

Cleaner Sustainable Route to Developer UV Protective and Colorful Wool Yarns: Natural Flavonoid-based Colorants from *Millettia Laurentii* Sawdust

S. Safapour^{*1}, M. Shabbir², L. J. Rather^{**3}, M. A. Assiri⁴

¹ Key Laboratory of Advanced Eco-Dyeing and Functional Finishing of Textiles, Faculty of Carpet, Tabriz Islamic Art University, P. O. BOX 51385-4567, Tabriz, Iran

² Department of Applied Sciences and Humanities (Chemistry), GL Bajaj Institute of Technology and Management, Greater Noida, UP, 201306, India

³ College of Sericulture, Textile and Biomass Science, Southwest University, Chongqing, 400715, PR China

⁴ Department of Chemistry, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

ARTICLE INFO

Article history:

Received: 24 Dec 2023

Final Revised: 6 Mar 2024

Accepted: 10 Mar 2024

Available online: 13 Mar 2024

Keywords:

Millettia Laurentii

Textile coloration

Biomordants

Color parameters

UV protection

ABSTRACT

Synthetic dyes have gained much of the textile dyeing market by offering various colors. Synthetic dyes have been a worry for the environment owing to their hazardous nature running in parallel. In recent decades, there has been a movement to substitute natural compounds due to their biocompatibility, biodegradability, and biological advantages. This study investigated using *Millettia Laurentii* sawdust as a natural colorant source. Eco-friendly metal salts (aluminium sulfate, ferrous sulfate, and copper sulfate) under ecologically permitted concentration levels and biomordants (tannic acid, pine bark, oak fruit hull, and eucalyptus leaves) were used to broaden the color range (CIEL*a*b*C*h° and K/S) with significant improvements in the fastness attributes (washing, rubbing, and light) and UV protection properties. Fastness results were found in the commercially acceptable range. All the metal salts provided enhanced color yields with a maximum performance by iron and the corresponding iron-biomordant combinations (iron/pine bark and iron/oak fruit hull). Among the biomordants, pine bark extract provided better performance and higher color depth (9.16) than other biomordants. The findings of this research work showed a significant influence of metal salts and biomordants in combination with *Millettia Laurentii* sawdust (supposed to be a waste) for enhancing the color characteristics and functional attributes of wool yarns. Prog. Color Colorants Coat. 17 (2024), 351-363© Institute for Color Science and Technology.

1. Introduction

Humans have long been intrigued by colors, and coloring garments have been fashionable since ancient times. In the past, people dyed their clothing using natural colors derived from plants and insects [1]. Synthetic dyes superseded natural dyes due to their ability to generate various colors and better fastness properties. Synthetic dyes negatively impact the

environment, although they are used to meet consumer demands [2]. Due to the significance of sustainability, the use of natural dyes and mordants is increasing since they provide environmental stability [3-6]. Natural dyes have been revived due to their biocompatibility, eco-friendly nature, and natural origin. Increased public awareness of the advantages of natural goods for individuals and the environment has also boosted using

*Corresponding author: * s.safapour@tabriziau.ac.ir

** luqmanjameel123@gmail.com

natural dyes to colorate textiles [7, 8]. Sustainable approaches have been implemented using eco-friendly metal salts within permissible thresholds, biomordants, surface modification, and radiation treatments [9-13]. Adding features like antibacterial, antifungal, UV protection, fluorescence, and antioxidant properties improves the effectiveness of natural dyes as alternatives to synthetic dyes, which are associated with environmental and health hazards [14-20]. *Millettia Laurentii* sawdust is being explored as a novel natural dye to improve the sustainability of textile dyeing. It is classified as a yellow natural dye according to its chemical makeup and the hues it produces on wool yarns.

Millettia Laurentii is a tree of about 30 meters with spreading branches, most commonly above 20 meters in height. *Millettia Laurentii* De Wild. (*Millettia Laurentii*) is belonging to the Leguminosae–*Millettia*, which is found in the rain forests of Congo, Cameroon, North Gabon, and Zaire [21]. *Millettia Laurentii* bark treats many diseases, such as diabetes, dermatological problems, fever, hernia, rheumatism, liver disorders, constipation, wound healing, smallpox, epilepsy, and abscesses [22, 23]. This tree is commonly harvested for the timber used in furniture making. Purple-blue flowers make it look beautiful and are sometimes grown in gardens and parks for ornamental purposes. Recent studies suggest that many plant parts besides bark, such as the roots and leaves, also possess qualities that may combat tumors, parasites, viruses, and inflammation [24]. Biological activities are associated with bioactive chemical components from different solvent extracts, including isoflavan-quinone, isoflavones, flavonols, and alkaloids [25, 26]. *M. Laurentii*'s wood entices the carpentry industry with its attractive color and polish, making it desirable for furniture items. This process produces a significant quantity of sawdust as a byproduct. This wood is sturdy in composition and exhibits a deep and lustrous chocolate-brown coloration that is intricately interwoven with black streaks. This obscure and distinctive shade is being used for the color categorization technique. The steaming procedure may achieve consistent wood color in *Millettia Laurentii* and other wood species [27]. *M. Laurentii* wood is cited in the literature as a source of coloring material and has lately been used in textile dyeing, facilitated by using different metal mordants [28, 29].

Natural dyes have a lower affinity towards textile substrates than synthetic dyes, reducing their frequent use. Several methods have been used to deal with this to enhance the fastness properties of natural dyes on synthetic and natural textiles. The use of different metal salts helps to widen the shade palette with enhanced characteristic features (color strength, fastness properties, functional finishing, etc.) [30, 31]. Mordants work as a bridge between textile substrates and dye molecules via several chemical interactions. Metal mordants (in ecological permissible limits) help via coordination complexation between dye molecules and textile substrates. This complexation ability of metal salts determines the washing, rubbing, and light fastness of natural colorants on textiles. In the last two decades, research has shifted its attention towards more sustainable and eco-friendly approaches using tannin-rich mordants of plant extracts. The rich polyphenolic compounds found in different plant extracts, such as barks, galls, and leaves, have been shown to improve color properties similar to metal mordants and provide a variety of environmentally acceptable hues [32-34].

Tannic acid is a polyphenolic compound generally obtained from *Quercus* species and acts as a weak acid. Numerous research studies have provided evidence regarding using tannic acid as a biomordant in textile dyeing that helps enhance dyed textiles' fastness [35-37]. Tannic acid was combined with iron sulfate to enhance the color strength and color fastness values [38]. The pine bark extracts exhibit an absorption peak in the low wavelength area, which is typical of condensed tannins. The Eucalyptus bark contains a significant concentration of tannins, phenols, and flavonoids. Eucalyptus bark extract has a wide band due to the abundance of gallotannins and ellagitannins, which exhibit an additional absorption peak between 350 and 450 nm. Hydrolysable and gallotannins are important for textile dyeing [39, 40]. *Quercus* species (Oak) are deciduous or evergreen trees that are highly regarded throughout history for their medicinal, ecological, and economic significance. Oak trees contain high amounts of polyphenolic components, which can be employed as natural mordants to enhance the color characteristics of dyed yarns [41, 42]. So, in continuation of our earlier research work on the use of *M. Laurentii* sawdust as a source of natural yellow dye [28], the present research employs the use of different metal salts (alum, copper, and iron), biomordants (tannic acid, pine bark, oak fruit hull, and eucalyptus

leaves) and the corresponding metal-biomordant combinations to develop a wide range of shades with high potential to scavenge or block the UV radiations.

2. Experimental

2.1. Wool substrate and chemicals

100 % wool yarn (20/4 Nm), used as pile yarn for handmade carpet production, was employed in the current research. The fine sawdust powder of *Millettia Laurentii* was collected during a Tabriz Islamic Art University workshop. Laboratory grade aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) (CAS: 7784-31-8), copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (CAS: 7758-99-8), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (CAS: 7782-63-0), tannic acid (CAS 72401-53-7), and acetic acid (CAS 64-19-7) were purchased from Merck (Germany). Pine bark, oak fruit hull, and eucalyptus leaves used for biomordanting process were purchased from the local market in Yazd, Iran. Non-ionic detergent (Nikogen SDN) was used to scour wool yarns.

2.2. Mordanting and dyeing process

The mordanting and dyeing were conducted in a temperature-regulated Glycerin bath (TE-182) with a precision control of ± 0.1 °C. Before mordanting, wool yarns were scoured by immersing them in a solution containing 5 g/L of Nikogen SDN (a non-ionic detergent) at 50 °C for 30 minutes with a liquor ratio of 40:1 to remove impurities and enhance surface wettability [43]. 5.0 % (o.w.f.) each of the metal mordants (aluminum sulfate, copper sulfate, and ferrous sulfate) and biomordants (tannic acid, pine bark, oak fruit hull, and eucalyptus leaves) were used to assess their effect on the color characteristics of dyed wool yarns. Briefly, 5 g of scoured wool yarns were drenched in the mordant solutions at room temperature (25 °C). The temperature was raised to 90 °C at a constant rate of 2 °C/min and kept at this temperature for 60 min with constant stirring [44]. The second set of experiments involves using binary combinations of metal salts and biomordants via a two-step mordanting process. i) First, 2.5 % (o.w.f.) each of aluminum sulfate (Al), copper sulfate (Cu), and ferrous sulfate (Fe) were applied to scoured wool yarns at 90 °C for 45 min with constant stirring. ii) The second step involves the addition of 2.5 % (o.w.f.) of each tannic acid (TA), pine bark (PB), oak fruit hull (OH), or eucalyptus leaves (EU) to the cooled (40 °C) mordant solutions and further keeping at

90 °C for another 45 min. After mordanting, the samples were rinsed with tap water using 5 g/L non-ionic detergent to remove weakly adsorbed/unfixed mordants.

The dyeing of wool yarn samples (untreated and treated) was carried out under optimized dyeing conditions at a liquor ratio of 40:1 with 75.0 % (o.w.f.) *Millettia Laurentii* sawdust. The dye bath temperature was raised at a constant rate (2 °C/min) to 90 °C and kept at that temperature for 60 min. The dyeing solution was constantly stirred to achieve uniform dyeing [16, 28]. The dyeing pH of 4 was maintained by using acetic acid. Finally, all the dyed samples were washed with tap water using 5 g/L non-ionic detergent.

2.3. Color measurements

The colorimetric analysis, i.e., CIELab values (L^* , a^* , b^* , C^* , and h°) and color strength (K/S) of dyed wool yarns were measured using a Color-eye XTH spectrophotometer under D65 illuminant and 10° standard observer. For each sample, three individual measurements from different places of the sample were done, and the average resultant values were reported. The K/S values were calculated using the Kubelka-Munk equation as follows (Eq. 1) [45]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the wool samples dyed with 75.0 % (o.w.f.) of *M. Laurentii* sawdust extract. This research reported the average color strength $(K/S)_{\text{AVG}}$ values within the 360-750 nm range. Chroma (C^*) and hue angles (h°) were calculated using the following equations (Eqs. 2 and 3) [46]:

$$\text{Chroma } (C^*) = \sqrt{a^{*2} + b^{*2}} \quad (2)$$

$$\text{Hue angle } (h^\circ) = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (3)$$

2.4. Fastness determination

The lightfastness testing was carried out as per ISO 105 B02:1988 (E) standard using SOLARBOX 1500. The fastness was determined using Digi wash SSTM (Lauderometer) according to ISO 105-C10:2006 (E) specifications. The rubbing fastness (dry and wet) was determined using a Digi crockTM (Crockmeter) as per ISO 105-X12:1993 (E). The wool yarn samples were

closely mounted on a solid panel and given ten strokes for both tests. The stains on an adjacent white fabric were assessed using a grey scale [20].

2.5. UV protection properties of dyed wool

Transmittance values of wool samples were measured using the Analytik Jena SPECORD 250 instrument equipped with a diffuse reflectance accessory with an integrating sphere for SPECORD® PLUS. Then, the ultraviolet protection factor (UPF) was calculated as per Australian and New Zealand standards (AS/NZS 4399: 1996) method in the range 290-400 nm [47]. Three measurements for each sample were done, and the results were averaged and reported.

3. Results and Discussion

3.1. Color characteristics

This study presents a systematic approach to examine the potential of using eco-friendly metal mordants (Al, Cu, and Fe), biomordants (tannic acid, pine bark, oak fruit hull, and eucalyptus leaves), and their corresponding binary combinations (a two-step mordanting process) in conjunction with 75.0 % (o.w.f.) *Millettia Laurentii* sawdust extract to develop a wide range of color palettes (K/S and CIEL*a*b*C*h°) on the wool yarns. A total of 20 distinct shades were created by utilizing different metal, biomordants, and metal-biomordant combinations, which exhibited notable UV protective properties compared to control dyed and undyed wool yarns.

3.1.1. Color coordinates

The color coordinates (L^* , a^* , b^* , C^* , and h°) and images of unmordanted, metal-mordanted, biomordanted, and binary combinations of metal-biomordanted wool yarn samples are given in Tables 1 and 2. It is quite clear that the use of metal salts (copper and ferrous sulfate) provided dominating effects on shade development. In contrast, the biomordants provided similar shades with marginal changes in a^* and b^* values and hue angles (h°) ranging between 61° and 66° . The application of ferrous sulfate provided significant variations in L^* , C^* , and h° values followed by copper sulfate. Low lightness values of 21.29 and 28.73 reflect dark shades with decreased color saturation. The color appearance of

biomordanted samples showed slight variations compared to control dyed wool yarn, which is also apparent from values of colorimetric parameters (a^* and b^*). Dyeing performed on PB mordanted samples resulted in relatively darker shades compared to TA, OH, and EU, which provided lighter shades with high L^* values compared to the control dyeing. The application of metals provided a wide range of hues, with hue angles ranging between 64 - 69° . Figure 1 depicts the effect of different metals and biomordants on the color space diagram. All shades fall in the yellow-red coordinate of the color space diagram. Pretreatment with Cu and Fe showed low a^* and b^* values compared to the control dyed sample, indicating a shift towards the red coordinate. In contrast, Al pretreatment showed a shift away from the yellow coordinate of the color space diagram. The use of biomordants didn't affect the position of coordinates, as was confirmed by slight variations in lightness (L^*) values and hue angle (h°) variations with almost similar color saturation (C^*).

Applying the binary combinations of metal and biomordants provided better results with a wide range of variations in the color coordinates along the yellow and red axis of the color space diagram (Table 2). While comparing binary combination with control dyed wool yarns, a significant increase in lightness (L^*) values was observed for Al/biomordant combinations indicating a cumulative/synergetic effect on the lightening of shades with a shift away from the red coordinate of color space diagram (Figure 2). The effect of Al/biomordant combinations was evident in increasing the color saturation (C^*) of samples compared to the control dyed, metal-treated, and biomordant-treated samples. The pretreatment of Fe and Cu/biomordant combinations provided better-decreased lightness (dark shades) results with significant variations in a^* and b^* values. Fe combinations produced brown to dark grey shades with low a^* and high b^* values, while Cu combinations produced reddish-brown shades with similar a^* and low b^* values compared to control dyed samples. There was a decrease in color saturation in both Fe and Cu combinations with an almost similar range of hues. Overall, using metal-biomordant combinations broadened the shade range compared to single metal and bio-mordants.

Table 1: Colorimetric characteristics ($L^*a^*b^*C^*h^0$) of different metal and biomordant- treated wool yarns dyed with 75.0 % (o.w.f.) *Millettia Laurentii* sawdust natural dye.







S. No.	Sample	Colorimetric properties					Images
		L*	a*	b*	C*	h ⁰	
1	Un-mordanted (UM)	35.13	9.46	17.81	20.17	62.02	
Metal salt mordants							
2	5.0% (o.w.f.) Al	35.29	8.32	20.63	22.25	68.04	
3	5.0% (o.w.f.) Fe	21.29	3.88	8.23	9.09	64.75	
4	5.0% (o.w.f.) Cu	28.73	7.13	17.17	18.59	67.45	
Biomordants							
5	5.0% (o.w.f.) TA	36.69	8.70	17.47	19.51	63.51	
6	5.0% (o.w.f.) PB	34.12	9.15	16.73	19.07	61.32	
7	5.0% (o.w.f.) OH	38.75	8.21	17.73	19.54	65.16	
8	5.0% (o.w.f.) EU	37.21	8.44	17.74	19.65	64.56	

Al: Aluminium sulfate; Fe: Ferrous sulfate; Cu: Copper sulfate TA: Tannic acid; PB: Pine bark; OH: Oak fruit hull; and EU: Eucalyptus leaves

Table 2: Colorimetric characteristics ($L^*a^*b^*C^*h^0$) of different binary combinations of metal salts and biomordants dyed with 75.0 % (o.w.f.) *Millettia Laurentii* sawdust.

S. No.	Sample	Colorimetric properties					Images
		L*	a*	b*	C*	h ⁰	
9	2.5 % Al + 2.5 % TA	46.26	8.92	23.10	24.76	68.88	
10	2.5 % Al + 2.5 % PB	42.80	7.34	26.66	27.65	74.61	
11	2.5 % Al + 2.5 % OH	43.18	7.73	22.29	23.60	70.88	
12	2.5 % Al + 2.5 % EU	44.06	6.73	23.87	24.80	74.25	
13	2.5 % Fe + 2.5 % TA	30.98	2.98	7.74	8.30	68.93	
14	2.5 % Fe + 2.5 % PB	28.92	3.87	12.65	13.23	72.97	

Table 2: Continue.

S. No.	Sample	Colorimetric properties					Images
15	2.5 % Fe + 2.5 % OH	30.79	3.42	10.72	11.26	72.29	
16	2.5 % Fe + 2.5 % EU	31.01	3.76	12.73	13.28	73.54	
17	2.5 % Cu + 2.5 % TA	33.25	7.40	19.72	21.06	69.44	
18	2.5 % Cu + 2.5 % PB	30.76	7.35	17.17	18.67	68.83	
19	2.5 % Cu + 2.5 % OH	30.80	7.95	18.11	19.77	66.30	
20	2.5 % Cu + 2.5 % EU	30.43	7.66	17.60	19.20	66.48	

Al: Aluminium sulfate; Fe: Ferrous sulfate; Cu: Copper sulfate TA: Tannic acid; PB: Pine bark; OH: Oak fruit hull; and EU: Eucalyptus leaves

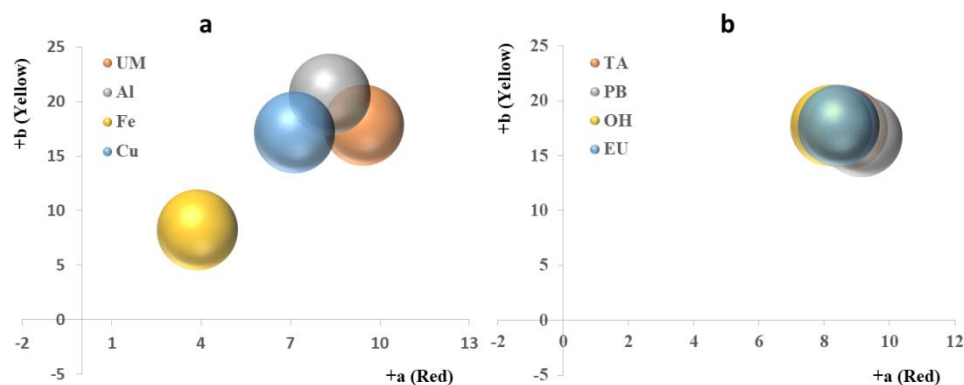


Figure 1: Color coordinates plotted in red-yellow quadrants (a^*-b^*); (a) metal-treated wool yarns, and (b) biomordant-treated wool yarns.

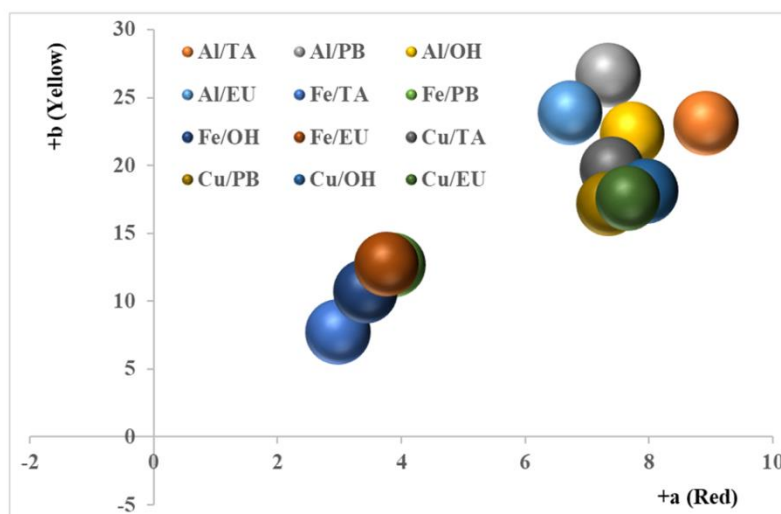


Figure 2: Color coordinates plotted in red-yellow quadrants (a^*-b^*) of binary mixtures of metal and biomordants.

3.1.2. Color strength

The color strength represented as K/S is an important parameter reflecting the shade depth produced during dyeing. The application of metal salts and biomordants on wool yarns dyed with an optimized dye concentration of 75.0 % (o.w.f.) of *Milletia Laurentii* sawdust natural dye at 90 °C under pH 4 for 60 min significantly altered the color depth values and color appearance of dyed yarns. Among the metal salts, the highest impact on color depth was produced by Fe and Cu pretreatment with an average K/S value of 16.21 and 11.82 over the wavelength range of 360-750 nm with 87.39 and 36.64 % increase in color depth, respectively (Figure 3a). However, Al pretreatment didn't significantly alter the color strength pattern with only 4.73 % increase in K/S compared to the control dyed sample. The higher adsorption of color components in the metal-treated samples, especially Fe and Cu, is due to the higher binding affinities of metal-dye components via coordination complexation between metal and dye components [48]. Al is considered a weak metal in coordinate complex formation compared to Fe and does not alter color strength much [49]. It is a general trend of achieving higher color strength values with different metal salts by forming stable coordination complexes with dye components (flavonoids) [35]. The variation of color appearance is also affected by the use of metal salt mordants and depends upon the extent and nature of chemical interactions (Table 1) [28]. On the other hand, slight variations in color depth values were observed with biomordants with the highest K/S value for pine bark extract (Figure 3b). The increased color depth via the use of biomordants and their activity sequence (PB > TA > EU > OH) is in direct correlation with the tannin content present in the mordant extracts [37].

However, the use of metal salts and biomordants in combination produced synergetic effects of increasing the color depth values of the dyed wool yarns with the

highest average K/S value of 11.02 and 10.10 for Cu/EU and Fe/PB mordanted samples (Figure 4). This reflects an average percentage increase of 27.39 and 16.76 % K/S values compared to control dyed wool yarns. However, the percentage increase in the color strength values of Cu/EU and Fe/PB compared to EU and PB are 33.25 and 40.08 %, respectively, which reflects the synergetic role and successful utilization of using metal salts in combinations with biomordants. The present study's findings enhanced shade range with metal-biomordant combinations much better than our earlier research on using other commercially available biomordants with different natural dyes [50-53].

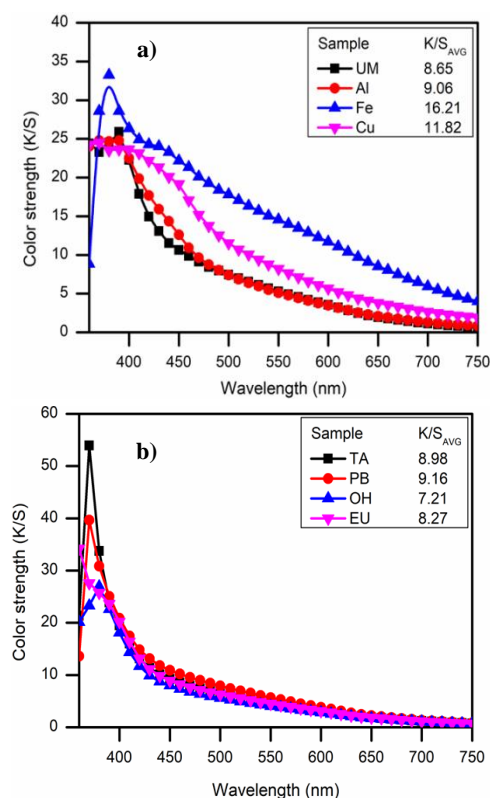


Figure 3: Color strength (K/S) variations of (a) metal salts-treated wool yarns, and (b) biomordants-treated wool yarns.

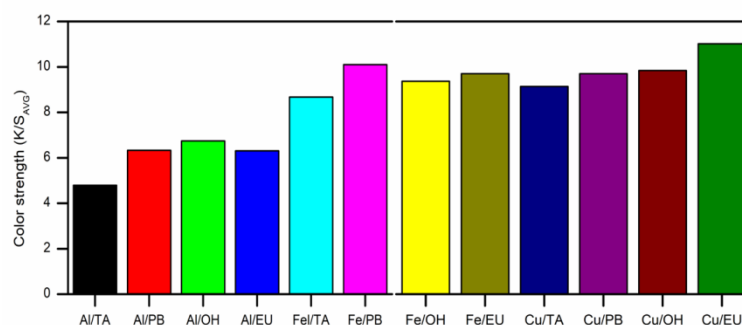


Figure 4: Color strength (K/S) variations of (a) metal salts-treated wool yarns, and (b) biomordants-treated wool yarns.

3.2. Color fastness properties

The colorfastness of all dyed samples against washing and rubbing was evaluated and rated on grayscale, whereas the fastness to light was rated on a blue scale (Table 3). For washing fastness, the color change (c.c.), color stain on wool (c.w.), and color stain on cotton (c.s.) were evaluated and compared with that of the control dyed sample. Resistance to rubbing was evaluated in dry and wet conditions to check the practical compatibility of dyed wool in conditions of dryness and perspiration. The fastness ratings of control dyed wool yarns were found in the region fair to the very good with ratings of 2-4. However, applying mordants (metal and biomordants) significantly improved the fastness ratings,

especially color staining properties on adjacent wool and cotton fabrics. The enhanced fastness of metal mordants might be due to the sandwiching of textile substrate-metal ion-dye molecules via coordination complexation. Results with Al, Fe, and Cu metal salts mordanting were highly improved. Strong coordination bonding helps prevent photolytic degradation by protecting chromophores, and energy dissipates through the chelate structure formed with metal ions. Using biomordants also improved fastness results to significant levels (very good to the excellent range of rating, 4-5) by working either of the two ways; act as a dye via mixed dyeing procedure and as a sandwiching molecule between wool surface and dye molecules.

Table 3: Colorfastness properties of wool yarns (unmordanted and mordanted) dyed with 75.0 % (o.w.f.) *Milletia Laurentii* sawdust natural dye.

S. No.	Sample	Wash fastness			Rub fastness		Lightfastness
		c.c.	c.w.	c.s.	Dry	Wet	
1	Un-mordanted	4	2-3	3-4	3-4	3	3
Metal mordanted samples							
2	5.0 % (o.w.f.) Al	4	4	4-5	4-5	4	6
3	5.0 % (o.w.f.) Fe	4-5	5	4-5	5	4	6
4	5.0 % (o.w.f.) Cu	4-5	4-5	4-5	5	4-5	6
Bio-mordanted samples							
5	5.0 % (o.w.f.) TA	4	4-5	4-5	5	4	6
6	5.0 % (o.w.f.) PB	4	4	4-5	4-5	4	6
7	5.0 % (o.w.f.) OH	4	4-5	4-5	5	4	5
8	5.0 % (o.w.f.) EU	4	4	4-5	4-5	4	5-6
Metal-Biomordant binary combinations							
9	2.5 % Al + 2.5 % TA	4	4-5	5	5	4	6
10	2.5 % Al + 2.5 % PB	4	4-5	4-5	4-5	4	6
11	2.5 % Al + 2.5 % OH	4	5	5	5	4	6
12	2.5 % Al + 2.5 % EU	4	4-5	4-5	4-5	4	6
13	2.5 % Fe + 2.5 % TA	5	5	5	5	4-5	7-8
14	2.5 % Fe + 2.5 % PB	4-5	5	4-5	5	4	6-7
15	2.5 % Fe + 2.5 % OH	4-5	5	4-5	5	4	7
16	2.5 % Fe + 2.5 % EU	4-5	5	5	5	4	6
17	2.5 % Cu + 2.5 % TA	5	5	5	5	4-5	6
18	2.5 % Cu + 2.5 % PB	4-5	5	5	5	4-5	6
19	2.5 % Cu + 2.5 % OH	5	5	5	5	4-5	6
20	2.5 % Cu + 2.5 % EU	4-5	5	5	5	4-5	6

c.c. = color change; c.w. = color staining of wool; c.s. = color staining of cotton. Wt. % of mordant and dye raw material is taken for 5.0 g of wool fabric

The metal-biomordant combinations provided better results with improved color staining properties, with most samples having excellent ratings of 5. The color change properties of Fe and Cu combinations were better than the Al combination due to the better complexation properties of Fe and Cu. The lightfastness properties of Fe/TA, Fe/PB, and Fe/OH were found to be in the very good to excellent range of 7-8 and is due to the higher stability of Fe-flavonoid chelate complex via 3- and 5-hydroxyl groups, introducing rigidity in molecules which increases the stability to ultraviolet radiations [49].

3.3. UV protection properties

Plants use sunlight for photosynthesis, whereas mammals rely on it for physiological functions. A small fraction of these radiations consist of harmful UV radiations with wavelengths ranging from 150 nm to 400 nm [47, 54]. Normally, UV radiation is absorbed by the ozone layer in the stratosphere, and only a small amount reaches the Earth's surface. Exposure to UV rays may result in many skin problems, including skin cancer in extreme cases. Several natural and artificial methods are available to avoid the consequences of UV radiation. Melanin in the skin provides natural protection against damage from UV light [55]. Sunscreens and UV protection wear are artificial methods to shield against UV rays [56]. Textile features such as weaving, dyeing, and surface treatments are crucial for imparting UV protection properties [57]. Natural colorants derived from various plants, animals, and microbiological sources might be a practical option for imparting UV protection and beautiful, eco-friendly shades. They can

block UV radiation by absorbing high-energy radiation. Researchers provide detailed insights into how natural plant extracts scavenge UV energy [47, 58]. The use of different metal salts, biomordants, and their corresponding binary combinations in conjunction with *M. Laurentti* sawdust natural dye have been used in this research for enhancing the UV protection properties of wool yarns and is represented as ultraviolet protection factor (UPF) (Figure 5) [59-61].

The UV protection provided by natural wool yarns used in this study was low, with a value of 15.92. The application of 75.0 % (o.w.f.) *M. Laurentti* sawdust natural dye improved its UV scavenging performance with a UPF value of 22.04 by 38.44 % compared to undyed (UN) wool yarns. The use of three metal salts, namely Al, Fe, and Cu, which acted as mordants for enhancing the color characteristics and the shade depth, proved very beneficial in improving the UV protection levels by a significant amount of 31.12, 162.56, and 126.67 %, respectively. This significant increase in the percentage UPF values is attributed to the higher dye adsorption and retention via the formation of stable metal-dye complexes. Metal salts play a significant role in UV protection by forming coordination complexes and dissipating energy via their extended chemical structure [62]. Alternatively, using biomordants also provided very good protection levels with maximum protection offered by PB and EU (Figure 5a). This is due to more polyphenolic hydroxyl groups than control dyed wool yarns. Enhancement of UPF values of the wool yarns via biomordants suits the conclusion that the more dye components on the wool surface, the higher the UV protection owing to the more energy dissipation on the surface through the adsorbed molecules.

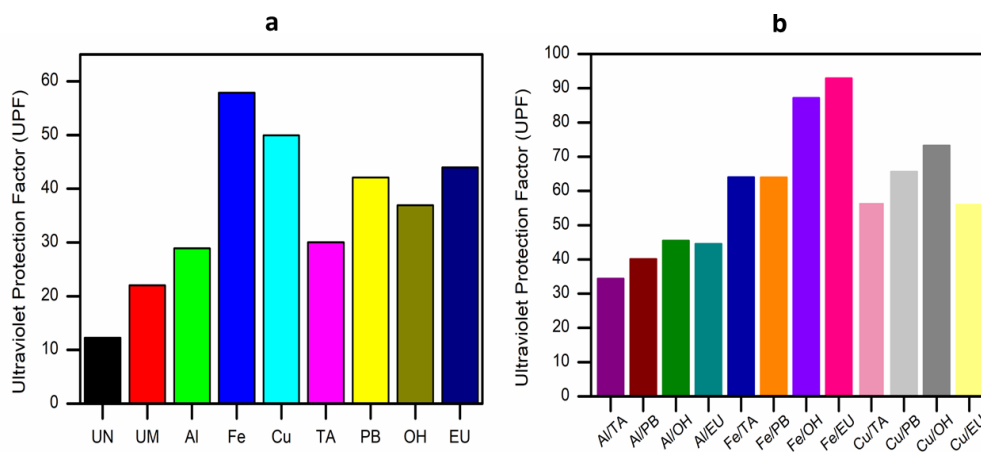


Figure 5: UV protection capacity of undyed (UN), control dyed (UM), and mordanted wool yarns in terms of UPF (UV protection factor) values.

In the case of binary metal-biomordant combinations, iron mordant combinations showed the incremental effect on UPF values followed by copper mordant combinations (Figure 5b). The maximum protection among all mordanted samples was offered by Fe/OH and Fe/EU combinations with a percentage increase of 295.55 and 321.55 %, respectively compared to the control dyeing. The role of dye flavonoid components from *Millettia Laurentii* sawdust natural dye in increasing the protection levels by blocking/scavenging the UV radiations from the surface of wool yarns was evident with a substantial increase in UPF values compared to the undyed samples [47].

4. Conclusion

The sawdust waste generated by *Millettia Laurentii* carpentry was used in this study for wool coloration and simultaneous UV protective functionalization. Different metal salts, biomordants, and their corresponding binary combinations were used to enhance the binding affinities of dye compounds to the textile substrate. The effect of metal salts and biomordants was assessed on color parameters (L^* , a^* , b^* , C^* , h° , and K/S), and UV protective functionalization. Among the metal salts, Fe provided the best results of higher color depth (16.21)

with a wide range of shade performances (hues). The fastness properties were significantly improved using metal and biomordants with much better performance by binary mordant combinations. Ferrous sulfate in combination with TA, PB, and OH, provided shades with excellent lightfastness with a rating between 7 and 8. The UV protection levels were significantly improved by using binary combinations of metals and biomordants with maximum protection offered by Fe/OH and Fe/EU followed by Cu/OH and Cu/PB. The findings of this research work showed a significant influence of metal salts and biomordants in combination with *Millettia Laurentii* sawdust (supposed to be a waste) for enhancing the color characteristics and functional attributes of wool yarns. With the aid of this research study, the textile industry will be able to reduce its reliance on synthetic dyes and heavy metal mordants, which will assist in increasing the utilization of waste raw materials (*Millettia Laurentii* carpentry sawdust) as a source of natural dye.

Acknowledgments

Tabriz Islamic Art University is gratefully acknowledged for supporting this research study.

5. References

- Atav R, Ergünay U. Screening of vegetal dyes for wool dyeing: selection of feasible alternatives for industrial applications. *Fibers Polym.* 2024; 25(1): 193-209. <https://doi.org/10.1007/s12221-023-00415-1>
- Kasiri MB, Safapour S. Exploring and exploiting plants extracts as the natural dyes/antimicrobials in textiles processing. *Prog Color Colorants Coat.* 2015;8(2):87-114. <https://doi.org/10.30509/pccc.2015.75856>.
- Ardila-Leal LD, Poutou-Piñales RA, Pedroza-Rodríguez AM, Quevedo-Hidalgo BE. A brief history of colour, the environmental impact of synthetic dyes and removal by using laccases. *Molecules.* 2021; 26(13):3813. <https://doi.org/10.3390/molecules26133813>.
- Khattab TA, Abdelrahman MS, Rehan M. Textile dyeing industry: environmental impacts and remediation. *Environ Sci Pollut Res.* 2020;27:3803-18. <https://doi.org/10.1007/s11356-019-07137-z>.
- Safapour S, Mazhar M, Moradnejad J, Liaghat F. A facile route to extend the color gamut of cochineal, *Dactylopius coccus costa*, natural dye on wool textiles. *J Text Inst.* 2023;1-12. In press. <https://doi.org/10.1080/00405000.2023.2283247>.
- Shahmoradi Ghaheh F, Haji A, Daneshvar E. Sustainable Dyeing Process for Nylon 6 Fabrics by Rhubarb Flower Using Different Bio-Mordants. *Sustainability.* 2023;15(12):9232. <https://doi.org/10.3390/su15129232>.
- Hosseinezhad M, Safapour S. Sources, chemistry, classification, challenges, and prospects of renewable Dyes Pigm. *Renewable Dyes Pigm.* 2024: 1-18. <https://doi.org/10.1016/B978-0-443-15213-9.00001-6>.
- Kasiri MB, Safapour S. Natural dyes and antimicrobials for green treatment of textiles. *Environ Chem Lett.* 2014;12(1):1-13. <https://doi.org/10.1007/s10311-013-0426-2>.
- Haji A, Naebe M. Cleaner dyeing of textiles using plasma treatment and natural dyes: A review. *J Cleaner Prod.* 2020;265:121866. <https://doi.org/10.1016/j.jclepro.2020.121866>.
- Rather LJ, Ali A, Zhou Q, Ganie SA, Gong K, Haque QMR, et al. Instrumental characterization of merino wool fibers dyed with *Cinnamomum camphora* waste/fallen leaves extract: An efficient waste management alternative. *J Cleaner Prod.* 2020;

- 273:123021. <https://doi.org/10.1016/j.jclepro.2020.123021>.
11. Sadeghi-Kiakhani M, Safapour S, Golpazir Y. Impact of chitosan-poly (amidoamine) dendreimer hybrid treatment on dyeing and color fastness properties of wool yarn with madder natural dye. *Prog Color Colorants Coat.* 2019; 12(4):241-50. <https://doi.org/10.30509/pccc.2019.81595>.
 12. Safapour S, Rather LJ, Safapour R, Mir SS. Valorization of bio-colorants extracted from *Hypericum scabrum* L. plant for sustainable and ecological coloration of wool yarns. *Heliyon.* 2023. <https://doi.org/10.1016/j.heliyon.2023.e19439>.
 13. Zhou Q, Rather LJ, Mir SS, Ali A, Haque QMR, Li Q. Bio colourants from the waste leaves of *Ginkgo biloba* L. tree: Wool dyeing and antimicrobial functionalization against some antibiotic-resistant bacterial strains. *Sustainable Chem Pharm.* 2022;25:100585. <https://doi.org/10.1016/j.scp.2021.100585>.
 14. Baseri S. Agricultural crop of *Scrophularia striata* as a new dye for eco-friendly dyeing and bioactive finishing of handwoven piles. *Sustainable Chem Pharm.* 2023;33:101088. <https://doi.org/10.1016/j.scp.2023.101088>.
 15. Hosseinneshad M, Gharanjig K, Adeel S, Mahmoudi Nahavandi A. Clean dyeing of wool yarns using oleaster fruit components as new bio-mordant: a step toward reducing agricultural waste. *Clean Technol Environ Policy.* 2023;25(10):3149-60. <https://doi.org/10.1007/s10098-023-02563-7>.
 16. Rather LJ, Akhter S, Padder RA, Hassan QP, Hussain M, Khan MA, et al. Colorful and semi durable antioxidant finish of woolen yarn with tannin rich extract of *Acacia nilotica* natural dye. *Dyes Pigm.* 2017;139:812-9. <https://doi.org/10.1016/j.dyepig.2017.01.018>.
 17. Rather LJ, Azam M, Shabbir M, Bukhari MN, Shahid M, Khan MA, et al. Antimicrobial and fluorescence finishing of woolen yarn with *Terminalia arjuna* natural dye as an ecofriendly substitute to synthetic antibacterial agents. *RSC Adv.* 2016;6(45):39080-94. <https://doi.org/10.1039/C6RA02717B>.
 18. Safapour S, Liaghat F. A review on multifunctional coating of textiles via silver nanoparticles synthesized with plant sources. *J Studies Color World.* 2022; 12(2):133-58. DOR:20.1001.1.22517278.1401.12. 2. 3.0.
 19. Safapour S, Rather LJ, Mazhar M. Coloration and functional finishing of wool via *Prangos ferulacea* plant colorants and bioactive agents: colorimetric, fastness, antibacterial, and antioxidant studies. *Fibers Polym.* 2023; 24(4):1379-88. <https://doi.org/10.1007/s12221-023-00156-1>.
 20. Safapour S, Rather LJ, Moradnejad J, Mir SS. Functional and colorful wool textiles through ecological dyeing with lemon balm bio-dyes and mordants. *Fibers Polym.* 2023;24(12):4357-70. <https://doi.org/10.1007/s12221-023-00397-0>.
 21. Kamnaing P, Free SYF, Fomum ZT, Martin M-T. Millettoneine, a guanidine alkaloid from *Millettia Laurentii*. *Phytochem.* 1994; 36(6):1561-2. [https://doi.org/10.1016/S0031-9422\(00\)89766-6](https://doi.org/10.1016/S0031-9422(00)89766-6).
 22. Ma F, Huang A-m. Rapid identification and quantification three chicken-wing woods of *Millettia leucantha*, *Millettia Laurentii* and *Cassia siamea* by FT-IR and 2DCOS-IR. *J Mol Struct.* 2018; 1166:164-8. <https://doi.org/10.1016/j.molstruc.2018.04.037>.
 23. Ngamga D, Free SF, Fomum Z, Chiaroni A, Riche C, Martin M, et al. Millaurine and acetylmillaurine: Alkaloids from *Millettia Laurentii*. *J Nat Prod.* 1993; 56(12):2126-32. <https://doi.org/10.1021/np50102a015>.
 24. Banzouzi J, Prost A, Rajemiarimiraho M, Ongoka P. Traditional uses of the African *Millettia* species (Fabaceae). *Int J Bot.* 2008; 4(4):406-420. <https://doi.org/10.3923/ijb.2008.406.420>.
 25. Jena R, Rath D, Rout SS, Kar DM. A review on genus *Millettia*: Traditional uses, phytochemicals and pharmacological activities. *Saudi Pharm J.* 2020; 28(12):1686-703. <https://doi.org/10.1016/j.jsps.2020.10.015>.
 26. Kamnaing P, Free SNF, Nkengfack AE, Folefoc G, Fomum ZT. An isoflavan-quinone and a flavonol from *Millettia Laurentii*. *Phytochem.* 1999;51(6):829-32. [https://doi.org/10.1016/S0031-9422\(99\)00043-6](https://doi.org/10.1016/S0031-9422(99)00043-6).
 27. Bechtold T, Mussak R. *Handbook of Natural Colorants*: John Wiley & Sons; 2009. <https://doi.org/10.1002/9780470744970>.
 28. Safapour S, Rather LJ, Mir SS, Dar QF. Upscaling *Millettia Laurentii* carpentry sawdust into natural dyes: imparting antimicrobial, antioxidant, and UV-protective finish to wool yarns through an ecological and sustainable natural dyeing process. *Biomass Convers Biorefin.* 2023: 1-13. In press. <https://doi.org/10.1007/s13399-023-04184-y>.
 29. Weigl M, Kandelbauer A, Hansmann C, Pöckl J, Müller U, Grabner M. Application of natural dyes in the coloration of wood. *Handbook of Natural Colorants* Wiley, New York. 2009: 277-313. <https://doi.org/10.1002/9780470744970.ch17>.
 30. Shabbir M, Rather LJ, Bukhari MN, Ul-Islam S, Shahid M, Khan MA, et al. Light fastness and shade variability of tannin colorant dyed wool with the effect of mordanting methods. *J Nat Fibers.* 2019; 16(1):100-113. <https://doi.org/10.1080/15440478.2017.1408521>.
 31. Hassan MM, Saifullah K. Sustainable dyeing and functionalization of jute fabric with a Chinese sumac gall-derived gallotannin using eco-friendly mordanting agents. *Cellulose.* 2021; 28(8):5055-70. <https://doi.org/10.1007/s10570-021-03805-x>.
 32. Guesmi A, Ladhari N, Hamadi NB, Msaddek M, Sakli F. First application of chlorophyll-a as biomordant: sonicator dyeing of wool with betanin dye. *J Cleaner Prod.* 2013;39:97-104. <https://doi.org/10.1016/j.jclepro.2012.08.029>.
 33. İsmal ÖE. Greener natural dyeing pathway using a by-product of olive oil; prina and biomordants. *Fibers Polym.* 2017;18:773-85. <https://doi.org/10.1007/>

- s12221-017-6675-0.
34. Shabbir M, Mohammad F. Sustainable coloration and bioactive functionalization of wool fabric via plant-based naphthoquinone compounds. *Fibers Polym.* 2023; 24(1):179-86. <https://doi.org/10.1007/s12221-023-00131-w>.
 35. Shahmoradi Ghaheh F, Moghaddam MK, Tehrani M. Comparison of the effect of metal mordants and biomordants on the colorimetric and antibacterial properties of natural dyes on cotton fabric. *Color Technol.* 2021;137(6):689-98. <https://doi.org/10.1111/cote.12569>.
 36. Lohtander T, Arola S, Laaksonen P. Biomordanting willow bark dye on cellulosic materials. *Color Technol.* 2020;136(1):3-14. <https://doi.org/10.1111/cote.12442>.
 37. Ke G, Mulla MS, Peng F, Chen S. Dyeing properties of natural Gardenia on the lyocell fabric pretreated with tannic acid. *Cellulose.* 2023; 30(1):611-24. <https://doi.org/10.1007/s10570-022-04896-w>.
 38. Burkinshaw S, Kumar N. The mordant dyeing of wool using tannic acid and FeSO₄, Part 1: Initial findings. *Dyes Pigm.* 2009;80(1):53-60. <https://doi.org/10.1016/j.dyepig.2008.05.008>.
 39. Kim YS, Bae SE. Dyeabilities with various fabrics and chemical composition of brown colorants from pine bark. *Fashion Text Res J.* 2013; 15(1):138-46. <http://dx.doi.org/10.5805/SFTI.2013.15.1.138>
 40. Santos J, Monteiro S, Oliveira S, Magalhães P, Magalhães FD, Martins JM, et al. Application of forest by-products in the textile industry: dyeing with pine and eucalyptus bark extracts. *Environ Sci Proc.* 2022;22(1):30. <https://doi.org/10.3390/IECF2022-13053>.
 41. Şöhretoğlu D, Renda G. The polyphenolic profile of Oak (*Quercus*) species: A phytochemical and pharmacological overview. *Phytochem Rev.* 2020; 19(6):1379-426. <https://doi.org/10.1007/s11101-020-09707-3>.
 42. Hosseinnezhad M, Gharanjig K, Jafari R, Imani H, Razani N. Cleaner colorant extraction and environmentally wool dyeing using oak as eco-friendly mordant. *Environ Sci Pollut Res.* 2021;28:7249-60. <https://doi.org/10.1007/s11356-020-11041-2>.
 43. Matlhoko KS, Vermaas JF, Cronjé N, van der Merwe S. Assessing the effectiveness of traditional wool scouring for small-scale farmers in South Africa: a study on detergents and scouring time. *Res J Text Apparel.* 2023. In press. <https://doi.org/10.1108/RJTA-02-2023-0017>.
 44. Safapour S, Mazhar M, Abedinpour S. Broadening color shade range of rubia tinctorum L. natural colorants on wool fibers via combination of metal mordants: color characteristics and fastness studies. *J Nat Fibers.* 2023; 20(1):2157923. <https://doi.org/10.1080/15440478.2022.2157923>.
 45. Safapour S, Mazhar M, Abedinpour S. Color shade extension of Reseda luteola L. natural colorant on wool textiles via binary combination of metal salts: colorimetric and fastness studies. *Fibers Polym.* 2023;24(9):3221-33. <https://doi.org/10.1007/s12221-023-00296-4>.
 46. Safapour S, Rather LJ. Effect of single and binary mixed metal mordant combinations on colorimetric and fastness characteristics of wool yarns dyed with *Melissa officinalis* L. natural colorants. *J Text Inst.* 2024; 115(1):97-105. <https://doi.org/10.1080/00405000.2022.2157941>.
 47. Rather LJ, Shabbir M, Li Q, Mohammad F. Coloration, UV protective, and antioxidant finishing of wool fabric via natural dye extracts: cleaner production of bioactive textiles. *Environ Prog Sustainable Energy.* 2019;38(5):13187. <https://doi.org/10.1002/ep.13187>.
 48. Safapour S, Rather LJ. Assessment of colorimetric and fastness properties of prangos ferulacea (jashir) dyed wool yarns in conjunction with mixed metal mordant combinations via reflectance spectroscopy. *J Nat Fibers.* 2023;20(1):2134267. <https://doi.org/10.1080/15440478.2022.2134267>.
 49. Rather LJ, Mohammad F. Study on the application of *Acacia nilotica* natural dye to wool using fluorescence and FT-IR spectroscopy. *Fibers Polym.* 2015;16(7):1497-505. <https://doi.org/10.1007/s12221-015-4879-8>.
 50. Rather LJ, Shahid-ul-Islam, Shabbir M, Bukhari MN, Mohammad F, Khan MA. *Adhatoda vasica* in conjunction with binary combinations of metal salts and biomordants as an effective textile dye to produce novel shades on wool. *J Nat Fibers.* 2018;15(4):611-23. <https://doi.org/10.1080/15440478.2017.1349712>
 51. Safapour S, Sadeghi-Kiakhani M, Doustmohammadi S. Chitosan-cyanuric chloride hybrid as an efficient novel bio-mordant for improvement of cochineal natural dye absorption on wool yarns. *J Text Inst.* 2019;110(1):81-88. <https://doi.org/10.1080/00405000.2018.1503384>.
 52. Shabbir M, Rather LJ, Bukhari MN, Shahid-ul-Islam, Khan MA, Mohammad F. First-time application of biomordants in conjunction with the *Alkanna tinctoria* root extract for eco-friendly wool dyeing. *J Nat Fibers.* 2019;16(6):846-54. <https://doi.org/10.1080/15440478.2018.1441085>.
 53. Shahid-ul-Islam, Rather LJ, Shabbir M, Sheikh J, Bukhari MN, Khan MA, et al. Exploiting the potential of polyphenolic biomordants in environmentally friendly coloration of wool with natural dye from *Butea monosperma* flower extract. *J Nat Fibers.* 2019;16(4):512-23. <https://doi.org/10.1080/15440478.2018.1426080>.
 54. Hatch KL, Osterwalder U. Garments as solar ultraviolet radiation screening materials. *Dermatologic clinics.* 2006;24(1):85-100. <https://doi.org/10.1016/j.det.2005.09.005>.
 55. Brenner M, Hearing VJ. The protective role of melanin against UV damage in human skin. *Photochem Photobiol.* 2008;84(3):539-49. <https://doi.org/10.1111/j.1751-1097.2007.00226.x>.

56. Chavda VP, Acharya D, Hala V, Vora LK, Dawre S. Sunscreens: A comprehensive review with the application of nanotechnology. *J Drug Delivery Sci Technol.* 2023; 104720. <https://doi.org/10.1016/j.jddst.2023.104720>.
57. Grifoni D, Bacci L, Zipoli G, Albanese L, Sabatini F. The role of natural dyes in the UV protection of fabrics made of vegetable fibres. *Dyes Pigm.* 2011; 91(3):279-85. <https://doi.org/10.1016/j.dyepig.2011.04.006>.
58. Feng X, Zhang L, Chen J, Zhang J. New insights into solar UV-protective properties of natural dye. *J Cleaner Prod.* 2007; 15(4):366-72. <https://doi.org/10.1016/j.jclepro.2005.11.003>.
59. Shabbir M, Rather LJ, Mohammad F. Economically viable UV-protective and antioxidant finishing of wool fabric dyed with *Tagetes erecta* flower extract: Valorization of marigold. *Ind Crops Prod.* 2018; 119:277-82. <https://doi.org/10.1016/j.indcrop.2018.04.016>.
60. Zhou Y, Zhang J, Tang R-C, Zhang J. Simultaneous dyeing and functionalization of silk with three natural yellow dyes. *Ind Crops Prod.* 2015; 64:224-32. <https://doi.org/10.1016/j.indcrop.2014.09.041>.
61. Zhou Y, Tang R-C. Modification of curcumin with a reactive UV absorber and its dyeing and functional properties for silk. *Dyes Pigm.* 2016; 134:203-11. <https://doi.org/10.1016/j.dyepig.2016.07.016>.
62. Gulzar T, Farooq T, Kiran S, Ahmad I, Hameed A. *The Impact and Prospects of Green Chemistry for Textile Technology.* Elsevier; 2019. <https://doi.org/10.1016/C2017-0-01957-2>.

How to cite this article:

Safapour S, Shabbir M, Rather LJ, Assiri MA. Cleaner Sustainable Route to Develop UV Protective and Colorful Wool Yarns: Natural Flavonoid-based Colorants from *Millettia Laurentii* Sawdust. *Prog Color Colorants Coat.* 2024;17(4):351-363. <https://doi.org/10.30509/pccc.2024.167264.1278>.

