Environmental Engineering and Management Journal
July 2019, Vol. 18, No. 7, 1439-1456
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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CURRENT APPROACHES FOR RAW WOOL WASTE MANAGEMENT AND UNCONVENTIONAL VALORIZATION: A REVIEW

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Abstract

Since the middle of the past century, when the synthetic fibers began their rise, wool has steadily lost importance in the textile sector, and now is a marginal fiber on the textiles market. Great amounts of non-marketed raw wool have turned from an income source for sheep farmers into a problematic waste, which is, at best, burn or landfill. With increasing interest for sustainable use of natural resources, wool was reconsider as an underrated, underused renewable resource, worthy of a better exploitation. Lately, intensive research has done on finding solutions for wool waste valorization in non-clothing applications. Two main directions to add value to wool waste have developed: in applications that exploit the native fiber properties, and in applications that use the keratin biopolymer, extracted from fibers by chemical solubilization or enzymatic bioconversion. Wool fibers in native state are most used for technical applications like green building insulation, polymer-fiber composites or sorbent materials for water pollution treatment. Keratin and its derivatives are main considered for the production of protein-based biomaterials for regenerative medicine. Bioconversion has a significant potential for transforming wool waste into high-value products like fertilizers for organic farming or proteolytic enzymes. The aim of this paper is to present the current management options for raw wool waste and to review literature on actual and emerging solutions for converting raw wool waste into useful and profitable materials and products.

Key words: natural fibers, renewable resources, waste management, waste valorization, wool

Received: October, 2017; Revised final: February, 2018; Accepted: March, 2018; Published in final edited form: July, 2019

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1. Introduction

Wool is a valuable natural fiber and has a long history as raw material for textile purposes. It was amongst the first commodities to be trade internationally and is still important to the agricultural economies of many countries. Between the 17th and the first half of the 20th centuries, the wool textile sector was a front ranking global industry, but competition from synthetic fibers, combined with consumer preferences shifting in favor of lighter weight and casual products, has negatively affected the demand for the woolen products. Wool production has also been constrained by its poor environmental performance related to sheep grazing and fiber industrial processing, which is water and resource intensive, and highly polluting (Henry, 2012).

The share of wool in total world fiber supply fell, in volume terms, from 9.9 % (in 1960) to 3.2 % (in 2000) (Kilduff, 2002). In the 2011/2012 season, when wool production fell to reach the lowest in 70 years, the share of the wool fibers on the global market was 1.3%, while the synthetics share was 61.4%. In 2013, world wool production lifted by 3% and has kept

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a steady trend since then, with about 1.2 million metric tons of clean wool per year (PADC, 2015). With respect to these figures, wool is currently perceive as a marginal fiber, reserved mainly for luxury products.

Market reports record only the traded wool, which enters the manufacturing chain and is process into different consumer products in the textile industry. The statistics do not take in consideration the raw wool that is produced in sheep farms, (i.e. shorn off sheep) but is not on the market, for different reasons: low quality not suitable for textile manufacturing, lack of potential buyers even for high grade wool, lack of wool collecting, washing and trading facilities etc. (Pattinson et al., 2015). In the last years, sheep shearing was sometimes only an animal welfare activity with no profit for the farmer and the shorn wool turned from an income source into a burden. Apart from the raw wool, that does not enter the textile process chain; the wool supply chain produces huge amounts of pre-consumer and post-consumer woolen wastes. Wool waste of different proveniences has become an issue of solid waste management, requiring rational actions.

With little prospect for growth in wool supply for the textile sector, the opportunity lies in benefiting from wool's advantage as a natural, renewable and biodegradable fiber, by finding unconventional uses and feasible processing technologies to obtain value-added products.

This paper aims to present an overview of the current situation of wool waste management, and a literature review of approaches and practical methods for raw wool fiber valorization for non-clothing common and advanced applications, in the context of renewable resources exploitation.

2. Chemistry and morphology of wool fiber

Wool is a natural protein material, whose unique properties rely on its chemical composition and morphological characteristics. Wool is graded in accordance with fineness, i.e. the fiber diameter, which varies from one sheep breed to another. Basically, there are four wool grades: fine grade, with maximum fiber diameter (Ø) of 22.04 µm, medium grade with Ø = 22.05-30.99 µm, coarse grade, with Ø = 31-36.19 µm, and very coarse, with Ø over 36.2 µm.

The histological structure of wool fiber comprises the cuticle, the cortex and the cell–membrane complex. The inner channel named medula exists only in coarse and medium grade fibers. The cuticle, or the outer layer, plays a barrier role against external physical and chemical damage. It is made up of overlapping scales or cuticle cells, which render roughness and toughness to the fiber surface. The cuticle surface is hydrophobic, due to the presence of fatty acids covalently bonded to the protein substrate. As the cortex is hydrophilic, the fiber has a core-shell structure, with a hydrophobic outer surface wrapping a hydrophilic core (Popescu and Höcker, 2007). This explains why wool surface is inherently water and dirt repellent, but the fiber in its whole is able to absorb high amounts of water vapors.

The cortex is the major body of the hair fiber, and is composed of many elongated spindle-shaped cells, which contain keratin in up to 93 percent by weight (Cardamone, 2010). The primary structure of keratin comprises 18 α-aminoacids, whose relative ratios, sequencing and side chains reactivity dictate the polypeptide chain conformation. The particular amino acid in keratin is cysteine, which accounts for the disulfide bridges that crosslink the adjacent polypeptide chains and determine the self-assembly of individual macromolecules into highly-ordered supramolecular aggregates. Disulfide bridges are responsible for the particular properties of keratin: hydrophobicity, water insolubility, high chemical resistance, low biodegradability, high mechanical resistance. Solubilization is possible under the action of certain chemical reagents (alkaline, reducing or oxidizing) or keratinolytic enzymes, which split the disulfide bridge. Besides cysteine, keratin is rich in glutamic acid, serine, leucine, glycine, proline. Two main classes of proteins are found within the cortex of the wool fiber, depending on the sulfur content: (1) low-sulfur, "alpha-keratins" (LSK), with molecular weight (MW) in the 40 – 60 kDa range, and (2) high-sulfur, matrix proteins (HSK), with MW in the 10-25 kDa range. The alpha-keratin macromolecules, or "dimers", are made up of two right-handed coiled polypeptide chains; the dimer is considered the unit cell of the fibrous assembly. Groups of four dimers stack together, to form protofibrils. Groups of 8-11 protofibrils further assemble in accordance with an alpha-helix folding pattern, to form highly ordered microfibrous structures known as keratin intermediate filaments (IFs) or microfibrils. Intermediate filaments closely pack together to form macrofibrils. Macrofibrils are embedded in an amorphous matrix containing high-sulfur proteins, together with others rich in glycine and tyrosine (Plowman, 2003). The matrix proteins, also termed as keratin-associated proteins (KAPs), act as a binder that holds the cortical superstructure together.

The cell-membrane complex performs the function of cementing cortical and cuticle cells together (Maclaren and Milligan, 1981). A graphical representation of wool fiber morphology and hierarchical organization of keratin is given in Fig. 1. Presence of macrofibrils embedded in the matrix is clearly proved by TEM micrographs of cross-section of cortical cells (Fig. 2). The cortex of the wool fiber can be considered as a natural polymer matrix-fiber reinforced composite elastomer, with advanced hierarchical organization. According to the two-phase model proposed for keratin fibers (Feughelman, 1997), the amorphous interfibrillar matrix is equivalent to the continuous phase, and the highly ordered system of intermediate filaments is analogous to the reinforcement fibers (Fig. 3). The tensile properties of wool are largely explained in terms of the two-phase composite model (Wang et al., 2016a).

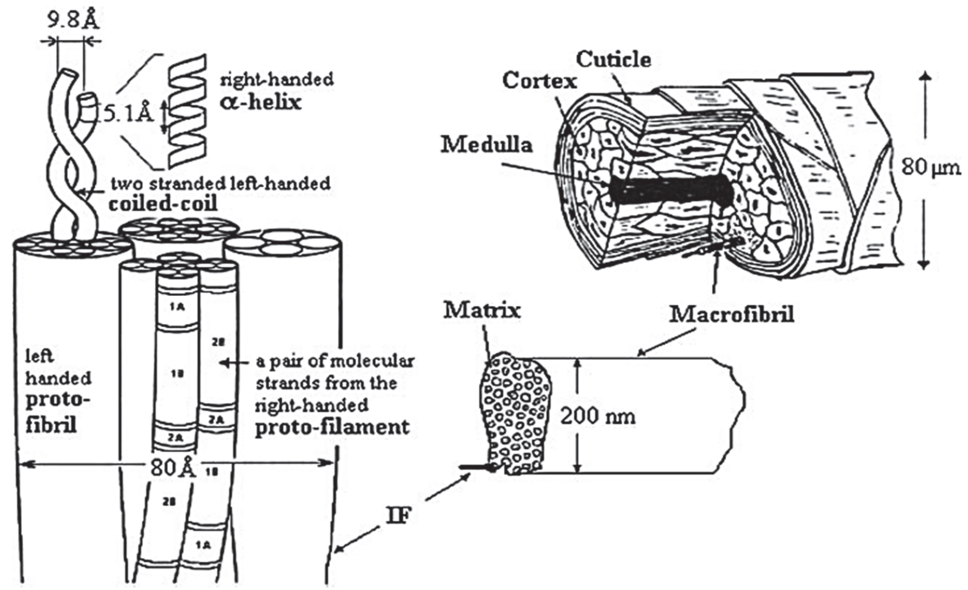

Fig. 1. Schematics of wool fiber morphology and hierarchical organization of keratin macromolecule (Popescu and Höcker, 2007, modified from Robbins, 1994).Reproduced with permission from Royal Society of Chemistry

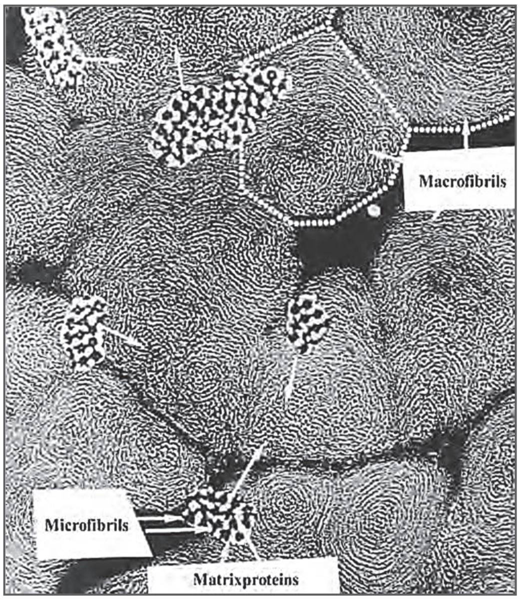

Fig. 2. TEM image of cross-section of wool cortical cells (Höcker, 2002)

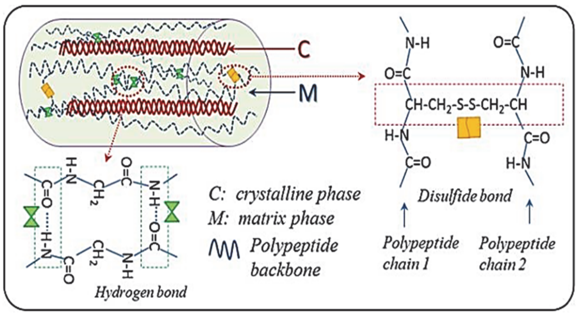

Fig. 3. Two-phase model for keratin fiber (Xiao and Hu, 2016)

Keratin macromolecule acts as an amphoteric polyelectrolyte, whose overall charge depends on the pH of the surrounding aqueous media. The pH at which the net positive charge of the side chains is balanced by the net negative charge of the side chains, and the macromolecule is electrically neutral, is called the isoelectric point (pI). At this point, the protein precipitates and can be recovered from solution. Native proteins exhibit pI intervals rather than a pI point; keratins specific to hair or wool have a pI interval of 4.7–6.1 (Coulombe et al., 2013).

When the pH is higher than the pI, the wool fiber surface carries negative charges with affinity for positively charged ions in solution. When the pH is lower than the pI, the wool surface carries positive charges, which enhance the affinity for negatively charged ions in solution (Fig. 4). This property is essential for the behavior of wool and keratin-based protein forms in solution, and interaction with other charged species.

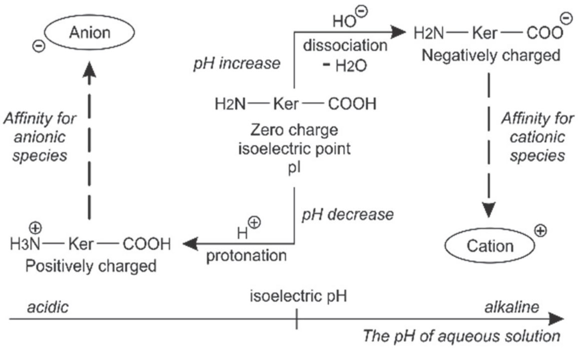

Fig. 4. Dependence of keratin macromolecule charge on pH, and affinity for charged species

The physical and chemical characteristics make wool fiber a valuable raw material for applications beyond the textile industry. As a traditional textile fiber, wool is valued for properties like high thermal insulation ability, hygroscopicity, low flamability, low density, felting, mechanical strength and durability. These attributes can be exploited in technical applications, of which technical textiles are representative. Keratin, the main chemical constituent of wool fiber, is a protein that can play its role within the general interest for biopolymers and bio-based materials.

As every year a sheep produces at least one new fleece, wool can be considered a renewable resource.

3. Classes of wool waste. Principles and general practices of wool waste management

Woollen waste is generated in different forms throughout the whole wool supply chain: as raw wool from the sheep farms, fibers and fabric leftovers from the textiles manufacturing process, worn clothing from consumers. The main sources and classes of wool waste are presented in Fig. 5. Amongst other solid wastes, wool wastes represent a matter of increasing concern, because of huge accumulated volumes, and difficulties in finding solutions for their effective management.

Raw wool i.e. wool as shorn from the sheep, is the most problematic waste because it affects the wool supply chain from the start. The worldwide production of raw wool can only be estimated, based on sheep number. For example, in Europe in 2011, there were more than 127 million sheep, which accounted for a total wool production of about 260,000 tons, comprising hundreds of different breeds, with a great variability of wool grades (Chaupin, 2013). Only a small part of it, represented by fine grades, is suitable for the textile industry and enters into the market. In Italy, for instance, the annual production of raw wool is estimated at about 14,000 tons, of which only around 5% finds cost-effective applications, mainly in niche markets like luxury apparel (Vagnoni et al., 2016).

In agreement with the waste management terminology, some comments should be made on terms like *by product*, *co-product*, *waste*, as regards the shorn-off wool. Recent studies on major agro-ecological zones showed significant differences depending on the sheep breed and wool grade (Wiedemann et al., 2015). In the UK, most wool is coarse-textured, sheep production is focused primarily on meat, and wool is regarded as a low-value by-product, which seldom accounts for more than 4% of the regular farm-gate income. New Zealand sheep farming is based on sheep bred for both meat and wool; the bulk of the income comes from meat, but wool also contributes with 20-25% of the typical farm-gate sales. Most of Australia's sheep flock comprises the Merino breed, which produces fine-grade wool for high-quality clothing. In New Zealand and Australia, the production systems are managed to optimize production of both wool and meat, and wool is considered as a co-product. The term *waste* is reserved for raw wool that cannot find any use, and must be managed in accordance with the waste management options.

The **Waste Framework Directive** (EC Directive 98, 2008), establishes the waste management hierarchy principle: disposal minimization and implementation of recovery strategies and actions for reuse and recycling. Minimization and avoidance of waste generation are the most preferred but less attainable options. At present, the low-level options - no action, landfilling and burning - are largely applied for wool waste. As wool waste avoidance is impossible and minimization is improbable within the actual economic and population growth, reuse and recycling remain the most feasible options for keratinous waste management.

The current situation of wool waste is framed within the European regulation context with EC Regulation 1069 (2009), and EU Regulation 142 (2011) implementing **EC Regulation 1069 (2009)** (2011). These regulations: (1) define wool as an animal by-product that must be thrown into landfill as a solid waste, if it is not directed towards the textile supply chain, and: (2) set rules on the management of raw wool and hair, which are regarded as category **3** animal by-products (ABPs), which means they are classed as low risk. Rules are set concerning handling, treating and disposal, and transportation. Disposal of unwanted wool must be done as quickly as possible, by different disposal methods approved for category **3** ABPs: sending to a landfill site, incineration, composting, applying to land as fertilizers, or processing to make fertilizers or cosmetic products, feed for farm animals, etc. According to regulations concerning safe disposal, wool cannot be buried in a farm dump or burned without a permit. Unless it is washed or disinfected, raw wool waste must be sent to incineration or landfilling specialized sites.

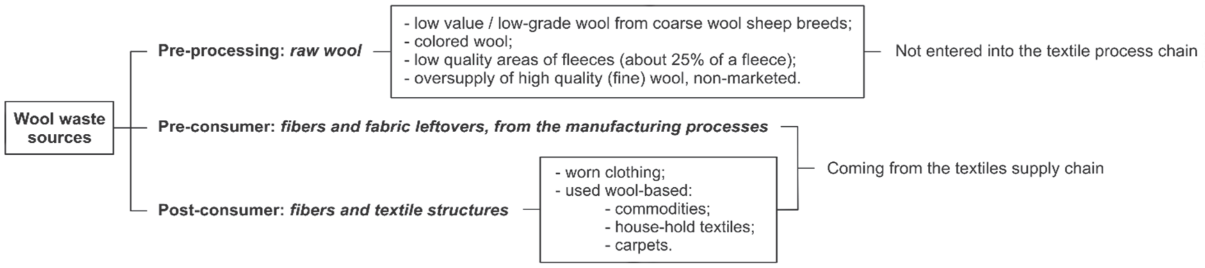

Fig. 5. Sources and classes of wool waste

In other words, environmental regulations force farmers to treat wool or to get rid of it in a short time. With increasing waste landfilling fees, illegal practices of storage, transportation and disposal are not improbable. This makes hard to estimate the real amount of waste wool that is disposed of in Europe (Zoccola et al., 2015). Sheep farming plays an important role in the agrarian economy of many countries worldwide and is a fundamental factor for rural development, mainly in mountain and arid regions. Finding rational ways for wool valorization is decisive for the survival of many communities whose main source of income is sheep breeding. An actual trend responding to the sheep breeders and wool industry hardship is the reconsideration of wool as a natural fiber and its traditional use as raw material for the textile industry. Bacci et al. (2013) carried out a qualitative research on coarse Sardinian wool and found that yarns and fabrics produced with coarse wools could undergo the same textile processing phases as those applied to wools commonly used in the clothing-fashion sector. Several projects were completed in Italy, to promote local wool valorization. Wool found uses for high quality traditional handmade textiles and carpets, insulating materials or agricultural mulches, assuring both a right profit to sheep breeders and environmental benefits (Vagnoni et al., 2016).

The wool supply chain also produces huge amounts of pre-consumer and post-consumer woolen wastes, which have found valuable applications in the textile sector. High quality fibrous waste coming from the manufacturing process is reintroduced in the process or directly used for nonwovens. Post-consumer wool waste can be reused or recycled. Worn clothing re-wearing is a sustainable option, because it decreases the volumes of textile waste. Recent studies on discarded textiles impact show that reuse of 100% woolen textiles gives superior benefits for the environment compared to incineration and recycling (Schmidt et al., 2016). Wool fabrics and knittings are recycled to obtain yarns, which can be reused. Recycling increases the environmental performance of woollen textile products, since the environmental impact of critical wet processes, like dyeing, is considerably reduced (Bamonti et al., 2016). However, most recycling is mechanical and constitutes a downcycling to a lower quality product; this is a barrier to finding markets for clothes from recycled natural fibers (Nicolli et al., 2012).

The unavoidable generation of wool waste is a drive for finding rational, cost-effective solutions for this solid waste/ natural resource management and valorization, with social and environmental benefits.

4. Practical solutions for exploitation of raw wool waste in non-conventional applications

4.1. Main pathways for wool valorization

Interest in keratin-based animal waste is focused on feathers discarded by poultry farms (Figueiredo and Freitas, 2013; Reddy, 2015), but wool has also come to researchers' attention. The main practical solutions for wool waste valorization in accordance with the high-level management options for solid waste, and in the actual context of renewable resources valorization, is presented in Fig. 6.

Valorization of raw wool for non-clothing applications have been developed in two main ranges: (1) applications that exploit the properties of natural wool fiber, subjected to non-destructive pretreatments, and (2) applications that exploit the properties of the keratin biopolymer, which involve fiber solubilization and keratin extraction.

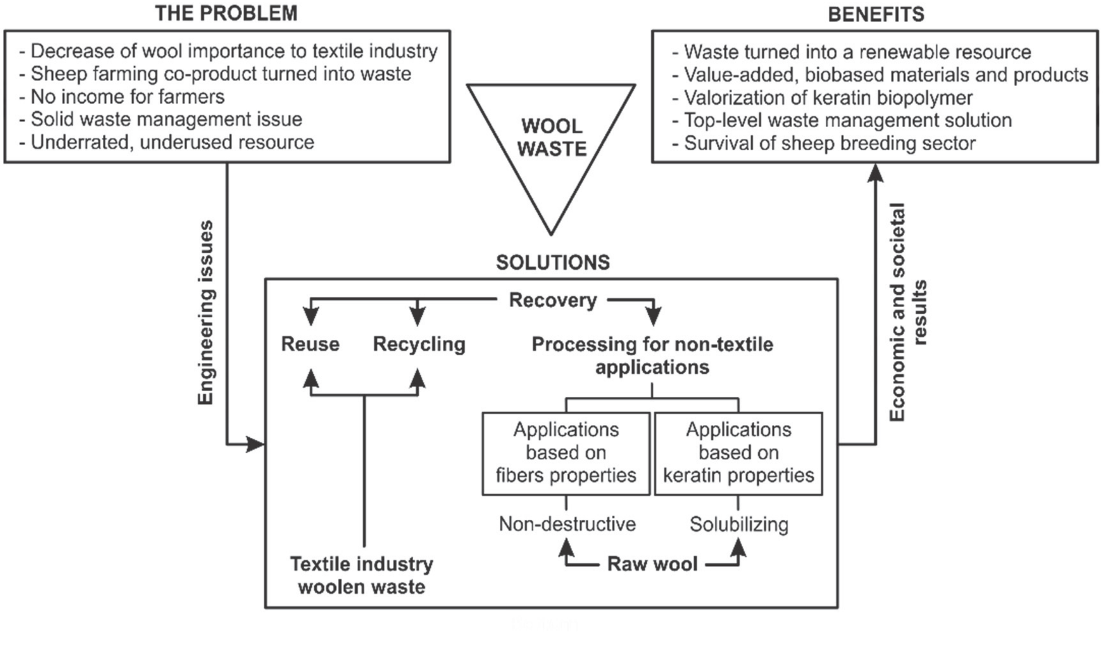

Fig. 6. Drives, benefits and practical solutions for wool waste valorization

The first pathway mainly makes use of low quality raw wool, but can also use pre-consumer and post-consumer wastes. Applications are mainly directed towards technical textiles, for which function is the key factor, and fiber fineness is unimportant. Recovery of keratin proteins by solubilization seems to be the most advanced way of raw wool fibers valorization.

The recovered keratin biopolymer is susceptible of further processing into value-added materials and products, with applications mainly in the regenerative medicine and cosmetics. An overview of wool solubilization pathways and main application areas of keratin forms thus obtained is presented in Fig. 7.

Even if potential applications are very attractive in the context of renewable resources, wool has received limited attention so far. There are two main reasons for this. Firstly, most applications use clean wool, but wool scouring is polluting and requires specific processing facilities, Secondly, keratin solubilization and recovery involves application of intricate processes, and use of different chemical reagents in high concentration. Hence, feasibility of wool processing for keratin extraction on large scale must be carefully considered.

4.2. Wool as thermal and sound insulation material for green building

Green or sustainable building is an actual response to societal concerns regarding the environmental impact of construction materials and practices. Insulation is essential to increasing the energy efficiency of a structure and to minimizing noise pollution. The demand for integration of more renewable resources into the construction industry drove the replacement of conventional insulators with natural substitutes, of which wool is gaining ground lately. Apart from its native thermal properties, wool's main advantages as insulator come from its breathability and air humidity buffering capacity, low flammability, self-extinguishing behavior. Objections are mainly related to the use of preservatives, anti-rodents and moth repellents with potential toxic effects on humans. Another objection is related to the decrease of insulating capacity with moisture content, since wool water uptake is high, up to 35wt%; it was shown that the increase in wool water content from 0% to 30% determined the decrease of thermal conductivity by 28% (Zach et al., 2012). Significant properties of wool as an eco-friendly insulator, reported in existing literature, are given in Table 1.

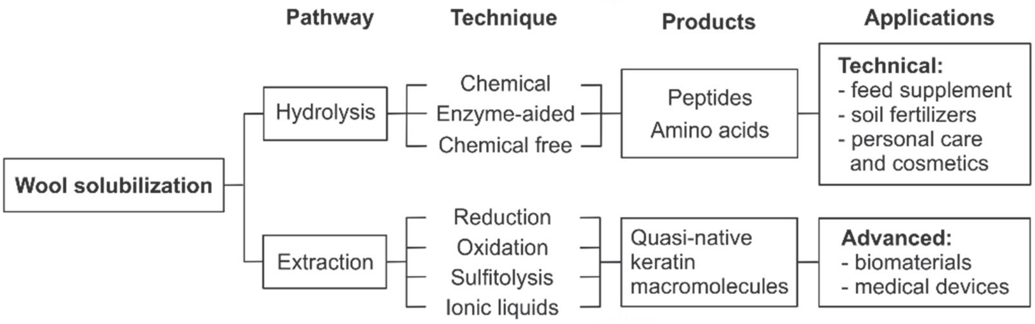

Fig. 7. Keratin biopolymer exploitation by wool solubilisation: methods and applications

Table 1. Significant properties of wool insulation materials

Property / Behavior / Characteristic	*Values / Description*	*Reference*
K value - thermal conductivity (W/mK)	0.034 – 0.067 0.034 – 0.048	Ye et al. (2006 Zach et al. (2012)
R value - thermal resistance, 82 mm thick, 17% moisture content (m^2K/W)	1.68 horizontal; 1.70 vertical	Ye et al. (2006)
Density (kg/m^3)	22 -23	Corscadden et al. (2014)
Sound absorption coefficient (500 -2000 Hz frequency range, 60 mm thick)	0.572 at 500 Hz; 0.966 at 2500 Hz	Zach et al. (2012)
Embodied energy **(**GJ/m^3**)**	0.11	Wooley et al. (2005)
Health hazards	Organic dust release during manufacture, presence of toxic anti-moth agents Growth of mould strains	Mansour et al. (2014) Stefanowski et al. (2017)
Health benefits	Improvement of indoor air quality by sorption of VOCs	Huang et al. (2007); Mansour et al. (2016)
Environmental impact	Global warming potential LCA profile and biodegradability	Murphy and Norton, (2008) Korjenic et al. 2015
Cost per unit - mfg cost ($\$/m^2$)	7.75	Corscadden et al. (2014)

Unlike many conventional insulators, wool by itself does not represent a health hazard, as it causes no irritation to eyes, skin or lungs. Mansour et al. (2014) assessed environmental and health benefits associated with the presence of natural insulation material in buildings, and concluded that possible health hazard related to wool dust particles (associated with irritation of the airways and eyes) comes from the manufacturing process, and can be managed to an economically viable minimum. Most references classify wool dust as a potential allergen due to the presence of microscopic growths on its surface (Haghi, 2001). Recently, tests on durability and susceptibility to mold growth of different bio-based insulating materials like fiberboard, hemp, or wood fiber, showed that despite its high water absorption coefficient, wool exhibited the lowest growth intensity of common mold strains (Stefanowski et al., 2017). For best performances in terms of density and mechanical strength, wool is used in combination with other recycled fibers, usually low-density polyester, in a wool-other fiber ratio of 3:1 (Patnaik et al., 2015).

Sheep wool insulation is currently produced as soft bats - mainly used for the insulation of pitched roofs, and semi-rigid panels - designed for application in walls. The manufacture of self-standing panels with high thermal and sound insulating properties, made entirely from wool stiffened by a thermo-chemical treatment was reported (Bosia et al., 2015). The availability of a 100% sheep wool stiff panel leads to new applications for insulation of external walls and internal insulation of walls or ceilings. A clay-wool composite with 5% wool had a K value of 0.19 W/mK, while the K value of clay alone was 0.51 W/mK, which means an improvement of 63%. This composite could control the external heat flow in dry climate area, when used as unfired insulation and building material (Mounir et al., 2015).

A comparative Life Cycle Assessment of different insulators - wool, hemp, mineral wool - showed that the wool-based insulator offered a net negative Global Warming Potential in 100 year time-frame (GWP_{100}) of – 0.323 kg CO_2-eq over its entire lifecycle, while the hemp had a GWP_{100} of 0.345 kg CO_2-eq, and the mineral wool had a much higher value of GWP_{100}, equal to 1.2 kg CO_2-eq (Murphy and Norton, 2008). The end of life scenarios showed that landfilling and composting are the best options for natural fiber insulators. A comparison between the environmental performances of insulated buildings, showed that the GWP_{100} of sheep wool insulated construction is about 4.7 kg CO_2-eq and the mineral wool isolated construction has a GWP100 of 5.3 kg CO_2-eq, which means about 13% less for the natural insulation (Korjenic et al., 2015).

Apart from its insulating function, wool can improve the indoor air quality (IAQ), due to its ability to act as an effective filter and adsorbent for hazardous VOCs such as formaldehyde and toluene in low concentrations, which are released from building materials, furniture and household appliances (Huang et al., 2007). The maximum sorption capacity of aldehyde on white scoured wool was 4 g/kg, while the uptake on unscored white wool was 5.5 g/kg, and the black wool could retain as much as 10 g/kg. (Mansour et al., 2016).

Besides the functional effectiveness, economics and manufacture-related issues must be taken into account when wool insulator is considered for a sustainable building material. In this respect, Corscadden et al. (2014) showed that manufacture of wool insulator on a small scale, using low cost, non-marketed raw wool, might offer small but significant benefit to sheep producers as well as consumers. Using the least valuable sheep's wool available did not have a negative impact on productivity or product performance.

Sheep's wool insulation is still a new and expensive product on the market, preferred by environmentally aware companies and final consumers, but with real prospects to expand its market share.

4.3. Wool as fiber reinforcement in polymer-fiber composites

Fiber reinforced polymer composites (FRPC) are a class of engineering materials, suited for both consumer products and advanced applications such as packaging, disposables, automotive or civil infrastructure. Conventional reinforcing fibers like carbon or glass fibers are expensive and their preparation or use may be hazardous. Natural fibers of vegetable and animal origin can replace conventional reinforcement fibers and apart from being cheap, renewable resources, they can impart some additional properties to the composite, such as biodegradability, low density, and good thermal and mechanical properties (Väisänen et al., 2017).

Wool has certain applications in fiber - reinforced composite materials. It is used in native state or after some chemical surface treatments that improve the compatibility with the polymer matrix. Isotropic polypropylene-matrix composites, reinforced with up to 60 wt% of short, fine wool fibers, were prepared by simple melt blending; the synergic interaction between wool fibers and the polypropylene matrix improved thermal and thermo oxidative stabilities of the composite material, but strength lowering was noticed as compared with the polypropylene matrix, mainly because the melt blending process had a detrimental effect upon the wool fibers length, which decreased below the 2 cm critical value (Conzatti et al., 2013). An optimized process for the fabrication of wool fiber-reinforced polypropylene composites by compression molding was reported (Govindaraju et al., 2014); composites obtained at 176°C, and 35 bar exhibited the best mechanical behavior in terms of tensile, flexural, and impact strength. Recently, a wool fiber-reinforced cementitious mortar, with mechanical and environmental performances similar to those of hemp-based composites, was reported for the first time (Fantilli et al., 2017b); the addition of 1% (w/v) wool fibers with average diameter 19 µm and 16 mm length to the mortar improved its flexural strength and bending fracture toughness by 18% and 300%, respectively.

Wool sensitivity to alkaline aqueous media limits its uses as filler in cement-based materials. Thus, Fantilli et al. (2017a) showed that wool fibers were effective in reducing the brittleness of plain mortars mortar even after 28 days, when the composite was cured in dry conditions. In water, the cracks bridging ability was entirely preserved for only 3 days, *i.e.* the approximate time required for wool fibers to disintegrate in alkaline aqueous media, and was completely lost after 28 days. Polypropylene composites reinforced with biochar and wool exhibited significantly lower peak heat release rate (PHRR), and smoke production; hybridization with wool proved to be beneficial for enhancing the limiting oxygen index (LOI) (Das et al., 2017). New aluminosilicate geopolymers prepared from kaolinite-type clay reinforced with 5 wt% wool, exhibited flexural strength and fracture characteristics improved by 40 % compared with the matrix, and higher thermal stability (Alzeer and MacKenzie, 2012); environmentally friendliness and relatively low cost make these composites attractive for some construction applications as well.

4.4. Wool as sorbent for oil spill cleanup

Accidental or systemic oil spills are a major source of fresh and seawater pollution, which require rapid and effective solutions, in order to diminish the environmental and economic impact. Synthetic oil adsorbents are largely used due to their high effectiveness, but their poor biodegradability raises disposal issues. Natural fibers are viable candidates for alternative sorbent materials, due to their biodegradability, availability from renewable resources, and low-cost, even if their lower efficiency makes them suitable rather for small-scale oil spills (Dong et al., 2015). Raw wool or recycled wool fabrics are viable candidates for oil spill cleanup. The irregular scaly and rough surface, crimp, and the presence of waxy matter on cuticle have a synergic influence upon the oil adsorption and ability to spread over the wool fiber surface (Choi and Moreau, 1993). Radetić et al. (2003) developed recycled wool-based non-woven mats (RWNM) made from 78% wool/22% polyester worn pullovers, and tested their sorption affinity towards crude oil, diesel and base oil. She found that the loose fibers had more than 100% better sorption capacity than the non-woven material. No significant difference between the sorption capacity in demineralized water and seawater could be noticed. About 88% of the adsorbed oil was removed during squeezing and after five cycles, the adsorption capacity was about 81% of the initial capacity, which proved good reusability. Investigation of sorption capacities of RWNM for different oil types (see Table 2) showed that wool-based sorbent was able to retain more than 10 fold oil as its weight and there were no significant differences between sorption from oily water and sorption from oil per se (Radetić et al., 2008).

Table 2. Sorption capacity of RWNM for different oil types (Radetić et al., 2008)

Oil type	*Viscosity cSt, 40°C*	*Sorption capacity (g/g)*	
		In oily water	*In oil without water*
Diesel fuel	3.07	9.62	10.6
Crude oil	9.56	11.06	12.46
Base oil	30.6	12.98	14.78
Vegetable oil	31.2	13.16	14.48
Motor oil	114	15.8	15.73

The sorbent efficiency for motor oil (MO) removal from water was investigated in a laboratory batch system, using clean wool fibers in loose state (NWF), RNWM (78% wool/22% polyester) mats, and mineral sorbents like sepiolite. Maximum uptake values of wool-based materials were significantly higher than those of the mineral sorbents: 34 g/g NWF, 18 g/g RNWM and 0.22 g/g sepiolite (Rajaković-Ognjanović et al., 2008). In real oily wastewater contaminated with the same MO, adsorption capacities were significantly lower, of about 5.56 g/g NWF and 5.48 g/g RNWM, because real oily wastewater occurred mainly in the form of stable emulsions (Rajakovic et al., 2007).

Comparable performances to those of conventional adsorbents were reported when greasy raw wool, as shared, was tested for the removal of a marine fuel oil from seawater surface (Periolatto and Gozzelino, 2015): after 15 sorption/impregnation-squeezing cycles on a laboratory system, wool recovered oil 140 times its initial weight, while on the pilot prototype simulating the real recovering conditions of a ship on the sea, an overall yield of 98% was achieved after 22 reuse cycles. Column experiments using pristine sheep fleece as filler showed a fairly good removal efficiency as compared to those of a polypropylene-based synthetic adsorbent - 84% vs. 93% - for the adsorption of high concentrations of oil in runoff (50- 230 mg/L) at high filtering rates (10 m/h), but the clogging in wool packed column was present after short treatment time, no longer than 30 min (Mažeikienė et al., 2014).

4.5. Wool-based sorbents for the treatment of water pollution with heavy metals

Heavy metals, present in wastewaters coming from different industries, are considered priority pollutants due to their toxicity, carcinogenicity, mutagenicity, even in concentrations below the allowable limits (Jaishankar et al., 2014). Treatment of heavy metal pollution by adsorption is a well-established technique, and in recent years, there was an increasing interest in biobased active solids with metal-binding capacities, as a sustainable alternative to the conventional activated carbon (Lim and Aris, 2014). Keratinous materials like feathers and hair exhibit good sorption capacity of different heavy metals, which makes them candidates for low-cost biosorbents for wastewater treatment (Zhang, 2014). The dependence of the protein macromolecule charge on the solution pH is the key factor that controls the sorption and desorption of charged species like heavy metals ions from aqueous solution (Fig. 3). The binding mechanism is related to electrostatic interaction between the metal cation and the negatively charged side groups like carboxyl or sulfhydryl (Friedman et al., 1973; Yang et al., 2007). Any chemical attack that creates new negatively charged groups will enhance the adsorption capacity of keratin for cations (Ki et al., 2007).

The raw wool fiber is not easily prone to sorption, because of the cuticle hydrophobicity and the tightly packed architecture of cortex, which limits the access to active sites. The adsorptive capacity can be improved by physical and/or chemical treatments, as given in Table 3. The comminuting degree also affects the fiber adsorptive capacity. Naik et al. (2010) showed that the Cu(II) uptake rate of the wool powder was significantly faster (about 42 fold) than that of the wool fiber; he also found that in comparison with commercial cation exchange resins, the wool powders had two to nine fold higher metal ion loading capacity.

Wool-based functional materials exhibit enhanced ability to retain heavy metal anions and cations. Wool graft polyacrylamidoxime obtained from coarse wool waste proved its ability to remove both metal cations and anions, and to withstand several regeneration cycles with minor loss of adsorption capacity (Cao et al., 2014); the reported adsorption capacities followed the order: $Hg^{2+} > Pb^{2+} > AsO_2^{-} > AsO_4^{3-} > Cd^{2+}$, with maximum uptake of 20 mg Hg^{2+}/g , and 12 mg Cd^{2+}/g. Wool modified by graft copolymerization with ethylacrylate (Monier et al., 2010) or by acylation with EDTA dianhydride (Taddei et al., 2003) exhibited selective affinity for Cu(II). Amino acids and small peptide fractions obtained by enzyme-aided hydrolysis of wool proved an excellent chelating agent for Cu(II) and improved phytoextraction of metal-contaminated soils, by selective mobilization (Evangelou et al., 2008). Use of wool for chromium removal from wastewater has attained much attention. Tests performed on Cr(VI) using different low-cost adsorbents like sawdust, pine needles, almond shells, charcoal or wool, showed that wool had the best efficiency, with a removal rate of 81% and high selectivity in the presence of Al, Mg, and Ca (Dakiky et al., 2002). A two-step process was proposed by Jumean et al. (2015) for the removal of Cr(VI), based on fast adsorption of hexavalent Cr on the wool fiber, followed by slow reduction of Cr(VI) to Cr(III) and desorption of Cr(III) into solution. The removal rate was more than 99% and the benign Cr(III) was recovered by precipitation. Continuous flow experiments on wool-packed columns showed a maximum adsorption capacity of 23 mg/g Cr(VI), without attaining saturation (Manassra and Khamis, 2010).

Literature reports on the performances of wool and wool-derived materials for removing heavy metal ions from aqueous solutions are reunited in Table 3.

Wool can be processed in different fibrous configurations (knitted, nonwoven, loose fibers), useful as filter materials with both hydraulic conductivity and adsorptive capacity. A porous material obtained by immobilization of Bauxsol adsorbent on wool fiber, and used as filler in a packed column system, removed Pb(II) and Co(II) with efficiencies of 100% and 96%, respectively (Hassan and Davies-McConchie, 2012).

Table 3. Performances of wool-based sorbents for removing heavy metals from solution

Wool-based adsorbent	***Maximum metal removal efficiency, R (%) and uptake, Q_{max} (mg/g)***	***Initial concentration (mg/L)***	***pH***	***Reference***
Cleaned raw wool, cut in short pieces	Cr(VI) Q_{max} = 39.3 mg/g	100 – 400	2	Jumean et al. (2015)
Wool powder from raw and chemically modified wool	Co(II) R = 75%; Q_{max} = 0,913 mg/g	0.59 – 295	8-10	Wen et al. (2010)
Keratin colloidal solution from reduced wool	Pb(II) R = 87%; Q_{max} = 43.3 mg/g	62 - 514	5	Sekimoto et al. (2013)
Nanofiber membrane from S-sulfokerateine	Cu(II) R = 95%; Q_{max} = 4.55 mg/g Ni(II) 65%; Q_{max} = 3.42 mg/g Co(II) 59%’; Q_{max} = 3.05 mg/g	0.8 0.8 0.8	6	Aluigi et al. (2013)
Chemically modified by graft copolymerization of ethyl acrylate (EA)	Cu(II) R=93%; Q_{max} = 133 mg/g Hg(II) R=40%; Q_{max} = 42 mg/g Ni(II) R=26%; Q_{max} = 38 mg/g	50-400	5	Monier et al. (2009)
Chemically modified by grafting of maleic anhydride	Cr(III) Q_{max} = 43.3 mg/g	134-563	4.5	Li and Ye (2015)
Wool keratose / silk fibroin blend	Cu(II) R = 82.5%; Q_{max} = 2.88 mg/g	3.49 mg	7	Ki et al. (2007)

4.6. Wool powders and their applications

Mechanical powderization is a promising pathway for environmentally friendly processing of wool in non-clothing applications. Wool powders are obtained by cutting and grinding the fibers. Due to high break and elongation strength of wool fiber, grinding is difficult and energy consuming, so certain surface chemical pretreatments are performed to promote fiber brittleness. The working conditions dictate the powder fineness. By fiber comminution, the specific surface increases and more functional groups are exposed; thus, the powder gains the characteristics of an active solid (Wen et al., 2009). Little change of the X-ray diffraction pattern and FTIR spectra, as compared with the native wool, proved no significant attack to the keratin macromolecule (Xu et al., 2004). Wool powders reported in the literature and their characteristics are given in Table 4. It must be noticed that fine grade wools are preferred for this application. Biobased thermoplastics can be obtained from mixtures of superfine wool powder with plasticizers and other synthetic or natural polymers, subjected to hot pressure molding or extrusion. Blend films were produced by hot pressing, from superfine wool powder and poly(propylene) (PP) (Xu et al., 2007). The powder was uniformly incorporated with PP and no substantial changes occurred in the chemical structure of both PP and wool powder. Thermal stability and mechanical properties significantly declined with an increase in the wool powder content of the blend film. Wang et al. (2008) mixed wool powder with an average particle size of 1.7 μm with glycerol plasticizer at 10-50 wt% and subjected the blend to a molding pressure of 1-9 MPa at 100-160°C for 1 – 9 min, when thermoplastic films with acceptable properties in terms of mechanical strength, tensile strength, swelling capacity, water resistance and ductility were obtained; the wool powder was intimately embedded into a continuous phase and the film surface was smooth. Ke and Xu (2012) reported the obtaining of a membrane from a blend of wool powder and chitosan, by solution casting, which exhibited high affinity for a natural cationic dye. These biodegradable thermoplastics can replace the synthetic plastics, which are very difficult to be degraded in nature, for different commercial applications such as packaging, disposable housewares, agricultural films etc. (Ashter, 2016).

4.7. Advanced carbonaceous materials from wool

Activated carbons (ACs) are traditionally obtained from wood charcoal, and used as versatile adsorbents for different organic species. Activated carbon fibers (ACFs) have several advantages over classical ACs: narrower pore size distribution in the micropore range, higher surface areas and adsorption capacity, direct exposure of micropores to fiber surface (Mays, 1999). Lately, production of activated carbons from low cost renewable resources as carbonaceous precursors have been developed (Yahya et al., 2015). Lignocellulosic materials are mainly targeted, but elemental composition and fiber morphology make keratinous wastes feasible precursors of carbonaceous materials. According to Zahn et al. (2003), pure organic carbon makes up 50% of the weight of wool, and the ash content is 0.5 wt%. Von Holstein et al. (2014) reported a carbon content of approximately 46.53 wt%, comparable to those of wood, and a very low ash content of about 0.067 wt%. Wool and feather subjected to pyrolysis at up to 500°C produced a carbonaceous residue with a yield of 43 % and 37%, respectively (Brebu and Spiridon, 2011). Carbons obtained from animal hairs and lignocellulosic materials exhibit significant differences concerning their porous structure, surface morphology, surface functional groups and sorption performances (Kong et al., 2015).

Table 4. Wool powders: techniques for obtaining and main characteristics

Native wool/grade	*Pretreatment*	*Mechanical treatment*	*Powder particles characteristics*	*Reference*
Australia 25 μm	Chemical: mild oxidation	Cutting Pan- milling	Needle shaped Diameter 2 μm, 5-10 μm length Almost intact XRD pattern Increased thermal stability: 150°C vs. 120°C for the control fiber	Xu et al. (2004)
Merino 20.4 μm	Chemical: mild oxidation	Cutting Milling in a rotary ceramic mill Air-jet milling	Irregular shape Diameter 51.4 - 4.5 μm Breakdown of the cell cuticle BET surface area 6.1 m^2g	Wen et al. (2009)
Merino 23 μm	Chemical: acid treatment for cuticle removal; mild oxidation	Ultrasonic disintegration	Cortical cells and microfibrils Diameter 3μm, length 50 μm	Fan and Yu (2012)
Australia 17.5 μm	No chemical pretreatment	Cutting Wet attrition at room temperature Air jet milling	Diameter 1.5 μm, BET surface area 14.89 m^2g Low bulk density Exposed macrofibrils Strong cohesion and poor flowability	Rajkhova et al. (2012)
Merino 17.9 μm	Hydrothermal (130°C)	Ball milling	Diameter 3-15 μm, Lower solubility in mixture solution of urea, sodium hydrogen sulfite, and SDS	Hou et al. (2014)

Feathers are the preferred keratinous precursor for the obtaining of activated carbon fibers (Senoz and Wool, 2010). Chen et al. (2013) reported the first attempt to produce powdered AC from fine merino wool. The AC obtained by impregnation with K_2CO_3 and pyrolysis at 600°C exhibited a relatively high surface area (438 m^2/g) and pore volume of 0.197 cm^3/g, with average pore diameter in the micropore range (0.858 nm). SEM micrographs showed that the activated solid had a particular tubular morphology due to the cuticle/cortex structure of wool fiber, irrespective of the activation agent. Activation with H_3PO_4 and microwave-assisted heating of wool waste resulted in carbon materials of the microporous class, with over 73% micropores; the carbon yield was 40.2% (Gao et al., 2013).

The feasibility of using wool-based carbon fibers as fillers in thermoplastic composites was investigated (Hassan et al., 2015); the obtained ACFs exhibited reasonable carbon yield (25.8%), high surface hydrophilicity but relatively low values of the ultimate tensile strength as compared to commercially available carbon fibers (160 MPa vs. 3.5 GPa), so the resulting fibers could have applications only as low modulus filler.

Recently, wool was used as carbon source for the obtaining of nitrogen-doped carbon nanodots (N-CDs) through an eco-friendly process (Shi et al., 2016). The prepared N-CDs exhibited high fluorescent quantum yield, excellent biocompatibility, low toxicity, and were applied in multicolor cell imaging, patterning, and biosensing. Wang et al. (2016b) reported the obtaining of photoluminescent carbon dots from wool, with an average diameter of 2.8 nm, which proved effective in the trace quantification of glyphosate herbicide in cereals. Hard carbon fibers with well-defined and homogeneously dispersed fiber networks were obtained from worn-out wool clothes, carbonized at 1100°C;; the interlayer space of 0.376 nm and the high capacity of 303 $mAhg^{-1}$, stable over 80 cycles, make them a promising anode material for Na-ion batteries (Zhu et al., 2016).

4.8. Wool waste bioconversion. Production of organic fertilizers, animal feed supplements, and keratinases

Even if keratinous biological materials are recalcitrant to biodegradation, certain classes of microorganisms - bacteria, fungi and actinomycetes - naturally present in soil, birds plumage or mammal hair, are able to attack and breakdown the keratin macromolecule. The keratinolytic microorganisms exploit the keratinous material as a nutritional substrate and produce extracellular enzymes named *keratinases*, which catalyze the biodegradation process (Gupta and Ramnani, 2006). The keratinolytic process proceeds through a cooperative action of two kinds of keratinases: (1) disulfide bond-reducing, which catalyze the cleavage of disulphide bonds, and (2) proteolytic, which split the protein backbone through hydrolytic effect upon the peptide bonds (Yamamura et al., 2002). The final products of the hydrolytic process are soluble low molecular weight species - peptides and amino acids (Korniłłowicz-Kowalska and Bohacz, 2011).

Use of raw wool as organic fertilizer is based on its ability to slowly degrade when buried into soil, and to release nutrients essential to crops, like nitrogen (N) and sulfur (S). There are unofficial accounts of farmers using low-grade greasy wool as fertilizer - laid directly in the bottom of the planting pits, or as weedmats. The main problem that arises when taking wool in consideration for use as fertilizer is the rate of nitrogen release into the soil. The degradation of burried wool is obvious in terms of months: the keratin macromolecule start to split after 4 weeks, and in hydrophylic conditions, the weight loss is 33% in three months (Arshad et al., 2014). These figures prove that wool can act as an excellent slow-release organic fertilizer. Due to its fibrous structure and water-holding capacity, it acts as a soil amendment as well.

Experiments performed to assess the fertilizing potential of clean wool (10 g /dm^3 substrate) on tomato, sweet pepper and eggplant cultures showed that wool amendment improved water retention and caused changes in nutrients content of substrate and plants leaves; yields were up to 33% higher, especially for tomato and pepper (Górecki and Górecki, 2010). Wool waste was reported to increase yields of basil, peppermint and garden sage, and the addition of only 0.33% per weight of uncomposted wool would support 2 to 3 harvests without the addition of other fertilizers (Zheljazkov et al., 2008). An innovative composite from raw wool scraps incorporated in a geopolymer resin was successfully used for the manufacture of environmentally-friendly agricultural pots, as an alternative to the traditional peat ones (Natali Murri et al., 2014). The mixture exhibited a synergic action in providing a controlled release of nutrients and preserving a higher and long lasting level of moisture in soil. The presence of wool positively influenced the plant growth ratio. Böhme et al. (2012) showed that pellets from uncleaned wool and different supplements (cellulose, potato starch, casein) could successfully substitute mineral fertilizers for organic cultures of tomatoes or iceberg lettuce. Cultivation tests on parsley, using defibered and pelletized wool waste, showed that wool was not suitable as solely nitrogen source for organically grown potted herbs; the combination of sheep wool with a rapidly mineralized fertilizer may prevent that plants temporarily suffer from nitrogen deficiency or excess (Seibold et al., 2015).

A novel pelleted organic fertilizer, based on low grade coarse greasy wool, exhibited the characteristics of an organic NK fertilizer, with an effect duration of up to 10 months. It also proved soil loosening ability by swelling effect, as it absorbed water up to 3.5 times of its weight (IASP, 2008).

Composting experiments on low quality sections of fleece showed that wool by itself did not generate enough nitrogen in order to produce high quality compost and incorporation of other organic materials, like grass clipping (50 wt%) and horse manure (25 wt%) provided the optimal results for composting in a large scale manner. Defibration of compacted wool to a loose state proved essential for allowing sufficient decomposition of the waste wool (Hustvedt et al., 2016). Innovative geotextiles for erosion control, fabricated from coarse ropes filled with sheep wool and wrapped with woolen nonwoven, were assessed for mechanical deterioration during one year of soil exposure. Due to slow biodegradation, the ropes maintained their soil reinforcing potential for one vegetation session, which was sufficient for the development of the protective vegetation on slopes (Broda et al., 2016).

In recent years, demand for keratinolytic proteases is increasing due to their manifold applications in biotechnology. Controlled proteolytic degradation of raw wool waste can be the basis for large-scale production of keratinases, with the keratinous waste acting as substrate for the culture of enzyme-producing microorganism. A keratinase produced by the thermophilic actinomycete strain *Thermoactinomyces candidus* was induced by sheep wool as the sole source of carbon and nitrogen in the cultivation medium. The purified product displayed higher proteolytic activity against native keratins than other proteinases. The optimal pH and temperature were 8.6 and 70°C, respectively (Ignatova et al., 1999). Fang et al. (2013) reported high yield production of a keratinase from *Stenotrophomonas maltophilia BBE11-1*, using wool waste and glucose as culture substrate. Wool fibers were solubilized after four days fermentation and the hydrolysate was rich in essential aminoacids. Two bacteria of the genus *Bacillus,* isolated from sand soil, completely degraded wool to powder at pH 7 and 37°C within 5 days. The extracted keratin-degrading proteases were stable in most of the used organic solvents and enhanced by metals, suggesting their potential use in biotechnological applications (Hassan et al., 2013). Gong et al. (2015) identified a novel keratinase from a *Streptomyces aureofaciens* strain, using wool as the sole carbon and nitrogen source. The extracted keratinase displayed significant activity toward casein, keratin, BSA and wool, and exhibited extreme stability at alkaline pH values between 6 and 12 and at a high reaction temperature of 65 °C, even in the presence of surfactants.

Due to their resistance to alkaline media and surfactants, keratinases can replace toxic chemicals in clean technologies for leather and wool processing (Anzani et al., 2017; Zhang and Wang, 2015) and have a significant application potential in the detergent industry (Rai and Mukherjee, 2011).

Controlled keratinolytic process is also exploited in biotechnology, as an environmentally friendly pathway for obtaining hydrolysates with high nutritional value from keratinous wastes, like feather and wool (Onifade et al., 1998). Compared with the alkaline hydrolysis which results mainly in peptides of higher molecular weight, the enzymatic hydrolysis produces mainly low molecular weight peptide fractions, and even aminoacids. Nutritionally essential amino acids such as phenylalanine and methionine, which are rare in wool keratin, were produced in considerable amounts as metabolites of keratinolytic microorganisms (Gousterova et al., 2005), along with aspartic acid, tyrosine, histidine, and lysine (Fellahi et al., 2014).

Zaghloul et al., (2011) reported wool degradation by a recombinant *Bacillus subtilis* strain, at 30°C, and pH 7; the highest net levels of released end products were achieved after approximately 3 days of incubation. Bacterial strains belonging to the genus *Bacillus*, collected from Merino wool, exhibited high keratinolytic activity towards wool, hair and feathers, which were broken down to soluble protein forms useful in animal feed formulation (Queiroga et al., 2012).

Fakhfakh et al. (2013) reported complete solubilization of wool by a new keratinolytic bacterium *Bacillus pumilus A1*, in an optimized process (2 days, at 45°C and at initial pH of 10. The protein hydrolysate exhibited a high *in vitro* digestibility (97%) as compared with the untreated wool (3%), and antioxidant potential in terms of radical scavenging activity, which makes it a useful source of protein and antioxidants in animals' diets.

A keratinolytic proteinase cloned from thermophilic bacterium *Geobacillus stearothermophilus AD-11* and expressed in *Escherichia coli BL21(DE3)* exhibited high substrate specificity toward keratin from wool at pH 9 and 60 °C. Low alleregenicity small peptides (~ 3.4 kDa) were obtained, which are suitable for use as nutritional additives in various feeds (Gegeckas et al., 2015).

Enzyme-aided hydrolysis is a feasible, cheap, reproducible, efficient and rapid biotechnological approach towards wool waste valorisation into high value-added products.

4.9. Biomaterials from wool keratins and their applications in the regenerative medicine

Extraction of proteins from natural sources, with the aim of obtaining biomaterials, has a solid research foundation (Gagner et al., 2014). Besides human hair (Xu et al., 2016), wool is becoming a preferred source of keratins for biomedical applications. Keratin is a versatile biopolymer, which became very attractive for such applications, despite the difficulties related to solubilization and extraction from the keratinous sources. These applications are based on native keratin properties: biocompatibility, biological activity, self-aggregation and crosslinking ability, cytocompatibility (in terms of cell attachment, viability and proliferation), biodegradability. The extraction process must produce quasi-native keratin macromolecules, which preserve these attributes to a high extent. The feasible chemical methods for the extraction of quasi-native keratins are: (a) *reduction* with thiols in denaturing media, which results in keratin forms known as “kerateines” (Nakamura et al., 2002; O'Donnell and Thompson, 1964); (b) *sulphitolysis* with alkali metal sulfites in denaturing media, which results in keratin forms known as "S-sulfo-kerateines" (Bailey and Cole, 1959; Vasconcelos et al., 2008); (c) *oxidation* with peroxy compounds, which produces sulfonated keratins known as "keratoses" (Alexander and Earland, 1952; de Guzman et al., 2011). The solubilization techniques were established in the middle of the 20th century, but are still in use with minor improvements. Recently, an environmentally friendly method that uses ionic liquids (ILs) as solubilizing agents has been developed (Idris et al., 2014; Xie et al., 2005). It results in kerateine-like proteins, which can be regenerated into films (Ghosh et al., 2014; Li and Wang, 2013). Hydrolysis under certain conditions can also produce soluble protein forms useful for biomaterial fabrication (Li et al., 2012). Kerateines and S-sulfo-kerateines preserve hydrophobicity and ability to regenerate the starting keratin through crosslinking, while keratoses are hydrophilic and loses the crosslinking ability. Thus, biomaterials with different physical configurations and functions in relation with the living bodies can be fabricated, as given in Table 5. Particularly, scaffolds for cell culture have been developed (Table 5), even if they exhibit lower cytocompatibility than collagen or gelatin, which are currently preferred for tissue engineering applications (Wang et al., 2016c).

Cosmetic applications of keratin solubilisates are directed mainly to proprietary hair-care products, owned by the producing companies.

Table 5. Solubilization methods and biomedical applications of wool solubilization products

Solubilization method	***Solubilization product / physical state and characteristics***	***Application***	***Reference***
Reduction	Kerateine-calcium alginate blend / high porosity sponge	Cell culture substrate	Hamasachi et al. (2008)
	Kerateine / sponge-like porous hydrogel	Scaffold for animal cell culture	Ozaki et al. (2014)
	Kerateine / Hydrogel	Drug carrier, cell culture substrate	Nakata et al. (2015)
	Kerateine / injectable and cytocompatible gel	Pulp-dentin regeneration	Ajay Sharma et al. (2016)
	S-carboxymethylated kerateine / nanofibrous mats	Scaffold for vascular tissue engineering	Li et al. (2016)
	Kerateine reduced with L-cysteine / hydrophilic nanonets	Cell culture substrate with enhanced cell adhesion and proliferation properties	Zhu et al. (2017)
Oxidation	Keratose / hydratable fibers or powder	Wound dressing, filler for implant applications	Van Dyke et al. (2001)
	Alpha-keratose / stable hydrogel	Cell scaffolding for adhesion and proliferation of fibroblasts	Sando et al. (2010)
	Keratose / matrix composition	Acellular scaffold for nerve regeneration	Van Dyke (2011)
	Keratose and sulfonated keratin homologs / solution	Additive in self-care products	Cardamone et al. (2014)
Sulfitolysis	S-sulfokerateine / microparticles (~6 μm)	Microparticulate drug delivery system	Cilurzo (2013)
	S-sulfokerateine / filler in poly(L-lactic) acid based biocomposite films	Culture media for human bone-marrow mesenchymal stem cells	Fortunati et al. (2015)
	S-sulfokerateine / photo-active film with antibacterial activity	Wound healing and tissue engineering	Aluigi et al. (2015)
	S-sulfokerateine doped with polydopamine nanoparticles / sponge with tunable morphology	3-D scaffold for cell culture, with antioxidant properties. Tissue engineering, drug delivery.	Posati et al. (2016)
	Photofunctionalized S-sulfokerateine / sponge with tunable porosity	3D scaffold with antimicrobial activity, for human fibroblast cells growth	Ferroni et al. (2016)
Mild alkaline hydrolysis	Keratin hydrolysate / Nanoparticles	Biomimetic keratin/hydroxyapatite nanocomposite for osteoblast culture and bone tissue regeneration	Li et al. (2012)
Ionic liquids	Keratin-cellulose-chitosan composite films	Drug delivery substrate	Tran and Mututuvari (2015)
	Alpha-keratin / powder/ electrospun nanofibers	Bandages or hydrogels for wound healing	Moore et al. (2016)
	Keratin-cellulose blend regenerated by casting	Scaffold for biomimetic hydroxyapatite mineralization	Salama and El-Sakhawy (2016)

5. Conclusions

With the rise and development of manmade fibers, the wool textile sector faced a dramatic decline. During the last decades, the share of wool fibers on the global market kept around 1.3%, with no prospects for increase. Huge amounts of raw wool, rejected by the textile industry, turned from an income source into a waste management issue. EU Regulations set the principles of wool waste management, together with practical rules concerning handling, treating, transportation and disposal.

The search for sustainable resources determined the reconsideration of raw wool waste as a biodegradable renewable resource, with particular fibrous structure and high content of keratin protein. It came into the attention of researchers and economic actors, who found effective and economically feasible pathways for converting a problematic waste into value-added materials and products. Various non-clothing applications, ranging from building insulation, oil spill sorbents and soil fertilizers, to carbon nanofibers and scaffolds for tissue engineering were developed. Finding non-conventional uses for wool can contribute to the survival of sheep farming, which is an important and traditional activity in worldwide mountain and arid regions, where there are few alternative forms of production or income.

Valorization of wool as a renewable and biodegradable resource has social, economic and environmental benefits, and can contribute to the sustainable development concept.

Acknowledgements

This work has been financially supported by Erasmus Mundus Joint Doctorate Programme SMDTex – Sustainable Management and Design for Textile [Grant number 532704-1-FR-2012-1-ERA MUNDUS-EMJD].

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