



Valorization of bio-colorants extracted from *Hypericum scabrum* L. plant for sustainable and ecological coloration of wool yarns

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ABSTRACT

Recently, natural dyes are being explored all over the world as safer and highly sustainable bio-based alternatives to synthetic dyes. Agricultural wastes and plant by-products are the most commonly explored alternatives with dual benefits of waste reclamation and sustainable dye production with extra value-adds. *Hypericum scabrum* plant contains interesting bio-dye molecules with high flavonoids and tannin contents. The present study aims at exploring the potential of *H. scabrum* plant extract to color wool textiles with a focus on sustainable bio-dye production and fastness properties. The extracted bio-dye was quantitatively (for total phenolic (2.733 mg per CE/g) and total flavonoid (1.140 mg per GAE/g) content using the Folin–Ciocalteu method) and qualitatively (UV–Vis, FT-IR, and EDX) characterized. The effect of dyeing parameters like pH (2–8), temperature (60–90 °C), dry-weight content of plant material as a dye (25–150% o.w.f.), and dyeing time (15–120 min) on color strength (K/S) values were assessed. Color fastness assays showed good resistance to light, washing, and rubbing. The effect of artificial aging (Xenon arc lamp) on the color strength of dyed wool yarns under different exposure times (0–48 h) was explored. The highest color fading occurred in control dyed samples with a first-order rate constant of 131.57 h⁻¹ and a half-life period of 5.26 × 10⁻³ h. Color difference (ΔE) values suggested that mordanted samples showed less fading compared to control dyed samples at equal times of Xenon exposure. Additionally, the dyed samples were washed in double distilled water, tap water, and 4 g/L NaCl solution to check their effects on the corresponding K/S values while 4 g/L NaCl solution mimics the real conditions of perspiration. Maximum color leaching occurred in 4 g/L NaCl washing with a first-order rate constant of 11.57 min⁻¹. Cost analysis of the dye extraction and dyeing procedure revealed that the process is sustainable and economical. Thus, the use of *H. scabrum* whole plant can provide a clean, economical, and sustainable source of alternative natural dyes that can be used to substitute synthetic analogs.

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1. Introduction

Dyes extracted from natural plant sources have been used in China since 2600 B.C., making them an ancient and environmentally friendly coloring technique. The process of extracting natural dyes encompasses the use of many botanical constituents, such as stem barks, roots, flowers, leaves, fruits, and peels. In earlier times, not too many resources were exploited as indicated by the archeological evidence [1]. The cultivation of dye plants arose as a prominent economic factor across Europe throughout the Middle Ages. The use of *Isatis tinctoria* and *Rubia tinctorum* to dye various textile substrates was seen in Germany, the Netherlands, and the southern regions of France. However, during the 19th century, synthetic dyes were available in the market due to the industrial revolution and almost replaced all the natural dyes from the textile and food industries [2,3]. The well-defined structures of synthetic dyes have many advantages over natural plant extracts in handling, performance, and most importantly reproducibility of shades. With high performances, these synthetic dyes were applied globally in modern dye houses [4]. The rough estimate of the use of synthetic dyes goes up to 1.3 million tons which cost around 23 billion dollars [5]. Nevertheless, the presence of several synthetic dyes and their byproducts within dyeing wastewater presents a substantial risk to both human well-being and the natural environment [6]. Numerous nations have implemented regulations to limit the use of synthetic dyes (azo dyes) and hazardous finishing compounds due to their detrimental impacts on human health and the environment [7].

Nowadays textile researchers are in constant search of new and environmentally friendly dyeing alternatives with natural dyes as the potential alternative that will help to minimize the adverse environmental impact of synthetic dyes [8]. One of the key advantages attributed to natural dyes is their capacity to provide gentle and sophisticated hues, while also exhibiting environmental compatibility, biodegradability, and notable biological attributes [9–12]. Many researchers have outlined the functional properties of different natural and synthetic textiles irreversibly coated with natural dyes derived from several botanical sources [13–15]. Further investigation into the comparative analysis of synthetic and natural dyes will provide more empirical support for the advantages and environmental sustainability of natural colors [16]. The primary focus of current research is to enhance color yield and colorfastness properties via the use of different types of unconventional natural dye and dyeing processes [17]. However, it is of utmost importance to address the concurrent examination of environmental, socioeconomic, and sustainability aspects [18]. The primary objective of this study is to provide novel data about the use of natural dyes in contemporary commercial textile applications, with a particular emphasis on their eco-friendly and sustainable attributes [19,20]. Considering the new influence of natural colorant usage in textile dyeing, *Hypericum scabrum* is one such candidate that will provide a wide range of new, eco-friendly, and elegant shades for wool dyeing with and without the use of metal mordants.

H. scabrum L. is a perennial herbaceous plant with yellow-colored flowers and red-colored glands. It belongs to the genus *Hypericum* (family: Hypericaceae) and possesses medicinal values which date back to 2499 years ago [21,22]. This plant grows up to a length of 40–50 cm and has naturalized itself to rough hillsides, forest clearances, and steppes in Turkey. *H. scabrum* is also found in Iran, Afghanistan, and other South Asian countries. Recent studies have shown that *H. scabrum* has substantial potential to be used as a cytotoxic [23], anti-inflammatory, antioxidant [24], antifungal [25], and antidepressant [26] agent. The random use of antibiotics and subsequent antibiotic resistance have compelled scientists to search for alternative drugs which will act quickly and effectively. *H. Scabrum* aerial plant parts possess many aromatic compounds of which three compounds with unusual skeletons were extracted and exhibited moderate level of effectiveness against *T. brucei* and *P. falciparum* [27]. The isolated chemical components of *H. scabrum* have antioxidant and antibacterial properties that are attributed to the presence of phenolic groups or oxygen-bound derivatives [28]. The most prevalent phenolic chemicals observed in *H. scabrum* were coumarins, cinnamic acid derivatives, and flavonoids [29].

Until now, there has been little data gathered or created addressing the secondary use of the *H. scabrum* L. plant. In the present research efforts, the authors have tried to explore the secondary usage of the *H. scabrum* plant in terms of a potential source of yellow natural dye which will ease the burden of the textile industry. So, the present research work is focussed on the valorization of whole plant parts of *H. scabrum* L. for developing eco-friendly shades of high color and fastness properties. The extracted dye powder was subjected to functional group analysis by UV–Vis, FT-IR, SEM, and EDX analysis. Additional phytochemical analysis was done in terms of total phenol and total flavonoid contents. The optimization of dyeing parameters was conducted in order to determine the optimal dyeing conditions with respect to pH, temperature, duration of dyeing, and quantity of plant material. For the first time, fastness with respect to 4 g/L of sodium chloride solution washing and Xenon lamp irradiation (aging) are being presented. The current study offers an innovative and environmentally friendly method for valuing entire plant extract, which is widely cultivated throughout Turkey, Iran, and other South Asian nations.

2. Material and methods

2.1. Materials and chemicals

100% commercial wool yarns (20/4 Nm, average fiber diameter of 30.4 μm) used to make hand-made carpets purchased from Azarbarf Co., Iran, were used in this research study. *H. scabrum* plant material was collected in June 2022 from the mountain areas of Hargalan village, Ajab Shir County, East Azerbaijan province, Iran. Different metal salts like aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) (99.99%), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) ($\geq 99\%$), copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) ($\geq 99\%$), stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) (98%), ferric chloride (FeCl_3) (97%), sodium chloride (NaCl) ($\geq 99\%$), sulfuric acid (H_2SO_4) (95–98%), chloroform (CHCl_3) ($\geq 99\%$), glacial acetic acid (CH_3COOH) (99–100%), and sodium carbonate (Na_2CO_3) ($\geq 99\%$) were purchased from Merck Germany (Laboratory grade). The pH of the dye solution was adjusted by means of acetic acid and sodium carbonate. The wool souring method included the use of a non-ionic detergent (Nikogen SDN), procured from a local retail shop.

2.2. Extraction of natural dye from *H. scabrum*

The finely powdered whole plant of *H. scabrum* was extracted thrice at neutral pH with 50% ethanolic aqueous solution (50:50 V/V) for 3 h at 60 °C. Briefly, the finely powdered plant material was soaked in an ethanolic aqueous solution at 25 °C for 1 h. The temperature was incrementally increased to 60 °C and maintained for further 2 h under continuous magnetic stirring. Whatman No. 42 was used to filter the mixture and the resulting filtrate characterized by its golden-yellow hue was employed for dyeing purposes without undergoing any further purification. A portion of the filtrates containing golden-yellow dye was subjected to evaporation in an oven maintained at a temperature of 60 °C. The resulting residue was then finely ground into a powder to facilitate Fourier-transform infrared (FT-IR) spectrum analysis.

2.3. Characterization of the extracted natural dye

The qualitative phytochemical analysis of *H. scabrum* whole plant extract was done to check the presence of different classes of phytochemicals as per the previously developed methods [30]. As mentioned earlier, the major phytochemicals present in the plant are phenolic and oxygen-bound derivatives. The Folin-Ciocalteu method outlined in our earlier published research was used to determine the total phenolic and total flavonoid content [31]. The outcomes were quantified as catechin (CE) and gallic acid (GAE) equivalents, using calibration curves spanning from 0.2 to 2.0 mg/ml [32]. The extracted dye powder from the *H. scabrum* whole plant was subjected to phytochemical characterization with UV-Vis and FT-IR analysis. The UV-Vis spectrum (200–700 nm) of the golden-yellow dye filtrate and FT-IR spectra (4000–500 cm⁻¹) of dried powder were documented on an Analytik Jena Specord 250 Plus UV-Visible spectrophotometer and Jasco 680-plus FT-IR spectrometer, respectively. The SEM analysis of the extracted dye powder was done by Tescan Mira3 microscope (Czech Republic) under 15 kV. The weight percentage of various metal ions and thus carbon to oxygen ratio (C:O ratio) present in the extracted dye was recorded on Zeiss Siga 300 EDX instrument under an extra voltage of 20 kV.

2.4. Mordanting and dyeing procedure

Native wool yarn samples (5 g) were scoured at 50 °C for 30 min under a liquor ratio of 40:1 with 2 g/L non-ionic detergent. After souring, the samples were pre-mordanted with single and binary metal salt combinations, details of which are provided in Table 1. These mordants were applied prior to dyeing alter the colorimetric and fastness characteristics of the dyed wool yarns. Weakly adsorbed metal salts were washed off by washing the mordanted samples with tap water.

The optimization process included varying the dyeing pH within the range of 2–8, adjusting the dyeing temperature between 60 and 90 °C, altering the quantity of plant material used as a dye within the range of 25–150% o.w.f., and modifying the dyeing duration between 15 and 120 min. This optimization was carried out utilizing the one-factor-at-a-time (O.F.T) optimization approach based on highest color strength (K/S) values. The process of dyeing of the mordanted samples was conducted under optimized dyeing variables of pH, temperature, concentration, and time at M:L ratio of 40:1. After the dyeing was complete, the samples were washed in the aqueous solution of 2 g/L non-ionic detergent (Nikogen SDN).

2.5. Measurements

The pH of the dye solutions was determined using a pH/mV meter (DB 1011). The researchers used the reflectance color-eye XTH spectrometer, manufactured by X-Rite Inc., to assess the color properties (L*, a*, b*, C*, and h°) of the dyed wool yarns. The K/S values of the dyed yarns were derived from reflectance data (R) using the below-mentioned equation (Kubelka-Munk) within the wavelength range of 360–700 nm.

$$K/S = (1 - R)^2/2R$$

Color difference (ΔE) of the samples was calculated from the colorimetric values (L*, a*, and b*) using the following equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5}$$

Comparisons regarding the wash and rub fastness properties were done using Grayscale following the guidelines outlined in ISO 105-C10:2006 (E) and ISO 105-X12:1993 (E) standards, respectively. The light fastness ratings (blue scale) were determined according to the ISO 105 B02:2013 (E) standard. The dyed wool yarns were also subjected to Xenon lamp (SOLARBOX 1500) irradiation (1100 W/m²) for different periods (0–48 h) to mimic the real exposure to solar radiation within the wavelength range of 290–800 nm.

Table 1

The symbolization of different mordanted dyed wool yarn samples.

S. No.	Sample	Code	S. No.	Sample	Code
1	5.0% (o.w.f.) Al ³⁺	Al	6	2.5% (o.w.f.) Al ³⁺ + 2.5% (o.w.f.) Cu ²⁺	Al/Cu
2	5.0% (o.w.f.) Fe ²⁺	Fe	7	2.5% (o.w.f.) Al ³⁺ + 1.5% (o.w.f.) Sn ²⁺	Al/Sn
3	5.0% (o.w.f.) Cu ²⁺	Cu	8	2.5% (o.w.f.) Fe ²⁺ + 2.5% (o.w.f.) Cu ²⁺	Fe/Cu
4	3.0% (o.w.f.) Sn ²⁺	Sn	9	2.5% (o.w.f.) Fe ²⁺ + 1.5% (o.w.f.) Sn ²⁺	Fe/Sn
5	2.5% (o.w.f.) Al ³⁺ + 2.5% (o.w.f.) Fe ²⁺	Al/Fe	10	2.5% (o.w.f.) Cu ²⁺ + 1.5% (o.w.f.) Sn ²⁺	Cu/Sn

Further, to mimic the real conditions of sweating during hot summer days, the dyed wool yarns were also washed in 4 g/L sodium chloride solution, deionized water (double distilled), and normal tap water to find out their direct effects on the color strength (K/S) values.

3. Results and discussion

3.1. Phytochemical analysis of the extracted dye

3.1.1. Qualitative color change experiments

The qualitative phytochemical analysis of *H. scabrum* L. whole plant extract was carried out using simple qualitative experiments reported in our earlier research [30]. The analysis yielded the identification of many bioactive components, including Saponins, Terpenoids, Glycosides, Flavonoids, Tannins, and Phenolic substances (Table 2). The observation of color variations throughout the process of qualitative analysis serves as further evidence supporting the existence of diverse phytochemical compounds.

3.1.2. Total phenolic and flavonoid content

The flavonoid and polyphenolic (tannin) compounds in the *H. scabrum* extract was quantified in terms of catechin (CE) and gallic acid (GAE) equivalents, respectively (Table 3). Standard curves were generated using equations $y = 0.938x + 1.58$ ($R^2 = 0.98$) and $y = 0.24x + 0.01$ ($R^2 = 0.99$) to determine the concentrations of these compounds [22].

3.1.3. Spectral analysis of the extracted dye

The FT-IR spectra of the powdered dye extract from *H. scabrum* whole plant extract is shown in Fig. 1a. The broad absorption band in the range of 3500–3100 cm^{-1} is due to the presence of polyphenolic (-O-H) structures that indicate intramolecular hydrogen bonding. Aromatic -C-H groups may be seen as a tiny, merged low-intensity peak at 2932 cm^{-1} [33,34]. The presence of a high-intensity absorption peak at 1609 cm^{-1} , followed by a shoulder at 1731 cm^{-1} , indicates the occurrence of the aromatic -C=O stretch in the flavonoid nucleus bearing quinone structures [35,36]. The peak seen at a wavenumber of 1433 cm^{-1} corresponds to the basic bending vibration of the -O-H bond [37]. The peak at 1057 cm^{-1} is referred to as the aromatic -C-O stretch [38,39]. The existence of -C-O groups of esters and phenols with C-C stretch is indicated by the appearance of many peaks at 817, 772, and 603 cm^{-1} [33,40,41].





The UV-Visible spectrum of the aqueous solution of *H. scabrum* yellow natural dye is shown in Fig. 1b. The fingerprint absorption bands of the basic chemical components of this dye are seen at wavelengths of 231 and 246 nm (major band), 260 nm (minor bands), and throughout the range of 315–350 nm (broadband). The peaks at 231 and 246 nm correspond to the presence of high tannin and phenolic content [42]. The peak at 260 nm represents the $\pi \rightarrow \pi^*$ transition of the carbonyl group (-C=O). This absorption peak indicates the HOMO to LUMO transition of the -C=O group of ring B of flavonoid molecules and reflects the presence of condensed tannins along with catechin and catechin gallates [31]. The broadband in the region of 315–350 nm is assigned to the $\pi \rightarrow \pi^*$ transition over the B-ring of the flavonoid.

The findings of Llorent-Martinez et al. (2018), who performed phytochemical analysis of methanolic extracts of aerial sections of the plant, are in consistent with the present FT-IR and UV-Visible spectral results of *H. scabrum* whole plant extract. In addition to phenolic acids and saccharides, the chemical profiles of the plant employing HPLC-ESI-MS indicated the presence of flavonoids as important chemical components [43,44]. The most common flavonoids were quercetin and myricetin glycosides (deoxyhexosides, hexosides, glucuronides, and pentosides) and their derivatives [45]. Kaempferol, isorhamnetin-O-rutinoside, taxifolin, and isorhamnetin were also observed in the *H. scabrum* extract [46]. Type A- and B-proanthocyanidins were also identified and characterized in addition to trimers of epicatechin [47]. HPLC-ESI-MS also revealed the presence of abiflavone with a characteristic m/z value of 537 [48]. Among the phenolic acids caffeoylquinic acid derivatives, ferulic acid, and several hydroxycinnamic acid derivatives were also analyzed and characterized [46,49]. The structures of the major chemical components present in the *H. scabrum* L. extract are given in Fig. 2.

3.1.4. SEM and EDX analysis of the extracted dye

The structural characteristics (SEM) and elemental composition (EDX) of the extracted dye powder is shown in Fig. 3. The surface morphology showed a coarse surface of the dye powder which will help to increase the relative forces of adsorption onto the wool surface. The quantitative findings demonstrated the relative abundance of carbon, oxygen, and nitrogen in the extracted dye

Table 2
Phytochemical analysis of *H. scabrum* L. yellow natural dye.

Ethanolic aqueous extract	Saponin	Terpenoids	Glycosides	Phenols and Tannins
<i>H. scabrum</i> L. whole plant	+	+	+	+
Color change				

Note: (+) means presence and (-) means absence of chemical constituents.

Table 3
Total phenolic and flavonoid content of *H. scabrum* L. extract.

S. No.	Chemical compounds	Amount per gram of the extract
1	Flavonoids	1.140 mg per CE/g
2	Polyphenols (tannins)	2.733 mg per GAE/g

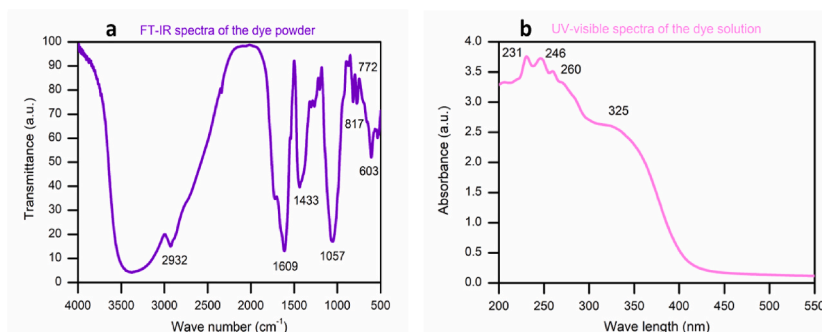


Fig. 1. (a) FT-IR spectra of the extracted dye powder, and (b) UV-Visible spectra of the extracted dye solution.

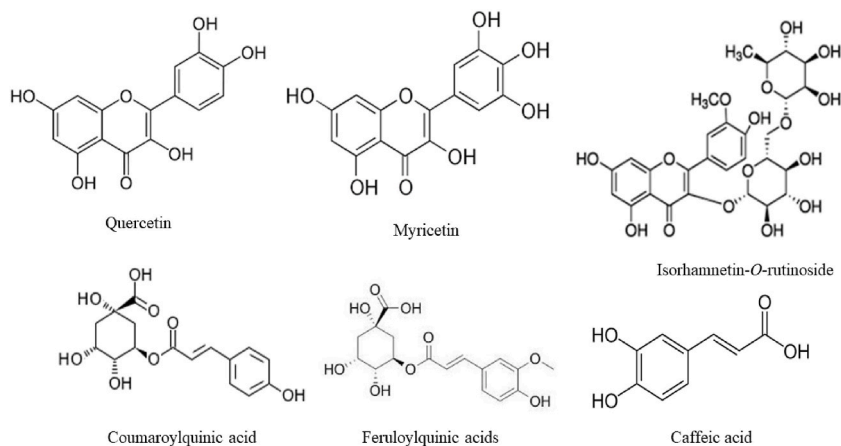


Fig. 2. Structures of the major chemical components present in *H. scabrum* L. whole plant extract.

powder, as well as their weight and atomic percentages. The carbon-to-oxygen weight percentage ratio of 0.91 suggests the existence of hydroxylated flavonoids with a greater abundance of polymeric forms [48,50].

3.2. Wool yarn dyeing optimization

Wool is a non-homogenous protein fiber that is amphoteric and can adsorb both anionic and cationic dyes. At lower pH values (<4), wool attains a net positive charge and adsorbs only anionic dyes (tannins- and flavonoids-based dyes) whereas, at pH value higher than 8, cationic dyes are freely adsorbed [51]. However, the rate of dye adsorption is largely determined by the movement of dye molecules in the dye bath and the adsorption capacity of wool fibers (transfer of dye molecules across the fiber surface) [52]. Therefore, the adsorption of dye molecules is contingent upon the physical attributes of the dye, such as the kind of functional groups it has. Additionally, the pH and temperature of the dye bath, as well as the concentration of dye and the presence of inorganic salts, all play significant roles in this process [53]. During this part of the research, the optimization of dyeing parameters such as pH, temperature, dye concentration, and dyeing duration was conducted by evaluating the color strength (K/S) using a one-factor-at-a-time (O.F.T) optimization approach [54,55] (Fig. 4).

3.2.1. Effect of pH and temperature

From the spectral analysis of extracted dye and phytochemical analysis, it is revealed that flavonoids (quercetin and myricetin) and tannin components (epicatechin-derivatives) are the major phytochemicals present in *H. scabrum* whole plant extract and can be categorized as yellow-flavonoid based natural dye. Thus, the polyphenolic nature (anionic) of the extracted dye will show maximum

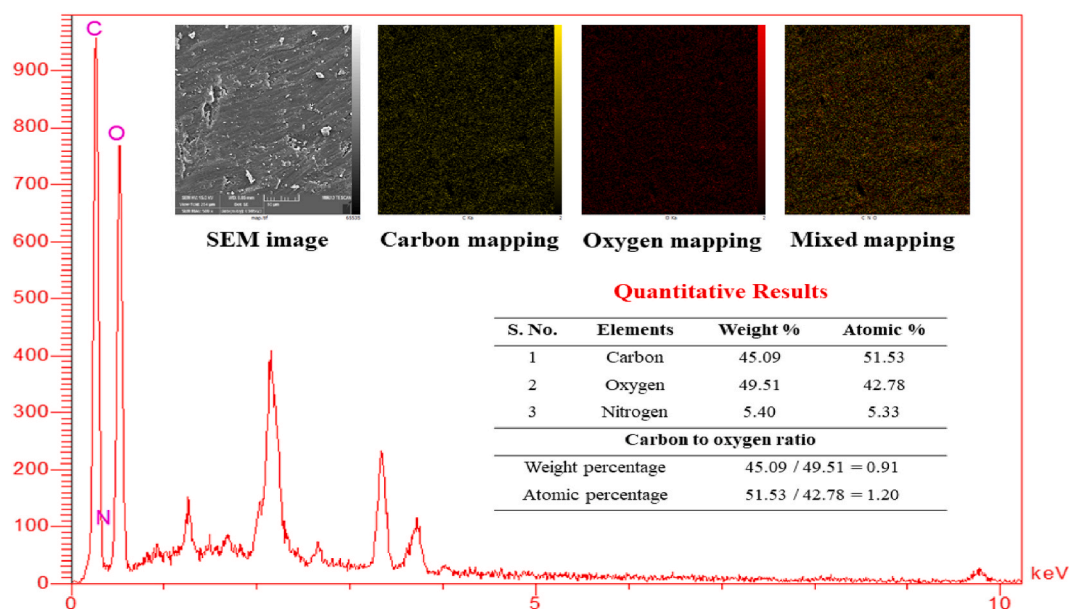


Fig. 3. SEM and EDX mapping of the extracted dye powder.

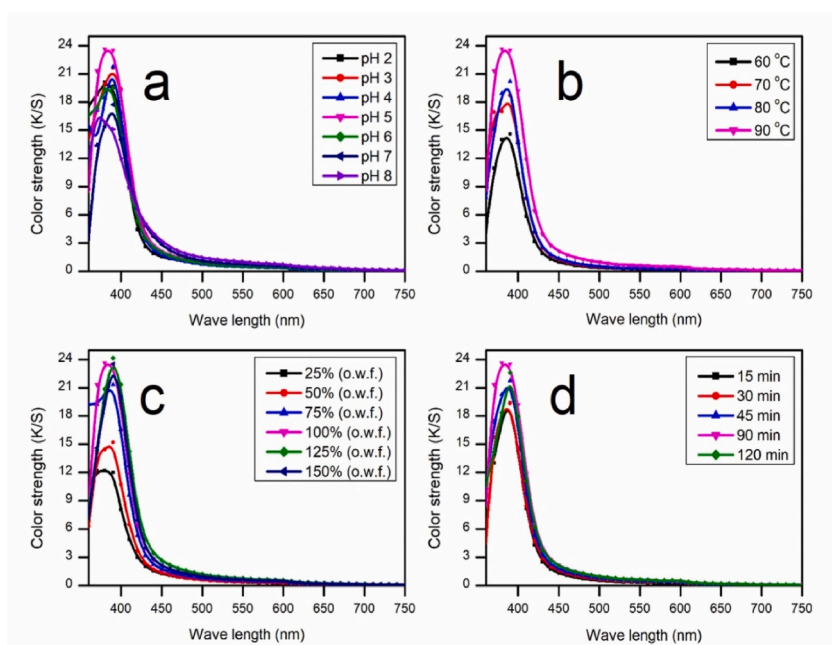


Fig. 4. Optimization of dyeing variables (a) dyeing pH, (b) dyeing temperature ($^{\circ}\text{C}$), (c) dye concentration (o.w.f.), and (d) dyeing time (min).

adsorption under acid conditions which were supported by the experimental results of maximum dye adsorption (highest K/S value) at a pH value of 5. The observations were conducted at different pH values of 2–8 for 75% (o.w.f.) *H. scabrum* whole plant extract adsorption onto the wool yarn surface at 90°C with a liquor ratio of 40:1 (Fig. 4a). The reason for the higher adsorption capacity under acid conditions of pH 5 is the increased electrostatic and ion-dipole attractions between anionic dye molecules (phenoxide ions) and positively charged wool surface ($-\text{NH}_3^+$) [52]. Hydrogen bonding between polyphenolic groups and wool fiber functional groups (amino and carboxyl groups) also contributes to the high adsorption of dye molecules. However, with lower adsorption capacity under alkaline conditions of pH 8, the side chain hydroxide ($-\text{O}^-$) and carboxylate ($-\text{COO}^-$) groups of wool yarn surface show increased repulsive forces with the ionized polyphenolic ($-\text{O}^-$) dye molecules [54]. Also, at higher pH values, the oxidation of polyphenolic dyes might result in the destruction of their conjugate structures which leads to low dye adsorption [56]. Similarly, lower adsorption at pH 3

is due to the high aggregation and low solubility of polyphenolic dyes.

The effect of temperature within the range of 60–90 °C on the *H. scabrum* natural dye adsorption on wool yarn surface is shown in Fig. 4b. Upon increasing temperature from 60 to 70 °C, there was a 20.79% increase in the color depth value. Further, an increase in temperature from 60 to 80 °C, increased color depth by an amount of 27.48%. However, the maximum increase in K/S values (40.14%) was achieved by further increasing the temperature to 90 °C. A rise in temperature results in a corresponding rise in dye adsorption, mostly attributable to an augmented diffusion rate of high molecular weight polyphenolic dyes which require higher temperatures to get disseminated into the interior of wool yarns [57]. Furthermore, it should be noted that a rise in the temperature of the dye bath results in an elevated level of swelling in wool fibers, increasing the size of cavities which aids in the diffusion of dye molecules. Also, an increase in the temperature increases the chemical reactivity of the ionized dyes with the amine groups of the wool, which increases the rates of dye adsorption and subsequent color depth of dyed wool yarns [57].












3.2.2. Effect of initial dye concentration and dyeing time

The affinity between wool skeins and dye molecules may be described by a proportional relationship to the logarithm of the ratio of absolute activities (concentrations) of the dye in solution and on the surface of the wool yarn [52]. The variation in color intensity as the amount of dye in the dye bath increases from 25 to 150% (o.w.f.) with a liquor ratio of 40:1, while maintaining ideal conditions of pH 5 and temperature of 90 °C, is depicted in Fig. 4c. The color strength values were significantly enhanced due to the concentration gradient ranging from 25 to 100% (o.w.f.) [55]. The maximum color depth value was achieved when the dye concentration was at 100% (on weight of fabric basis). Moreover, the augmentation of the dye-bath concentration after 100% (o.w.f.) exhibits minimal impact on the K/S values, suggesting the achievement of equilibrium [58]. The experiment determined that the most favorable duration for dyeing was 90 min, as illustrated in Fig. 4d.

3.3. Color parameters

Table 4 presents the color parameters of the un-mordanted and mordanted wool yarns dyed with 100% (o.w.f.) *H. scabrum* whole plant extract. The use of several metal mordants and their binary combinations has resulted in substantial modifications to the colorimetric properties of dyed wool yarns, specifically in terms of lightness (L^*), chroma (C^*), and hue angle (h°). However, it is worth noting that this effect is not well pronounced while using Al^{3+} and Al^{3+}/Fe^{2+} combination. Application of Al^{3+} and Sn^{2+} have slightly

Table 4
CIEL*a*b* and CIEL*C*h° values of control and mordanted dyed wool yarns.

S. No.	Mordants	Colorimetric data					Sample
		L^*	a^*	b^*	C^*	h°	
1	Control	67.47	3.15	30.84	31.00	84.16	
2	Al	67.33	2.50	31.40	31.50	85.45	
3	Fe	45.15	0.37	21.44	21.44	89.01	
4	Cu	52.80	2.02	34.75	34.80	86.68	
5	Sn	62.82	17.79	64.23	66.65	74.52	
6	Al/Fe	64.64	0.76	33.28	33.29	88.68	
7	Al/Cu	58.92	2.12	33.22	33.29	86.35	
8	Al/Sn	64.12	11.80	63.08	64.18	79.40	
9	Fe/Cu	44.08	0.26	25.25	25.26	89.40	
10	Fe/Sn	59.31	14.58	58.37	60.16	75.98	
11	Cu/Sn	58.30	0.66	42.99	42.99	89.12	

changed the lightness (L^*) values in comparison to un-mordanted dyed wool yarns. Nevertheless, the use of single and mixed mordant combinations other than Al^{3+} and Sn^{2+} resulted in the production of deeper hues characterized by lower brightness (L^*) values. Fe^{2+} mordanting produced darker shades (chocolate brown) while as Sn^{2+} application produced lighter shades (Reddish-yellow) with high color saturation (C^*). The introduction of Sn^{2+} in conjunction with Fe^{2+} has increased the color saturation to 60.16 compared to Fe^{2+} and Sn^{2+} mordanting acting synergistically with each other. In contrast to our previous research endeavors concerning the implementation of *M. laurentii* flavonoid-based natural dye on wool yarns, the present research results in terms of hue angle are diverse and much higher ($74-90^\circ$).

Fig. 5a and b illustrate the color coordinates, namely the a^* and b^* values, of both the control and mordanted wool yarns that underwent dyeing with a 100% (o.w.f.) concentration of *H. scabrum* natural dye. All color coordinates are located inside the yellow-red quadrant of the color space diagram. A notable alteration/shift was seen in a^* and b^* values of the samples mordanted with Sn^{2+} , resulting in a vivid yellow hue. The effect of Sn^{2+} mordanting was also seen in Al/Sn and Fe/Sn combinations, which showed a shift red region of color space diagram compared to singly applied Al and Fe samples.

Fig. 6 illustrates the relationship between color depth and the specific metal salts used for mordanting. The application of Fe^{2+} and Cu^{2+} metal mordants individually yielded the most favorable outcomes, as shown by the greatest K/S values, resulting in a chocolate brown hue (Fig. 6a). Among the binary mix mordant combinations, Al/Sn and Cu/Sn exhibited superior outcomes of higher K/S values (Fig. 6b). Higher K/S values indicate increased dye absorption due to the metal complexation characteristics of the flavonoid components [57]. In comparison to other metal mordants, iron mordant undergoes oxidation from ferrous (Fe^{2+}) to ferric (Fe^{3+}) resulting in darker and dull shades which are further aided by its strong complex forming ability within the interior of the dyed substrate [59, 60]. Moreover, the coexistence of Fe^{2+} and Fe^{3+} ions on the dyed fiber leads to the overlapping of their spectra, resulting in a shift of λ_{max} towards darker hues [61]. The enhanced color depth value of Cu-mordanted wool yarn may be attributed to the development of an insoluble Cu-flavonoid or Cu-tannate complex on the surface of the fiber [62,63].

3.4. Fastness properties

Table 5 presents the wash, rub, and light fastness values of the wool yarns dyed with 100% (o.w.f.) *H. scabrum* natural dye. The samples that were not treated with a mordant exhibited a notable color change, receiving a grade of 3, which indicates a satisfactory outcome. The provided sample also exhibited a light fastness grade of 4, indicating a satisfactory level of resistance to fading when exposed to light. The staining property on the adjacent fabrics was observed in the good region with a rating of 2–3. The use of several metal salts and their binary combinations led to enhanced color change characteristics within the 4–5 range (indicating very high to outstanding quality), along with significant advancements in staining qualities. The reduction in dye molecule leaching with repeated washing procedures is attributed to the coordination interactions among metal ions, wool, and color molecules [57].

Dry rub fastness (4–5) properties were better as compared to wet rub fastness (3–4). Among different mordanted samples iron and copper-treated samples showed better light fastness results which are due to the higher stability of Fe and Cu-chelate complex. The mordanted samples exhibit strong wash and light fastness capabilities, falling within the very good to outstanding range. This may be attributed to the enhanced dye adsorption (K/S), as seen from the visual documentation of dyed samples shown in Table 4. Among different adjacent fabrics, acrylic, polyester, and poly acetate fabrics showed very high staining properties compared to wool and cotton fibers.

3.5. Photoaging of dyed wool yarns (fastness against xenon lamp irradiation)

The dyed wool samples were photo-aged under a Xenon light equipped with a temperature control system. The color strength (K/S)

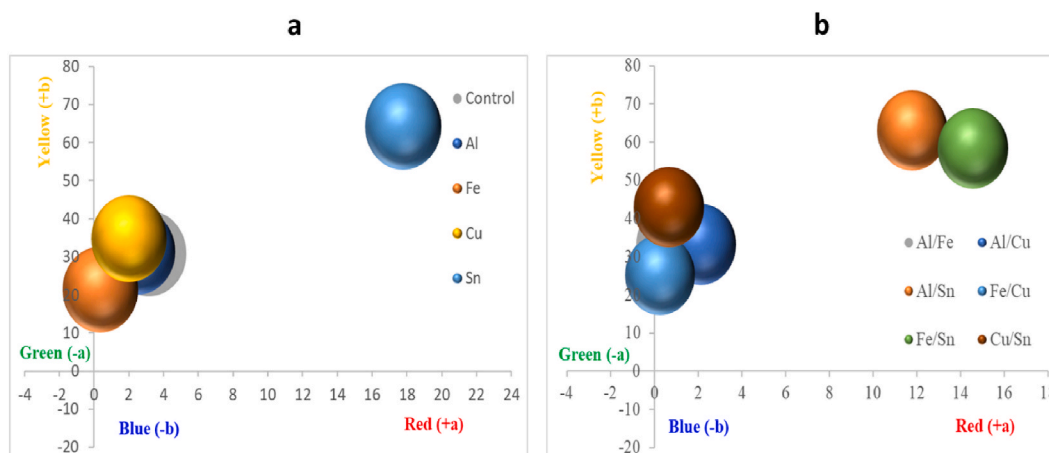


Fig. 5. a^* - b^* plot of dyed wool samples (a) control and singly applied metal mordants, (b) mixed metal mordant combinations.

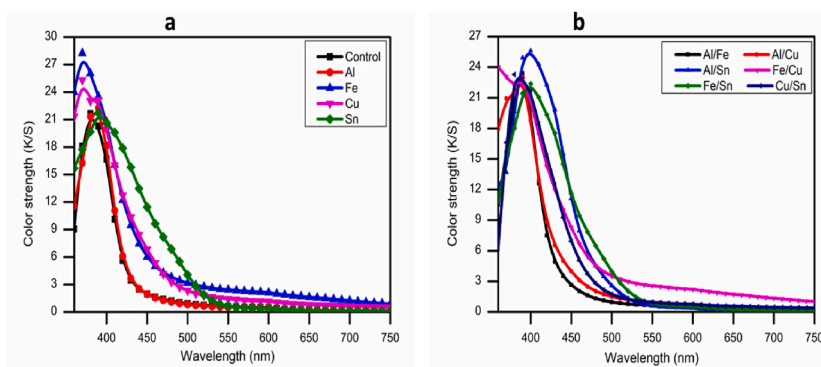


Fig. 6. Color strength (K/S) variations of (a) Singly applied metal mordants, and (b) binary mix metal combinations.

Table 5

Wash, rub, and light fastness properties of dyed wool yarns.

S. No.	Sample	Color change	Color staining properties on different adjacent fabrics						Rub fastness		Light fastness
			s.w.	s.c.	s.ar.	s.pe.	s.pa.	s.ac.	Dry	Wet	
1	Control	3	3	3	5	5	4	5	3	2-3	4
2	Al	3	4	4	5	5	4	5	4-5	4	5
3	Fe	4-5	5	5	5	5	5	5	5	4	6
4	Cu	4-5	5	5	5	5	5	5	5	4	6
5	Sn	4	4-5	4-5	5	5	4	5	4-5	4	4
6	Al/Fe	4-5	4-5	5	5	5	4	5	5	4	5
7	Al/Cu	4-5	4-5	5	5	5	4	5	5	4	5
8	Al/Sn	3	4	4-5	5	5	4	5	4	3	4
9	Fe/Cu	4-5	5	5	5	5	5	5	5	4	6-7
10	Fe/Sn	3	4-5	4-5	5	5	4	5	4	3	4
11	Cu/Sn	3-4	4-5	4-5	5	5	4	5	4	3	5

s.w., s.c., s.ar., s.pe., c.pa., and s.ac. represent the color staining of wool, cotton acrylic, polyester, polyamide, and acetate fabric respectively.

and ΔE values of the irradiated samples (control dyed and mordanted dyed) were measured using a reflectance color-eye XTH spectrometer at their corresponding λ_{\max} values every 12 h up to a total exposure time of 48 h. The effect of continuous Xenon irradiation on the color strength (K/S) and color difference (ΔE) values of dyed wool yarns is shown in Figs. 7 and 8, respectively. With an increase in the Xenon irradiation time from 0 to 48 h, the K/S values steadily decrease in all control, singly metal (Fig. 7a), and binary mix metal mordanted samples (Fig. 7b).

However, it was found that the rate of decrease in the color strength was high in control (un-mordanted) dyed samples compared to the mordanted samples indicating the role of mordants in natural dyeing processes. The quantitative analysis of the color degradation (decrease in K/S values) was assessed using the first-order decay rate law [64]. The rate constant and half-life period of color degradation study confirms that the rate of decrease in the color strength was high in control dyed samples (131.57 s^{-1}) compared to most of the mordanted samples. Mordanting with different metals has increased the half-life period of color degradation and significantly decreased the rate constant of first-order color degradation. The activity sequence of rate constants was found in the order of: Sn (51.81 s^{-1}) < Fe (62.11 s^{-1}) < Al (77.52 s^{-1}) < Cu (108.69 s^{-1}) < Control dyed (131.57 s^{-1}) samples (Table 6). Our results are well established in comparison to the earlier research studies of the photo-stability of quercetin and kaempferol-based-yellow dyes which rapidly degrade upon UV light exposure. The complexation of metal ions with polyphenolics dye chromophores (3-hydroxy-4-keto or 5-hydroxy-4-keto complexation site) increases the UV stability of the metal-polyphenolic dye complex [63,65]. The enhanced photo-stability of the metal complexed-flavonols (metal-dye complex) relative to the flavonols with a free 3-OH group is attributed to a larger triplet state population and/or a higher reactivity with singlet oxygen in metal-dye polyphenolic complexes.

The color difference (ΔE) values of almost all mordanted samples were considerably larger than the control dyed samples. The ΔE of the control dyed sample exceeds 5.9 after an exposure time of 48 h (Fig. 8a). The ΔE values for Al^{3+} and Sn^{2+} mordanted samples are 4.96 and 11.63 higher than that of the control dyed sample at equal times (48 h) of UV radiation exposure. Among the binary mixed mordant combinations, Al/Sn and Fe/Sn showed higher color difference values compared to other metal combinations at equal times of UV light exposures (Fig. 8b). This suggests that after the mordanting process, the photostability of the adsorbed colorants has increased [66].

3.6. Fastness against sodium chloride solution washing

The color change properties with respect to sodium chloride solution will nearly mimic the real conditions of perspiration. The

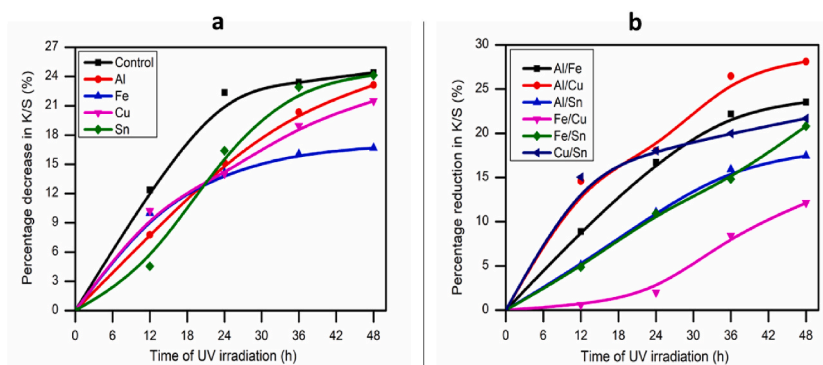


Fig. 7. Photoaging properties of dyed wool samples with respect to the percentage decrease in the color strength (K/S) values (a) control and singly applied metal mordants, (b) mixed metal mordant combinations.

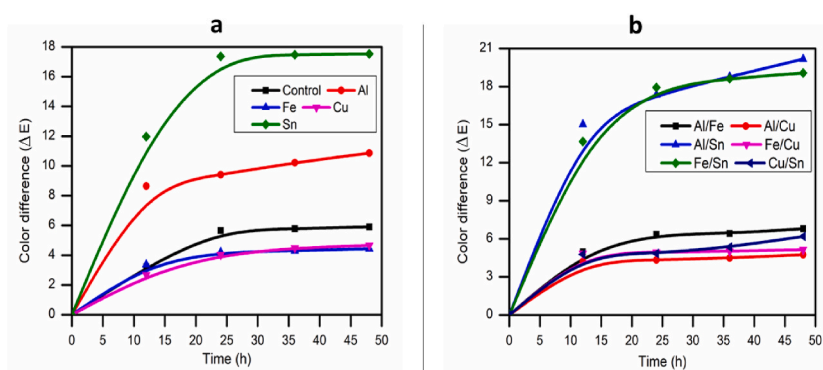


Fig. 8. Photoaging properties of dyed wool samples with respect to the color difference (ΔE) values (a) control and singly applied metal mordants, (b) mixed metal mordant combinations.

Table 6

First-order decay variables of dyed wool samples subjected to artificial UV irradiation for 48 h.

S. No.	Samples	First-order color decay variables			
		Rate constant (K_2)	Half-life (h)	R^2	STDEV
1	Control	131.57	5.26×10^{-3}	0.705	0.139
2	Al	77.52	8.90×10^{-3}	0.865	0.101
3	Fe	62.11	1.61×10^{-2}	0.865	0.211
4	Cu	108.69	6.37×10^{-3}	0.969	0.144
5	Sn	51.81	1.33×10^{-2}	0.781	0.337

human sweat contains an average of 2 g/L NaCl concentration along with calcium, potassium, magnesium, phosphate, and bicarbonate as primary constituents with average pH of 5.3 [67]. So, in this study, we have used 4 g/L NaCl solution at 40 °C at a liquor ratio of 40:1 for different time intervals to check its effect on the color depth (K/S) of wool yarns dyed with 100% (o.w.f) of *H. scabrum* natural dye. Fig. 9 shows the correlation of color depth variation after continuously washing samples in the double distilled, tap water, and 4 g/L NaCl solution for 75 min with a break of 15 min. The rate constant for the decrease in the percentage color strength values according to the first-order rate equation was found to be high in 4 g/L solution (11.57 min^{-1}) followed by tap water (8.48 min^{-1}) and double distilled water (3.99 min^{-1}).

4. Cost analysis

Many researchers working on environmentally friendly textile dyeing try to reduce the cost of natural dye processes which is still a major concern in comparison to the use of synthetic dyes. So, cost analysis is critical to evaluate the cost of the present research which will provide a rough estimate and an opportunity to compare with other textile dyeing procedures. The detailed cost analysis is provided in Table 7.

The control dyeing procedure costs an amount of \$9.56 to dye one kg of wool yarn. However, mordant dyeing costs are a little

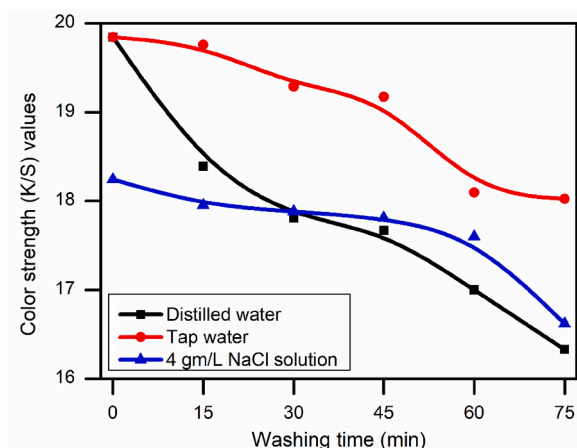


Fig. 9. Variation of color strength (K/S) of un mordanted dyed samples washed in double distilled water, tap water, and 4 g/L NaCl solution.

higher than control dyeing processes. The present cost analysis does not involve the effluent treatment costs of the wastewater produced by this dyeing process. However, we have used eco-friendly metal mordants within ecologically permitted concentration levels. The concentration of stannous chloride was further reduced to 3% (o.w.f.) (0.3%). The comparison was made on the basis of K/S values.

5. Conclusion

Scientific research on the dyeing of textile materials has seen a tremendous rise in the demand for environmentally friendly textile materials keeping in view the environmental and human-health benefits of natural dyes. Although natural dyes have been effectively used in textile dyeing processes but still need to be proven with respect to better fastness qualities and productivity at industrial levels. Thus, the purpose of this work was to investigate the dyeing behavior of *Hypericum scabrum* whole plant extract for wool yarn dyeing in conjunction with some eco-friendly metal mordants. The extracted dye powder showed high content of flavonoid (1.140 mg per CE/g) and polyphenol (2.733 mg per GAE/g) content which was quantitatively characterized by Folin–Ciocalteu method. The best dyeing results of the highest K/S values were achieved at acid conditions of pH 5, temperature of 90 °C, dye concentration of 100% (o.w.f.), and dyeing time of 90 min. Mordanting with different metal salts and their binary combinations has broadened the color palette and significantly improved wash, light, and rub fastness values. Artificial aging experiments with respect to Xenon arc lamps and washing in 4 g/L NaCl solution have negatively affected the color production of dyed wool yarns over different UV exposure and washing times. Color difference (ΔE) values suggest that mordanted samples showed less fading compared to the control dyed samples at equal times of UV exposure. Thus, the use of *H. scabrum* whole plant can provide a clean, economical, and sustainable source of natural dyes that can be used to substitute synthetic analogs as was further confirmed by the cost analysis.

Author contribution statement

Siyamak Safapour: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools, or data; Wrote the paper. Luqman Jameel Rather: Conceived and designed the experiments; Contributed reagents, materials, analysis tools, or data; Analyzed and interpreted the data; Wrote the paper. Reza Safapour: Performed the experiments; Contributed reagents, materials, analysis tools, or data. Shazia Shaheen Mir: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools, or data; Wrote the paper.

Table 7

Cost of *H. scabrum* natural dyeing process of wool yarns.

S. No.	Sample	Produced K/S value	Shade cost per kg of the wool yarns
1	5 g of wool yarn	–	0.01
2	100% (o.w.f.) <i>H. scabrum</i> ^a	21.23	6
3	12.50% (o.w.f.) $Al_2(SO_4)_3 \cdot 18H_2O$	21.71	0.00125
4	12.50% (o.w.f.) $FeSO_4 \cdot 5H_2O$	27.24	0.001
5	12.50% (o.w.f.) $CuSO_4 \cdot 5H_2O$	24.35	0.005
6	7.50% (o.w.f.) $SnCl_2 \cdot 2H_2O$	21.47	0.015
Total cost		6.031 \$ = 254,767 Iranian Rials	

^a The dye costs involve only the labor charges from collection to grinding processes.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the author(s) have not used AI and AI-assisted technologies in the writing process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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