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Enhancing the color shade and depth of linen fabrics dyed with *Caesalpinia sappan* L. wood extract using metallic salt mordants

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Abstract

This study demonstrated natural dyeing of linen with a dye extracted from sappan wood (Caesalpinia sappan L.). Four metallic salt mordants, namely $(NH_4)_2Fe(SO_4)_2$, $CuSO_4$, $SnCl_2$, and $AlK(SO_4)_2$, referred to as Fe, Cu, Sn, and Al, respectively, were used to improve the dyeing properties. The influences of the pH, dye concentration, mordant type and concentration, and mordanting technique on the dyeing properties were investigated. Dyeing without mordants resulted in a reddish-brown fabric; however, different mordants produced a variety of color shades. In general, the mordant containing Fe yielded the highest color strength, generating a dark gray color very close to black. Crimson and magenta fabrics were obtained using Sn, and pink fabrics were obtained using Al. The samples with the Cu mordant showed a dark and dull purple color. The color strength due to post-mordanting was higher than those due to pre- and meta-mordanting. Dyeing and mordanting increased the ultraviolet protection factor (UPF) of the fabrics. Only the fabrics post-mordanted with Fe exhibited good ultraviolet protection (UPF 15). The concentrations of extractable heavy metals (Fe and Cu) were also determined.

1. Introduction

Natural dyeing of textiles is perceived as more eco-friendly and sustainable than dyeing with synthetic colorants. Natural dyeing also helps preserve local traditions and cultural heritage as well as improve the rural economy. Some plants and animals are rich in natural colorants, and the extracted dyes have been used as textile dyes, paint pigments, and food additives. However, since the discovery of synthetic petroleum-based dyes, large-scale production of natural dyes has significantly declined, and natural dyestuffs have been rapidly superseded by synthetic ones. A major disadvantage of natural dyes is their cost because a larger amount of natural dyes may be needed to dye a certain amount of fabric as opposed to synthetic dyes. Moreover, poor shade reproducibility, inadequate fastness properties, difficulty in color standardization, and lengthy dyeing procedures hinder the industrial applications of natural dyes [1]. Synthetic dyes are preferred for large-scale manufacturing because of the simpler dyeing process, better control of color shades, and superior color fastness properties compared to natural dyes. However, some synthetic dyes induce allergies and are carcinogenic, thus posing serious health risks to humans; they could have negative environmental impacts. Consequently, many countries such as China, Japan, the USA, and the European Union have banned the use of azo dyes, which constitute the largest category of synthetic dyes [2]. As people are more concerned about to health and environmental impacts related to synthetic dyes, the demand for textile products manufactured using natural dyes has been increasing. One attractive characteristic of natural dyes is that the shades they produce are usually soft, lustrous, and soothing to the human eye.

Sappan wood (*Caesalpinia sappan* L.) is a small leguminous tree commonly found in tropical Asia. Its orange-red heartwood can be used to produce a red dye called "brazilin" suitable for dyeing fabrics as well as producing paints and inks [3]. Brazilin is a homoisoflavonoid, which is a group of polyphenolic compounds. The color of this dye depends on the pH of the solution, varying from yellow in acidic solutions to orange and red with increasing alkalinity. Brazilin is readily converted to brazilein upon exposure to atmospheric oxygen and light. The structures of brazilin and brazilein are shown in Figure 1. These compounds are the main components in the aqueous extracts obtained from the heartwood of *C. Sappan* [4]. Textiles dyed with the extract from *C. sappan* generally exhibit poor color fastness. Therefore, a mordant is used to overcome this issue. A mordant is a substance capable of fixing dyes on fabrics by forming insoluble dye-mordant complexes. Common mordants include weak organic acids, such as acetic or tannic acid, and metal salts such as alum and ferrous sulfate. Dye-metal complexation tends to affect the color shade because of charge-transfer processes and increased conjugation lengths [5].

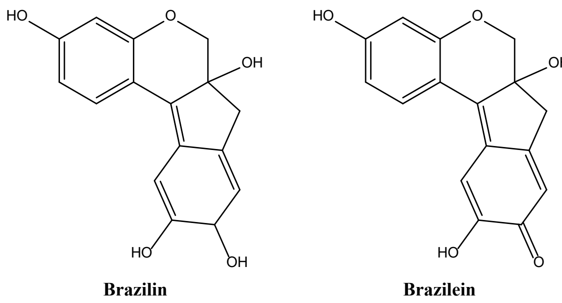


Figure 1. Chemical structures of brazilin and brazilein.

Many research groups have reported the use of natural dye extracts from *C. sappan* to dye textiles. Studies have reported the presence of brazilein in both aqueous and alcoholic extractions. Most studies chose fabrics produced from natural fibers such as cotton [6], wool [7], silk [8,6,9], and jute [10]. Dyeing of synthetic fabrics produced from poly(ethylene terephthalate) has also been reported [9]. In some cases, textile dyeing was carried out using a mixture of *C. sappan* and another natural dye to expand the range of color shades [10,11]. Both metallic salt mordants and biomordants have been used to improve dyeing properties. Improved color strength was achieved using $AlK(SO_4)_2$, $ZnSO_4$, and $CuSO_4$ as mordants for dyeing wool. These mordants did not significantly alter the color fastness to washing and rubbing [7]. One study on the effects of post-mordanting with $CuSO_4$, $FeSO_4$, and $Al(NH_4)(SO_4)_2$ on the color shades of cotton fabrics indicated that the dyed cotton appeared reddish brown without the mordant [6]. Mordanting cotton with $CuSO_4$, $FeSO_4$, and $AlK(SO_4)_2$ produced dark purple, dark lavender, and wine red, respectively. Biomordants such as gelatin [12], chitosan [9], soy protein, and sodium casein [8] also improved the color strength of fabrics dyed with *C. sappan,* without changing the color shades.

Linen fabric is made from flax fibers and therefore is viewed as an eco-friendly material. Flax fiber is lignocellulosic and one of the strongest natural fibers, surpassing even cotton [14]. Fabrics produced from flax show adequate water absorbency and air permeability [15]. Wearing linen clothes can keep the skin cool owing to the excellent moisture-wicking properties [14]. Despite drawbacks such as a low degree of wrinkle recovery, poor abrasion, and low dimensional stability, linen fabrics have found widespread use in apparels and household textiles [16].

To the best of our knowledge, this is the first study demonstrating the use of *C. sappan* extract to dye linen fabric. We prepared the spray-dried, orange dye powder from an aqueous extraction of the heartwood. Linen was dyed using the dye powder and four different metallic salt mordants namely, ammonium ferrous sulfate, copper(II) sulfate, tin(II) chloride, and aluminum potassium sulfate. These are referred to as Fe, Cu, Sn, and Al, respectively. The effects of the mordanting procedure, pH, and the dye and mordant concentrations on the dyeing properties and color fastness were studied. The ultraviolet protection factor and the extractable heavy metal contents were also determined.

2. Experimental

2.1 Materials

The heartwood parts of sappan wood and plain-woven linen fabric were obtained from local stores in Thailand. The mordants used i.e., ammonium iron (II) sulfate hexahydrate (Morhr's salt), $(NH_4)_2Fe(SO_4)_2(H_2O)_6$, copper(II) sulfate ($CuSO_4$), tin(II) chloride ($SnCl_2.2H_2O$), and aluminum potassium sulfate (alum, $AlK(SO_4)_2$), were of analytical grade, Deionized (Dl) water was used throughout this study.

2.2 Methods

2.2.1 Dye extraction

The sun-dried heartwood of *C. sappan* was crushed into smaller slices (approximately 10 cm × 0.5 cm). These slices were soaked in DI water for 3 d, using 8 kg heartwood with 40 L of water. Then the mixture was heated at 60°C for 1 h. The extract was filtered to remove solid residue. The aqueous solution was then spray-dried by adding 2% maltodextrin to produce the dye powder. The inlet and outlet temperatures of the spray-drying machine were set at 200°C and 100°C, respectively.

2.2.2 Dyeing and mordanting of linen fabrics

The fabric was cut into pieces with dimensions of 15 cm × 20 cm. (4.7 g). Dyeing and mordanting were carried out in an infrared dyeing machine (Starlet DL-6000). The dyeing solution was prepared in deionized water and the final pH was adjusted using sodium hydroxide or acetic acid. The pH of the as-prepared dye solution was 6.04. The mordant solutions were also prepared by dissolving each mordant in deionized water at neutral pH. The dye concentration was varied from 25 %owf to 75 %owf (i.e., on weight of fabric), and the mordant concentration ranged from 0.25 %owf to 2 %owf. The mordanting process included pre-mordanting, meta-mordanting, and post-mordanting. Unless specified otherwise, the mordanting and dyeing profiles used throughout our experiments are shown in Figure 2 and Figure 3, respectively. The dye pots were rotated at a fixed speed of 45 rpm. Excess dye was removed by heating the samples in 2 $g\cdot L^{-1}$ of a standard detergent solution at 60°C for 15 min at an L:R ratio of 30:1. The samples were then rinsed with water until clean and then air-dried.

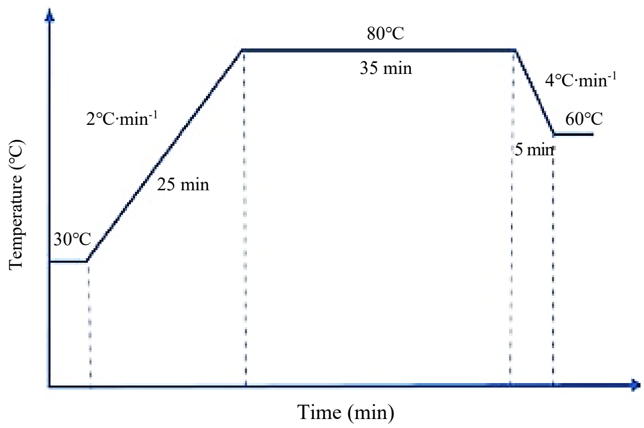


Figure 2. Fabric mordanting profile

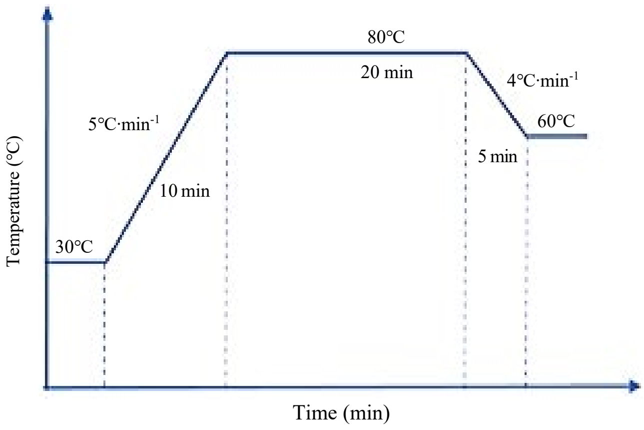


Figure 3. Fabric dyeing profile

2.2.3 Measurement of color parameters

The CIELab color parameters including L* (lightness), a* (red-green), b* (yellow-blue), C* (chroma), h° (hue angle), and color strength (K/S) were measured using a spectrophotometer (GretagMacbeth color i5). The color values of each sample were determined in triplicate.

2.2.4 Color fastness test

The dyed samples were tested for color fastness to washing following the ISO 105-C10: 2007 Method A1 protocol. In brief, a 100 mm × 40 mm fabric specimen was attached to a multifiber DW and washed using a GyroWash machine with 5 $g\cdot L^{-1}$ of a standard detergent and 50:1 liquor ratio at a washing temperature of 40°C for 30 min. Further, color fastness to perspiration (acid and alkaline) was evaluated by following the ISO105-E04: 2013 standard. An alkaline solution with a pH of 8 and acid perspiration pH of 5.5 were freshly prepared according to the standard. The specimen was treated in the prepared solution (L:R 50:1) for 30 min and then placed in a perspiration tester (each sample was sandwiched between two acrylic plates under a pressure of 12.5 kPa). The test device was then placed in an oven at 37°C for 4 h and dried by hanging in air at room temperature. The color fastness ratings were determined using a spectrophotometer (GretagMacbeth color i5).

2.2.5 Assessment of UV protection properties

The UV protection properties of the fabrics were measured in terms of ultraviolet protection factor (UPF). UPF is the ratio of the average effective UV radiation irradiance transmitted through air to the average effective UV radiation irradiance transmitted through the fabric. The UPF of a sample can be determined using the following Equation:

$$UPF = \frac{\sum_{200nm}^{400nm} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{280nm}^{400nm} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda}$$

where E(λ) is the relative erythemal spectral effectiveness, S(λ) is the solar spectral irradiance ($W\cdot m^{-2}\cdot nm^{-1}$), Δλ is the measured wavelength interval (nm), and T(λ) is the average spectral transmittance of the fabric.

The fabric with a high UPF rating showed a high UV shielding performance. In this study, the UPF ratings of the samples were measured using a UV-visible spectrophotometer (Camspec M550SPF double beam scanning spectrophotometer) by following the AATCC TM183: 2020 standard. The measurements were performed in triplicate, and the average of the three values were recorded as the final UPF rating of each sample.

2.2.6 Determination of the extractable heavy metal contents in the fabrics

The extractable heavy metal contents in the post-mordanted fabrics were analyzed. An artificial acid perspiration solution was used to extract the heavy metals from the fabrics using an in-house method (THTI-E03 based on ISO 105-E04: 2013/ ISO11885: 2007). The perspiration extract was then analyzed by inductively coupled plasma optical emission spectroscopy (Varian 730-ES, USA) to determine the concentrations of copper and iron present in the samples; the limit of detection was 0.5 $mg\cdot kg^{-1}$.

3. Results and discussion

3.1 Effects of pH (no mordant)

Table 1 lists the CIELAB color parameters of the fabrics dyed without a mordant at different pH values. The color shade is defined by the hue angle (h°) and can be calculated using arctan (b*/a*). Varying the pH of the dye solution yielded similar color shades, except for dyeing at pH 12; here, a slightly higher h° value was obtained than that when dyeing at other pH values. All the samples were reddish brown, as confirmed by the similar hue angles. Without mordanting, the K/S values were typically low, implying low dye pickup by the fabric, which led to weak colors. According to a previous study [17], brazilein is sensitive to heat and pH. The authors investigated the effects of pH (3, 7, and 9) and heating on the color, structure, and thermal stability of brazilein. They claimed that brazilein underwent degradation upon heating at high pH values of 7 and 9. At pH 3, brazilein contained no net charge and appeared yellow. This yellow color was not affected when the sample was heated at 80°C or 100°C for 1 h, indicating the satisfactory thermal stability of brazilin. At pH 7 and 9, partial and full deprotonation of the structure occurred, and the dye appeared orange and red, respectively. Because brazilein became more prone to degradation upon heating at higher pH values, the thermal degradation and color change at pH 9 were more pronounced than those at pH 7. The color changed from yellow to red only when the sample was heated at a high temperature of at least 80°C for a long time (60 min); however at pH 9, a heating temperature of 60°C was sufficient to induce significant structural changes. In our study, we did not observe any obvious change in the color from pH 4 to pH 11, probably because the heating duration was not long enough to induce thermal degradation. We obtained a different hue angle and color strength, and detected a reduction in redness (a*), only at pH 12. At this pH, the solution was strongly alkaline, causing the fully deprotonated dye molecules to undergo extensive thermal degradation. Therefore, pH 6.04 was chosen for dyeing during the remaining experiments, as we could achieve adequate color stability and higher K/S values; moreover, pH adjustment was not required because this pH was readily obtained for the as-prepared dye solutions.

Table 1 . Effects of pH on the color parameters of unmordanted linen fabrics dyed with 75 %owf dye, dyeing time of 35 min, dyeing temperature of 80°C, and dyeing L:R of 15:1.

pH	*L**	*a**	*b**	*C**	*h°*	*K/S*	Photographic image
4	61.43	11.58	7.80	13.96	33.96	1.89	
5	60.58	11.98	8.14	14.48	34.20	1.85	
6	60.57	12.20	8.53	14.89	34.98	2.09	
7	60.50	12.10	8.07	14.54	33.69	1.91	
8	59.98	12.42	7.97	14.75	32.70	1.96	
9	59.92	12.88	8.01	15.17	31.86	1.97	
10	59.32	12.15	7.12	14.08	30.36	2.00	
11	60.88	11.89	8.90	14.85	36.79	1.95	
12	66.15	8.92	8.77	12.51	44.53	1.62	

3.2 Effects of dye concentration (studied using a pre-mordanting technique)

Table 2 indicates that different color shades *(h°)* were obtained by dyeing the linen fabric using different mordants; we obtained reddish brown for the unmordanted fabrics, dark gray for those mordanted with the Fe salt, purple for the Cu salt, Crimson for the Sn salt, and pink for the Al salt. Except for the Al salt, all the mordants generally led to a higher *K/S.* This increase was attributed to the formation of insoluble complexes between the metal ions and brazilein. Certain metal ions exhibit unique complex formation properties, producing different color shades. In general, increasing the dye concentration produced higher *K/S* and lower *L*,* as expected. However, extremely high dye concentrations might result in dye agglomeration and reduced dye diffusion into the fabric, leading to a lower dye uptake. Low *K/S* values were obtained for the unmordanted fabrics and those pre-mordanted with the Cu salt at high dye concentrations.

3.3 Effects of L:R (studied using a pre-mordanting technique)

L:R is important for the uniform dyeing of fabrics. For dyes with high affinity to fibers, a higher L:R is needed for dyeing because an uneven shade would be obtained otherwise. Because at a low L:R, the effective concentration of the dye molecules is high, and there is a high probability that some dye molecules may adhere to the same site of the fiber. As this ratio is increased, the dye bath becomes more diluted, and it is thus unlikely that more than one dye molecule can reach the same point on the fiber surface [18]. However, using a high L:R generates a large amount of wastewater.

In this study, we used L:R values of 15:1 and 30:1 for dyeing the pre-mordanted samples. Most of the samples showed a decrease in color strength when dyed at a higher L:R, as expected (see Figure 4). This is because the liquor ratio *(L)* and dye affinity to the fiber *(K)* are the key parameters that control exhaustion *(E)*; $E = K(K+L)$ and $K = C_f/C_s$, where C_f and C_s are the equilibrium concentrations of the dye in the fiber and solution, respectively. When *L* increases, *E* decreases and less dye is exhausted into the fiber [19].

3.4 Effects of different mordanting techniques

Although meta-mordanting is the simplest technique because it is the only single-step process, we observed that this technique tended to produce weaker shades compared to the other techniques. This could have happened probably because, during the mixing of the mordant and the dye in a single dye bath, the dye-mordant complexation occurred rapidly. Therefore, a large number of these complexes remained in the solution. Evidently, the color strength of the fabrics subjected to post-mordanting was higher than those of the fabrics subjected to the other mordanting techniques. From Table 3, the color shades appeared slightly different to the naked eye, and these differences were further confirmed by the different *h°* values.

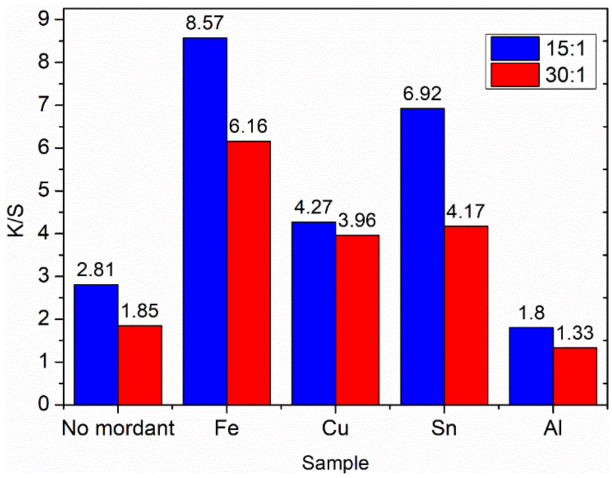


Figure 4. Effects of L:R on the color strength (K/S) of the fabrics pre-mordanted with a 3 %owf mordant and 30 %owf dye for a mordanting time of 20 min and dyeing time of 35 min; the dyeing temperature and pH were 80°C and 6, respectively.

Table 2. Effects of dye concentration on the color parameters of fabrics dyed using a pre-mordanting technique, with 3 %owf mordant and a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80℃, dyeing pH of 6, and dyeing L:R of 30:1.

Mordant type	Dye concentration (% owf)	*L**	*a**	*b**	*C**	*h°*	*K/S*
No mordant	25	63.10	10.16	7.41	12.58	36.11	1.77
	50	57.31	9.33	5.00	10.59	28.17	2.38
	75	62.01	9.60	7.25	12.03	37.05	1.85
Fe	25	48.90	4.91	-0.93	4.99	349.25	5.24
	50	47.95	5.74	0.39	5.76	3.91	5.60
	75	46.56	6.73	1.39	6.87	11.64	6.16
Cu	25	41.73	4.64	-11.11	12.04	292.67	4.73
	50	44.70	4.83	-9.33	10.51	297.35	3.83
	75	43.90	5.93	-9.31	11.04	302.51	3.96
Sn	25	56.88	28.27	3.61	28.50	7.27	2.39
	50	55.05	24.13	6.50	24.99	15.07	3.33
	75	53.36	27.50	6.86	28.35	14.01	4.17
Al	25	67.10	14.84	2.12	14.99	8.15	0.96
	50	64.55	15.77	3.81	16.22	13.6	1.28
	75	63.11	16.21	2.89	16.47	10.1	1.33

Table 3. Comparison of the color parameters obtained from pre-mordanting, meta-mordanting, and post-mordanting techniques. All fabrics were dyed with 3 %owf mordant and 75 %owf dye at a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80℃, dyeing pH of 6, and dyeing L:R of 15:1.

Mordant type	Mordanting technique (%owf)	*L**	*a**	*b**	*C**	*h°*	*K/S*	Photographic image
No mordant	–	57.37	13.34	8.40	15.77	32.18	2.81	 Reddish brown
Fe	Pre	46.56	6.73	1.39	6.87	11.64	6.16	 Dark gray
	Meta	57.02	3.67	-5.12	6.30	305.64	1.42	 Dark gray
	Post	30.04	5.59	-3.34	6.51	329.16	12.50	 Dark gray
Cu	Pre	40.70	8.52	-6.42	10.67	322.99	4.27	 Purple
	Meta	38.63	4.87	-10.26	11.35	295.40	5.55	 Dark purple
	Post	32.06	8.69	-2.73	9.11	342.57	10.76	 Dark purple
Sn	Pre	44.01	27.96	7.47	28.94	14.97	6.92	 Crimson
	Meta	80.26	16.17	1.92	16.28	6.78	0.44	 Bright Pink
	Post	44.09	34.95	8.20	35.9	13.2	7.23	 Crimson
Al	Pre	55.82	20.51	0.43	20.52	1.19	1.81	 Magenta
	Meta	64.40	19.15	0.75	19.16	2.25	1.02	 Carmine
	Post	44.80	20.95	6.26	21.87	16.63	5.07	 Pink

3.5 Effects of mordant concentration (studied using the post-mordanting technique)

The effects of the mordant concentration were investigated for the post-mordanted samples and the color parameters are reported in Table 4. All the mordants led to an increased color strength on increasing the mordant concentration. Metallic salt mordants are known to improved dyeability and color fastness by forming insoluble complexes with the dye which may result in a shade that is darker, brighter, or even a drastically different one [20]. According to [4], when using transition metals as mordants, brazilein forms a complex with Al (III) in an octahedral arrangement with two molecules of the dye acting as ligands via the ionized 10-hydroxyl group and 9-carbonyl oxygen to form coordinate bonds with Al(III), and two water molecules serve as co-ligands. Ferrous sulfate mostly forms octahedral complexes with the dye molecules [20], and it allows for some coordination sites to be occupied by the hydroxyl groups of the cellulosic fibers, leading to a higher dye uptake and a deeper shade. Copper (II) ion complexes are generally four-coordinated, but in some cases, a coordination number greater than four has been reported (such as complexation with azo dyes substituted in the *ortho* positions) [21]. Al and Sn salts are brightening mordants, whereas Cu and Fe salts are dulling mordants. Compared to the Fe ion, Sn and Al ions tend to form weaker coordination complexes with the dye and do not interact effectively with the fiber, leading to a lower color depth [20].

3.6 Color fastness results (studied using the post-mordanting technique)

The dyed samples were evaluated for color fastness against washing (Table 5) and perspiration (Table 6). In terms of color change, only Fe increased color fastness, from 2 to 3 (poor to fair) for the control, to 3 to 4 (fair to good). The following is the order of the fastness in terms of color change: Fe > Al, no mordant > Cu, Sn. Evaluation of color staining to an adjacent fabric revealed that in most cases, using mordants did not improve fastness ratings except for Fe and Cu, which provided a slight improvement in color transfer to wool and acrylic fibers, respectively. A drastic reduction in the fastness rating was found when using the Cu mordant, with a very poor rating for color transfer to adjacent cotton. All samples were rated 4 (good) and 3 to 4 for color transfer to adjacent polyester and nylon.

Table 4. Effects of mordant concentration on the color parameters of fabrics dyed using the post-mordanting technique with 75 %owf dye and a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80°C, dyeing pH of 6, dyeing L:R of 15:1.

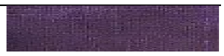
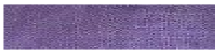
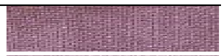
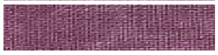
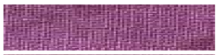
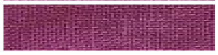
Mordant type	Mordant concentration (%owf)	*L**	*a**	*b**	*C**	*h*°	*K/S*	Photographic image
No mordant	–	40.64	6.04	0.39	6.05	3.68	6.93	
Fe	0.25	40.64	6.04	0.39	6.05	3.68	6.93	
	0.5	37.27	5.70	-0.67	5.73	353.3	9.09	
	1	34.14	5.42	-0.75	5.47	352.14	10.21	
	2	31.40	5.49	-1.80	5.78	341.83	13.30	
Cu	0.25	38.04	7.36	-4.58	8.67	328.13	6.00	
	0.5	35.48	8.01	-3.79	8.86	334.68	7.52	
	1	32.29	7.28	-4.26	8.44	329.7	10.01	
	2	31.63	7.93	-4.35	9.04	331.26	10.18	
Sn	0.25	48.75	20.93	7.60	22.27	19.97	4.71	
	0.5	48.23	21.83	7.83	23.19	19.73	5.04	
	1	47.63	22.53	8.16	23.97	19.92	5.79	
	2	44.49	25.5	8.32	26.82	18.07	7.35	
Al	0.25	52.39	13.52	6.91	15.19	27.06	3.47	
	0.5	49.76	15.91	6.06	17.02	20.86	3.84	
	1	50.07	15.93	6.18	17.09	21.22	3.92	
	2	48.87	17.01	7.20	18.47	22.94	4.46	

Table 5. Color fastness to washing ratings of fabrics dyed using a post-mordanting technique with 2 %owf mordant and 75 %owf dye at a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80°C, dyeing pH of 6, and dyeing L:R of 15:1.

Technique	**Mordant**	**Color change**	**Color staining**					
			Wool	**Acrylic**	**Polyester**	**Nylon**	**Cotton**	**Acetate**
No mordant		2-3	3	4	4	3-4	3-4	4
Post	Fe	3-4	3-4	4	4	3-4	2-3	4
	Cu	2	2-3	4-5	4	3-4	1	4
	Sn	2	2-3	4	4	3-4	3-4	3-4
	Al	2-3	3	4	4	3-4	3	3-4

Table 6. Color fastness to perspiration ratings of fabrics dyed using a post-mordanting technique with 2 %owf mordant and 75 %owf dye at a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80°C, dyeing pH of 6, and dyeing L:R of 15:1.

Technique	**Mordant**	**Color change**	**Color staining**					
			Wool	**Acrylic**	**Polyester**	**Nylon**	**Cotton**	**Acetate**
Acid perspiration	No mordant	4	3	4	4	2	3–4	3
	Fe	3-4	2	3-4	3	1	1	1
	Cu	1-2	1-2	3	2-3	1	1	1
	Sn	3	3-4	4	3-4	1-2	2-3	2
	Al	3-4	3	3-4	3-4	1	1	1-2
Alkaline perspiration	No mordant	3	3	4-5	4-5	3	3-4	4
	Fe	4	1-2	4-5	4-5	2	2-3	2
	Cu	1-2	1-2	3-4	3	1	1	1
	Sn	3	3	4-5	4-5	2	2-3	3
	Al	3	2-3	4-5	4-5	2	3-4	2–3

Table 6 shows the color fastness to perspiration ratings. Without mordanting, the fabric was rated good (4) under acidic conditions and fair (3) under alkaline conditions. When tested for color fastness to acid perspiration, none of the mordant types showed any improvement in the color fastness ratings in terms of color change. The following trend was observed: no mordant > Fe, Al > Sn > Cu; alkaline perspiration showed the following trend: Fe > no mordant, Sn, Al > Cu. The staining tests for acidic and alkaline perspirations revealed a wide range of ratings from 1 to 4-5. Staining on acrylic and polyester fabrics appeared to be less than that on wool, nylon, cotton, and acetate. Cu was the worst mordant based on color change and color staining in all color fastness tests. Furthermore, considering the higher toxicity of Cu compared to the other mordants used in this study, we can conclude that Cu is the least promising mordant to dye linen with *C. sappan* unless the purple shade is specifically desired. The better or comparable fastness ratings of the unmordanted linen fabrics with respect to the post-mordanted ones can be ascribed partly to the weaker color of the former; therefore, color changes and chances of color staining are less pronounced than that observed for the mordanted samples with stronger color depths.

3.7 UV protection properties

The UV protection efficiency of the samples was rated according to the AATCC 183: 2020. The pristine linen fabric provided only a UPF rating of 4.88±0.47. As can be seen from Figure 5, both dyeing and mordanting improved the UV protection properties as reflected in the higher UPF ratings. Evidently, post-mordanting with Fe resulted in higher UPF values than those obtained with the other mordants. Further, a high mordant concentration generally increased the UPF value, because the UPF rating was enhanced with dark hues and high concentrations of the colorant in the fabric [22,23]. According to the AATCC 183 standard, the fabrics with a UPF rating of less than 15 were not UV-protective. Fabrics with UPF rating of 15-24, 25-39, and 40-50+ were classified as good, very good, and excellent UV-protective fabrics, respectively. Figure 5 demonstrates that only post-mordanting with 1 %owf and 2 %owf of the Fe salt resulted in good UV-protective fabrics (UPF 15.3±1.3 and 15±0.8, respectively). The other fabrics exhibited UPF values < 15 and thus could not be classified as UV-protective.

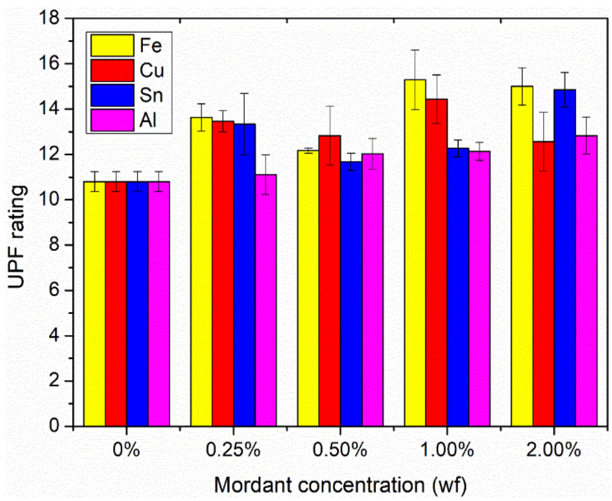


Figure 5. Effects of dyeing, mordanting, and mordant concentration on the UPF ratings of the linen fabrics (75 %owf dye and a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80°C, dyeing pH of 6, dyeing L:R of 15:1).

Table 7. Extractable heavy metal analysis of the fabrics dyed by post-mordanting with a 0.25 %owf to 2 %owf mordant and 75 %owf dye at a mordanting time of 20 min, dyeing time of 35 min, dyeing temperature of 80°C, dyeing pH of 6, and dyeing L:R of 15:1.

Extractable element	Mordant concentration (%owf)	Extractable heavy metal concentration ($mg\cdot kg^{-1}$)
Fe	0.25	2.07
	0.5	2.59
	1	1.49
	2	1.72
Cu	0.25	1320.72
	0.5	1392.58
	1	1592.91
	2	1694.70

3.8 Extractable heavy metal contents in the post-mordanted fabrics

Because of the presence of heavy metals in the mordanted fabrics, their contact with skin can be hazardous to human health. Thus, the concentrations of heavy metals in the samples containing Fe and Cu were measured via extraction by perspiration. Table 7 indicates that the extractable Fe content is very low, ranging between 1.49 $mg\cdot kg^{-1}$ to 2.59 $mg\cdot kg^{-1}$. Fe is an essential micronutrient that becomes toxic to biological systems, when they are excessively exposed to Fe, but only under pathological or harsh situations [24]. Therefore, the fabrics mordanted with Fe in this study can be considered safe. Cu, although being an essential trace element in human tissues, can induce cellular toxicity through participation in the formation of reactive oxygen species [25]. The Oeko-Tex Standard 100 set the limit value of Cu for textile products at 25.0 $mg\cdot kg^{-1}$ for babies and at 50.0 $mg\cdot kg^{-1}$ for other textile products, including products that come in direct contact with skin, with no direct contact with skin, and decoration materials [26]. Table 7 shows that the amount of Cu that can be extracted from the fabrics (treated with Cu) exceeds that of the Oeko-Tex guidelines; thus, their use is a safety concern.

4. Conclusions

Linen fabrics were dyed with a sappan wood extract using metallic salt mordants. The fabrics subjected to post-mordanting exhibited deeper color shades than those subjected to pre-mordanting and meta-mordanting. Although the unmordanted fabric appeared reddish brown, mordanting with Fe, Cu, Sn, and Al salts produced different color shades and generally improved the color strength. Upon post-mordanting, the Fe, Cu, Sn, and Al mordants produced dark gray, dark purple, crimson, and magenta colored fabrics, respectively. Tests conducted to determine color fastness to washing and perspiration indicated that the metallic salt mordants did not improve the fastness properties. Among the mordants, Cu resulted in the lowest fastness ratings. Dyeing and mordanting generally enhanced the UV protection efficiency, and Fe was found to be the most effective in producing UV-protected fabric. In other words, only the dyed fabrics treated with 1%owf to 2 %owf of the Fe mordant exhibited good UV protection. Extractable heavy metal concentration analyses revealed that the Fe content was within the safe limit, whereas that of Cu far exceeded the Oeko-Tex 100 guidelines.

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References

[1] S. S. Affat, "Classifications, advantages, disadvantages, toxicity effects of natural and synthetic dyes: A review," *University of Thi-Qar Journal of Science*, vol. 8, pp.130-135, 2021.

[2] M. M. Hasan, K. A. Nayem, and A. Azim, "Dyeing of cotton and silk fabric with purified natural curcumin dye," *International Journal of Scientific Engineering and Technology,* vol. 3, pp. 838-844, 2014.

[3] K. Mekala, and R. Radha, "A review on sappan wood-a therapeutic dye yielding tree," *Research Journal of Pharmacognosy and Phytochemistry,* vol. 7, p. 227, 2015.

[4] K. Wongsooksin, S. Rattanaphani, M. Tangsathitkulchai, V. Rattanaphani, and J. B. Bremner, "Study of an Al(III) complex with the plant dye brazilein from *Ceasalpinia sappan* Linn," *Suranaree Journal Scicene Technology,* vol. 15, pp. 160-163, 2008.

[5] A. P. Manian, R. Paul, and T, "Bechtold. Metal mordanting in dyeing with natural colourants," *Coloration Technology,* vol. 132, pp. 107-113, 2016.

[6] P. Ohama, and N. Tumpat, "Textile dyeing with natural dye from sappan tree (*Caesalpinia sappan* Linn.) extract," *International Journal of Materials and Textile Engineering,* vol. 8, pp. 432-434, 2014.

[7] M. K. Datta, M. E. Talukder, A. M. Faisal, A. Sarker, and H. Jiang, "The sustainable coloration of wool fabric using naturally extracted dyes from sappan heartwood," *Journal of Natural Fibers,* pp. 1-15, 2021.

[8] S. H. Hwang, and J. D. Jang, "The effects of the pre-treatments with proteins on dyeing of silk fabric with *Caesalpinia sappan*," *Textile Coloration and Finishing,* vol. 28, pp. 208-218, 2016.

[9] Y. Park, "Dyeing characteristics of fermented *caesalpinia sappan* L. Wood extract with chitosan-acetic acid solution and illite powder," *Textile Coloration and Finishing,* vol. 31, pp. 268-275, 2019.

[10] A. K. Samanta, P. Agarwal, D. Singhee, and S. Datta, "Application of single and mixtures of red sandalwood and other natural dyes for dyeing of jute fabric: studies on colour parameters/ colour fastness and compatibility," *The Journal of The Textile Institute,* vol. 100, pp. 565-587, 2009.

[11] Y. Park, K. Koo, S. Kim, and J. Choe, "Improving the colorfastness of poly (ethylene terephthalate) fabrics with the natural dye of *Caesalpinia sappan* L. Wood extract and the effect of chitosan and low-temperature plasma," *Journal of applied polymer science,* vol. 109, pp. 160-166, 2008.

[12] E. Hwang, Y. H. Lee, and H. D. Kim, "Dyeing and deodorizing properties of cotton, silk, and wool fabrics dyed with various natural colorants," *Textile Coloration and Finishing,* vol. 19, pp. 12-20, 2007.

[13] J. Y. Lee, and J. D. Jang, "Improving the dyeability of cotton fabric with *Caesalpinia sappan* through pretreatment with gelatin," *Fashion & Textile Research Journal,* vol. 21, pp. 509-514, 2019.

[14] N. Senthil, and B. Dhurai, "Knittability enhancement study of 100% linen yarn using softeners," *Journal of Natural Fibers,* vol. 19, pp. 4393-4402, 2021.

[15] A. Farouk, S. E. Saeed, S. Sharaf, and M. A. El-Hady, "Photo-catalytic activity and antibacterial properties of linen fabric using reduced graphene oxide/silver nanocomposite," *RSC advances,* vol. 10, pp. 41600-41611, 2020.

[16] B. Dornyi, E. Csiszár, and P. Somlai, "Improving quality of linen-cotton fabrics with liquid ammonia treatment," *Journal of Natural Fibers,* vol. 4, pp. 41-57, 2008.

[17] L. Ngamwonglumlert, S. Devahastin, N. Chiewchan, and G. Raghavan, "Color and molecular structure alterations of brazilein extracted from *Caesalpinia sappan* L. under different pH and heating conditions," *Scientific reports,* vol. 10, pp. 1-10, 2020.

[18] J. N. Chakraborty, "Introduction to dyeing of textiles," *Fundamentals and Practices in Colouration of Textiles,* pp. 1-10, 2010.

[19] SR. Shukla, *Pollution abatement and waste minimisation in textile dyeing.* Environmental Aspects of Textile Dyeing, Elsevier., 2007.

[20] M. G. Uddin, "Effects of different mordants on silk fabric dyed with onion outer skin extracts," *Journal of Textiles,* vol. 2014, pp. 1-8, 2014.

[21] H. B. Jonassen, and J. R. Oliver, "Metallated dye complexes. IV. The stereochemistry of copper(II)-dye complexes," *Journal of the American Chemical Society,* vol. 80, pp. 2347-50, 1958.

[22] S. K. Ajoy, "An evaluation of UV protection imparted by cotton fabrics dyed with natural colorants," *BMC dermatology,* vol. 4.1, pp. 1-8, 2004.

[23] P. Pisitsak, J. Hutakamol, S. Jeenapak, P. Wanmanee, J. Nuammaiphum, and R. Thongcharoen, "Natural dyeing of cotton with *Xylocarpus granatum* bark extract: Dyeing, fastness, and ultraviolet protection properties," *Fibers and Polymers*, vol. 17, pp. 560-568, 2006.

[24] R. Eid, A.T.T. Rawan, and M.T. Greenwood, "Iron mediated toxicity and programmed cell death: A review and a re-examination of existing paradigms," *Biochimica et Biophysica Acta (BBA)-Molecular Cell Research,* vol. 1864.2, pp. 399-430, 2017.

[25] L. M. Gaetke, and C. K. Chow, "Copper toxicity, oxidative stress, and antioxidant nutrients," *Toxicology*, vol. 189, pp. 147-163, 2003.

[26] OEKO-TEX® STANDARD 100 [https://www.oeko-tex.com/en/our-standards/oeko-tex-standard-100].