Phenolic Dyed Textile Fabrics

Subjects: Materials Science, Textiles

Contributor: Tiago Barros Afonso , Teresa Bonifácio-Lopes , Eduardo Manuel Costa , Manuela Estevez Pintado

Textile dyeing is known to have major environmental concerns, especially with the high use of toxic chemicals. The use of alternatives such as natural dyes rich in phenolic compounds has become extremely appealing in order to move towards a more sustainable circular economy. Phenolic dyes have the potential to functionalize textile fabrics with properties such as antimicrobial, antioxidant, and UV protection.

phenolic compounds by-products textiles sustainable dyeing

1. Introduction

The textile industry is known to have major environmental issues of concern regarding the high use of energy, water, and chemicals. The huge amount of chemical usage in its processes makes this industry a major global source of pollution [1]. Synthetic dyes, in particular, pose major challenges as environmental contaminants in textile wastewater due to their non-biodegradable nature, making them difficult to remove from water. Thus, a need has risen to move the textile industry towards a sustainable circular economy [2]. This awareness of eco-safety and increased environmental concern has led to the use of green and sustainable natural dyes as the needed trend in the textile industry [3].

Natural dyes have been used for the coloration of synthetic and natural textile materials since prehistoric times [4]. With the arrival of synthetic dyes in the Industrial Revolution, the use of natural dyes declined to a great extent and practically stopped [4][5]. During the last few decades, researchers' attention has turned once again towards various aspects of natural dye applications.

Natural dyes are commonly considered eco-friendly as they are obtained from renewable sources and because they are non-toxic, non-carcinogenic, and biodegradable [6]. However, the production and use of natural dyes is not free from environmental concerns as they can be derived from rare, endangered, and threatened (RET) species (e.g., RET plants of Madhya Pradesh, India) or mordant dyes containing heavy metals as part of the dye molecule (e.g., zinc phthalocyanine, acid blue, copper (II) phthalocyanine, lead (II) phthalocyanine, cadmium phthalocyanine) [1][7][8]. According to the latest (4.0) version of the Global Organic Textile Standard (GOTS), dyes obtained from RET species or dyes containing heavy metals are prohibited [9]. Among sources of natural dyes, the use of different raw plant materials and by-products represents an economically and ecologically useful path [10].

Phenolic plant compounds or polyphenols have been gaining interest due to their application as in situ textile dyes as they have colors and have been widely used as natural colorants in the food industry [11]. These compounds are the main plant-derived substances formed by their secondary metabolism. They have always been present throughout human history, long before their formal discovery. Polyphenols have applications in several industries such as the food, pharmaceutical, cosmetic, packaging, and textile industries [12][13][14]. Their use is extremely valuable due to their range of bioactivities, including antimicrobial, antioxidant, anti-proliferative, and anti-inflammatory, among others [11]. They are also responsible for pigmentation and can act as UV protectors, as well as protecting against insects and parasites [15][16]. These compounds can be found in a myriad of diverse matrices including fruits, vegetables, wild plants, etc. An extremely important approach is obtaining phenolic compounds from wastes/by-products of different industries, mainly food processing, but also wood processing and wine-making [17][18][19]. Agri-food bioresidues with no economic value represent a significant percentage of the food processing industries. Consequently, wastes/by-products serve as a natural source of these compounds, being both cheap and abundant while concurrently aiding in the reduction in waste [11].

Chemically, phenolic compounds are formed by one or more aromatic rings bonded to one or more hydroxyl (–OH) groups. For this reason, these compounds can be divided into five different groups: phenolic acids, flavonoids, tannins, stilbenes, and lignans [20] (**Figure 1**).

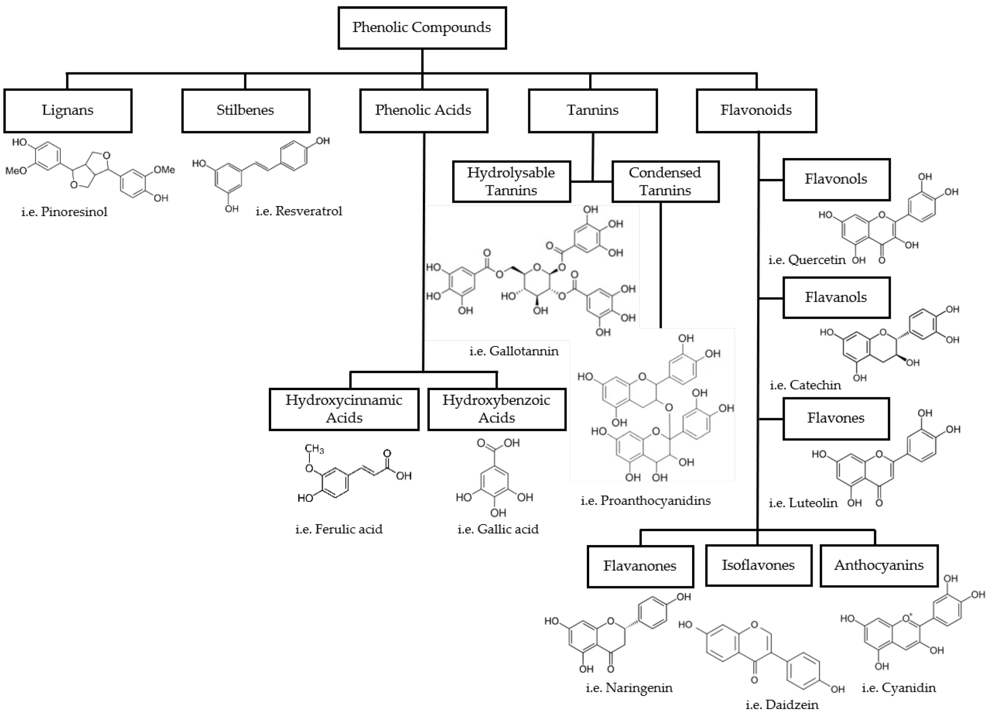

Figure 1. Classification and structural examples of phenolic compounds.

Phenolic acids are the simplest class of polyphenolic compounds present in foodstuff and their basic structure is characterized by one phenolic ring and a carboxylic acid function. They are derived from two main phenolic compounds, thus being divided into two groups: hydroxybenzoic acids (C6–C1) derived from benzoic acid and hydroxycinnamic acids (C6–C3) derived from cinnamic acid (**Figure 1**) [20]. The latter is composed of the most common phenolic acids, such as ferulic and caffeic acids, and is responsible for several important bioactivities [20][21].

The most abundant phenolic compounds are flavonoids. They generally comprise a skeleton of carbon atoms (C6–C3–C6) that is built into two benzene rings (A and B), linked by a heterocyclic pyrane ring (C) [11][20]. Depending on the bond between the B and C rings and the substitution patterns of the C ring, they can be divided into six subgroups: flavonols, flavanols, flavones, flavanones, isoflavones, and anthocyanins (**Figure 1**) [20]. Flavonoids are widespread in several food matrices and are deeply investigated for their range of bioactivities [12].

Tannins are higher-molecular-weight phenolic compounds and are divided into two subgroups: hydrolyzable tannins and condensed tannins, also called proanthocyanidins [20]. They are the most common phenolic compounds found in plant tissues and are responsible for the bitter taste in a variety of fruits [11]. Condensed tannins are oligomers and polymers consisting of two or more monomers of flavan-3-ols units, linked together by bonds between the A rings of the flavanol units and the pyrane rings of other flavanols [20]. Hydrolyzable tannins are mixtures of simple phenols such as ellagic and gallic acids, with a carbohydrate. Gallotannin is an example of a hydrolyzed tannin structure formed from gallic acid (**Figure 1**) [20]. They are also known to possess a wide range of biological properties [22].

Stilbenes are chemically characterized by two benzene rings linked by a double bond with the structure C6–C2–C6, with the E isomer configuration being the most common [20]. The most known stilbene is resveratrol, with its bioactivities being broadly studied (**Figure 1**) [20][23].

Lignans are widespread secondary plant metabolites with different chemical structures. However, their common structure is composed of a combination of two phenylpropanoid C6–C3 units, linked by the central carbons of the side chains [20]. One of the main dietary lignans is pinoresinol (**Figure 1**). Their main properties are related to estrogenic and anti-estrogenic activities [20].

2. Functional Properties of Phenolic Dyed Textile Fabrics

Functional finishing is always an exciting treatment in which fabrics can be given interesting performance/functional properties during textile processing. Natural dyes rich in polyphenols can directly provide desirable finishing properties during the dyeing process without the need for a separate finishing. Due to different functional groups, these dyes can form different interactions between the dye and the fabric, allowing for different functional properties to be achieved [20]. While some dyes only report one function, most of them can be responsible for different functionalities at the same time. The two main reported functionalities provided to textile fabrics are antimicrobial/antibacterial and UV protection, followed by antioxidant performance. To a lesser extent, other functionalities have also been reported, i.e., flame retardance, hydrophobicity, insect resistance, and moth proofing.

2.1. Antimicrobial/Antibacterial

The human body is constantly being exposed to a variety of microorganisms such as bacteria and other microbes. While clothing fabrics usually cover a significant part of the human skin, they inherently lack effective antimicrobial resistance. On the contrary, they have been recognized as a medium for supporting bacterial growth and proliferation [24]. For instance, some fabrics such as wool, due to its proteinaceous nature, under ambient conditions of moisture and temperature, can serve as a growth promoter for a large number of bacterial strains [25]. Subsequently, this bacterial growth can lead to the discoloration and degradation of textile fabrics or more importantly, to an increased risk of dermal infection and allergic responses [25]. For these reasons, providing antimicrobial/antibacterial properties to textile fabrics becomes crucial.

Different methodologies have been used to test the antimicrobial/antibacterial properties of textile fabrics dyed with natural dyes rich in polyphenols. These include methodologies such as zone of inhibition and agar diffusion tests, percentage reduction assays, spectrophotometric assays, and minimum inhibitory concentration determinations, among others [25][26][27][28]. These have usually been performed in accordance with standardized methodologies, i.e., AATCC TM 100 [29], AATCC TM 90:2016 [30], ASTM E2149 [31], ISO/DIS 20743 [32], and GB/T 20944.3-2008 [24][26][28][33][34][35].

The two most tested microorganisms for evaluating antimicrobial/antibacterial properties of dyed fabrics are bacterial strains such as *Escherichia coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive) [6][36][37][38]. Other commonly used bacteria are *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *B. cereus*, while *Candida albicans* is the most commonly selected fungus [27][39][40][41][42].

Phenolic compounds attach onto fabrics by forming a complex, and when microorganisms come into contact with the fabrics, these compounds can disrupt their enzyme production which eventually results in the death of the cell. For instance, several dyed fabrics were able to achieve a great percentage of inhibition against bacteria. These include dyed fabrics with pure phenolic compounds such as pyrogallol, phloroglucinol, pyrocatechol, and resorcinol, which were able to inhibit >99.9% of *S. aureus* and >99.6% of *E. coli* in cotton and wool fabrics [43]. A dye obtained from Keemun black tea, with theaflavins as the major polyphenol in its composition, was able to inhibit >99.9% of *S. aureus* in flax fabric [44]. Aqueous chestnut shell extracts, having condensed tannins and gallic and ellagic acids, were able to achieve percentage inhibitions of >99.9% against *S. aureus* and *K. pneumoniae* in cotton fabric [45][46]. Several other dyes were also able to achieve over 90% inhibition against microbes. Fang et al. [47] reported percentage inhibitions of >98% against *S. aureus* and *E. coli* with an extract containing tannins and flavonoids obtained from *I. batatas* leaves, in wool, cotton, nylon, polyester, and silk fabrics. Interestingly, these fabrics maintained very good inhibition percentages (>84%) even after 30 wash cycles. Other natural dyes were able to maintain some of their antimicrobial activity after washing. Wool fabric dyed with an extract obtained from rice straw showed >98% inhibition against *S. aureus* and >80% was maintained after 20 washing cycles [48]. In addition, cotton fabric dyed with *G. ericarpum* leaf extracts showed >80% inhibition against *E. coli* after five washing cycles [49].

In some cases where the extract itself did not display strong antimicrobial activity, a combination with different mordants was able to enhance this functionality. For example, Sadeghi-Kiakhani et al. [50] showed that wool fabrics dyed with extracts from pomegranate peels and walnut green husks displayed around 65% inhibition against *E. coli* and *S. aureus*. In the same study, when the wool fabric was pretreated with Ag or Cu before being dyed with the extract, it was able to achieve >99.9% inhibition. In addition, after 10 washing cycles, the fabric maintained >91%

inhibition against both bacteria. Thus, the application of mordants (i.e., aluminum, tannic acid, chitosan), crosslinking, or other surface modifications with cationization or by applying a biopolymer are responsible for increasing functionality and providing washing stability [51][52][53][54][55].

2.2. UV Protection

Several diseases are directly linked to the exposure of skin to solar UV radiation, such as freckles, sunburns, and in extreme cases, skin cancer [15]. With the harmful changes occurring in our climate, these problems are becoming more common and exacerbated, resulting in the need for protection against UV radiation. Solar UV light radiation contains three parts: UV-A (400 − 315 nm), UV-B (315 − 290 nm), and UV-C (290 − 200 nm). The main concern regarding damage to human skin is UV-A as most of the UV-B and UV-C are filtered by the ozone layer [56].

Different synthetic UV absorbers are currently available for the textile industry, but there is an obvious need to search for more sustainable alternatives. The UV protective property of dyed fabrics is typically analyzed using their ultraviolet protection factor (UPF) as an indicator. This UV protective analysis is usually completed in accordance with standardized methods, i.e., AATCC 183 [57], GB/T 18830-2009 [58], AS/NZS 4399:1996 [59], and EU standard 13758-2001 [36][48][60][61][62]. The UPF scale is the following: 15–24, good; 25–39, very good; and 40–50+, excellent.

Textile fabrics by themselves have poor UPF values (<15) and thus, cannot offer sufficient UV protection [38]. The application of natural dyes rich in polyphenols onto textile fabrics can significantly increase their UPF. For instance, cotton fabric dyed with *S. nigrum* or *A. viridis* displayed UPF values of 60+ and 100+, respectively. This excellent UPF was attributed to the presence of polyphenols and flavonoids as *A. viridis* extract had a higher content of these compounds [63]. Flavonoids are known for their capacity as UV absorbers, and present wavelength selectivity for UV-B which may prevent the accumulation of UV-B-induced damage [63]. The excellent UV protective properties (100+ UPF) of wool fabrics dyed with orange peel extracts were reported to not only be due to the absorbability of UV rays by colored phenolic components, but also by the presence of other colorless phenolic compounds [64]. Cotton fabric, dyed with a natural dye obtained from groundnut testa, revealed an excellent UPF of 50+. This UV protective functionality was attributed to the presence of tannins, phenols, and flavonoids as these compounds exhibit free radical scavenging capability [65]. Other fabrics dyed with extracts rich in flavonoids and tannins have also reported a 50+ UPF, such as wool fabric dyed with rice straw and *A. auriculiformis* extracts [48][66]. Guo et al. [18], reported that the excellent UV protection of cotton fabric dyed with grape seed extract was due to the high number of aromatic rings present in proanthocyanins.

The same dye can provide different UPF values on different fabrics. For instance, cotton dyed with an extract obtained from roasted peanut skin showed <15 UPF, while silk and wool fabrics dyed with the same extract showed 50+ UPF [67].

Although natural dyes improve the UV protective properties of fabrics, there are some limitations associated with them. After long exposure to UV rays as well as several washing steps, this protection might be reduced or even lost. Otaviano et al. [68] reported a good UPF (25) for cotton dyed with pomegranate peel extract, but after 10 washing cycles, no UV protection was detected. To address this issue, mordants can be used. In this same study, with the combination of natural dye with Fe (II), the fabric was able to maintain a good UPF throughout the washing cycles [68]. In addition, the use of chitosan as a mordant allowed cotton fabric dyed with *G. ericarpum* to maintain a UPF of 30 after five repeated washing cycles [49]. Nevertheless, other natural dyes were able to provide their UV protective function to textiles after laundry cycles without any mordant. For example, cashmere dyed with grape seed proanthocyanins, wool fabric dyed with Sorghum husk extract, and silk fabric dyed with *A. vera* rind extract all maintained an excellent (50+) UPF even after 20, 30, and 25 washing cycles, respectively [69][70][71].

2.3. Antioxidant

Free radicals present in the atmosphere are considered a major cause of several specific human diseases, making antioxidant activity a subject of intense interest. However, the antioxidant activity of textiles has not attracted proper attention in the past, while in reality, clothes with an antioxidant function can provide the skin with protection against free radicals that are responsible for skin aging [18]. Phenolic compounds present in natural dyes are well known for their antioxidant properties, being considered their most effective feature. The antioxidant activity of these compounds is mainly owed to their redox properties, which help to captivate and neutralize free radicals [56]. For instance, phenolic acids usually display antioxidant activity by trapping free radicals, while flavonoids can scavenge them [37]. Thus, when applied to clothing materials, phenolic compounds will help protect the skin from various types of damage by slowing the effects of free radicals [51].

The two main reported methodologies for evaluating the antioxidant activity of dyed fabrics with natural dyes are 1,1-diphenyl l-2-picrylhydrazyl free radical ($DPPH^{\bullet}$) and ABTS radical cation ($ABTS^{\bullet +}$) scavenging activities [37][72][73]. Results are typically shown in terms of percentages of inhibition.

Undyed textile fabrics have a poor ability to catch free radicals and poor antioxidant function [74][75]. Linen fabric dyed with *S. baicalensis* showed 84% free radical scavenging activity. This was due to the presence of the phenolic compound baicalin [36]. Polyamide fabric dyed with quercetin showed above 90% free radical scavenging activity [37]. Guinot et al. [76] reported excellent antioxidant activity in hemp and wool fabrics dyed with *S. officinalis*, *T. vulgaris*, and *A. cepa* extracts. This was attributed to the high content of flavonoids and hydroxycinnamic acid derivatives in their composition. Different natural dyes obtained from by-products were also able to functionalize textile fabrics with high antioxidant activity. Among others, wool fabric dyed with *S. sebiferum* fallen leaf extract, silk fabric dyed with tea stem waste extract, and viscose fabric dyed with orange peel extract showed antioxidant activity above 90% [27][46][56][70][75][77].

Several dyed fabrics were also able to maintain some of their antioxidant activity after washing cycles. For instance, wool fabric dyed with *A. nilotica* bark extract showed a decrease to 30% of its antioxidant activity after 20 washing cycles, while initially showing 87%. In this study, the use of mordants allowed for a slightly better (40%)

antioxidant activity after washing cycles [78]. In another study, cotton and wool fabrics dyed with *Hibiscus* flower extract showed over 75% free radical scavenging activity with and without mordants after five washing cycles [74]. As observed for other functionalities, the use of mordants or crosslinkers also allowed for the obtention of better antioxidant activities [51][52][55][79]. Nevertheless, wool fabric dyed with an extract obtained from pineapple peel showed distinctly better antioxidant activity without a mordant when compared to that of wool dyed using a ferrous mordant [80].

These differences in textile dye efficacies require further research to achieve optimal treatment and dyeing conditions in order to maximize the functionalities of fabrics.

2.4. Flame Retardance

Flame-retardant treatment is used to reduce the risk of fire in textiles because they are quite flammable and capable of burning well. There are inorganic and organic flame-retardant compounds commercially available. Organic compounds are the most utilized as they can be applied to almost all textiles whereas inorganic compounds are mainly applied to wool fabrics [34]. The most used organic flame-retardant compounds are bromine-, chlorine-, phosphorus-, and nitrogen-containing compounds, but some of them are toxic or not eco-friendly [34]. Although numerous polyphenolic natural dyes are reported to provide functionalities such as those described in the previous sections, not enough attention has yet been given towards their application as flame retardants.

Few studies have reported the flame retardance functionality of fabrics dyed with polyphenolic extracts. The studies that reported this functionality evaluated flame-retardant properties through the limited oxygen index (LOI) in addition to vertical flammability tests according to the standardized methods GB/T 5454-1997 [81], ASTM D2863 [82], GB/T 5455-2014 [83] and ASTM D6413 [34][48][75][84][85]. Fabrics exhibiting LOI values higher than 25% are considered flame-retardant.

A natural dye obtained from *D. cirrhosa* tubers was able to provide silk fabric with flame retardance properties, even after 20 washing cycles (LOI higher than 28%). The flame retardance function provided by this dye was attributed to the presence of condensed tannins [34]. Tannins possess high chemical and thermal stability alongside low thermal conductivity due to their specific aromatic structure, which makes them suitable for providing textiles with flame retardance properties for various applications [34]. Tea stem waste extract was also able to provide silk fabric with good flame retardance properties (LOI of 25.6%). With metallic salt mordants, this property was slightly increased (LOI of 26.75%) [75]. This property was attributed to the polymerized products in tea stem extract and the formation of natural polyphenols/metal ions/silk fabric complexes [75]. Proanthocyanins from grape seeds were also able to impair silk fabric with durable flame retardance properties (LOI of 27%). This property was maintained after 20 washing cycles [84]. Wool fabric dyed with rice straw extract also showed flame retardance properties due to the presence of phenolic compounds in combination with different mordants (LOI of 27.5%). However, after 20 washing cycles, the LOI value decreased below 25% [48].

2.5. Other Functionalities

To a lesser extent, other functionalities are reported to textile fabrics dyed with phenolic dyes. For instance, highly hydrophobic fabrics were able to be fabricated by using nature-inspired polyphenol chemistry. Using tannic, ferulic, and caffeic acids for coating fabrics such as viscose and cotton enabled the loading of hydrophobic particles (i.e., silver nanoparticles, Fe (III), and DTM@Ti$(OH)_4$) onto them [86][87][88]. These metal-organic systems coated the fabrics and affected their surface roughness, making the textiles hydrophobic. All of the fabrics revealed an excellent hydrophobic capacity even after several washing cycles (25 to 50 washing cycles). Other authors reported that lotus leaf extract containing polyphenols and flavonoids was able to enhance the hydrophobicity of dyed polyester yarns [89].

Insect resistance has also been reported. For instance, a polyphenolic extract obtained from mango seed kernel was able to provide wool fabric with insect repellence activity against larvae of *Tineola bisselliella*. These insects can digest keratin protein causing premature damage to wool-made fabrics [16]. In addition, orange peel extract was also able to provide linen fabric with insect resistance activity [56]. Moreover, anti-moth properties were reported in wool fabric dyed with *M. azedarach* bark extract against the larvae of the black carpet beetle (*Attagenus unicolor*) [90].

References

1. Agnhage, T.; Perwuelz, A.; Behary, N. Towards Sustainable Rubia tinctorum L. Dyeing of Woven Fabric: How Life Cycle Assessment Can Contribute. J. Clean. Prod. 2017, 141, 1221–1230.
2. Rahman, S.S.; Siddiqua, S.; Cherian, C. Sustainable Applications of Textile Waste Fiber in the Construction and Geotechnical Industries: A Retrospect. Clean. Eng. Technol. 2022, 6, 100420.
3. Wang, F.; Gong, J.; Ren, Y.; Zhang, J. Eco-Dyeing with Biocolourant Based on Natural Compounds. R. Soc. Open Sci. 2018, 5, 171134.
4. Shabbir, M.; Rather, L.J.; Shahid-ul-Islam; Bukhari, M.N.; Shahid, M.; Ali Khan, M.; Mohammad, F. An Eco-Friendly Dyeing of Woolen Yarn by Terminalia Chebula Extract with Evaluations of Kinetic and Adsorption Characteristics. J. Adv. Res. 2016, 7, 473–482.
5. Javaid, R.; Qazi, U.Y. Catalytic Oxidation Process for the Degradation of Synthetic Dyes: An Overview. Int. J. Environ. Res. Public. Health 2019, 16, 2066.
6. Jia, Y.; Liu, B.; Cheng, D.; Li, J.; Huang, F.; Lu, Y. Dyeing Characteristics and Functionability of Tussah Silk Fabric with Oak Bark Extract. Text. Res. J. 2017, 87, 1806–1817.
7. Yadav, S.; Tiwari, K.S.; Gupta, C.; Tiwari, M.K.; Khan, A.; Sonkar, S.P. A Brief Review on Natural Dyes, Pigments: Recent Advances and Future Perspectives. Results Chem. 2023, 5, 100733.

8. Velusamy, S.; Roy, A.; Sundaram, S.; Kumar Mallick, T. A Review on Heavy Metal Ions and Containing Dyes Removal Through Graphene Oxide-Based Adsorption Strategies for Textile Wastewater Treatment. Chem. Rec. 2021, 21, 1570–1610.
9. Global Organic Textile Standard (GOTS). Version 4.0. Available online: www.global-standard.org (accessed on 6 November 2023).
10. Danila, A.; Costea, M.; Profire, L.; Rimbu, C.M.; Baican, M.; Lupascu, F.; Tatarusanu, S.M.; Profire, B.S.; Muresan, E.I. A Sustainable Approach to a Cleaner Production of Antimicrobial and Biocompatible Protein Fibers. Polymers 2022, 14, 3194.
11. Albuquerque, B.R.; Heleno, S.A.; Oliveira, M.B.P.P.; Barros, L.; Ferreira, I.C.F.R. Phenolic Compounds: Current Industrial Applications, Limitations and Future Challenges. Food Funct. 2021, 12, 14–29.
12. Mark, R.; Lyu, X.; Lee, J.J.L.; Parra-Saldívar, R.; Chen, W.N. Sustainable Production of Natural Phenolics for Functional Food Applications. J. Funct. Foods 2019, 57, 233–254.
13. Brudzyńska, P.; Sionkowska, A.; Grisel, M. Plant-Derived Colorants for Food, Cosmetic and Textile Industries: A Review. Materials 2021, 14, 3484.
14. Zeng, P.; Chen, X.; Qin, Y.R.; Zhang, Y.H.; Wang, X.P.; Wang, J.Y.; Ning, Z.X.; Ruan, Q.J.; Zhang, Y.S. Preparation and Characterization of a Novel Colorimetric Indicator Film Based on Gelatin/Polyvinyl Alcohol Incorporating Mulberry Anthocyanin Extracts for Monitoring Fish Freshness. Food Res. Int. 2019, 126, 108604.
15. Grifoni, D.; Bacci, L.; Di Lonardo, S.; Pinelli, P.; Scardigli, A.; Camilli, F.; Sabatini, F.; Zipoli, G.; Romani, A. UV Protective Properties of Cotton and Flax Fabrics Dyed with Multifunctional Plant Extracts. Dye. Pigment. 2014, 105, 89–96.
16. Hassan, M.M. Enhanced Insect-Resistance, UV Protection, and Antibacterial and Antistatic Properties Exhibited by Wool Fabric Treated with Polyphenols Extracted from Mango Seed Kernel and Feijoa Peel. RSC Adv. 2021, 11, 1482–1492.
17. Gómez-Moreno, H.; Duran-Serra, A.; Prieto-Fuentes, R.; Álvarez del Castillo, M.D.; Macanás, J.; Carrillo-Navarrete, F. Almond Skin, a Bio-Waste for Green Dyeing of Wool Fibres. Text. Res. J. 2023, 93, 1030–1042.
18. Guo, L.; Yang, Z.Y.; Tang, R.C.; Yuan, H. Bin Preliminary Studies on the Application of Grape Seed Extract in the Dyeing and Functional Modification of Cotton Fabric. Biomolecules 2020, 10, 220.
19. Rossi, T.; Silva, P.M.S.; De Moura, L.F.; Araújo, M.C.; Brito, J.O.; Freeman, H.S. Waste from Eucalyptus Wood Steaming as a Natural Dye Source for Textile Fibers. J. Clean. Prod. 2017, 143, 303–310.

20. Durazzo, A.; Lucarini, M.; Souto, E.B.; Cicala, C.; Caiazzo, E.; Izzo, A.A.; Novellino, E.; Santini, A. Polyphenols: A Concise Overview on the Chemistry, Occurrence, and Human Health. Phytother. Res. 2019, 33, 2221–2243.

21. Sun, S.S.; Xing, T.; Tang, R.C. Simultaneous Coloration and Functionalization of Wool, Silk, and Nylon with the Tyrosinase-Catalyzed Oxidation Products of Caffeic Acid. Ind. Eng. Chem. Res. 2013, 52, 8953–8961.

22. Pizzi, A. Tannins Medical / Pharmacological and Related Applications: A Critical Review. Sustain. Chem. Pharm. 2021, 22, 100481.

23. Alonso, C.; Martí, M.; Martínez, V.; Rubio, L.; Parra, J.L.; Coderch, L. Antioxidant Cosmeto-Textiles: Skin Assessment. Eur. J. Pharm. Biopharm. 2013, 84, 192–199.

24. Zhang, B.; Wang, L.; Luo, L.; King, M.W. Natural Dye Extracted from Chinese Gall–The Application of Color and Antibacterial Activity to Wool Fabric. J. Clean. Prod. 2014, 80, 204–210.

25. Zhou, Q.; Rather, L.J.; Mir, S.S.; Ali, A.; Rizwanul Haque, Q.M.; Li, Q. Bio Colourants from the Waste Leaves of Ginkgo biloba L. Tree: Wool Dyeing and Antimicrobial Functionalization against Some Antibiotic-Resistant Bacterial Strains. Sustain. Chem. Pharm. 2022, 25, 100585.

26. Raji, Y.; Nadi, A.; Chemchame, Y.; Mechnou, I.; Bouari, A.E.L.; Cherkaoui, O.; Zyade, S. Eco-Friendly Extraction of Flavonoids Dyes from Moroccan (Reseda luteola L.), Wool Dyeing, and Antibacterial Effectiveness. Fibers Polym. 2023, 24, 1051–1065.

27. Zhou, Q.; Rather, L.J.; Ali, A.; Wang, W.; Zhang, Y.; Rizwanul Haque, Q.M.; Li, Q. Environmental Friendly Bioactive Finishing of Wool Textiles Using the Tannin-Rich Extracts of Chinese Tallow (Sapium sebiferum L.) Waste/Fallen Leaves. Dye. Pigment. 2020, 176, 108230.

28. Inprasit, T.; Pukkao, J.; Lertlaksameephan, N.; Chuenchom, A.; Motina, K.; Inprasit, W. Green Dyeing and Antibacterial Treatment of Hemp Fabrics Using Punica Granatum Peel Extracts. Int. J. Polym. Sci. 2020, 2020, 6084127.

29. AATCC TM 100; Test Method for Antibacterial Finishes on Textile Materials: Assessment of. American Association of Textile Chemists and Colorists (AATCC): Research Triangle Park, NC, USA, 2019.

30. AATCC TM 90; Antimicrobial Activity Assessment of Textile Materials: Agar Plate. American Association of Textile Chemists and Colorists (AATCC): Research Triangle Park, NC, USA, 2016.

31. ASTM E2149; Standard Test Method for Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions. American Society for Testing and Materials: West Conshohocken, PA, USA, 2020.

32. ISO/DIS 20743; Textiles—Determination of Antibacterial Activity of Textile Products. International Organization for Standardization: Geneva, Switzerland, 2013.

33. Bouaziz, A.; Dridi, D.; Gargoubi, S.; Chelbi, S.; Boudokhane, C.; Kenani, A.; Aroui, S. Analysis of the Coloring and Antibacterial Effects of Natural Dye: Pomegranate Peel. Coatings 2021, 11, 1277.

34. Yang, T.T.; Guan, J.P.; Tang, R.C.; Chen, G. Condensed Tannin from Dioscorea Cirrhosa Tuber as an Eco-Friendly and Durable Flame Retardant for Silk Textile. Ind. Crops Prod. 2018, 115, 16–25.

35. GB/T 20944.3-2008; Textiles-Evaluation for Antibacterial Activity-Part 3: Shake Flask Method. National Standard of the People’s Republic of China, China Standard Press: Beijing, China, 2008.

36. Li, H.; Li, Z.; Liu, Y.; Li, M. Advantages of Scutellaria baicalensis Extracts over Just Baicalin in the Ultrasonically Assisted Multi-Functional Treatment of Linen Fabrics. Cellulose 2020, 27, 4831–4846.

37. Li, Y.D.; Guan, J.P.; Tang, R.C.; Qiao, Y.F. Application of Natural Flavonoids to Impart Antioxidant and Antibacterial Activities to Polyamide Fiber for Health Care Applications. Antioxidants 2019, 8, 301.

38. Jose, S.; Pandit, P.; Pandey, R. Chickpea Husk–A Potential Agro Waste for Coloration and Functional Finishing of Textiles. Ind. Crops Prod. 2019, 142, 111833.

39. Andriamanantena, M.; Razafimbelo, F.F.; Raonizafinimanana, B.; Cardon, D.; Danthu, P.; Lebeau, J.; Petit, T.; Caro, Y. Alternative Sources of Red Dyes with High Stability and Antimicrobial Properties: Towards an Ecological and Sustainable Approach for Five Plant Species from Madagascar. J. Clean. Prod. 2021, 303, 126979.

40. Lee, Y.H.; Hwang, E.K.; Baek, Y.M.; Kim, H.-D. Deodorizing Function and Antibacterial Activity of Fabrics Dyed with Gallnut (Galla chinensis) Extract. Text. Res. J. 2015, 85, 1045–1054.

41. Xia, W.; Li, Z.; Tang, Y.; Li, Q. Sustainable Recycling of Café Waste as Natural Bio Resource and Its Value Adding Applications in Green and Effective Dyeing/Bio Finishing of Textile. Sep. Purif. Technol. 2023, 309, 123091.

42. Ghaheh, F.S.; Nateri, A.S.; Mortazavi, S.M.; Abedi, D.; Mokhtari, J. The Effect of Mordant Salts on Antibacterial Activity of Wool Fabric Dyed with Pomegranate and Walnut Shell Extracts. Color. Technol. 2012, 128, 473–478.

43. Hong, K.H. Phenol Compounds Treated Cotton and Wool Fabrics for Developing Multi-Functional Clothing Materials. Fibers Polym. 2015, 16, 565–571.

44. Wang, P.; Wu, H.; Zheng, X.; Bian, L.; Sun, Y.; Wang, Z.; Li, C. High-Binding-Fastness Dye from Functional Extracts of Keemun Black Tea Waste for Dyeing Flax Fabric. Color. Technol. 2022, 138, 255–265.

45. Hong, K.H. Sustainable Functional Finishing for Cotton Fabrics Using Chestnut Shell Extract. Cellulose 2021, 28, 11729–11743.

46. Hong, K.H. Sustainable Functionalization for Cotton Fabrics by Printing with a Mixture of Chestnut Shell Extract and Alginate. Polym. Bull. 2023, 80, 6675–6692.

47. Fang, J.; Meng, C.; Zhang, G. Agricultural Waste of Ipomoea Batatas Leaves as a Source of Natural Dye for Green Coloration and Bio-Functional Finishing for Textile Fabrics. Ind. Crops Prod. 2022, 177, 114440.

48. Kadam, S.; Sharma, A.; ul-Islam, S.; Bramhecha, I.; Sheikh, J. Utilization of Rice Straw as a Source of Biomolecules for Sustainable Multifunctional Finishing Vis a Vis Dyeing of Wool. J. Nat. Fibers 2020, 17, 1508–1518.

49. Zhou, Y.; Tawiah, B.; Wang, L.; Li, Q. Enhancing the Affinity and Adsorption Efficiency of Glochidion Ericarpum Champ Leave Extract to Cotton for Colouristic and Functional Properties Integrating Trimethyl Chitosan and Ultrasonic Technique. Ind. Crops Prod. 2022, 186, 115255.

50. Sadeghi-Kiakhani, M.; Tehrani-Bagha, A.R.; Gharanjig, K.; Hashemi, E. Use of Pomegranate Peels and Walnut Green Husks as the Green Antimicrobial Agents to Reduce the Consumption of Inorganic Nanoparticles on Wool Yarns. J. Clean. Prod. 2019, 231, 1463–1473.

51. Hong, K.H. Crosslinking Phenolic Compounds with Cotton Fabrics Using Succinic Acid to Develop Functional Clothing Materials. Fibers Polym. 2016, 17, 705–711.

52. Shahid-ul-Islam; Butola, B.S.; Roy, A. Chitosan Polysaccharide as a Renewable Functional Agent to Develop Antibacterial, Antioxidant Activity and Colourful Shades on Wool Dyed with Tea Extract Polyphenols. Int. J. Biol. Macromol. 2018, 120, 1999–2006.

53. Kim, S. Dyeing Characteristics and UV Protection Property of Green Tea Dyed Cotton Fabrics - Focusing on the Effect of Chitosan Mordating Condition. Fibers Polym. 2006, 7, 255–261.

54. Shahmoradi Ghaheh, F.; Mortazavi, S.M.; Alihosseini, F.; Fassihi, A.; Shams Nateri, A.; Abedi, D. Assessment of Antibacterial Activity of Wool Fabrics Dyed with Natural Dyes. J. Clean. Prod. 2014, 72, 139–145.

55. Koh, E.; Hong, K.H. Functional Fabric Treatment Using Tannic Acid and Extract from Purple-Fleshed Sweet Potato. Text. Res. J. 2017, 87, 790–798.

56. Rehan, M.; Abdel-Wahed, N.A.M.; Farouk, A.; El-Zawahry, M.M. Extraction of Valuable Compounds from Orange Peel Waste for Advanced Functionalization of Cellulosic Surfaces. ACS Sustain. Chem. Eng. 2018, 6, 5911–5928.

57. AATCC TM 183; Transmittance or Blocking of Erythemally Weighted Ultraviolet Radiation through Fabrics. American Association of Textile Chemists and Colorists (AATCC): Research Triangle Park, NC, USA, 2020.

58. GB/T 18830-2009; Textiles—Evaluation for Solar Ultraviolet Radiation Protective Properties. National Standard of the People’s Republic of China, China Standard Press: Beijing, China, 2009.

59. AS/NZS 4399:1996; Sun Protective Clothing–Evaluation and Classification. Standards Australia International Limited: Sydney, Australia, 1996.
60. Gong, K.; Pan, Y.; Rather, L.J.; Wang, W.; Zhou, Q.; Zhang, T.; Li, Q. Natural Pigment during Flora Leaf Senescence and Its Application in Dyeing and UV Protection Finish of Silk and Wool–A Case Study of Cinnamomum Camphora. Dye. Pigment. 2019, 166, 114–121.
61. Silva, P.M.d.S.; Fiaschitello, T.R.; de Queiroz, R.S.; Freeman, H.S.; da Costa, S.A.; Leo, P.; Montemor, A.F.; da Costa, S.M. Natural Dye from Croton Urucurana Baill. Bark: Extraction, Physicochemical Characterization, Textile Dyeing and Color Fastness Properties. Dye. Pigment. 2020, 173, 107953.
62. EU Standard 13758-2001; Textiles—Solar UV Protective Properties—Part 1: Method of Test for Apparel Fabrics. European Standards: Pilsen, Czech Republic, 2001.
63. Saleem, M.A.; Nazir, A.; Nazir, F.; Ayaz, P.; Faizan, M.Q.; Usman, M.; Hussain, T. Comparison of UV Protection Properties of Cotton Fabrics Treated with Aqueous and Methanolic Extracts of Solanum Nigrum and Amaranthus Viridis Plants. Photodermatol. Photoimmunol. Photomed. 2019, 35, 93–99.
64. Hou, X.; Chen, X.; Cheng, Y.; Xu, H.; Chen, L.; Yang, Y. Dyeing and UV-Protection Properties of Water Extracts from Orange Peel. J. Clean. Prod. 2013, 52, 410–419.
65. Pandit, P.; Jose, S.; Pandey, R. Groundnut Testa: An Industrial Agro-Processing Residue for the Coloring and Protective Finishing of Cotton Fabric. Waste Biomass Valorization 2021, 12, 3383–3394.
66. Chakraborty, L.; Pandit, P.; Roy Maulik, S. Acacia Auriculiformis–A Natural Dye Used for Simultaneous Coloration and Functional Finishing on Textiles. J. Clean. Prod. 2020, 245, 118921.
67. Pandey, R.; Patel, S.; Pandit, P.; Nachimuthu, S.; Jose, S. Colouration of Textiles Using Roasted Peanut Skin- an Agro Processing Residue. J. Clean. Prod. 2018, 172, 1319–1326.
68. Otaviano, B.T.H.; Sannomiya, M.; de Queiroz, R.S.; Sánchez, A.A.C.; Freeman, H.S.; Mendoza, L.E.R.; Veliz, J.L.S.; Leon, M.M.G.; Leo, P.; da Costa, S.A.; et al. Natural Dye Extracted from Pomegranate Peel: Physicochemical Characterization, Dyeing of Cotton Fabric, Color Fastness, and Photoprotective Properties. Fibers Polym. 2023, 24, 1321–1332.
69. Wang, Y.; Huang, L.; Wang, P.; Ran, R.; Zhang, T. Silk Textile Finished with Natural Dyes and UV Resistance Agents from Agricultural Waste Aloe Vera Rinds. J. Text. Inst. 2023, 1–7.
70. Li, Q.; Zhang, N.; Ni, L.; Wei, Z.; Quan, H.; Zhou, Y. One-Pot High Efficiency Low Temperature Ultrasonic-Assisted Strategy for Fully Bio-Based Coloristic, Anti-Pilling, Antistatic, Bioactive and Reinforced Cashmere Using Grape Seed Proanthocyanidins. J. Clean. Prod. 2021, 315, 128148.

71. Wizi, J.; Wang, L.; Hou, X.; Tao, Y.; Ma, B.; Yang, Y. Ultrasound-Microwave Assisted Extraction of Natural Colorants from Sorghum Husk with Different Solvents. Ind. Crops Prod. 2018, 120, 203–213.
72. Chen, M.X.; Haider, M.K.; Kim, I.S.; Lee, J.S. Characterization of Antioxidant Houttuynia Cordata Extracts Loaded Polyurethane Nanofibers. Fash. Text. 2023, 10, 17.
73. Sanchez-Sanchez, J.; Fernández-Ponce, M.T.; Casas, L.; Mantell, C.; de la Ossa, E.J.M. Impregnation of Mango Leaf Extract into a Polyester Textile Using Supercritical Carbon Dioxide. J. Supercrit. Fluids 2017, 128, 208–217.
74. Rehan, M.; Ibrahim, G.E.; Mashaly, H.M.; Hasanin, M.; Rashad, H.G.; Mowafi, S. Simultaneous Dyeing and Multifunctional Finishing of Natural Fabrics with Hibiscus Flowers Extract. J. Clean. Prod. 2022, 374, 133992.
75. Cheng, T.H.; Liu, Z.J.; Yang, J.Y.; Huang, Y.Z.; Tang, R.C.; Qiao, Y.F. Extraction of Functional Dyes from Tea Stem Waste in Alkaline Medium and Their Application for Simultaneous Coloration and Flame Retardant and Bioactive Functionalization of Silk. ACS Sustain. Chem. Eng. 2019, 7, 18405–18413.
76. Guinot, P.; Benonge, I.; Nicolett, G.; Gargadennec, A.; Andary, C.; Rapior, S. Combined Dyeing and Antioxidative Properties of Some Plant By-Products. Acta Bot. Gall. 2007, 154, 43–52.
77. Lachguer, K.; Boudadi, I.; Fayzi, L.; El Merzougui, S.; El Bouchti, M.; Cherkaoui, O.; Serghini, M.A. Natural Extraction of Dyes from Saffron “Crocus Sativus L” Flower Waste, Cotton Dyeing, and Antioxidant Effectiveness. Pollution 2023, 9, 890–906.
78. Rather, L.J.; Akhter, S.; Padder, R.A.; Hassan, Q.P.; Hussain, M.; Khan, M.A.; Mohammad, F. Colorful and Semi Durable Antioxidant Finish of Woolen Yarn with Tannin Rich Extract of Acacia Nilotica Natural Dye. Dye. Pigment. 2017, 139, 812–819.
79. Hassan, M.M.; Saifullah, K. Sustainable Dyeing and Functionalization of Jute Fabric with a Chinese Sumac Gall-Derived Gallotannin Using Eco-Friendly Mordanting Agents. Cellulose 2021, 28, 5055–5070.
80. Sheikh, J.; Agrawal, A.; Garg, H.; Agarwal, A.; Mathur, P. Functionalization of Wool Fabric Using Pineapple Peel Extract (PPE) as a Natural Dye. AATCC J. Res. 2019, 6, 16–20.
81. GB/T 5454-1997; Textiles–Burning Behavior—Oxygen Index Method. National Standard of the People’s Republic of China, China Standard Press: Beijing, China, 1997.
82. ASTM D2863; Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index). American Society for Testing and Materials: West Conshohocken, PA, USA, 2023.

83. GB/T 5455-2014; Textile—Burning Behavior—Determination of Damaged Length, Afterglow Time and Afterflame Time of Vertically Oriented Specimens. National Standard of the People's Republic of China, China Standard Press: Beijing, China, 2014.

84. Guo, L.; Yang, Z.Y.; Tang, R.C.; Yuan, H. Bin Grape Seed Proanthocyanidins: Novel Coloring, Flame-Retardant, and Antibacterial Agents for Silk. ACS Sustain. Chem. Eng. 2020, 8, 5966–5974.

85. ASTM D6413; Standard Test Method for Flame Resistance of Textiles (Vertical Test). American Society for Testing and Materials: West Conshohocken, PA, USA, 2022.

86. Bu, Y.; Zhang, S.; Cai, Y.; Yang, Y.; Ma, S.; Huang, J.; Yang, H.; Ye, D.; Zhou, Y.; Xu, W.; et al. Fabrication of Durable Antibacterial and Superhydrophobic Textiles via in Situ Synthesis of Silver Nanoparticle on Tannic Acid-Coated Viscose Textiles. Cellulose 2019, 26, 2109–2122.

87. Gu, S.; Yang, L.; Huang, W.; Bu, Y.; Chen, D.; Huang, J.; Zhou, Y.; Xu, W. Fabrication of Hydrophobic Cotton Fabrics Inspired by Polyphenol Chemistry. Cellulose 2017, 24, 2635–2646.

88. Xing, L.; Wang, B.; Zhang, Y.; Yang, H.; Zhu, X.; Chen, G.; Xing, T. Universal Fabrication of Superhydrophobic and UV Resistant Cotton Fabric with Polyphenols. Cellulose 2021, 28, 11645–11663.

89. Zhu, Q.; Zhang, C.; Zhu, N.; Gong, J.; Zhou, Z.; Sheng, D.; Zhou, S.; Wang, X.; Fu, Z.; Xia, L. Preparation of Polyester Yarns with Bright Color and Enhanced Hydrophobicity Using Lotus Leaf Powders. Ind. Crops Prod. 2023, 193, 116152.

90. Tian, Y.; Lu, Y.; Zhang, Y.; Hou, X.; Zhang, Y. Extraction and Characterization of Natural Colorant from Melia Azedarach Bark and Its Utilization in Dyeing and Finishing of Wool. Sustain. Chem. Pharm. 2022, 27, 100647.