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ORIGINAL ARTICLE

Simultaneous dyeing and finishing of wool and natural silk fabrics using *Azolla pinnata* extract

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Abstract

The dyeing process is an important part of the textile industry, where a broad spectrum of dyes, including synthetic and natural dyes, is applied to improve the product's appearance and performance attributes. In order to avoid the environmental pollution that occurred from using synthetic dyes, there is a rapid movement towards natural dyes due to their eco-friendliness, non-toxicity, low cost, biodegradability, and antimicrobial properties. This work aims at extracting the coloring materials from the *Azollapinnata* plant via water or ethanolic extraction. Both extracted powders were utilized for the simulation dyeing and finishing of wool and silk fabrics at different pH values for 1 h at 90°C. The antioxidant properties and the ferric-reducing power of the aforementioned extracts were examined. FTIR was used to study the chemical structure of both the extracted colorant and the dyed substrates. The color intensity, fastness properties, and ultraviolet protection factor (UPF) of the dyed wool and natural silk fabrics were evaluated. The protection of the dyed fabrics against pathogenic microorganisms, besides the antioxidant properties of the extracted colorant, was also examined. The results show the successful dyeing of wool and natural silk fabrics by *Azollapinnata* extracts with a novel cumin color with high UV protection, antimicrobial activity, and antioxidant properties. The thermal behavior of the treated fabric was not highly affected as declared by thermogravimetric analysis (TGA).

Keywords *Azolla pinnata* · Extracts · Wool · Natural silk · Fabrics · Dyeing · Finishing

Abbreviations

AP	*Azolla pinnata*
FTIR	Fourier transforms infrared spectroscopy
UPF	Ultraviolet protection factor
DPPH	2-diphenyl-1-picryl hydrazyl radical
TPTZ	2,4,6-Tris(2-pyridyl)-*s*-triazine
AWB	*Azolla pinnata* water base
AOB	*Azolla pinnata* oil base
MLR	Material-to-liquor ratio
o.w.f.	on the weight of the fabric
FRAP	ferric reducing power
ABTS	2,2′-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid)
AP-E	*Azolla pinnata* ethanol extracts
AP-W	*Azolla pinnata* water extracts
NPs	nanoparticles

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1 Introduction

Wool and natural silk are the utmost commonly used proteinic natural fibers in the textile and clothing fields by virtue of their hygroscopic nature and appropriate physico-mechanical characteristics. Dyeing and printing are essential wet processes of textile fabrics in which synthetic and natural materials are applied to the textile substrates to impart a pleasant form with induced functions [1, 2]. However, the excessive use of synthetic dyes in the coloration of textile substrates led to the accumulation of polluting contaminants in the drained wastewater [3]. Most of the chemicals that are usually used during the synthesis and application of synthetic dyes are highly toxic [4]. Therefore, there is an increasing demand for the application of natural dyes as an eco-friendly alternative to synthetic ones [5]. Natural dyes have the advantages of being environmentally acceptable,

cheap, and non-toxic, with antimicrobial and antioxidant activities [6]. Natural dyes are usually derived from different parts of plants, animals, and microorganisms [7].

The hygroscopic nature of wool and natural silk fibers affords the proper medium for the growth and proliferation of microorganisms, such as bacteria and fungi [8]. To overcome this problem, various functional finishes with simultaneous coloration of the proteinic fibers have been proposed by different researchers [9–11]. High-performance textile fabrics were developed by one-pot dyeing and finishing using natural dyes with versatile properties, including superior resistance to microorganisms, insects, and UV radiation [12–14].

By virtue of their relatively low cost and excellent binding capacity with various textile substrates, currently 99% of synthetic dyes are consumed in the coloration of textiles, compared to only 1% of natural dyes [15]. Synthetic colorants (dyes and pigments) are diverse and usually classified according to the chromophore groups, such as the azo, anthraquinone, indigo, and triarylmethane groups. After the dyeing operation, the discharge of these synthetic colorants into the effluent of a dyehouse has a negative impact on the aquatic ecosystems because of their toxic and carcinogenic effects, as well as their limited biodegradability [16]. Through the food chains of aquatic fauna, these toxic colorants may reach humans, causing dangerous effects on our lives. The presence of these synthetic chemicals causes disruption of the photosynthesis mechanism of aquatic flora and defect in physiological processes due to a lack of oxygen circulation and absorption of light [17]. As per the environmental legislation across almost the entire globe, the removal of the residual dye from the dyehouse effluent is mandatory. One of the emerging technologies in this aspect is the use of hollow fiber membranes (HFMs) whose various applications have seen gigantic growth over the last two decades [18]. HFMs are very efficient for different remediation applications through the nanofiltration (NF) process [19]. Color removal was conducted through photocatalytic degradation of synthetic dyes within the dyehouse effluents using graphene-based nanostructure [20], TiO_2 nanoparticles (NPs) [21], keratin-based composites [19], oxidized cellulose nanostructure [22], PVA capped silver-doped ZnS NPs [23], chitosan-grafted silica bionanocomposite [24], and woolen-based formulations [25].

Azolla pinnata (AP) is a species of fern commonly encountered in some Asian and African countries with different nomenclatures, such as water velvet, feathered mosquito fern, and mosquito fern [26]. AP is a marine fern having a short, bulky stem together with bearing roots hanging beneath the surface of water. The AP leaves are consecutively settled; each leaf has its own thick airborne dorsal lobe encompassing green chlorophyll [27]. *Azolla pinnata* is rich in various bioactive compounds, the most important of which are proteineous components, essential amino acids, flavonoids, vitamins, β-carotene, minerals, and saponin [28].

Azolla pinnata is usually utilized in animal feeding and water purification. It is also considered as human food, medicine, green manure, and a source of hydrogen and biogas. It has been practically verified that *Azolla pinnata* exhibits antioxidant, bioremediation, plant growth promontory [29], hepato-protective [30], and bactericidal activities [31]. Some phyto-constituents, viz., tannins and flavonoids-rich phenolic compounds, within the *Azolla pinnata* extracts impart this antioxidant activity [32].

The ability of *Azolla pinnata* for absorption and removal of dyes from textile effluents was examined by many authors. Zazouli et al. evaluated the capability of AP in removing C.I. Acid Black 1 dye from a dye-house effluent [33]. *Azolla filiculoides* biomass has been successfully used as a biosorbent for C.I. Reactive Black 5 from the drained water of a textile mill [34]. Adopting artificial neural networks and random forest approaches, *Azolla pinnata* was effectively utilized in the remediation of Rhodamine B dye from aqueous solutions [35]. To the best of our knowledge, there are no published reports that deal with the use of *Azolla* extract in the finishing and coloration of textiles. Accordingly, this work aims at the extraction of green natural colorant material from the *Azolla pinnata* plant via water and ethanol extraction. Both green colorant extracts were utilized for dyeing wool and natural silk fabrics, producing novel cumin-colored fabrics. The aim of this work was extended to evaluate the antibacterial, antifungal, UV-protective, and antioxidant properties of the dyed fabrics.

2 Experimental

2.1 Materials and reagents

In this work, fresh green leaves of *Azolla pinnata* were provided by a local botanical farm. Degummed woven natural silk fabric from Chinese silkworm *Bombyx mori* (85 g/m^2) and plain weaved scoured crossbred wool fabrics with a mean fiber diameter of 22.1 µm in both the warp and weft directions were used. 2-diphenyl-1-picryl hydrazyl radical (DPPH) and 2,4,6-Tris(2-pyridyl)-*s*-triazine (TPTZ) were supplied by Sigma-Aldrich. All other chemicals are of laboratory grade and used as they are provided without further purification.

2.2 Methods

About 50 g of dried *Azolla pinnata* leaves were used to prepare the *Azolla pinata* extract (water and ethanol). The ratio of *Azolla pinnata* leaves to the solvent (water and ethanol)

was 1:100, and it was soaked with shaking for 24 h. After that, was drained using filter paper No. 4 and lyophilized.

2.2.1 Water extract of *Azolla pinnata*

Water extract was prepared by drying leaves of *Azolla pinnata* at 40 °C for 1 day. The dried leaves were milled into powder and impregnated in double distilled water (50 g/L) for 2 days with moderate shaking at ambient temperature. The contents were filtered and kept in a sealed vessel at −4 °C until usage.

2.2.2 Ethanolic extraction of *Azolla pinnata*

Adopting the method of Kunjiappan et al., the ethanolic extract was obtained from the dried leaves of AP [36]. The dried leaves (50 g/L) were collected and dried at 40 °C for 1 day, then milled into powder and impregnated in 70% (v/v) ethyl alcohol for 2 days at room temperature with gentle shaking. The contents were then filtered and preserved inside a sealed vessel at −4 °C until usage.

2.2.3 Treatment of wool and natural silk fabrics

Wool and natural silk fabrics were soaked, each separately, in 0.4% of *Azolla pinnata* water base (AWB) at pH 5 and 9.6 for 1 h at 90°C. In another experiment, each fabric was immersed in 0.4 or 0.8% of *Azolla pinnata* oil base (AOB) at pH 6.5 or 4.4, respectively for 1 hat 90°C. The material-to-liquor ratio (MLR) was1:50.

Meta mordanting of the dyed sample was adopted to assign the effect of adding a mordant to the treatment bath on the properties of the treated fabrics, 5% (on the weight of the fabric, o.w.f.) of tannic acid or tin (II) chloride ($SnCl_2$) was added to a treatment bath of both fabrics containing 0.8%AOB at pH 4.4 for 1 h at 90°C.

2.3 Analyses and testing

2.3.1 Characterization of *Azolla pinnata* extract

Antioxidant assay *Azolla pinnata* probes (10 mg/mL) were subjected to the antioxidant assay using the DPPH free radical method. A stock solution of DPPH was prepared by dissolving 0.0025 g in 10 of mL methyl alcohol. The free radical scavenging activity of the AP extract was determined as follows:

- Samples of AP extracts (10 µL and 20 µL) were transferred into a series of test tubes, and the volume was completed to 50 µL with methyl alcohol. A control sample of methyl alcohol only was used.
- An amount of 2 mL of DPPH stock solution was added to all test tubes containing AP extract as well as the control sample.
- The test tubes were kept in a dark place at ambient temperature for *ca.* 20 min.
- The extent of the decrease in absorbance was assessed by measuring the absorbance at 517 nm spectrophotometrically. Each test was conducted in duplicate.
- The free radical scavenging activity of the samples is a function of the extent of reduction in DPPH. The lower the absorbance of the sample, the higher the free radical scavenging activity.
- The free radical scavenging capability was determined using Eq. (1) [37]:

$$\text{DPPH scavenging effect (\%inhibition)} = \left(A_0 – A_1\right)/A_0 \times 100 \quad (1)$$

where A_0 and A_1 are the absorbance of the control and test samples, respectively.

Determination of ferric reducing power assay The FRAP assay is based mainly on the ability of the phenolic compounds in Azolla extract to reduce iron III cation into iron II cation. The FRAP reagent was made by combining 0.1 M acetate buffer (pH 3.6), 10 mM 2,4,6-tripyridyl-s-triazine (TPTZ), and 20 mM iron III chloride (10:01:01, v/v/v). A mixture of 150 µL of the prepared FRAP reagent and 20 µL of the previously diluted extract was prepared. The absorbance of the prepared mixture was measured at 593 nm using a microplate spectrophotometer. An aqueous solution of Trolox was adopted as a reference material. This procedure was conducted in triplicate, and the results were expressed as moles of Trolox equivalent/100 g of sample [38].

Fourier transforms infrared spectroscopy The FTIR spectra of both AP extracts and the treated wool and natural silk fabrics were obtained using the JASCO FTIR 4700 spectrometer within the range of 4000–400 cm^{-1}.

2.3.2 Fabric characterization

Antioxidant activity The antioxidant activity of the treated wool and natural silk fabrics is of prime importance to slow down the rate of fiber damage due to ageing. The antioxidant activity imparted to the AP-treated fabrics was evaluated in accordance with the radical cation decolorization assay reported by Re et al. using 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) [39]. An ABTS radical cation ($ABTS^{\cdot+}$) was created by reacting a 0.007 M aqueous solution of ABTS with a 0.00245 M potassium persulfate solution. The product was kept in a dark area at room temperature (*ca.* 30 °C) for 12 h. The $ABTS^{\cdot+}$ solution was then diluted with a phosphate buffer (0.1 M, pH 7.4) to attain an

absorbance of 0.7 at 734 nm. The examined fabric (10 mg) was impregnated in 10 mL of $ABTS^{\cdot+}$ solution for 30 min. Afterwards, the antioxidant activity of $ABTS^{\cdot+}$ was calculated at 734 nm using Eq. (2):

$$\text{Antioxidant activity } (\%) = \left[\left(A_1 - A_2\right)/A_1\right] \times 100 \quad (2)$$

where A_1 is the absorbance of the $ABTS^{\cdot+}$ before impregnation of the fabric sample, and A_2 is the absorbance of the remaining $ABTS^{\cdot+}$ after impregnation with the fabric sample. Each reported value is the average of three tests.

Antimicrobial activity The antimicrobial properties of the undyed, along with some dyed wool and silk fabrics, were evaluated using Gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*) and the pathogenic fungus *Candida albicans*, according to the standard methods ATCC 25922, ATCC 6538, and ATCC 10231, respectively.

Adopting the shake flask method, each tested sample (*ca.* 0.5 g) was applied to the aforementioned strains to evaluate their resistance to microbial attack, expressed as a (%) reduction in bacterial count. The resistance of the tested sample to microbial attack, expressed as "relative reduction %", was calculated using Eq. (3):

$$\text{Relative reduction } (\%) = \left(A_c - A_s/A_c\right) \times 100 \quad (3)$$

where "A_c" is the count of microorganisms in the control flask, which contains only the strain, and "A_s" is the count of microorganisms in the tested flask, which contains the tested sample [40].

Ultraviolet protection factor The resistance of the tested samples (2 × 2 cm) towards UV-rays, expressed as UPS, was determined according to the Australia/New Zealand standard AS/NZS 4399:1996 [41]. The ultraviolet protection factor (UPF) calculation system of a UV/Vis spectrophotometer was used in this analysis according to the AATCC Standard Test Method 183:2010-UVA Transmittance [42].

Color measurements and fastness characteristics The color intensity (K/S) and the colorimetric data (CIE LAB color space values: L*, a*, b*) of the dyed wool and natural silk fabrics were evaluated for 2 × 4 cm sample using a spectrophotometer equipped with a pulsed xenon lamp light source (Ultra Scan Pro, Hunter Lab, USA) and a 10° observer with D65 illuminant, d/2 viewing geometry, and a measurement area of 2 mm. The hue angle was adjusted in terms of a degree from 0° (red), 90° (yellow), 180° (green), 270° (blue), and again back to 0°. The standard test methods for color fastness of the dyed samples against washing [43] and light [44] were adopted.

Thermal properties About 4–5 mg of the tested sample was cut and used for thermo-gravimetric analysis (TGA). The TGA was measured using the SDT Q2000 Tzero TA instrument under N_2 atmosphere with a heating rate 10 °C/min.

3 Results and discussion

3.1 Antioxidant activity

The antioxidant activity of the aqueous and ethanolic extracts of *Azolla pinnata* (AP) was evaluated using the DPPH method, and the results are shown in Fig. 1. It is clear from this figure that the AP extracts are effective free radical scavengers, which makes them appropriate candidates as natural antioxidants at concentrations of 0.01 and 0.001% (w/v) for ethanol extract (AP-E) and 0.1 and 0.01% (w/v) for water extract (AP-W). Scavenging activity ranged from 30.4 to 65.2%. The highest scavenging activity was for ethanol extract at 0.01 concentrations. The higher antioxidant efficacy of AP extracts can be attributed to the relatively high contents of total phenolics and flavonoids compounds as reported by Mithraja et al. [45].

The antioxidant activity, expressed as a reducing power activity, was measured using the TPTZ method as µg Trolox eq/g sample (FRAP). In the present study, according to the screening of the antioxidant activity of AP extracted samples. AP-W (0.1%) had the highest reducing power (597.4 ±0.006) µg Trolox eq/g sample, $p < 0.05$). On the other side, the AP-E (0.01%) has a higher reducing power compared to the same concentration of the AP-W extract (494.612 ± 0.04 and 214.914 ± 0.03 µg Trolox eq/g sample, respectively). These findings suggest that further research plans should be directed towards the development of bioactive ingredients in

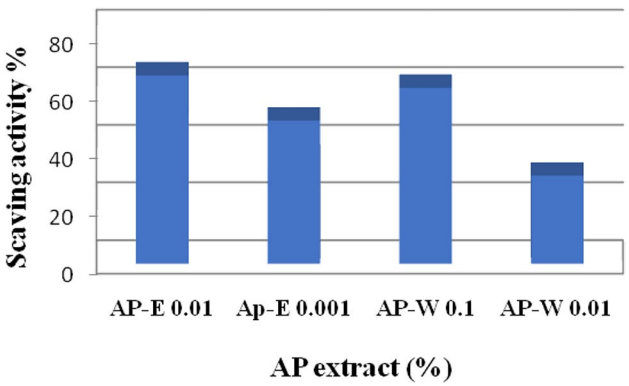


Fig. 1 Antioxidant activity of *Azolla pinnata* (AP) extracts by the DPPH method. PA-E0.01: ethanol extract 0.01%, PA-E 0.001: ethanol extract 0.001%, PA-W 0.1: water extract 0.1%, and PA-W 0.01: water extract 0.01%

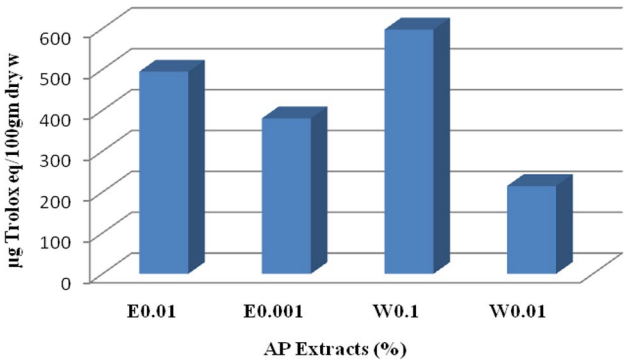


Fig. 2 Antioxidant activity of AP extracts by the TPTZ method. AP-E0.01: ethanol extract 0.01%, AP-E 0.001: ethanol extract 0.001%, AP-W 0.1: water extract 0.1%, and AP-W 0.01: water extract 0.01%

AP and their utilization as eco-friendly natural antioxidants in various applications (Fig. 2).

3.2 FTIR analysis

Figures 3 and 4 show the FTIR spectra of AP-E and AP-W extracts before and after being incorporated into wool or natural silk fabrics. The AP extracts showed a broad band at 3297 cm^{-1}, corresponding to O–H stretching vibration of carboxyl groups as well as N–H stretching vibrations of the secondary amide group. The weak bands at 2922 and 2853 cm^{-1} are associated with stretching vibrations of the aliphatic $–CH_3$ and $–CH_2$ groups. The medium bands at 1599, 1515, and 1418 cm^{-1} indicate the C–N stretching vibration, $–COO^-$ anions, and C=C of aromatic residues. The

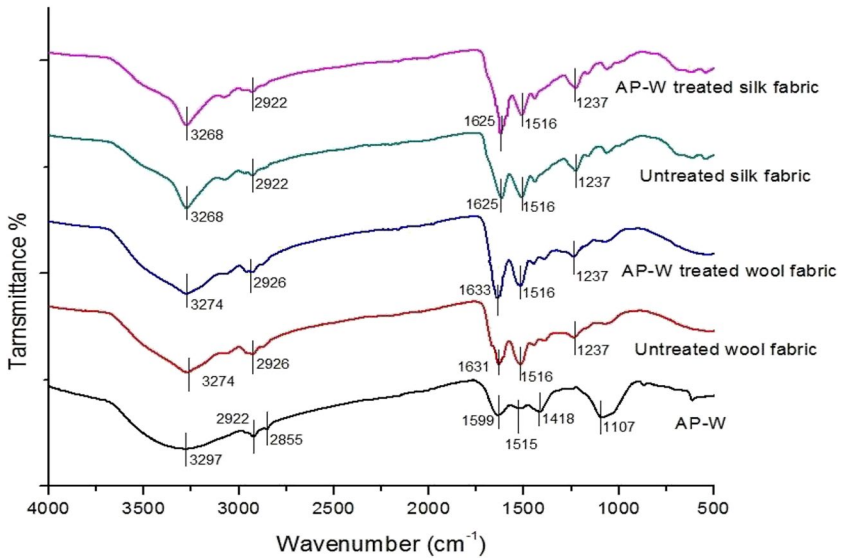


Fig. 3 FTIR chart of undyed as well as AP/W-dyed wool and natural silk

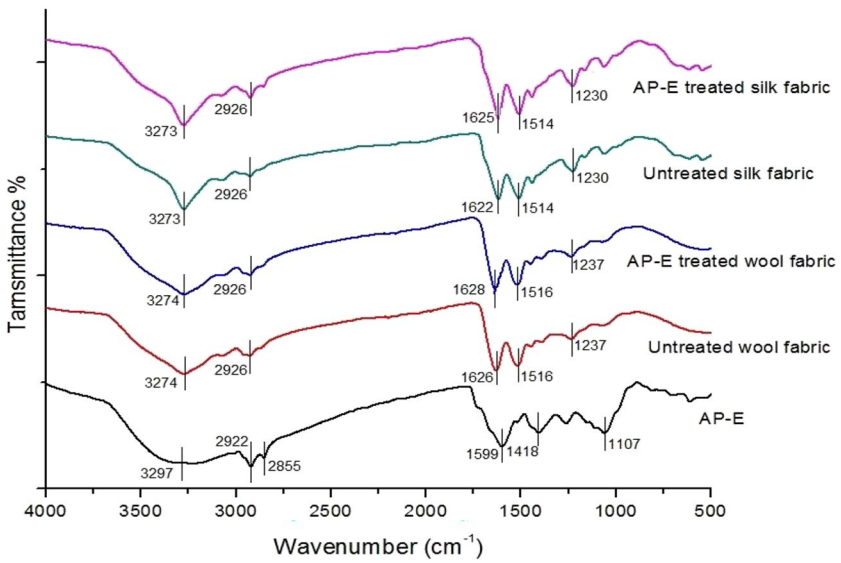


Fig. 4 FTIR chart of undyed as well as AP/E-dyed wool and natural silk

band at 1440 cm^{-1} is due to the bending vibrations of the C–OH alcoholic group and the C–O bond vibrations of an ether linkage. The C–N stretching vibration of an aliphatic amino group is responsible for the medium band appearing at 1107 cm^{-1}. The functional groups indicated by the bands that appeared in the FTIR chart of AP-W and AP-E exist in the chemical structure of AP, such as proteins, phenolic compounds, flavonoids, and terpenoids [46].

The FTIR spectra of undyed wool show the characteristic band beyond 3274 cm^{-1}, which is due to the stretching vibration of the $–NH_2$ and –OH within the side chains of some amino acid residues in proteins. The characteristic bands of wool appearing at 1631 cm^{-1}, 1516 cm^{-1}, and 1237 cm^{-1} are due to amide I, II, and III, respectively [47]. Being proteinic fibers, the FTIR spectra of both wool and natural silk are common in most of the characteristic bands [48]. Treatment of wool and natural silk fabrics with AP-E as well as AP-W extracts resulted in a slight decrease in the bands of the –OH of the carboxylic group and the $–NH_2$ group, together with a slight increase in the band corresponding to the C=O bond of the amide group. This implies that the AP extracts bind to wool and natural silk macromolecules via amide formation reaction.

3.3 Color strength

Treatment of wool and natural silk fabrics with AP extracts results in coloration of the fabrics with different hues depending on the extracting medium as well as the conditions of extraction. As shown in Table 1, wool and natural silk fabrics dyed with AP-W or AP-E in an acid medium resulted in higher K/S values. In an acid medium, the amino groups in wool and natural silk are protonated, creating cationic groups that are labile to form salt links with any anionic group in AP extracts, such as the carboxylate anions. The K/S values of wool or natural silk fabrics dyed with AP-E are higher than the corresponding samples treated with AP-W, presumably due to the presence of some compounds in the ethanolic extract that are completely absent in the aqueous extracts, viz., alkaloids, anthraquinones, and coumarins [46]. The data in Table 1 also indicate that upon increasing the concentration of the used extract to the double, the K/S of the treated fabrics increased almost by twofold.

The dyeing of wool and silk fabrics with an ethanolic or aqueous AP extract in the presence of $SnCl_2$ or tannic acid as a mordant led to a decrease in the K/S of the dyed samples to different extents depending in the change in the hue of the dyed sample.

3.4 Colorimetric data and color fastness

The effect of dyeing conditions on the L*, a*, b* data as well as the fastness properties of the dyed fabrics towards light and washing were evaluated, and the results were summarized in Table 2. As the "L*" value increases, the sample gets darker, while the increase in the positive values of a* and b* indicates shift of the color of dyed wool fabrics towards the red-blue color and their negative values imply shift towards the green-yellow region. The data of Table 2 indicated that the dyed fabrics have negative a* and positive b* values which correspond to greener and bluer hues rather than the redder and yellower hues. The color fastness to light of the dyed fabrics ranged between good/very good to excellent, whereas their wash fastness is very good in all samples.

3.5 Performance attributes

High-performance textiles are fabricated with unique properties to protect the human body from extreme surrounding conditions like fire, UV radiation, and microorganisms. The fabrication of highly microbial- and UV-resistant wool and silk products was the subject of many investigations [49–51]. The resistance of selected AP-E-treated fabrics to the microbial attack and UV rays was monitored, and the results are shown in Table 3. The resistance of wool and natural silk fabrics towards *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans* was assessed. The highest reduction in organism count was recorded in the case of the treated wool fabric against *C. albicans* (94.69%), compared to 76.25% in the case of untreated wool. In case of silk fabrics, the high reduction was found to be against *S. aureus*. The inhibitory effect induced on the treated fabric is due to the presence of some bioactive materials, viz., flavonoids, alkaloids, tannins, steroids, saponins, and glycosides [52]. It has been reported that alkaloids, tannins, flavonoids, and terpenoids exhibit good antimicrobial action [53]. Moreover, Vannini et al. reported that the antimicrobial activity of tannins is due to their capability to inhibit the extracellular enzymes, which are essential for the creation of the substrates required for microbial growth, or by suppressing the oxidative phosphorylation of microbial metabolism [54].

The results in Table 3 revealed also that the resistance of the treated fabrics against UV rays was greatly enhanced, and the extent of improvement is higher in the case of the treated wool fabrics, as indicated by the UPF values. The aromatic compounds within the AP extract might be the principal factor responsible for enhancing the UPF of the treated wool and silk. It has been agreed by many authors that most phenolic compounds are capable of scavenging any free radicals created by UV radiation, resulting in excellent protection against UV rays [55].

The free radical scavenging capability, expressed as antioxidant activity, of wool and natural silk fabrics treated with AP extract. It is clear from the results in Table 3 that the pristine fabrics exhibited limited antioxidant activity values, which did not exceed 19%. On the other hand, the

Table 1 Photographs and color intensity (K/S) values (at λ_{max} 365 nm) of wool and natural silk fabrics dyed with AZ-E or AZ-W extract

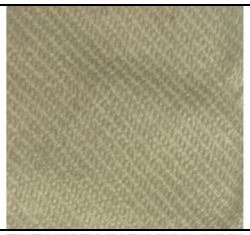
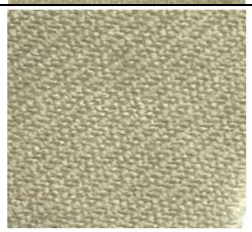
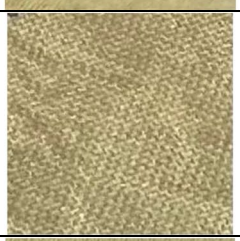
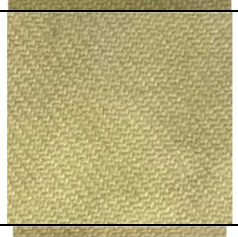
Treatment conditions	Wool	K/S	Natural silk	K/S
AP-W: 0.4%, pH 9.6, 1 h, 90°C.		1.74		1.02
AP-W: 0.4%, pH 5, 1 h, 90°C		2.44		1.22
AP-E: 0.4%, pH 6.5, 1 h, 90°C		4.49		1.8
AP-E: 0.4%, pH 4.4, 1 h, 90°C		6.78		2.57
AP-E: 0.8%, pH 4.4, 1 h, 90°C		13.11		5.08
AP-E: 0.8% pH 4.4, 1 h, 90°C in the presence of $SnCl_2$		12.9		4.02
AP-E: 0.8%, pH 4.4, 1 h, 90°C in presence of tannic acid		11.31		3.63

Table 2 Colorimetric data and color fastness to washing and light

Sample	L*	a*	b*	Light fastness	Washing fastness		
					St*	St**	Alt
Wool treated with AP-W: 0.4%, pH 9.6 for 1 h at 90°C	76.84	−1.18	13.62	5	4	4	4
Wool treated with AP-W:0.4%, pH 5 for 1 h, 90°C	71.26	−1.37	14.54	4-5	4	4	4
Wool treated with AP-E:0.4%, pH 6.5, 1 h at 90°C	74.35	−0.88	19.83	4	4	4	4
Wool treated with AP-E:0.4%, pH 4.4, 1 h, 90°C	69.17	−0.68	22.60	4	4	4	4
Wool treated with AP-E:0.8%, pH 4.4, 1 h, 90°C	69.42	−1.42	26.47	3-4	4	4	4
Wool treated with AP-E:0.8%, pH 4.4, 1 h, 90°C in presence of $SnCl_2$	78.99	−3.18	29.67	4	4	4	4
Wool treated with AP-E:0.8%, pH 4.4, 1 h, 90°C in presence of tannic acid	68.05	−0.72	25.37	3-4	4	4	4
Silk treated with AP-W:0.4%, pH 9.6, 1 h at 90°C	77.87	−0.66	11.16	4-5	4	4	4
Silk treated with AP-W:0.4%, pH 5, 1 h at 90°C	77.03	−0.51	12.63	4	4	4	4
Silk treated with AP-E: 0.4%, pH 6.5, 1 h, 90°C	75.61	−1.48	18.93	4	4	4	4
Silk treated with AP-E: 0.4%, pH 4.4, 1 h, 90°C	72.34	−0.71	21.72	3-4	4	4	4
Silk treated with AP-E: 0.8%, pH 4.4, 1 h, 90°C	70.55	−0.30	24.29	3-4	4	4	4
Silk treated with AP-E:0.8%, pH 4.4, 1 h, 90°C, in presence of $SnCl_2$	78.74	−3.36	24.23	3-4	4	4	4
Silk treated with AP-W:0.8%, pH 4.4, 1 h, 90°C, in presence of tannic acid	72.00	−0.85	23.15	4	4	4	4

*St** Stunning on cotton, *St*** stunning on wool, *Alt* changing in color

Table 3 The antimicrobial activity and UPF of wool and natural silk fabrics treated with AP-E (0.8 %, pH 4.4, 90 °C, 1 h)

Sample	Reduction in colony count (%)			UPF	Antioxidant activity (%)
	E. coli	*S. aureus*	*C. albicans*		
Untreated wool	67.11	76.25	76.25	23.7	19.0
AP-E treated wool	82.88	83.12	94.69	109.1	92.4
Untreated silk	69.13	57.20	76.12	14.4	17.3
AP-E treated silk	97.37	93.23	97.93	56.2	88.9

treated fabrics had relatively higher antioxidant activities. The enhanced antioxidant activity of the treated fabrics may be rationalized in terms of the presence of many phenolic hydroxyl groups in the structure of AP extracts, which are considered to be proper free radical scavengers [56]. This would result in high resistance of the treated fabric against ageing under the influence of a polluting environment.

3.6 Thermal properties

The thermal behaviour of wool and natural silk fabrics dyed with E-AP extract was compared to the respective samples. As shown in Fig. 5, dyeing of wool and natural silk fabrics with E-AP extract decreased the percent loss in weight at the maximum decomposition temperature (324 °C) by a factor of 15.4 and 10.5%, respectively. This indicates that during the dyeing process of wool and natural silk with E-AP, new bonds or crosslinks were created, leading to an increase in the ratio of the crystalline part on the expense of the amoprphous regions of the fibers' structure.

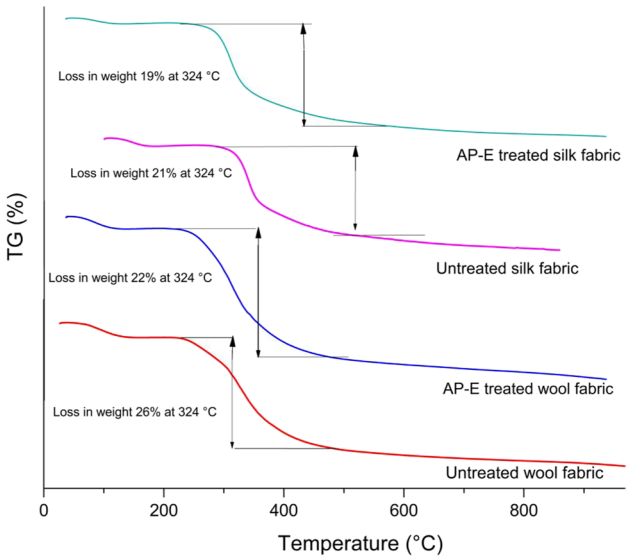


Fig. 5 Thermogravimetric analysis of untreated and treated wool and natural silk fabrics

4 Conclusion

Azolla pennata extract was successfully used for one-pot coloration and functionalization of wool and silk fabrics. *Azolla pinnata* extract is an appropriate candidate for improving the resistance of wool and natural silk towards Gram negative bacteria (*E. coli*), Gram positive bacteria (*S. aureus*), and the

pathogenic fungus (*C. albicans*) to different extents depending on the tested species. The AP extract is also effective in enhancing the UPF of the treated fabric to an excellent degree. A superior free radical scavenging capability was imparted to the AP-treated wool and natural silk fabrics. The treated fabrics exhibited various degrees of cumin color which varies according to the extracting medium (aqueous or ethanolic), the treatment conditions, and the presence of a mordanting agent. The colour fastness of the dyed fabric against light and washing ranged between good and excellent. *Azolla pinnata* has the advantage of being eco-friendly, non-toxic, cheap, biodegradable, and microbial-resistant, compared to the synthetic dyes that are usually used for dyeing wool and natural silk.

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Data availability Not applicable

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

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