Fibers and Polymers (2024) 25:1825–1833
https://doi.org/10.1007/s12221-024-00535-2

Online ISSN 1875-0052
Print ISSN 1229-9197

REGULAR ARTICLE

Dyeing of Cotton and Wool Fibers with the Aqueous Extract of *Alnus glutinosa*: Evaluation of Their Ultraviolet Protection Factor, Their Color fastness and the Antioxidant Activity of the Aqueous Extract

Niki Tsouka[1] · Diamanto Lazari[2] · Nikolaos Nikolaidis[3] · Kiriakos Dimitriadis[2] · Evangelia Vouvoudi[3] · Konstantinos Theodoropoulos[1]

Received: 3 October 2023 / Revised: 9 January 2024 / Accepted: 19 March 2024 / Published online: 7 April 2024
© The Author(s) 2024

Abstract
The aim of the present study is to evaluate the dyeing properties and behavior of the aqueous extract of *Alnus glutinosa* leaves when applied on cotton and wool fibers. The antioxidant activity and the total phenolic content of the aqueous extract were calculated. The colorfastness of the dyed samples such as washing, acid and alkali perspiration, wet and dry fastness and light fastness was performed. The ultraviolet protection factor (UPF) which is a measurement of the protection offered by the dyed fabric substrates against ultraviolet radiation was also assessed. It was found that *Alnus glutinosa* aqueous extract shows exceptionally high antioxidant activity and high phenolic content. The dyed samples showed astonishingly high light fastness approaching the light fastness of synthetic dyes such as the vat dyes or metal complex dyes. The conferred protection of the dyed samples against the distractive ultraviolet radiation is exceptionally high as this is demonstrated by the high UPF measurements of the dyed samples.

Keywords Natural dyes · Color fastness · Total phenolics · DPPH method · Forest plants

1 Introduction

Ancient peoples used natural dyes and pigments either to express themselves or to decorate various objects, since their appearance influenced their mood and activities. The use of natural dyes has been flourishing in Europe for thousands of years as part of the everyday and of higher cultural European identity. In ancient times, dyed textiles were symbols of status and, because of their expense and rarity, were reserved only for the wealthiest classes. Early dye sources included vegetable, animal and mineral extracts [1, 2]. Madder, indigo and saffron were the three ancient dyes used in India since *ca.* 2500 BC [3–6].

Later, in modern ages, with the manufacture of the synthetic dyes, natural dyes and pigments were replaced, since they were much cheaper and more efficient in their application for both natural and synthetic fibers. A large number of synthetic dyes produced today satisfy results for simple, reproducible application processes, and also meet consumers' demand for high-quality products at a reasonable price. Thus, even though natural dyes have been available for centuries, synthetic dyes are popular primarily due to their ease of large-scale production, affordability, wide range of colors and excellent color fastness. These qualities are essential to meet today's requirements [7, 8]. However, manufacturing synthetic dyes suffers from various disadvantages such as environmental unfriendliness due to the fact that the synthesis processes require the use of strong acids, alkalis, volumes of solvents, high temperatures and heavy metals [6]. For example, dyes accumulate in water to such an extent that light can no longer penetrate or with low O_2 content, which impairs the ability of plants to photosynthesize. Additionally, some dyes used in industry are toxic and carcinogenic

✉ Konstantinos Theodoropoulos
ktheodor@for.auth.gr

[1] Laboratory of Forest Botany-Geobotany, Department of Forestry and Natural Environment, Aristotle University of Thessaloniki, 54124 Thessaloniki, Macedonia, Greece

[2] Laboratory of Pharmacognosy, Department of Pharmacy, Aristotle University of Thessaloniki, 54124 Thessaloniki, Macedonia, Greece

[3] Laboratory of Polymers and Colours Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Macedonia, Greece

and can cause skin and eye irritation after prolonged exposure. Therefore, the main concerns for reducing synthetic dyestuffs include raw materials, energy requirements and waste handling. Additionally, environmental toxicity, allergic reactions to synthetic dyes and increasing consumer awareness are becoming more important [9].

However, natural, so-called "green" dyes can be considered as an alternative to the synthetic dyes if they can only be produced at a comparable price and exhibit similar fastness characteristics to the synthetic ones. Recently, plant dyestuffs have started to be used not only in the cosmetic industry and the food/packaging industry as active or coloring ingredients, but also in the textile industry for dyeing and printing, especially baby clothing [10]. Furthermore, the choice of plant species aimed to conserve natural resources, thereby contributing to sustainable development and the protection of the natural environment. Plants, being renewable resources, play a crucial role in achieving these goals. Natural dyes are a mixture of colorants whose chemistry is complex and the color of some natural dyes, especially those retrieved from plants, varies depending on local soil and environmental conditions [10]. The difference in final shades is a matter of great concern in textile dyeing.

Alnus glutinosa (commonly known as black alder or European alder) is a tree of the *Betulaceae* family widely spread through Europe, Southeastern Asia, the Caucasus mountains and Western Siberia [11]. N. Greece is an area where *Alnus glutinosa* is quite common, and since it can withstand excessive humidity, it grows along rivers and streams. It is a deciduous tree that thrives in wet soils and may grow up to 30 m high [12]. In an analysis of the leaves of *Alnus glutinosa*, it was found that they contain organic acids, specifically oxalic acid detected in the largest amount (1403.9 mg/kg), followed by citric acid (620.9 mg/kg), malonic acid (267.9 mg/kg) and malic acid (266.8 mg/kg), and to a lesser extent, hydroxycinnamic acid (157.0 mg/kg), α-hydroxy phenolic acid (104.9 mg/kg), fumaric acid and others [13]. In analysis of the bark and fruits of *Alnus glutinosa*, it was found that they contain, among others, diarylheptanoids, polyphenols (gallotannins, ellagitannins), flavonoids (flavonols), triterpenes, steroids, phenolic compounds, oregonin and hirsutenone [14]. Thus, many studies have shown that extracts from black alder bark display antimicrobial, anti-inflammatory and anticancer activities [11]. Textile materials provide an excellent environment for microorganisms to grow, because of their large surface area and ability to retain moisture. Microbial activity can be detrimental to textiles [15]. Diarylheptanoids are polyphenols typically found in *Alnus* and consist by far the most predominant bioactive compounds, although, to date, no quantitative phytochemical studies have been carried out. They include two aryl groups with certain substituents that significantly influence their biological activity. Diarylheptanoids have been reported to display antioxidant, cytotoxic, antibacterial, hepatoprotective, and anticancer activity [11, 16].

The aim of the present study is to investigate whether aqueous extracts of *Alnus glutinosa* can be used for the dyeing of cotton and wool fibers conferring satisfactory color and fastness properties (like wash, rubbing or perspiration fastness). Also, the color resistance of the dyed samples toward the sunlight and the protection from the UV irradiation was investigated, along with the antioxidant potential and the concentration of the total phenolics of the aqueous plant extract.

2 Experimental

2.1 Materials

Young leaves which were collected from the natural environment of Kilkis of Macedonia, Greece, were used for the aqueous extraction. The aqueous extracted liquor was used as the main dye bath for the dyeing. Two types of fabrics were used in the present study, neat knitted cotton fabric (185 g/m^2) and neat woven wool fabric (155 g/m^2). The samples used for the dyeing were 10 g each. In the aqueous extraction method, the plant is dried, powdered and boiled in water. The mixture is then filtered to extract the coloring substance. This method is not suitable for heat-sensitive and water-insoluble coloring substances [10].

The chemical reagents used in the study were: "Alum" $KAl(SO_4)_2{\cdot}12H_2O$ (Fluka GmbH, Switzerland), 2,2-dienol-1-picrylhydrazyl (DPPH, Merck Darmstadt, Germany), phenol (Folin–Ciocalteu reagent, Merck Darmstadt, Germany), anionic detergent (Standard Soap Without Optical Brightening Agent, ISO 105: C06 B2S, SDL International Ltd., England), NaOH (Riedel-de-Haen, Seelze, Germany), Histidine (*L*-Histidine monohydrochloride monohydrate $C_6H_{10}ClN_3O_2{\cdot}H_2O$, VWR International Ltd., England), sodium dihydrogen orthophosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$, VWR International Ltd., England), di-sodium hydrogen orthophosphate dihydrate ($Na_2HPO_4{\cdot}2H_2O$, VWR International Ltd., England) and NaCl (Merck KGaA, Germany). All reagents were used as received without further purification.

For the wet fastness tests, standard Multifiber Adjacent Fabric, Type "DW," (Warp Stripe, SDL International, Shirley Developments LTD England) and standard white cotton control samples (SDCE Cotton Lawn, according to the specifications of ISO 105-F09) were used, in dimensions 5×5 cm. For the light fastness, standard Blue Wool Reference Standards No.1-No.8 (conforming to requirements of BS EN ISO 105 B08) and Grayscale for Assessing Change in Color (ISO 105-A02: 1993, BS EN 20105-A02: 1995, BS 1006-A02: 1990, SDC Standard Methods, 5th Edition

A02 and BS1006-A03: 1990, SDC Standard Methods, 5th Edition A03) were used [17]. The visual observations were executed by the same experienced researcher in all cases, under the appropriate light spot.

2.2 Apparatus

A thermostatic open-type dye bath (Raypa, Spain) was used for all the dyeings. Color measurements were performed using a Microflash datacolor international spectrophotometer. A Xenon Q-Sun test chamber (Xe-1-B) (Q-LAB, USA) was used for the light fastness measurements. The Jasco V-550 UV–Vis spectrometer was used to collect the data for the UV Protection Index (UPF). The International model M231 Perspirometer (SDL ATLAS Textile Testing Solutions, USA) was used for the perspiration fastness test. UV-1700 PharmaSpec (Shimadzu, Kyoto, Japan) spectrophotometer was used to measure the total phenolics of the extract. The evaluation of the color change after the color fastness tests was performed in a VeriVide observation chamber with standard lighting D_{65} (Leslie Hubble Ltd, UK). Moreover, an electronic microprocessor pH meter (535 multical CWTW) was used for the pH measurements [15].

2.3 Methods

2.3.1 Determination of Antioxidant Activity and Total Phenolics of the Aqueous Extract

To evaluate the antioxidant activity of the extracts, interaction with 2,2-dienol-1-picrylhydrazyl (Sigma Aldrich, DPPH) in solution was performed and the absorbance was measured at $\lambda_{max} = 517$ nm relative to the corresponding samples without DPPH at two time intervals (20 and 60 min) [18]. Reduction in the reaction rate upon the addition of DPPH is used as an indicator of the radical behavior of the reaction. Three measurements were made for each extract and the average was calculated (the deviation does not exceed 10%). Results are expressed as a percentage of free radical scavenging capacity (% radical scavenging capacity, RSC) [19]:

$$\mathrm{RSC}\ (\%) = \frac{A_c - A_s}{A_c}$$

where A_s and A_c represent the absorbance of each sample and of the control sample, respectively.

The Folin–Ciocalteu phenol reagent method or the gallic acid equivalence method (GAE) was used for the colorimetric determination of the total phenolics of the aqueous extract. The expression of the results is a single number expressed as mg/L of gallic acid equivalence (mg GAE/L) [20]. In the present study, three measurements of total phenolics, for each sample, were made and the mean deviation does not exceed 10%, as calculated [21].

2.3.2 Dyeing Procedure

Young leaves in 30% wt in deionized water, were used for the experimental procedure. The extraction was done at 95 °C for 1 h. The mordanting process was done with an alum solution of 15 g/L at a bath ratio of 1:30 at a temperature of 80 °C for 20 min. All dyeings were performed at a 1:20 liquor ratio. The samples and extracts were placed in the dyeing machine, and the temperature was increased from 20 to 95 °C, at a constant rate of 2 °C/min. The dyeing process remained at this temperature for 10 min. Then NaCl was added at a ratio of 10 g/L, and the dyeing continued for another 20 min. The machine was then cooled at a constant rate of 2 °C/min up to 60 °C, where it remained for 10 min at this temperature. Then the fabric was rinsed with water only for dye excess removal (Fig. 1).

2.3.3 Color Measurements

The color of the dyed samples was measured using a Microflash datacolor international spectrophotometer. Reproducibility was checked by taking four measurements focusing on different spots, and the average reflectance values over the range 400–800 nm were taken [22]. The results are in the CIELAB color system, where each color is described by three coordinates or factors called L^*, a^* and b^*. The K/S values were calculated using the Kubelka–Munk equation which gives a numerical value of the amount of color in the substrate [23]:

$$\frac{K}{S} = A \times C = \frac{(1-R)^2}{2R}$$

where K is the absorption (%), depending on the amount of dye, S is the scattering (%), depending only on the substrate, A is a constant, depending on color, wavelength and substrate, C is the color concentration and R is the reflectance of a monochromatic light beam (of variable wavelength) in

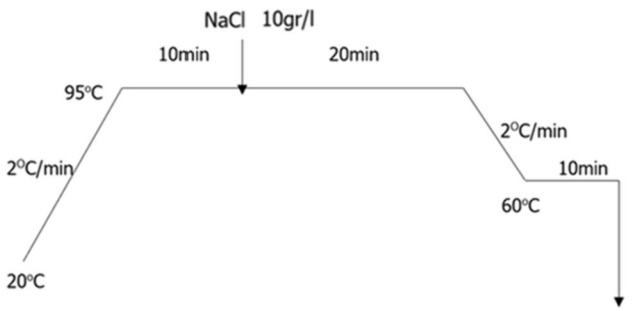


Fig. 1 Dyeing process of the fabrics, schematically

the region of the vis spectrum, with respect to the standard white surface of the instrument.

2.3.4 Fastness Properties, Wash, Light, Rubbing, Perspiration, and Ultraviolet Protection Factor (UPF)

The wash fastness of the dyed samples was performed according to the ISO 105-C06: 2010, A1 standard (colorfastness to domestic and commercial laundering), at 40 °C. The ISO 105-B02 (colorfastness to artificial light xenon arc fading lamp test) standard was used to measure the light fastness of the dyed samples. An initial exposure of 72 h was executed, followed by three additional exposures of 72 h each. The dry and wet rubbing fastness tests of the dyed samples were performed according to the ISO 105-X12: 2016 standard (textiles—tests for color fastness—Part X12: color fastness to rubbing). The acid and alkali perspiration fastness of the dyed samples were performed according to the standard ISO 105-E04:2013 (color fastness to acid and alkali perspiration) [17, 24].

The ultraviolet protection factor (UPF) was measured and evaluated according to the Australian/New Zealand standard AS/NZS 4399 (Sun Protective Clothing–Evaluation and Classification) and according to the European standard EN 13758-1: 2001 and EN 13758-2: 2003. In Table 1, there is a correlation of the UPF value, with the category of protection from UV irradiation and the percentage of the blocked UV radiation by the fabric [24].

3 Results and Discussion

3.1 pH Measurements, Antioxidant Activity, and Total Phenolics of the Aqueous Extract

To begin with, the characterization of the aqueous extraction of *Alnus glutinosa* leaves took place. As can be seen from the pH measurements in Table 2, the pH of aqueous extracts before dyeing was acidic, while after dyeing the pH was dropped to lower values for both cotton and wool. This can be attributed to the desorption of alum during dyeing which resulted in lowering the pH of the dyebath solutions. The optimal pH range for alum is approximately 5.5–6.5 and can reduce total alkalinity and pH by neutralizing carbonate and bicarbonate compounds with a greater decline in pH when applied to water.

Table 1 Categorization of UPF according to price rating and protection categories [24]

Grading UPF	Protection category	UV irradiation % blocked
1–14	Insufficient	< 93.3
15, 20	Moderate–good	93.3–95.9
25, 30, 35	Very good	96.0–97.4
40, 45, 50, 50+	Excellent	97.5 and up

Table 2 Measurements of pH, antioxidant activity and total phenolics of the aqueous extract *A. glutinosa*

	Cotton	Wool
pH before dyeing	5.59	5.59
pH after dyeing	4.05	4.37
Antioxidant activity of the extract at 20 min (% RSC)	88.47	
Antioxidant activity of the extract at 60 min (% RSC)	87.72	
Total phenolics of the aqueous extract (mg GAE/L)	357.55	

After the interaction of the aqueous extract of *Alnus glutinosa* with the substance DPPH for two different time periods (20 and 60 min), a high antioxidant activity was observed (Table 2). Specifically, the average of the three measurements (% RSC) at 20 min was 88.47 (a fairly high value), and over time, at 60 min, the average value decreased slightly to 87.72. The results demonstrate the high antioxidant capacity of the aqueous extract of *Alnus glutinosa*, which decreases negligible over the time studied.

The results of the measurements of the total phenolic content of the extract (Table 2) showed an average of 357.55 mg GAE/L, which represents an extremely high value that corresponds to the high content of the total phenolic in the extract. The high level of the phenolic content extracted from the leaves has been absorbed by the samples during the dyeing process, and it is believed to confer the unusually high light fastness of the dyed samples with *Alnus glutinosa* extract.

3.2 Color Measurements

The colorimetric coordinates a^*, b^*, L^*, C^*, $h°$, the percentage reflection $\%R$ and the K/S values of the dyed and non-dyed cotton and wool samples are given in Table 3. Both dyed samples have K/S values higher than undyed samples indicating that the aqueous extract of *Alnus glutinosa* leaves has high coloristic properties. The K/S value of the dyed wool sample is significantly higher compared to the corresponding one of the cotton samples. In fact, the K/S value of the wool sample was quite high resembling those of synthetic dyes. The K/S value of the cotton sample was lower than that for the wool but was still high for a natural dye. The difference in dye adsorption is due to the different bonds with which the dyestuff binds to the fibers of cotton (cellulose) and wool (proteins). *Alnus glutinosa* contains heptanoids, polyphenols, flavonoids, terpenes and steroids which have hydroxyl and carboxylic groups that are able to ionize and create negatively charged molecules.

Table 3 The colorimetric coordinates L^*, a^*, b^*, C^*, $h°$ and *K/S* values of the cotton and wool samples at $\lambda_{max} = 400$ nm are given

	*a**	*b**	*L**	*h°*	*C*	*R %*	*K/S*
Undyed cotton sample	−0.05	0.62	88.72	94.75	0.62	69.71	0.066
Dyed cotton sample	7.79	31.52	75.90	76.13	32.47	12.53	3.050
Undyed wool sample	3.36	14.55	79.59	76.99	14.94	27.06	0.983
Dyed wool sample	11.01	37.59	69.72	73.67	39.17	3.70	12.532

During the dyeing process, the wool fiber, which is positively charged due to the protonation of its amino groups, absorbs the negatively charged dye extract of *Alnus glutinosa*. In this respect, the dyestuff resembles an acid dye in the dyeing of wool [6, 25]. The adsorption on wool indicates a monolayer of molecules on infinite wool dye sites taking place mainly through electrostatic interactions between the cationically charged wool fiber and the anionically charged molecules of dyestuff [6, 25].

However, cotton fiber is negatively charged due to the ionization of cellulose hydroxyl groups in the aqueous environment of the dye and repels the negatively charged *Alnus glutinosa* molecules. The adsorption of the dye on cotton takes place mainly through Van der Waals interactions, meaning that cellulosic molecules and dye molecules, upon being planar and non-branched molecules, facilitate each other's approach enough to allow the development of Van der Waals interactions which operate at short distances [6, 25]. Therefore, there is much less and weaker adsorption of the dye from the cotton fiber compared to the impressively higher absorption (four times) by the wool fiber. The behavior of the aqueous extract of *Alnus glutinosa* during the dyeing process is similar to the behavior of the direct synthetic dyes in cotton where the presence of salt is necessary to increase the adsorption of the dye [6, 25].

The cotton sample had a higher lightness (L^*) value compared to wool which corresponds to less dye absorbed by the cotton (lower *K/S* value). The minimum value of the percentage reflection (*R%*) was at the same wavelength at 400 nm. The color factor b^* has very high values in both samples and agrees perfectly with the visual effect and the yellow color of the samples (Fig. 2). The hue ($h°$ value) of both the cotton and the wool sample was in the color range of yellow (between 70° and 90°) and corresponds to the orange part of the spectrum effect. The positive values of the color factor a^* are low and indicate that the dyed samples present also a reddish hue [26]. It is noted that for all tests, the fabrics were just rinsed with plenty of water for excess removal, but no soap was used, for further cleaning.

In a study by Guinot et al. [27], the dyeing of cotton and wool samples with leaves of *Alnus glutinosa* different extraction and dyeing methodologies were studied as well. The hue ($h°$) results are consistent with the present study for both samples. The lightness value (L^*) of the cotton sample agrees with the present research and is quite high. In the wool sample, the lightness was different between the two studies. In the measurements of the abovementioned research, it was found less than 60, while at the present it was close to 70. The difference is probably due to the different methodologies of extraction and dyeing. In the same study by Guinot et al. [27], the hue ($h°$) of the two samples was measured and the results are in complete agreement with the present study.

3.3 Colorfastness to Rubbing

The fastness to dry rubbing was found excellent in both samples. In wet rubbing, the color fastness of the wool

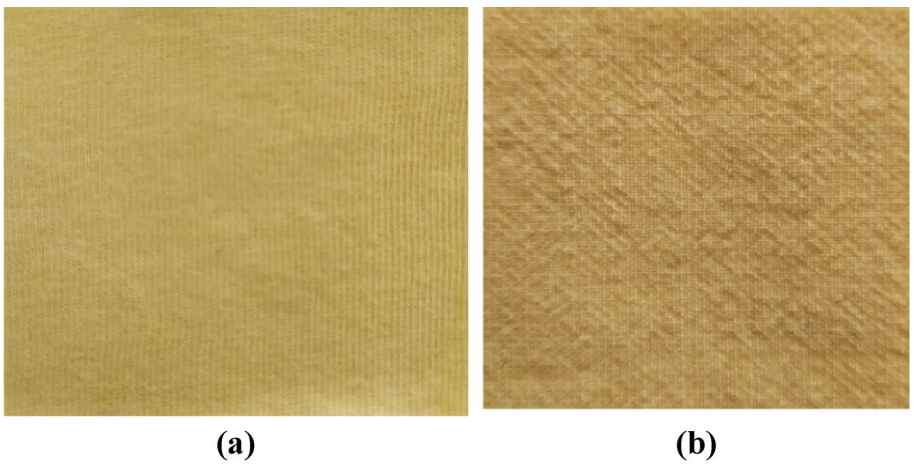


Fig. 2 Imaging of the color hue generated on **a** cotton and **b** wool fabric after dyeing with *Alnus glutinosa*

sample was also excellent while that of cotton was moderate (Table 4) due to the looser attachment of the dye to the surface of the cotton sample due to dye–substrate anionic repulsions.

3.4 Colorfastness to Washing, Acid, and Alkali Perspiration

The wash fastness of the dyed fibers during the test of color resistance to washing (Table 5) for both samples had excellent results regarding the color staining (C_S) of the multifiber, while the color change (C_C) of the dyed samples was of moderate stability. The cotton sample underwent a moderate washout, while the wool sample was more affected because it had absorbed a larger amount of dye. The above findings indicate that the desorbed dye during the wash fastness test does not stain the adjacent multifiber strips, but only has an effect on the color of the dyed samples, showing lower values and, thus, moderate color change.

The fastness to acid perspiration (Table 5) was excellent for both samples in terms of staining (C_S) of the multifiber. The grayscale has five contrast levels. In terms of color change (C_C), fastness was moderate for cotton (2–3) and very good (4–5) for the wool fiber. The color in the wool sample faded slightly, while the cotton sample was quite affected [26]. This can be attributed to the diminishing electrostatic attraction between the protonated hydroxyl groups of cotton and the *Alnus* ingredients. Consequently, there is repulsion between the chromophore groups and the cotton fiber and easier transfer of the colorants from the cotton substrate to the aquatic environment.

Fastness to the alkali perspiration in terms of staining (C_S) of the multifiber was excellent for the cotton samples and very good till excellent for the wool samples, while the color of the two dyed samples (C_C) was slightly affected (rate 4 of the grayscale). This indicates a strong "salt link" operating at the alkaline conditions of the test between the ionized hydroxyl groups of cotton and wool and positively charged groups of the *Alnus* dye extract.

3.5 Colorfastness to Artificial Light

The colorfastness of the dyed samples to the artificial light was assessed visually by using the Blue Wool Standards Scale (rating 1 is the lowest endurance and rating 8 is the highest). The light fastness of the dyed cotton samples (Table 6) was moderate, 5 on the blue wool scale. The light fastness of the dyed wool sample (Table 6) was excellent and was rated from 7–8 on the blue wool standard scale. It was noticed that after exposure of the cotton and wool samples to artificial light, the color became slightly darker than the original, and this can be possibly attributed to the color change of the phenolic groups. The excellent light fastness of the wool dyed samples obtained under the conditions specified by the ISO B02 was further confirmed by overexposing the dyed samples for another 144 h making the total exposure time 216 h, which overpasses the conditions specified by the ISO B02. The light fastness results obtained were surprisingly excellent and remained unchanged between 7 to 8 on the blue wool scale (Table 6) indicating that wool samples dyed with *Alnus glutinosa*

Table 4 Color fastness to rubbing on grayscale

	Dry rubbing	Wet rubbing
Cotton samples	4	3
Wool samples	4–5	4–5

Table 6 Fastness to artificial light

	Visual color difference
Undyed cotton sample after 48 h	8
Dyed cotton sample after 48 h	5
Undyed wool sample after 48 h	8
Dyed wool sample after 48 h	7–8
Dyed wool sample after (3 × 72 h)	7–8

Table 5 Indication of color fastness to washing at 40 °C, to acid perspiration or to alkali perspiration, on grayscale

Colorfastness	Spun diacetate (C_S)	Bleached cotton (C_S)	Spun polyamide (C_S)	Spun polyester (C_S)	Spun polyacrylic (C_S)	Worsted wool (C_S)	Color change (C_C)
Washed—cotton samples	5	5	5	5	5	5	3–4
Washed—wool samples	5	4–5	5	5	5	5	2–3
Acid perspiration—cotton samples	5	5	4–5	5	5	5	2–3
Acid perspiration—wool samples	5	4–5	4–5	5	5	5	4–5
Alkali perspiration—cotton samples	5	5	5	5	5	5	4
Alkali perspiration—wool samples	4–5	4	4	4–5	4–5	4–5	4

aqueous extract have extremely high light fastness to artificial light, matching the light fastness of some synthetic dyes: Vat dyes are recommended to specialized application where high light fastness is required such as automotive interiors.

In general, the colorfastness of plant dyes to solar radiation is quite low, due to the photochemical oxidation caused by the dyes (chromophore substituents). The extract from the leaves of *Alnus glutinosa*, although it is a plant pigment, had excellent resistance to solar radiation. In the study of Guinot et al. [27], the resistance of the dye to solar radiation was measured and the results are identical to the present study for the cotton sample where it was graded as 5 out of 8 on the blue wool scale. For the wool sample in the same research, it is mentioned that it belongs to the samples that became darker after the exposure to the solar radiation, and this agrees with the present research. It is noted that in the present study, both samples (cotton and wool) became darker than the original ones.

A study by Fedchenkova and Khvorost [28] found that the leaves of *Alnus glutinosa* contain large amounts of oxalic acid which is a powerful carboxylic acid. Oxalic acid forms complexes with heavy metal ions and is used as a stabilizer in paints [29]. The presence of oxalic acid in the extract probably creates stability of the dye, perhaps due to the strengthening of the bond between the alum fin and the chromophore groups. The use of oxalic acid as a mordant in the application of apple tree bark as a natural source for cotton dyeing indicated no greater auxiliary than the no-mordant dyeing [30]. The fading of the dyed cotton fiber (cellulose) after exposure to solar radiation is due to photooxidation of the flavonoids contained in the dye. The presence in the hydroxycinnamic acid extract [31] which is known for its antioxidant properties probably explains the fairly good color fastness of the cotton sample. The formation of a flavonoid complex with hydroxycinnamic acid which is stable in solar radiation explains the above behavior. The fading of the wool fiber (protein) is due to a reduction mechanism: This may explain the protection of polyphenols from oxidation and the high resistance of the dye to solar radiation. Also, the aqueous extract of the young leaves of *Alnus glutinosa*, according to the results of the measurements, has a high antioxidant activity (average % RSC 88.45 in 20 min and 87.72 in 60 min). Therefore, the high colorfastness of the dyed samples is also due to the high antioxidant capacity of the extract that prevented photooxidation. In addition, according to research by Ren et al. [4], *Alnus glutinosa* contains five derivatives of stilbene which is the main base of synthetic ultra-bleaches, where the sequence of single and double carbonyl bonds they possess absorbs high-energy ultraviolet radiation. This property of stilbene derivatives protects the chromophore groups of *Alnus glutinosa* from the destructive degradation of the dye.

3.6 Ultraviolet Protection Factor (UPF)

The ultraviolet protection factor (UPF) of fabrics dyed with *Alnus glutinosa* extract was measured as shown in Table 7. The UPF value of the samples increases significantly after dyeing with *Alnus glutinosa* compared to the corresponding UPF values of undyed control samples. The UPF value of the cotton sample is 104.18 and belongs to the category of excellent according to the Australian/New Zealand standard, which means that it provides excellent UV protection radiation, blocking over 97.5% of UV radiation. Moreover, according to the European standard, it belongs to the fabrics that can be labeled as protecting from UV sunlight because the UPF value is higher than 40 and the UV_A value is less than 2%. The dyed wool sample also had an excellent UPF value of 139.00 blocking over 97.5% of UV radiation according to the Australian/New Zealand standard. Analogously, regarding the European standard, it belongs to the fabrics that can be labeled as protecting from UV sunlight because the UPF value is higher than 40 and the UV_A value is less than 2%.

It is worth noting that while the shade of the fabrics is light the UPF value is excellent according to the Australian/New Zealand Standard AS/NZS 4399:1996 and the European Standard EN 13758. According to an announcement by the Australian Ministry of UV Protection [32], light colors usually have a low UPF value and do not protect enough from UV radiation. The results of the present study show that *Alnus glutinosa* dyed samples have extremely high UPF values matching or even exceeding the UPF values obtained by commercially available UV blockers used for the treatment of textiles. It is well known that plants activate various mechanisms to protect themselves from damage caused by UV_B radiation. They compose protective dyes mainly water-soluble flavonoids, such as flavonoids, flavonols and isoflavones. They accumulate anthocyanins which esterified to cinnamic acid also provide protection from UV irradiation [31]. Our studies showed that the aqueous extract of *Alnus glutinosa* contained a very high concentration of total phenolics (357.55 mg GAE/L) which is responsible for the high UPF values obtained and the ability to provide excellent protection against UV solar radiation. *Alnus glutinosa* perhaps is an amazing natural product that could be used in cosmetology to produce cosmetics that provide protection

Table 7 Measurements of UPF

	UV_A	UV_B	UPF
Undyed cotton sample	70.99	40.93	2.19
Dyed cotton sample	1.57	1.65	104.18
Undyed wool sample	47.93	9.76	6.31
Dyed wool sample	1.55	0.73	139.00

from ultraviolet radiation (UV_A, UV_B) by replacing synthetic (and often toxic) sun blockers.

4 Conclusions

Cotton and wool samples were dyed successfully with the aqueous extract of *Alnus glutinosa* leaves. High coloristic values were obtained on wool indicating the possible formation of electrostatic bonds between the protonated amino groups of wool and negatively charged *Alnus glutinosa* molecules. The dry and wet rubbing fastness was good for cotton and very good for the wool dyed sample. The protection against the UV irradiation of the dyed cotton and wool samples was excellent according to Australian/New Zealand standards and the European standards. The color fastness to washing was excellent in terms of multifiber staining and moderate in terms of color change indicating that a dye fixing stage may be required in order to stop the migration of the dye from the dyed material in the water phase. The color fastness to acid and alkaline perspiration was excellent for both cotton and wool in terms of multifiber staining. However, the color change was high under the conditions of acid perspiration for both cotton and wool indicating a weaker "salt link" formed between cotton and wool and *Alnus glutinosa* at acid pH. The alkaline perspiration was very high for both cotton and wool as far as both multifiber staining and color change are concerned indicating the presence of a strong "salt link" between cotton, wool and *Alnus glutinosa* molecules.

The light fastness of the wool samples was excellent, being equal to the most light-fast synthetic dyes. The light fastness of the cotton dyed samples was very good for a natural dye like *Alnus glutinosa*. High tinctorial values were obtained on cotton, and very high tinctorial values were obtained on wool indicating that an interaction between the positively charged amino groups and *Alnus glutinosa* plays an important role in *Alnus glutinosa* absorption by the wool. The wash, perspiration and rubbing fastness of the dyed cotton and wool samples can be characterized from excellent to exceptional. The unusually very high, for a natural dye, light fastness and ultraviolet protection properties conferred to cotton and wool open the way to further research.

This present work shows that *Alnus glutinosa* can be successfully used for the dyeing of cotton and wool fabrics with good overall dyeing characteristics and exceptionally high light fastness and ultraviolet protection properties. This plant species could possibly be a new alternative cultivation for the production of natural dyes, thus contributing to environmental protection and sustainable economic growth.

Funding Open access funding provided by HEAL-Link Greece.

Data availability Not applicable.

Declarations

Conflict of interest The authors declare no conflicts of interest regarding the content of this study.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. M.A. Rahman Bhuiyan, A. Islam, A. Ali, M.N. Islam, J. Clean. Prod. **167**, 14 (2017)
2. E.T. Güzel, R. Karadag, J. Nat. Fibers **18**(8), 1107 (2021)
3. Textile Industry and Fabrics History; Ancient, CIBA Review, 1968/2 (Ciba, Basel, 1968)
4. Plinius Secundus Gaius Historia Naturalis ca 79 AD, 1968 (Parallel Latin and English Translation) (Press, Harvard, 1968)
5. R.D. Lillie, J. Soc. Dyers Colour. **95**, 57 (1979)
6. P. Naidis, S. Lykidou, M. Mischopoulou, E. Vouvoudi, N.F. Nikolaidis, Color. Technol. **139**(5), 565 (2023)
7. H. Schweppe, Handbook der Naturgarbstoffe: Vorkommen, Verwendung, Nachweis (Ecomed, Landsberg/Lech, 1992)
8. B. Glover, J. Soc. Dyers Colour. **16**, 53 (1998)
9. OEKO-TEX® Standard 100, Edition 4/2010, OEKO-TEX, Zurich
10. R. Rana, K. Dhiman, M.S. Ashawat, J. Nat. Fibers **19**, 14755 (2022)
11. A. Smeriglio, V. D'Angelo, A. Cacciola, M. Ingegneri, F.M. Raimondo, D. Trombetta, M.P. Germanò, Plants **11**(19), 2499 (2022)
12. X. Fotios, K. Theodoropoulos, E. Eleftheriadou, D.A. Samaras, C. Damianidis, T. Papadopoulos, Acta Bot. Croat. **73**(1), 21 (2014)
13. S. Sukhikh, S. Ivanova, L. Skrypnik, A. Bakhtiyarova, V. Larina, O. Krol, A. Prosekov, A. Frolov, M. Povydysh, O. Babich, Plants **11**(18), 2415 (2022)
14. X. Ren, T. He, Y. Chang, Y. Zhao, X. Chen, S. Bai, L. Wang, M. Shen, G. She, Molecules **22**, 1383 (2017)
15. S. Lykidou, M. Pashou, E. Vouvoudi, N. Nikolaidis, Fibers Polym. **22**, 3336 (2021)
16. Ç. Altınyay, I. Süntar, L. Altun, H. Keleş, E.K. Akkol, J. Ethnopharmacol. **192**, 148 (2016)
17. BS1006, Methods of test for color fastness of textiles and leather, 5th ed. J. Soc. Dyers Colour. **107**, 84 (1991)
18. S. Kedare, R.P. Singh, J. Food Sci. Technol. **48**(4), 412 (2011)
19. L. Chaires Martinez, M. Perez Vargas, A. Cantordel Angel, F. Cruz Bermudez, H. Jimenez Avalos, Cereal Chem. **90**(3), 263 (2013)
20. V. Singleton, R. Orthofer, R. Lamuela-Raventos, Methods Enzymol. **299**, 152 (1999)
21. K. Kalaitsidis, E. Sidiropoulou, O. Tsiftsoglou, I. Mourtzinos, T. Moschakis, Basdagianni, S. Vasilopoulos, S. Chatzigavriel, D. Lazari, I. Giannenas, Animals **11**(4), 1063 (2021)

22. B. Rigg, Colorimetry and the CIE system in colour physics for industry. The Society of Dyers and Colourists, ed. by R. McDonald (Bradford, 1997 ISBN:0901956708), p. 83
23. I. Eleftheriadis, N. Nikolaidis, E. Tsatsaroni, Chemistry and Color Technology, Greek Academic Electronic Textbooks and Aids (Athens, 2016). https://repository.kallipos.gr/handle/11419/822
24. A. Hall, J. Soc. Dyers Colour. **112**(5–6), 144 (2008)
25. P. Naidis, S. Lykidou, M. Mischopoulou, E. Vouvoudi, N. Nikolaidis, J. Nat. Fibers **19**, 7885 (2022)
26. H. Ozdemir, Sustainability **15**, 14639 (2023)
27. P. Guinot, A. Rogé, A. Gargadennec, M. Garcia, D. Dupont, E. Lecoeur, L. Candeliera, C. Andary, Color. Technol. **122**, 93 (2006)
28. Y.A. Fedchenkova, O.P. Khvorost, News Pharm. **3**(79), 51 (2014)
29. F. Colmenero, Phys. Chem. Chem. Phys. **5**(21), 2673 (2019)
30. G. Radomska, A. Radomski, Ann. Warsaw Univ. Life Sci.-SGGW For. Wood Technol. **119**, 35–47 (2022)
31. J. Li, T.M. Ou-Lee, R. Raba, R.G. Amundson, R.T. Last, Plant Cell **5**(2), 171 (1993)
32. https://www.arpansa.gov.au/. Accessed in Sept 2022