AS) | Total Solids (TS) |
| | | FTIR | Total Suspended Solids (TSS) |
| | | | Total Disolved Solids (TDS) |

### (i) Chestnut fruit analysis

The analysis of horse and sweet chestnut fruits was carried out using methods for extracting the chestnut fruits in ethanol and isolating in water. These procedures was preceded by the preparation of the chestnut fruit by dividing it into four parts in order to obtain an approximately equal mass of both fruits. The fruits were dried and prepared gravimetrically using a Kern balance, model ALJ 220-5DNM, Germany. After accurate weighing of the dried fruits of horse (hc-f) and sweet chestnut (sc-f), the extraction procedure in 200 mL ethanol (Et-OH) and the isolation procedure in water (Wa) were started. Soxhlet extraction of chestnut fruits in Et-OH was carried



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out for 2 hours. Filtration and combined evaporation of extract in a Soxhlet and in a dryer were then carried out until a constant mass was obtained.

Isolation in water was carried out in an Erlenmeyer flask on a hot plate for 1 hour. After this time, the contents were filtered into previously weighed Erlenmeyer flasks using a sintering funnel. The filtrate was then evaporated to dryness on a water bath. The flasks with the residue were then placed in a desiccator, cooled and then weighed. After extraction in Et-OH, isolation in water (Wa) and evaporation, the content of extracted and isolated components from the horse and sweet chestnut fruits was determined.

**(ii) Horse and sweet chestnut fruit suspensions**

The pH value of horse (hc-s) and sweet chestnut (sc-s) suspensions was measured with a SevenCompact™ Duo S213 multimeter from Mettler Toledo, Hong Kong before and after crushing the fruit in a blender.

**(iii) Analysis of scoured wool**

To determine the wool yield (Yld), samples of raw wool were dried and weighed before and after scouring using the conventional procedure [50].

Samples of raw wool and wool scoured by the conventional method and suspensions of wild and sweet chestnut were analysed by the reflectance spectrophotometry method on a DataColor 300, Switzerland, to determine their reflectance curves (R), and samples of wool scoured in suspensions of chestnut fruits were measured for whiteness (W) and yellowness index (YI).

The evaluation of the wool fibre surface chemistry was performed with a Spectrum 100 FTIR spectrometer (Perkin Elmer, Buckinghamshire, UK) using the attenuated total reflection method. Five different measurements for each fibre were evaluated, and the average value was considered. All spectra were registered from 4000 $cm^{-1}$ to 380 $cm^{-1}$, with a resolution of 4 $cm^{-1}$ and four scans. To compare the FTIR spectra they were baseline corrected, smoothed and normalized on the amide I vibration at 1627 $cm^{-1}$.

The alkali solubility (AS) test was performed according to ISO 3072:1975, Wool — Determination of solubility in alkali and is sensitive for the detection of acid damage, because under normal, moderately strong alkaline conditions the amount of protein degraded provides a direct measure of the hydrolysis of the main chains. The procedure is carried out to process a mass of about 1 g of finely divided wool fibres ($w_1$) in 100 mL of NaOH solution (0.1 m) at a temperature of 65 °C for 60 minutes, shaking for 5 seconds every 15 minutes. The precipitate obtained is filtered and washed in several cycles with distilled water, twice with 200 mL acetic acid and in six cycles with water. The residue is dried ($w_2$) and the mass loss is determined, on the basis of which the alkali solubility (AS) is calculated according to equation 1:

$$S = \frac{w_1 - w_2}{w_1} \cdot 100 \quad (1)$$

**(iv) Analysis of scouring wastewater**

The wastewater from the pre-scouring process and the process of scouring raw wool in horse and sweet chestnut suspensions was analysed by measuring and determining pH, conductivity,



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turbidity, chemical oxygen demand (COD), total solids (TS), total suspended solids (TSS) and TDS (total dissolved solids). The physico-chemical properties of the wastewater were monitored by determining the pH by standard method according to HRN EN ISO 10523:2012: Water quality - Determination of pH and conductivity using a SevenCompact™ Duo S213 multimeter from Mettler Toledo, HRN EN 27888:2008: Water quality - Determination of electrical conductivity. Turbidity was measured according to HRN EN ISO 7027-1:2016: Water quality - Determination of turbidity with the TU5200 turbidimeter from Hach and COD using HRN ISO 15705:2003, Water quality - Determination of chemical oxygen demand index (ST-COD) - Small-scale sealed-tube method, with the HT200S Thermostat and DR3900 Laboratory Spectrophotometer for water analysis, both from Hach Lange GmbH, Germany. TSS, TS and TDS were determined according to in-house methods based on standard filtration (glass fibres filter, GF-pore size 0.7 µm, Ahlstrom-Munksjö, Germany) and gravimetric methods using the Kern balance, model ALJ 220-5DNM, Germany.

Results of preliminary analyses of the applicability of horse and sweet chestnut fruits for the process of scouring raw wool by four analytical approaches using adapted methods are presented.

The results of extraction of substances from horse and sweet chestnut fruits (f) in ethanol, Et-OH and isolation in water, Wa are presented in Table 21.

**Table 21:** Isolated substances content

| Sample | % extract (Et-OH) | % isolate (Wa) |
|---|---|---|
| hc-f | 1.15 | 18.66 |
| sc-f | 2.26 | 13.44 |

The results of the percentage of isolates in Et-OH and water differ in quantity. The mass fraction of the isolates extracted in ethanol is significantly lower than the fraction isolated in water. It can be assumed that the isolates in alcohol consist of saponins and some other alcohol-soluble substances, as this method is used to determine surfactants in detergents. The proportion of isolates from sweet chestnut is twice as high as that from horse chestnut, while the proportion of isolates in water is many times higher than that in alcohol and the proportion from horse chestnut is higher than that from sweet chestnut. A possible explanation for the higher proportion of isolates in the horse chestnut could be a starchy substance. The analysis of the horse chestnut and sweet chestnut suspensions included the pH of the supernatant and the suspension obtained by homogenisation of the supernatant and the crushed chestnut fruit, Table 22.

**Table 22:** pH suspensions of horse and sweet chestnuts

| Sample | pH | |
|---|---|---|
| | supernatant | suspension |
| hc-s | 5.89 | 6.11 |
| sc-s | 5.46 | 5.79 |

The results for the pH of the solution and the suspension differ by about 0.4 pH units, and higher values were measured for the horse chestnut for both the supernatant and the suspension. These relationships confirm the differences in the composition of these two fruits as described in the literature.

The yield of raw wool (Yld) scoured under laboratory conditions was 63.1%, which is consistent with previous analyses of wool from other breeds [51].

Figure 25 shows photos of raw wool (R-WO), wool scoured with chestnut fruits (hc-WO, sc-WO) and wool scoured under laboratory conditions (L-WO) to illustrate the effect achieved by the scouring process.

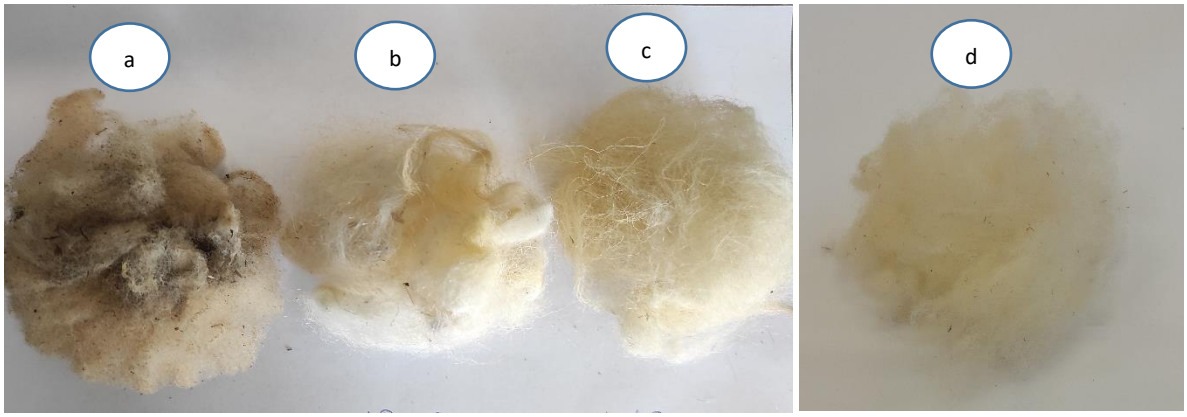



**Figure 25:** Photos of wool samples: a. R-WO, b. hc-WO, c. sc-WO; d. L-WO

The images of the samples in Figure 25b-d show that impurities and dirt were removed during the scouring process. The wool sample scoured in laboratory conditions using a stepwise process (L-WO) contained less residual vegetable impurities than the wool samples scoured in horse chestnut and horse chestnut suspensions.
The reflectance curves of the raw wool samples and the wool scoured by conventional and sustainable agents are shown in Figure 25, while the degree of whiteness, yellowing index and alkaline solubility of the wool samples scoured with chestnut fruits are shown in Table 23.



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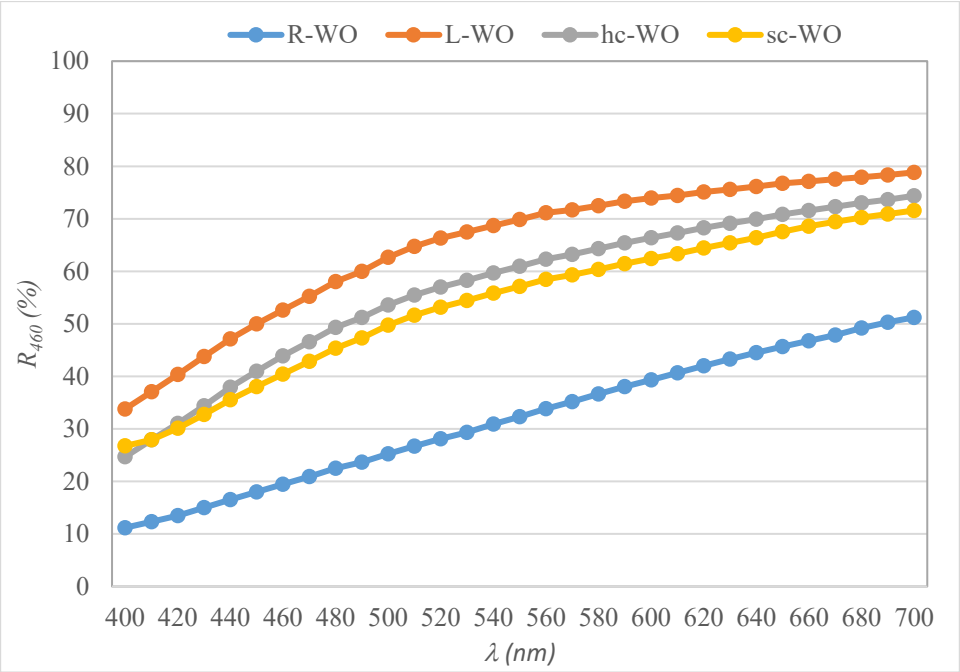



**Figure 26:** Reflectance curves of wools samples before and after scouring process

The reflectance curves of the wool scoured with conventional process and in horse chestnut and sweet chestnut suspensions, Figure 26, have the same shape in the entire spectral range (400 - 700 nm). The reflectance values of the wool sample scoured in the laboratory are the highest, confirming a better effect compared to the samples scoured in horse chestnut suspension. Considering the conditions of the scouring procedures, the differences obtained are as expected. The reflectance of the wool sample scoured in horse chestnut suspension is about 5 units higher in the 460 to 700 nm range than the values for the wool sample scoured in sweet chestnut suspension.

**Table 23:** Whiteness, yellowness index and alkali solubility of scoured wool samples

| Sample | W | YI | AS (%) |
|---|---|---|---|
| hc-WO | -42.2 | 39.24 | 11.87 |
| sc-WO | -46.9 | 40.07 | 15.10 |

The spectral values (whiteness and yellowing index) in Table 23 confirm the yellowish tone of the scoured samples. The differences in the yellowness index are small, while the whiteness values of the wool samples scoured in horse chestnut suspension are about 4 units higher than those of the samples scoured in sweet chestnut suspension. This is consistent with the reflectance values in the wavelength which belong to blue part of the spectrum, and Figure 27 show the FTIR of the raw wool sample, scoured under laboratory conditions and scoured in horse chestnut suspension.



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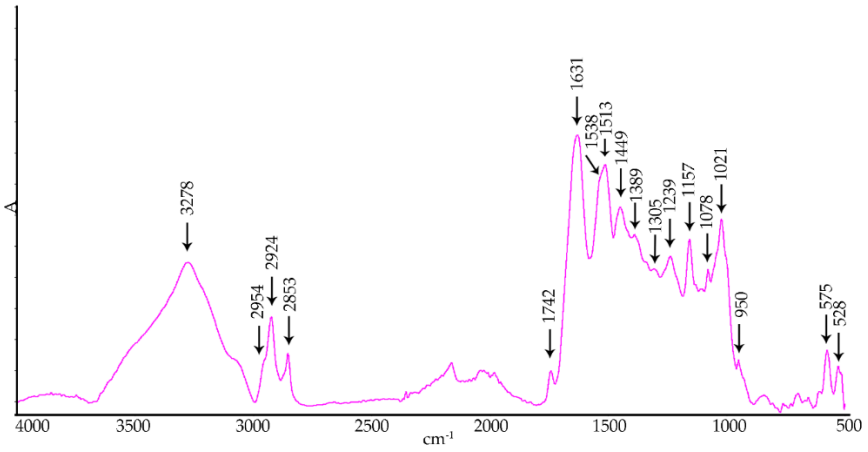



**Figure 27:** FTIR spectra of wool sample scoured in the laboratory conditions.

FTIR spectra of scoured wool is presented in Figure 27 and show peaks characteristic for the peptide bond that is a basis for protein chains. Bands within the range from 3700 $cm^{-1}$ to 2700 $cm^{-1}$ are attributed to N-H, O-H, $-CH_3$ and $-CH_2$ groups, while CH groups are determined with 1449 $cm^{-1}$ and 1389 $cm^{-1}$ peaks. Peaks attributed to CH groups are more pronounced in w-WO than in hc-WO or sc-WO suggesting less breaking of side chains in polypeptide chain during scouring process. Peaks at 1742 $cm^{-1}$ and 1305 $cm^{-1}$ indicate lanolin presence while disappearance of peaks at 1462-1468 or 1174 $cm^{-1}$ suggest less lanolin in comparison to the chestnut scoured wool (presented in Figure 28).

The stretching vibration of amide I is appeared at 1631 $cm^{-1}$ while amide II peaks are visible at 1538 and 1513 $cm^{-1}$. Peak at 1239 $cm^{-1}$ is visible in all tested samples and is assigned to the C-N group from amide III [2]. Peaks within the range 1200 -1000 $cm^{-1}$ are assigned to sulphur-oxygen groups of keratin. C-H bending is attributed to peak at 950 $cm^{-1}$. S-S stretching vibrations corresponds to peak at 528 $cm^{-1}$ while peak at 575 $cm^{-1}$ is attributed to C-S stretching from disulphide [52,53].

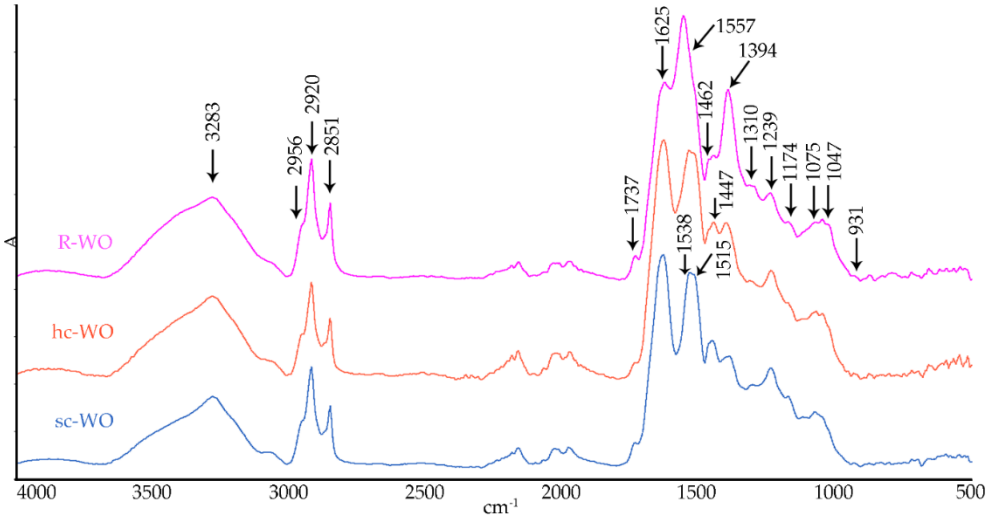



**Figure 28:** FTIR spectra of R-WO, hc-WO and sc-WO samples.

FTIR spectra of wool samples show bands associated to the peptide bond (-CO-NH-) which is characteristic for the polypeptide chain structure [53].
A broad absorption band is visible within the range 3500-3200 $cm^{-1}$ and is attributed to the overlapping of N-H and O-H groups [52].
Peak at 2956 $cm^{-1}$ is attributed to $CH_3$ group. Intensity of this band is highest for R-WO sample and lowest for hc-WO sample. Peaks at 2920 $cm^{-1}$ and 2851 $cm^{-1}$ are attributed to the symmetrical and asymmetrical stretching of the $CH_2$ group [54]. FTIR spectra suggest the lowest intensity of these peaks for hc-WO sample indicating less of vegetable and other organic impurities. Peaks in the range from 2700-1900 $cm^{-1}$ are not attributed to wool fibre, therefore we assumed they could be assigned to impurities found in raw wool fibre since intensities of these bands decrease in order R-WO, sc-WO and hc-WO.
Peaks at 1735-1737 $cm^{-1}$, 1462-1468 $cm^{-1}$, 1303-1312 $cm^{-1}$ and 1174 $cm^{-1}$ are associated with lanolin and they are more pronounced in the R-WO sample and less in hc-WO sample indicating better efficiency of the horse chestnut on scouring effects [55].
The stretching vibration of amide I (C=O bond) appeared at 1625 $cm^{-1}$ for R-WO sample and is slightly moved to the left region of spectra, to 1631 $cm^{-1}$ for hc-WO and sc-WO. Amide II peaks appeared at 1557 $cm^{-1}$ for R-WO and at 1538 and 1515 $cm^{-1}$ for other tested samples. Bending vibrations of C-N-H from amide II is assigned to 1515 cm-1 band. It is obvious shifting of peaks to lower wave numbers compared to raw wool. Peak at 1239 cm-1 is visible in all tested samples and is assigned to the C-N group from amide III [53].
There is significant difference in the two characteristic peaks (amide I and amide II) of raw wool but after scouring with both chestnut species this difference is almost unnoticeable. Therefore, less or no difference between the two peaks in intensity suggests better quality of scoured wool fibres [52].
Peaks at 1447 $cm^{-1}$ and 1386-1400 $cm^{-1}$ are attributed to -CH group and the less intensity of these peaks can be observed in sc-WO sample indicating minor amount of side chains in polypeptide chains and thus more close packing of the protein molecules [56].
Peaks at 1047 $cm^{-1}$ and 1075 $cm^{-1}$ are assigned to the sulphur-oxygen groups (i.e. S=O stretching vibrations from cysteic acid [52,54].
Peak at 931-930 $cm^{-1}$ is broad peak of low intensity assigned to C-O-C bond which decrease in order R-WO, sc-WO and hc-WO [54].
When analysing scoured wool, the alkali solubility (AS) of the scoured samples was taken into account, although this method is more suitable for bleached wool samples. Undamaged wool has a value of 9 to 12% and the solubility increases with the degree of damage. The alkali solubility of wool scoured in horse chestnut suspension (AS=11.87%) is lower than the value obtained for wool scoured in sweet chestnut suspension (AS=15.10%).

The analysis of wastewater from the process of pre-scouring in water (1-w, 2-w) and scouring in suspensions of horse chestnut (1-hc) and sweet chestnut (2-sc) included physico-chemical indicators in Table 24.

**Table 24:** Physico-chemical parameters of pre-scouring and scouring wastewaters

| Wastewater sample | pH | κ (µS/cm) | M (FNU) | COD (mg $O_2$/L) | TS (mg/L) | TSS (mg/L) | TDS (mg/L) |
|---|---|---|---|---|---|---|---|
| 1-w | 8.86 | 2019.10 | 1004 | 472 | 4036 | 485.3* | 2552.5 |
| 1-hc | 5.59 | 518.06 | 366 | 460 | 2091 | 521.6 | 1094.3 |
| 2-w | 9.23 | 2606.03 | 972 | 120 | 4778 | 724.7* | 3110 |
| 2-sc | 6.29 | 480.06 | 222 | 74 | 1880 | 1178.6 | 662 |

The values of the individual physico-chemical parameters of the wastewater from pre-scouring and scouring in suspensions of horse chestnut and sweet chestnut in Table 24 are different, which is to be expected.

The pH value in the pre-scouring cycles confirms the alkalinity of the wastewaters. However, the measured differences of around 0.4 pH units were not to be expected, as the same fleece was treated in water in a pre-scouring. These differences can be attributed to the conditions of the manual treatment with gentle kneading and defibrillation of the wool, which was carried out by different hands. The pH values of the wastewater resulting from the scouring of wool with horse chestnut and sweet chestnut are significantly lower and correspond to the values determined for pure suspensions.

A similar ratio of conductivity and turbidity values was determined for wastewater from the pre-scouring and scouring of wool in suspensions of horse chestnut and sweet chestnut.

According to [22] the environmental effect of various wastewaters is usually described by chemical oxygen demand (COD), which can be as high as 45 000 mg/L for wool scouring wastewater in industrial applications. The high COD values of the wastewater from the wool scouring process are caused by the emulsified wool grease, while water-soluble components, the suint, have a lower influence on the COD [7].
The COD values shown in Table 24 are extremely low for all wastewaters and are not consistent with other physico-chemical parameters and previously published data [26,38].
The total solids (TS) in the pre-scoured wastewaters are extremely high, while the TS of the two scouring wastewaters (1-hc, 2-sc) correspond to results of previous research [26]. The TDS value is extremely high in the pre-scouring wastewater and many times lower in the scouring wastewater. Some technical problems occurred during the determination of the TSS (*), therefore that a real explanation of the values obtained was not possible.

## Final remarks

The preliminary results of the analysis of the scouring process of raw wool fibres (R-WO) of the "Pramenka" breed with suspensions of horse chestnut and sweet chestnut showed the potential in the application, but also the need for further research and in-depth analysis of the fruits, the suspension, the properties of the scoured wool and the wastewater. Considering the nutritional value of sweet chestnut, further research will focus only on horse chestnut. In addition, the fleece of other Croatian sheep breeds, especially in the Majur region, was selected. A comparison of this



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natural and green agent with products available on the market was realized and results are shown in 2.4 subchapter of Green-Tex portfolio.

## 2.4 Scouring of raw wool with natural and petroleum-derived agents

Four agents, tri petroleum derived and one natural green - horse cheststnut were selected for a scouring process of raw wool - sample 0 (“Merino Wirtemberg”) sheep breed using bath ratio 1:20.

1. Felosan RG-N, alkalized with $Na_2CO_3$
2. Horse chestnut suspension
3. Sera Wash M-OWS with Sera Wet C-ANS
4. IEC 60456 Reference Wool Detergent

Felosan RG-N is a special compound with remarkable emulsifying properties for oil and grease stains, excellent wetting properties and a very good washing power, supplied by CHT, Germany alkalized with soda.
Sera Wash M-OWS is an alkyl polyethylene glycol ether, a low-foaming cleaning and dispersing agent combined with Sera Wet C-ANS, a preparation of anionic, non-ionic and complexing agent, low foaming, alkali resistant washing and wetting agent with excellent dispersing power for pre-treatment of all fibre types, both supplied by DySTAR, Germany.

Horse chestnut suspension prepared from fruits of local chestnut collected in September 2024 and freezed. IEC 60456 Reference Wool Detergent supplied by wfk Germany, formulated by following ingredients:

- Linear sodium alkyl benzene sulfonate, 50% aqueous solution 10 %
- Ethoxylated fatty alcohol $C_{13}/_{15}$ (7 EO) 5 %
- Anti Foam (fatty acid) 1 %
- Phosphonates 0.5 %
- Sodium Hydroxide to pH 8.5
- 1,2-Benzisothiazolin-3-on 100 ppm
- Water approx. 78 %

The process phases (pre-scouring, scouring-I, scouring-II, scouring-III and rinsing) and the basic technological parameters (mass of raw wool, temperature, time) were identical. The concentration of scouring agents used was adjusted to the manufacturer's recommendation, while natural scouring bath was prepared as a suspension of chestnuts.

Scouring parameters are presented in Tables 25 – 28.

**Table 25:** Scouring parameters with alkalized Felosan RG-N (FA)

| Bath | Step | Composition | Conditions | pH |
|---|---|---|---|---|
| 0 | Pre-scouring | Water | 50°C, 5 minutes | - |
| I | Scouring | 2 g/L Felosan RG-N<br>0.5 g/L $Na_2CO_3$ | 50°C, 10 minutes* | 8.8 |
| II | Scouring | 1 g/L Felosan RG-N<br>0.35 g/L $Na_2CO_3$ | 50°C, 10 minutes* | 8.4 |
| III | Scouring | 0.2 g/L Felosan RG-N | 50°C, 10 minutes | 5.4 |
| IV | Rinsing | Warm distilled water | 50°C, 5 minutes | |
| V | Rinsing | Cold distilled water | 5 minutes | |
| VI | Rinsing | Cold distilled water | 5 minutes | |

*the time was prolonged from 5 to 10 minutes as a result of use of scouring bath poured in cold cuvette

**Table 26:** Scouring parameters with horse chestnut suspension (HC)

| Bath | Step | Composition | Conditions | pH |
|---|---|---|---|---|
| 0 | Pre-scouring | Water | 50°C, 5 minutes | - |
| I | Scouring | Suspension of horse chestnut | 50°C, 10 minutes* | 4.8 |
| II | Scouring | Suspension of horse chestnut | 50°C, 10 minutes* | 4.8 |
| III | Scouring | Suspension of horse chestnut : water (1:1) | 50°C, 5 minutes | 5.6 |
| IV | Rinsing | Warm distilled water | 50°C, 5 minutes | |
| V | Rinsing | Cold distilled water | 5 minutes | |
| VI | Rinsing | Cold distilled water | 5 minutes | |

*the time was prolonged from 5 to 10 minutes as a result of use of scouring bath poured in cold cuvette

**Table 27:** Scouring parameters with Sera Wash M-OWS supplemented by Sera Wet C-ANS (SW2)

| Bath | Step | Composition | Conditions | pH |
|---|---|---|---|---|
| 0 | Pre-scouring | Water | 50°C, 5 minutes | - |
| I | Scouring | 1 g/L Sera Wash M-OWS<br>0.5 g/L Sera Wet C-ANS | 50°C, 10 minutes* | 5.1 |
| II | Scouring | 1 g/L Sera Wash M-OWS<br>0.5 g/L Sera Wet C-ANS | 50°C, 10 minutes* | |
| III | Scouring | 1 g/L Sera Wash M-OWS<br>0.5 g/L Sera Wet C-ANS | 50°C, 10 minutes | |
| IV | Rinsing | Warm distilled water | 50°C, 5 minutes | |

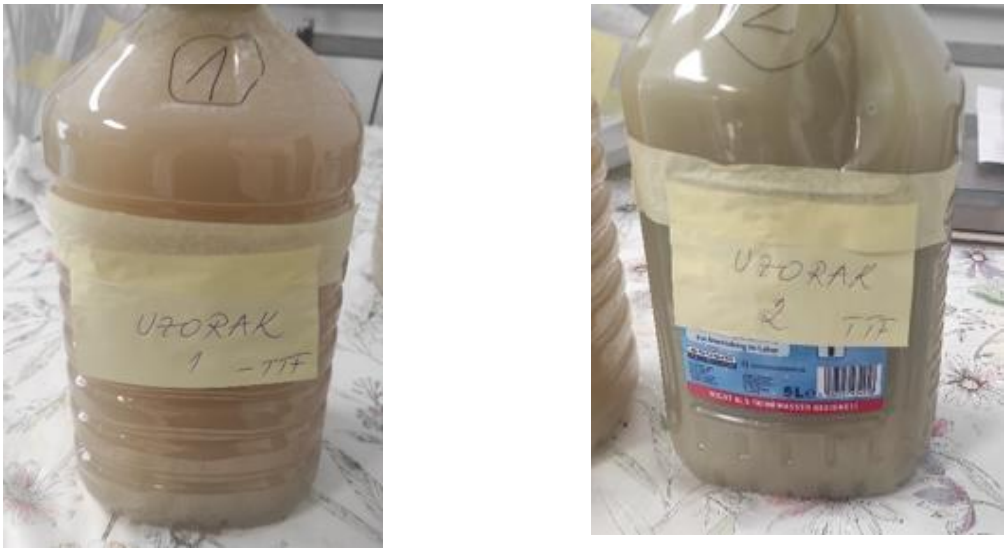
| | | | | |
|---|---|---|---|---|
| V | Rinsing | Cold distilled water | 5 minutes | |
| VI | Rinsing | Cold distilled water | 5 minutes | |

**Table 28:** Scouring parameters with IEC Wool Reference Detergent (RD)

| Bath | Step | Composition | Conditions | pH |
|---|---|---|---|---|
| 0 | Pre-scouring | Water | 50°C, 5 minutes | - |
| I | Scouring | 2 g/L IEC Wool detergent | 50°C, 10 minutes* | 5.2 |
| II | Scouring | 2 g/L IEC Wool detergent | 50°C, 10 minutes* | |
| III | Scouring | 2 g/L IEC Wool detergent | 50°C, 5 minutes | |
| IV | Rinsing | Warm distilled water | 50°C, 5 minutes | |
| V | Rinsing | Cold distilled water | 5 minutes | |
| VI | Rinsing | Cold distilled water | 5 minutes | |

Wastewaters from the pre-scouring, scouring and rinsing processes collected from two processes, alkalized Felosan RG-N (WW-FA) and horse chestnut (WW-HC) were analysed for its composition. The scoured wool samples were placed on a textiles mesh screen and allowed to air dry at ambient conditions.

Collected wastewaters prepared for analysis by standard methods are presented in Figure 29.




a. b.

**Figure 29:** Collected wastewaters: a. after scouring with alkalized Felosan RG-N (WW-FA); b. after scouring with suspension of horse chestnut (WW-HC)

The analysis of scoured wool with four agents and wastewaters from two agents (WW-AF and WW-HC) was performed by evaluation parameters specified in Table 29.

**Table 29:** Evaluation criteria

| Wool | Wastewater | Quality criteria |
|---|---|---|
| Alkali solubility (AS) | $BOD_5$ | The quality and health safety of water |
| Yield (Yls) | COD | |
| Residual grease (RG) | Sulphate | |
| Yelowness index (YI) | Ammonium | |
| pH of aqueous extract (pH) | Total nitrogen | |
| Dyeability | Total phosphorous | |
| | Dissolved sufides COD | |
| | Copper (Cu) | Analytical assessment of metal content |
| | Zinc (Zn) | |
| | Cadmium (Cd) | |
| | Total chrom | |
| | Manganese (Mn) | |
| | Lead (Pb) | |
| | Iron (Fe) | |
| | Lipophilic substances of low volatility (Total oil and grease) | Environmental hygiene |
| | Total Organic Carbon (TOC) | |
| | Dissolved Organic Carbon (DOC) | |



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# Results

### Wool samples reflectance

Reflectance curves of raw and scoured wool are shown in Figure 30.

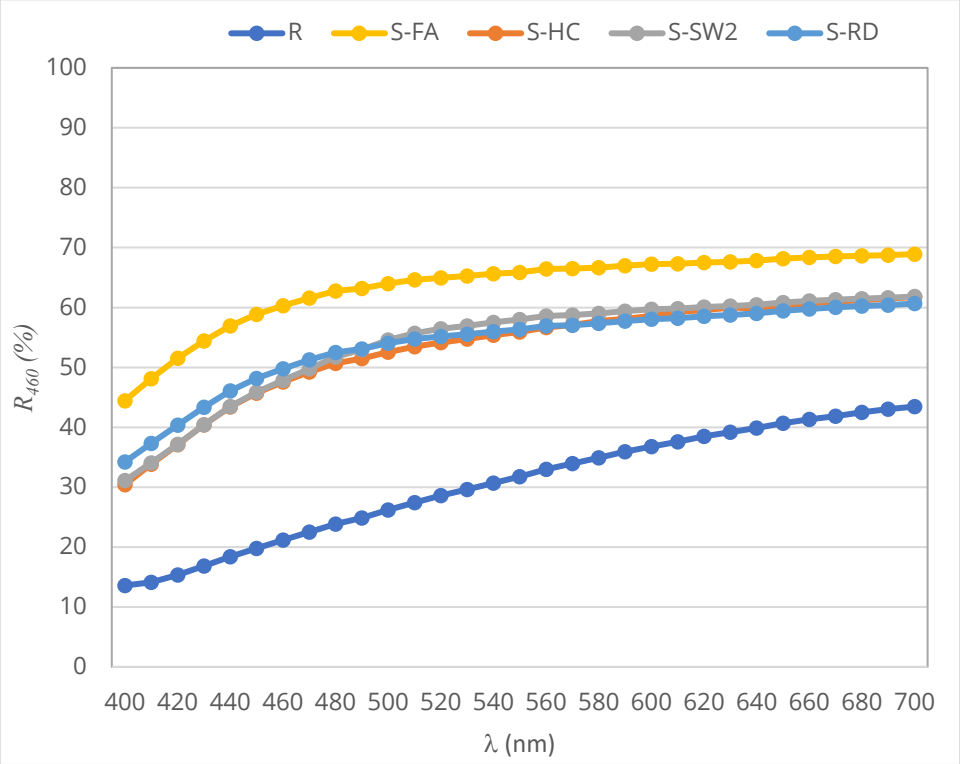



**Figure 30:** Reflectance curves of raw and scoured samples

The best scouring performance was achieved in a process with alkalized Felosan RG-N (S-FA). Other agents, chestnut (S-HC), SeraWash (S-SW$^2$) and IEC wool reference detergent (RD) gave similar reflectance values in the whole wavelength.

### Evaluation parameters of scoured wool

**Table 30:** Characteristic parameters of scoured wool

| Scoured fibers | AS (%) | Yls (%) | YI | $W_{CIE}$ | pH |
|---|---|---|---|---|---|
| S-FA | 9.9 | 64.2 | 12.74 | 32.3 | 6.4 |
| S-HC | 14.8 | 66.2 | 22.31 | -1.8 | 5.6 |
| S-SW$^2$ | 11.5 | 65.9 | 23.29 | -6.1 | 6.2 |
| S-RD | 14.0 | 62.8 | 17.41 | 10.6 | 6.1 |

Table 30 gives results of different evaluation parameters as follows: less alkali solubility (S-FA) and a high alkali solubility (S-HC and S-RD); very similar wool yields for all samples; yellowness index:



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the raw wool fibres as a reference have YI 48.95, descending followed by by S-SW[2], S-HC, S-RD and S-FA.

**Dyeability**

Sustainable approach which is respected in the Green-Tex project is promotion of natural sources, therefore scoured samples were tested by dyeability test with natural dye. Figure 31 gives a view of different natural dye sources, and from which the onion was selected for dyeing test on four scoured wool samples.

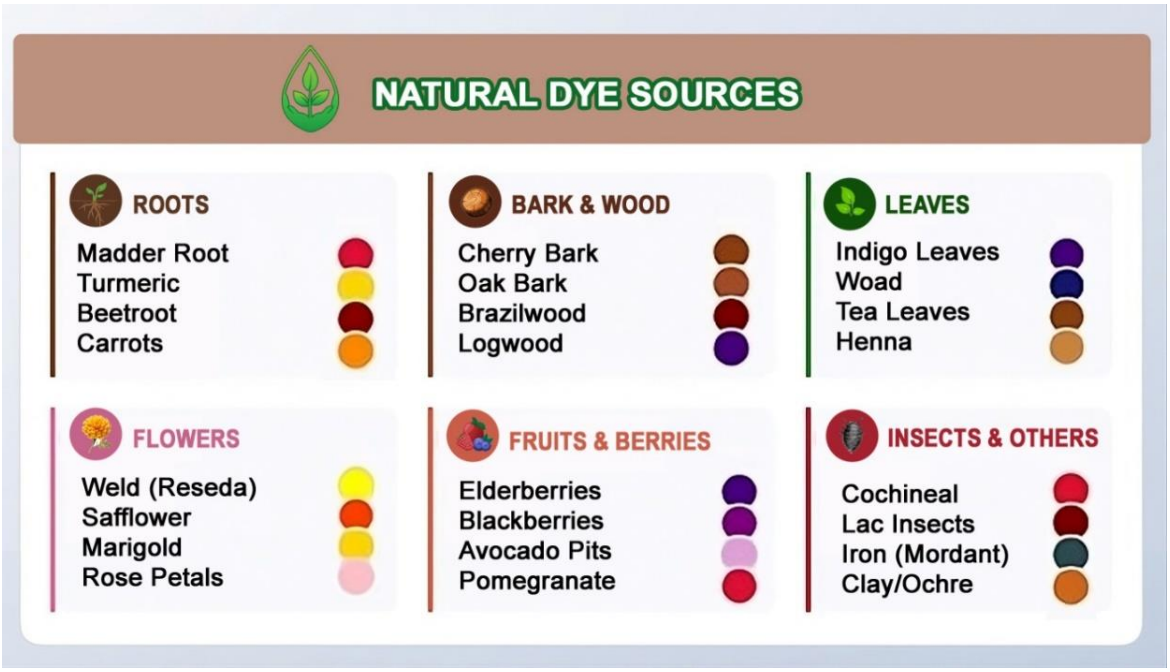



**Figure 31:** Sources for natural dyes (design by T. Dekanić)

Dyebility of scoured wool samples was test by natural dye prepared from red onion shells, Figure 32. Onion shells (red onion, *Allium cepa* L.) are rich in flavonoids, the most abundant of which is quercetin, followed by quercetin glucoside and kaempferol. Considering their chemical structure, flavonoids are the most common yellow plant dyes, therefore onion shell is also natural dye giving a dark yellow colour [58,59].



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**Figure 32:** Natural dye - red onion in different forms: powder, solution and shell

Scoured wool fibres and scoured wool fibres pretreated with potassium aluminum sulfate dodecahydrate in concentration of 2% were dyed with onion solution, Figure 33.

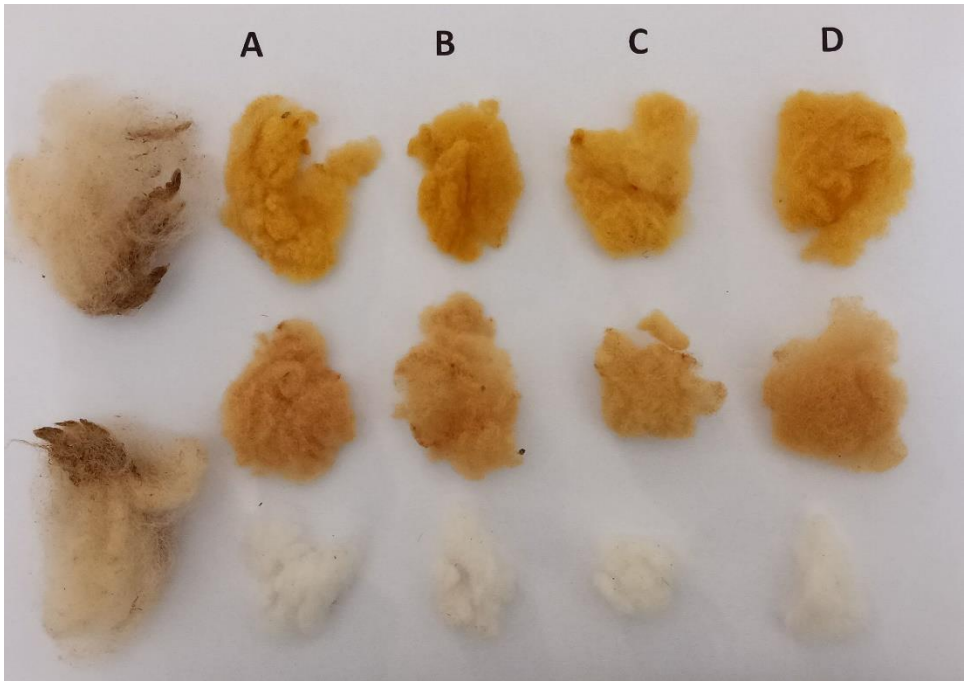



**Figure 33:** „Pramenka“ wool samples, raw, scoured, dyed and pretreated and dyed: A. S-FA; B. S-HC; C. S-SW$^2$; D. S-RD

Colour strength (K/S) of dyed wool fibres by both procedures is specified in Table 31.

**Table 31:** Color strength (K/S) value of scoured wool samples

| Dyed scoured wool fibers | K/S | K/S* |
|---|---|---|
| S-FA | 19.10 | 18.69 |
| S-HC | 28.95 | 24.02 |
| S-WS[2] | 22.29 | 19.75 |
| S-RD | 29.55 | 22.2 |

*Pretreated and dyed

K/S value represent colour strength, therefore scoured wool fibres dyed with onion have different K/S values; A higher K/S values have S-HC and S-RD. Pretreatment, and dyeing resulted with a change in K/S values, therefore a high K/S possesses S-HC.

### Characterisation of scouring wastewaters

Despite the positive properties mentioned, wool is considered solid waste, the disposal of which is challenging and complex. Therefore, the development and optimization of the row wool scouring process should be based on the purification of wastewater, the environmentally friendly extraction of lanolin and the use of environmentally friendly wool-based materials [60].

### The quality and health safety of water

| Parameter | Method |
|---|---|
| $BOD_5$ | HRN EN 1899-1:2004, modified |
| Sulphate | ASTM D516-22 |
| Ammonium | HRN ISO 7150-1:1998 |
| Total nitrogen | HRN EN 25663:2008; HRN EN 26777:1998; SM 24th Ed. 2023.4500-$NO_3$ B |
| Total phosphorous | SOP-203-051 (Version 01) |
| Dissolved sufides | HRN ISO 10530:1998 |
| COD | HRN ISO 15705:2003, |

**Table 32:** Wastewaters results of the quality and health safety

| Parameter | Unit | WW-FA | WW-HC | U** | MAC | CA |
|---|---|---|---|---|---|---|
| $BOD_5$ | mg/L $O_2$ | 746 | 3747 | | ≤ 250 | No |
| Sulphate | mg/L $SO_4^{2-}$ | 55 | 24.0 | | ≤ 200 | + |
| Ammonium | mg/L N | 0.69 | 7.73 | | | - |
| Total nitrogen | mg/L N | 29.7 | 169.3 | | ≤ 50 | + |
| Total phosphorous | mg/L P | 6.94 | 25.1 | ± 0.90 | ≤ 10 | + |
| Dissolved sufides | mg/L | < 0.050 | < 0.050 | | ≤ 1 | + |
| COD | mg/L $O_2$ | 4.350 | 11.260 | | | |

CA-conformity assessment



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**Analytical evaluation**

| Parameter | Methods |
|---|---|
| Copper (Cu) | HRN EN ISO 17294-1:2024; HRN EN ISO 17294-2:2023 (ISO 17294-2:2023, corrected version 2024-02; EN ISO 17294-2:2023) |
| Zinc (Zn) | HRN EN ISO 17294-1:2024; HRN EN ISO 17294-2:2023 (ISO 17294-2:2023, corrected version 2024-02; EN ISO 17294-2:2023) |
| Cadmium (Cd) | HRN EN ISO 17294-1:2024; HRN EN ISO 17294-2:2023 (ISO 17294-2:2023, corrected version 2024-02; EN ISO 17294-2:2023) |
| Total chrome | HRN EN ISO 17294-1:2024; HRN EN ISO 17294-2:2023 (ISO 17294-2:2023, Corrected version 2024-02; EN ISO 17294-2:2023) |
| Manganese (Mn) | HRN EN ISO 17294-1:2024; HRN EN ISO 17294-2:2023 (ISO 17294-2:2023, Corrected version 2024-02; EN ISO 17294-2:2023) |
| Lead (Pb) | HRN EN ISO 17294-1:2024; HRN EN ISO 17294-2:2023 (ISO 17294-2:2023, Corrected version 2024-02; EN ISO 17294-2:2023) |
| Iron (Fe) | DIN 38406-32:2000 |

**Table 33:** Wastewaters results of analytical evaluation

| Parameter | Unit | WW-FA | WW-HC | U** | MAC | CA |
|---|---|---|---|---|---|---|
| Copper (Cu) | mg/L | < 0.050 | 0.17 | - | ≤ 0.5 | + |
| Zinc (Zn) | mg/L | 0.17 | 0.32 | ± 0.014 | ≤ 2 | + |
| Cadmium (Cd) | mg/L | < 0.020 | < 0.020 | - | ≤ 0.1 | + |
| Total chrome | mg/L | < 0.050 | < 0.050 | - | ≤ 0.5 | + |
| Manganese (Mn) | mg/L | 0.062 | 0.10 | ± 0.0040 | ≤ 4 | + |
| Lead (Pb) | mg/L | < 0.050 | < 0.050 | - | ≤ 0,5 | + |
| Iron (Fe) | mg/L | 0.78 | 0.79 | ±0,080 | ≤ 10 | + |

**Analytical assessment of metal content**

| Parameter | Methods |
|---|---|
| Lipophilic substances of low volatility (Total oil and grease) | SM 24th Ed. 2023, 5520 B |
| Total Organic Carbon (TOC) | HRN EN 1484:2002 |
| Dissolved Organic Carbon (DOC) | HRN EN 1484:2002 |

**Table 34:** Wastewater results of analytical assessment of metal content

| Parameter | Unit | WW-FA | WW-HC | U** | MAC | CA |
|---|---|---|---|---|---|---|
| Lipophilic substances of low volatility (Total oil and grease) | mg/L | 187.5 | 488.8 | | ≤ 100 | No |
| Total Organic Carbon (TOC) | mg/L C | 1005 | 2285 | ± 649 | | - |
| Dissolved Organic Carbon (DOC) | mg/L C | 784 | 1457 | ± 414 | | - |

When the declaration of conformity for accredited methods issued, a binary decision rule based on simple acceptance is applied. The conformity assessment (CA) of the measurements result is determined without the contribution of the measurement uncertainty.



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**Declaration of conformity – Sample WW-FA**

The results of the tested parameters in the scouring wastewater sample, WW-FA before discharge into the public sewage system do NOT correspond to the maximum permissible concentrations according to Annex I. of the Regulation on Wastewater Emission Limits (Official Gazette, OG 26/2020), because of increased concentrations of organic substances ($BOD_5$) and non-volatile lipophilic substances (total oils and grease).

**Declaration of conformity – Sample WW-HC**

The results of the analysed parameters in the scouring wastewater sample, WW-HC before discharge into the public sewer system do NOT comply with the maximum permissible concentrations according to Annex I of the Regulation on Wastewater Emission Limits (OG 26/2020), as a result of increased concentrations of organic substances ($BOD_5$), total nitrogen, total phosphorus and semi-volatile lipophilic substances (total oils and grease). To remove the grease and the dirty substances large amounts of water and surfactants should be consumed; therefore, the scouring process generates a high contaminating wastewater, $BOD_5$ about 20.000-40.000 mg/L and COD of 100.000 mg/L. To reduce the generation of wastes, some washing plants recover part of the grease as a cream phase, containing mainly the wool wax, remains in the superficial layer of the different scouring tanks. Those superficial waters are centrifuged, and a cream phase - lanolin can be isolated by extraction and purification [27,40].

**Biodegradability**

Biodegradability is expressed as the ratio of scouring wastewaters parameters, biological oxygen demand ($BOD_5$) and chemical oxygen demand (COD). The results of their ratio indicate the quality of the water according to the criterion of biodegradability [61-63].

**Table 32:** Assessment criteria of biodegradability

| $BOD_5$/COD | Biodegradability |
|---|---|
| ≥ 0.5 | readily biodegradable |
| 0.4-0.5 | moderate biodegradable |
| 0.2 to 0.4 | poor biodegradable |
| ≤ 0.2 | non-biodegradable |

As this ratio expresses the biodegradability of scouring wastewater, characterization of analysed samples WW-FA and WW-HC is given in Table 33.

**Table 33:** Biodegradability of analysed scouring wastewaters

| Parameter | WW-FA | WW-HC |
|---|---|---|
| $BOD_5$ (mg/L) | 746 | 3747 |
| COD (mg/L) | 4350 | 11260 |
| $BOD_5$/COD | 0.17 | 0.33 |
| Biodegradability | *Non-biodegradable* | *Poor biodegradable* |



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This part of the wool portfolio (2.4), aimed to improve the understanding of horse chestnut suspension as a scouring agent, encourage further research and unlock the full potential of this valuable plant.



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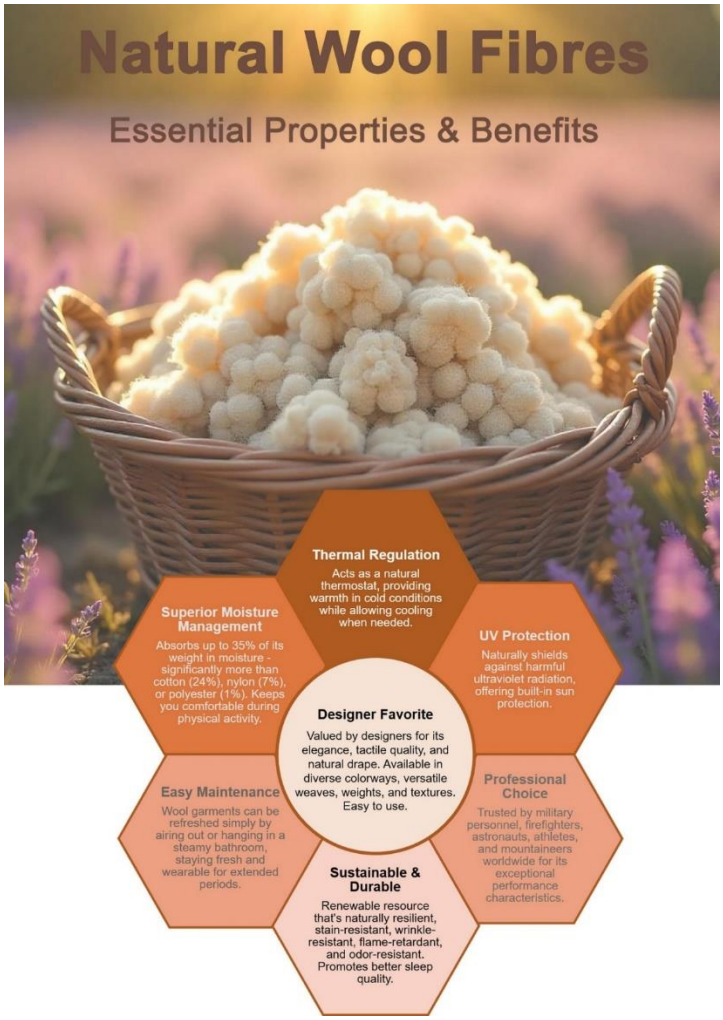
# Final remarks

## Wool fibres

## Green- Tex solution

***Natural raw material, valuable for clothing, interior textiles and technical applications - an opportunity for creators, designers, artists, artisans and sustainability promoters!***

APPROVED




Design by T. Dekanić according to [8]



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