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A Study on Combining Natural Dyes and Environmentally-friendly Mordant to Improve Color Strength and Ultraviolet Protection of Textiles

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Abstract: In this study, natural dyes were extracted from five plants, namely diospyros kaki, dioscorea cirrhosa, millettia (*jixueteng*), ecliptae, and macrocarpa nucuma, using environmentally-friendly solvents, including ethanol and deionized (DI) water. A plant mordant, tannin extracted from *Emblica officinalis G.*, and a metal mordant, copper sulfate, were used in the pre-dyeing process. Cotton and silk fabric samples were treated using the five natural dyes without and with mordanting for comparison on their color strength and characteristics as well as protection against ultraviolet radiation (UVR). Results revealed that *Emblica officinalis G.* had the highest total phenol content, followed by dioscorea cirrhosa. The presence of abundant phenolic groups in the natural dyes and mordant makes them effective coloration agents for fabrics. Cotton and silk fabrics dyed using ecliptae without pre-mordanting had the highest *K/S* values. Silk fabrics had higher *K/S* values than cotton fabrics, indicating greater color strength in pre-mordanted silk treated with DI water-extracted dyes. Natural mordant used before treatment with natural dyes contribute to significant enhancement in color strength, and *Emblica officinalis G.* alone could darken the color of cotton and silk fabrics dyed with plant pigment. Moreover, treatment with natural dyes after mordanting can increase ultraviolet protection factor (UPF) and the enhancement in UVR protection is greater and more significant in cotton fabrics than in silk fabrics, and in fabrics treated with DI water-extracted natural dyes than in those treated with ethanol-extracted ones. In conclusion, pre-dyeing with natural mordant followed by treatment with natural dyes extracted using environmentally-friendly solvents can enhance significantly *K/S* and UPF, offering directions for manufacturing textiles without environmental hazards but with good appearance and health benefits.

Keywords: Natural dyes, Natural mordant, Textiles, *K/S*, UPF, Total phenol content

Introduction

Advances in technology have led the textile industry to invest in research and development of innovative raw materials and dyeing techniques. However, excessive use of synthetic dyes in mass production of textiles causes environmental problems. In particular, water pollution caused by textile processing and chemical dyeing poses health hazards to humans. With an ever-increasing awareness for environmental protection and conservation, greater attention has been devoted by the industry and the Government to reducing pollution and conserving resources [1-5]. According to a report of the US textile industry, "natural fibers are back in demand. The emergence and popularity of a more natural way of life as reflected in a return to organic farming and natural foods has now extended into textiles where the resurgence of natural fibers and natural dyes is on the increase" [6].

Natural dyes refer to colorants of natural origins, with the majority from plant sources including wood, roots, stems, branches, leaves, flowers, fruits, seeds, and peels. Plant pigment is nontoxic and safe; it poses no health problem or environmental harm. People have long utilized plant pigment for centuries. In ancient times, natural dyes were used not only for dyeing wool, cotton, silk, and fur, but also they were applied as cosmetics and daily necessities. Some plant dyes show anti-bacterial activity while some can function as insect repellants [7-11]. However, most plant pigments are unstable and oxidize easily, resulting in discoloring. In addition, most natural dyes have low affinity for textile fibers. Hence, textile fabrication often involves a process known as mordanting, in which a mordant is employed to facilitate dye absorption by fibers and thus enhance color fixation and color strength [12-14]. Tannin, a naturally occurring plant polyphenol, has been the most widely used natural mordant [15]. In this study, tannin was extracted from *Emblica officinalis G.* (Hindi: Amla) for use as a natural mordant. Tannin accounts for 28 % of the fruit of *Emblica officinalis G* and contains the phenolic hydroxyl group that can promote color fixation of dyed molecules in natural textiles. In other words, tannin can enhance the affinity of plant dyes to fibers, thus increasing the color strength of dyed cotton and silk fabrics [12].

Besides aesthetic enhancement achieved by natural dyes along with natural mordants, dyes can also affect the ultraviolet protection factor (UPF) of fibers. According to the US National Toxicology Program (NTP), ultraviolet radiation (UVR) of wavelength ranging from 290 nm to 400 nm reduces the immunity of skin cells and is carcinogenic. Effects of over-exposure to UVR include freckling and

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sunburn, along with higher risk of skin cancers [16-21]. Hence, exploration on natural dyes that can increase shielding against UVR would be useful for human health protection.

In this study, natural pigments were extracted from different parts of five plants, namely diospyros kaki, dioscorea cirrhosa, millettia (*jixueteng*), ecliptae, and macrocarpa nucuma, using environmentally-friendly solvents, namely ethanol and deionized (DI) water. In the pre-dyeing process, tannin, a natural mordant extracted from *Emblica officinalis G.* and copper sulfate, a metal mordant, were used for comparing effects of different mordants on coloration. The total phenol content of each plant used as either dye or mordant was determined. The color strength (*K/S*) and UPF of the dyed cotton and silk fabrics with and without mordanting were analyzed. Results obtained can serve as useful references for the application of environmentally-friendly techniques to both dye extraction and textile dyeing, and for the development of UPF-enriching natural dyes for protection against UVR harmful to human health.

Experimental

Materials

To reduce carbon footprint, local plants from Taiwan were used in this study. The five plants used were diospyros kaki, dioscorea cirrhosa and ecliptae, millettia (*jixueteng*) and macrocarpa nucuma. *Emblica officinalis G.* (Amla) was procured from India. The cotton fabric (124GSM) was provided by the Hermin Textile Co. Ltd. of Taiwan, and the silk fabric (42 GSM) was purchased from Japan. Other materials used including ethanol 95 % (ECHO), acetic ether (ECHO), copper sulfate (ACROS), sodium carbonate (ACROS), gallic acid (ACROS), and folin-ciocalteu reagent (PanReac) were all of analytical grade.

Methods

Extraction of Natural Dyes

Rind of diospyros kaki, tuber of dioscorea cirrhosa, stem of millettia (*jixueteng*), whole plant of ecliptae, and stem of macrocarpa nucuma were dried under direct sunlight and ground into powder. Then, 100 g powder of each plant was weighed using a precision balance and extracted using ethanol and DI water as solvents.

Ethanol (95 %) extraction was performed three times using 200 m*l*, 200 m*l*, and 100 m*l* of ethanol, respectively. First, ethanol was added to the flask containing 100 g of plant powder. After 10-min thorough mixing, the solution was allowed to stand for 1 h at room temperature, and then filtered with air drawn out using a vacuum pump (Japan ULVAC GVD-050A). The ethanol was then evaporated using a rotary evaporator (EYELA N-1000) and a circulating aspirator (SIBATA WJ-20) with the plant extract dried using a vacuum oven (SHELLAB 1410D).

Similarly, DI water extraction was performed three times using 500 m*l*, 300 m*l*, and 200 m*l* of DI water, respectively. First, DI water was added to the flask containing 100 g of plant powder. Under 1-h magnetic stirring, the solution was heated using a hot stage (THMS600) to reach 65±5 ^{o}C, and allowed to stand for 2 h and then filtered. The solution was then evaporated using a rotary evaporator and a circulating aspirator with the plant extract dried using a vacuum oven.

Extraction of Natural Mordant

Fruits of *Emblica officinalis G.* were dried and ground into powder. Then 100 g of powder was extracted with 500 m*l* of ethanol under magnetic stirring for 12 h. The extract was concentrated under vacuum using a rotary evaporator. The semi-solid extract thus obtained was diluted with 300 m*l* of DI water, kept at 5 ^{o}C for 3 days and then filtered. The filtrate was further extracted three times, each with 200 m*l* of acetic ether. The yellow extract was then concentrated under vacuum using a rotary evaporator to yield a brown extract, which was dried in a vacuum oven at 75 ^{o}C for 7 h to yield tannin [12].

Determination of Total Phenol Content

The total phenol content of natural plants was determined using the Folin-Ciocalteu method [22]. In brief, 100 mg/*l* (ppm) of plant extract solution was put into a 1.5-m*l* cuvette, followed by addition of 8.5 m*l* of water and 100 μ*l* of the Folin-Ciocalteu reagent. After thorough mixing, the solution was allowed to stand for 8.5 min. Then 300 μ*l* of sodium carbonate solution (20 %) was added, followed by shaking. The mixed solution was then left to stand at 20 ^{o}C for 2 h and absorbance was determined using a UV/Vis spectrometer (BMG LABTECH SPECTROStar Nano) under the wavelength of 760 nm against the blank (0 m*l* of solution). All determinations were carried out in triplicate. The calibration curve was plotted using concentrations of 0, 1, 2, 5, 10, 15, and 20 mg/*l* of gallic acid. The total phenol content in the extracts is calculated using equation (1).

$$T = C \times V/M \tag{1}$$

where T: total phenol content, mg per g plant extract, in gallic acid equivalents (GAE), C: the concentration of gallic acid established from the calibration curve, mg per l, V: the volume of extract, l, and M: the weight of plant extract, g.

Mordanting

For comparison, there were three experimental groups. First, there was the control group (Nil) where no mordant was used. In the second group (10 % A), cotton and silk fabric samples were pre-dyed with *Emblica officinalis G.* (A) solution at 10 % concentration on weight of fabric (owf) at 85 ^{o}C for 45 min with the liquid to materials ratio maintained at 20:1. The third group (10 % A+0.5 % Cu) comprised fabric samples pre-dyed first with A solution at 10 % owf and then with copper sulfate (Cu) solution at 0.5 % owf, both at 85 ^{o}C for 45 min with the liquid to materials ratio maintained at 20:1 [12].

Dyeing of Cotton and Silk Fabrics

The above-mentioned three groups of fabric samples were put into dyeing solution of natural pigments at 20 % owf at room temperature in a water bath shaker (Model: B603D). The temperature was then increased to 85 °C at which dyeing proceeded for 60 min with the liquid to materials ratio maintained at 20:1. The dyed fabrics were then rinsed and air-dried [12].

Evaluation of Color Strength

Color strength of dyed fabric samples were evaluated using a UV-vis spectrometer (JASCO V-670) and the Color Diagnosis Software under light source D65 with a 10° standard observer. L^*, a^*, b^*, C^*, and h^o coordinates were measured according to the CIE $L^*a^*b^*$ system; L^*: lightness (0=black, 100=white); a^*: red-green coordinates (positive values=red, negative values=green); b^*: yellow-blue coordinates (positive values=yellow, negative values=blue); h^o: color index chromaticity angle 0-180 (0=purple, 90=yellow, and 180=bluish green); and C^* was calculated using equation (2)

$$C^* = (a^{*2} + b^{*2})^{1/2} \tag{2}$$

Reflectance of the dyed fabric samples was also measured in triplicate using a UV-Vis spectrometer (JASCO V-670). The mean was then taken to determine the *K/S* value, indicative of color intensity, of dyed samples using equation (3) [23,24].

$$K/S = \frac{(1-R)^2}{2R} \tag{3}$$

where K: absorption coefficient, S: scattering coefficient, and R: reflectance at complete opacity.

Penetration of UVR and Calculation of UPF

The dyed fabric samples were put under direct sunlight; and penetration of UVR, both UV-A of wavelength 320-400 nm and UV-B of wavelength 290-320 nm, through the samples was measured using a UV-Vis spectrometer (JASCO V-670). According to the Australian/New Zealand Standard (AS/NZS 4399) [25], UPF is defined as the ratio of average effective UVR irradiance calculated for unprotected skin to the average effective UVR irradiance calculated for skin protected by the test fabric, as expressed in equation (4) [26].

$$UPF = \frac{\sum_{\lambda=290}^{400} E_\lambda \cdot S_\lambda \cdot \Delta\lambda}{\sum_{\lambda=290}^{400} E_\lambda \cdot S_\lambda \cdot T_\lambda \cdot \Delta\lambda} \tag{4}$$

where E_λ: erythemal spectral effectiveness, S_λ: solar spectral irradiance in $Wm^{-2}\,nm^{-1}$, T_λ: spectral transmittance of fabric (%), $\Delta\lambda$: the bandwidth in nm (5 nm), λ: the wavelength in nm (290-400 nm). According to the estimation and classification standards of the Australian/New Zealand Standard (AS/NZS 4399), textiles with UPF rating of 15-24 are classified as "Good" with 93.3-95.9 % of UVR blocked, those with UPF of 25-39 are categorized as "Very Good" with 96-97.4 % of UVR blocked, and those with UPF of 40 or above are "Excellent" with ≥97.5 % of UVR blocked [27].

Results and Discussion

Total Phenol Content

Table 1 lists the total phenol content of the five natural dyes and natural mordant extracted from plants. As can be seen, dyes extracted from dioscorea cirrhosa using ethanol and DI water have the highest total phenol content, 75.7 GAE and 66.2 GAE, respectively; followed by those from macrocarpa nucuma, 61.7 GAE and 63.3 GAE, respectively. Moreover, the total phenolic content of *Emblica officinalis G.* was 98.9 GAE, even higher than that of natural dyes. Taken together, these high phenolic contents of various plants evidenced the presence of abundant phenolic (-OH) groups in the natural dyes and mordant [12], making them effective colorants for fabrics.

Color Strength without Mordanting

Table 2 shows the *K/S* value of cotton and silk fabrics

Table 1. Total phenol content of natural dyes and mordant extracted with ethanol and DI water

Natural plant	Solvent	
	Ethanol (95 %)	DI water
Diospyros Kaki	3.8±0.8	9.7±2.0
Dioscorea Cirrhosa	75.7±2.6	66.2±4.8
Millettia	36.5±2.1	50.8±1.8
Ecliptae	9.5±0.7	15.2±1.6
Macrocarpa Nucuma	61.7±2.2	63.3±1.0
Emblica officinalis G. 98.9±1.8		

Unit: GAE mg/g-plant extract.

Table 2. Color strength of cotton and silk fabrics treated with natural dyes without mordanting

Natural dye	Fabric	Solvent	
		Ethanol (95 %)	DI water
		K/S value	*K/S* value
Diospyros Kaki	Cotton	0.3733	0.4808
	Silk	0.0743	2.2310
Dioscorea Cirrhosa	Cotton	1.9323	2.0215
	Silk	0.2454	1.8714
Millettia	Cotton	1.2849	2.4744
	Silk	0.6683	0.9399
Ecliptae	Cotton	4.9734	3.2186
	Silk	5.4133	7.1148
Macrocarpa Nucuma	Cotton	1.4232	1.8257
	Silk	1.4929	2.8301

treated with the five natural dyes without mordanting. As can be seen, cotton and silk fabrics dyed with ecliptae had the highest *K/S* values. Moreover, the *K/S* value of silk fabrics dyed with ecliptae is higher than that of cotton fabrics dyed with ecliptae. In other words, among the five natural dyes, ecliptae gave the fabrics the best color strength without mordanting.

Effects of Different Mordants on Color Characteristics

Tables 3 and 4 show respectively the color characteristics of cotton and silk fabrics treated using ethanol-extracted natural dyes with and without mordanting. As can be seen, the pre-dyeing process increased the *K/S* value of both cotton and silk fabrics regardless whether one or two mordants were used. The most significant increase in *K/S*

Table 3. Color characteristics of cotton fabrics treated with ethanol-extracted natural dyes with and without mordants

Natural dye	Mordant	*K/S* value	Color coordinates				
			L^*	a^*	b^*	C^*	h^o
Diospyros Kaki	Nil	0.3733	95.91	-1.76	10.49	10.64	99.51
	10 % A	2.7826	73.9	-0.15	17.62	17.62	90.5
	10 % A+0.5 % Cu	5.8157	70.73	0.72	18.91	18.92	87.77
Dioscorea Cirrhosa	Nil	1.9323	65.49	18.13	27.35	32.82	56.46
	10 % A	8.6373	48.97	24.61	34.92	42.72	54.83
	10 % A+0.5 % Cu	10.5052	42.22	23.58	28.27	36.81	50.17
Millettia	Nil	1.2849	66.00	13.32	20.51	24.45	57.00
	10 % A	6.2841	48.62	15.86	21.55	26.75	53.66
	10 % A+0.5 % Cu	6.0535	50.77	12.76	22	25.43	59.89
Ecliptae	Nil	4.9734	73.07	-2.67	26.71	26.84	95.71
	10 % A	9.0976	57.43	-2.01	23.14	23.23	94.96
	10 % A+0.5 % Cu	12.3190	36.43	-4.71	11.11	12.07	112.98
Macrocarpa Nucuma	Nil	1.4232	73.00	5.24	14.94	15.83	70.67
	10 % A	7.2197	56.21	7.99	21.91	23.33	69.96
	10 % A+0.5 % Cu	6.8963	54.56	2.89	17.62	17.85	80.69

A: *Emblica officinalis G.* (Amla), Cu: Copper sulfate.

Table 4. Color characteristics of silk fabrics treated with ethanol-extracted natural dyes with and without mordants

Natural dye	Mordant	*K/S* value	Color coordinates				
			L^*	a^*	b^*	C^*	h^o
Diospyros Kaki	Nil	0.0743	98.29	-0.36	3.46	3.48	95.94
	10 % A	6.8501	66.27	0.12	21.75	21.76	89.69
	10 % A+ 0.5 % Cu	8.1762	60.61	2.31	24.38	24.49	84.60
Dioscorea Cirrhosa	Nil	0.2454	86.12	9.08	16.48	18.82	61.15
	10 % A	5.2891	60.03	9.85	25.93	27.74	69.21
	10 % A+ 0.5 % Cu	6.0935	51.73	13.73	30.37	33.33	65.68
Millettia	Nil	0.6683	85.56	7.01	18.31	19.61	69.06
	10 % A	6.2215	54.01	10.82	23.15	25.56	64.95
	10 % A+ 0.5 % Cu	5.7129	53.45	10.89	23.32	25.74	64.96
Ecliptae	Nil	5.4133	74.20	-4.31	29.20	29.52	98.40
	10 % A	11.4092	50.17	-0.25	16.29	16.30	90.88
	10 % A+ 0.5 % Cu	10.2888	36.71	-5.42	11.4	12.62	115.44
Macrocarpa Nucuma	Nil	1.4929	85.67	3.15	18.64	18.90	80.41
	10 % A	9.3114	54.40	5.66	22.47	23.17	75.86
	10 % A+ 0.5 % Cu	8.6343	50.99	4.61	20.53	21.04	77.34

A: *Emblica officinalis G.* (Amla), Cu: Copper sulfate.

value was observed in pre-mordanted cotton fabrics treated with ethanol-extracted dioscorea cirrhosa (from 1.9323 to 8.6373, Table 3) and in pre-mordanted silk fabrics treated with ethanol-extracted macrocarpa nucuma (from 1.4929 to 9.3114, Table 4). Increase in color strength was attributed to the complex formed by the phenolic hydroxyl group in the plant mordant with dye molecules, resulting in higher fixation of dye. Moreover, the extent of increase in *K/S* value was more significant when using the natural mordant alone than when using both natural and metal mordants. For cotton and silk fabrics treated with ethanol-extracted millettia and macrocarpa nucuma, and for silk fabrics treated with ethanol-extracted ecliptae, pre-dyeing with both mordants even attained a lower *K/S* value than using the natural mordant alone. In other words, natural mordant used before treatment with natural dyes contribute to significant enhancement in color strength, and *Emblica officinalis G.* alone could darken the color of cotton and silk fabrics dyed with plant pigment.

Table 5. Color characteristics of cotton fabrics treated with DI water-extracted natural dyes with and without mordants

Natural dye	Mordant	*K/S* value	Color coordinates				
			L^*	a^*	b^*	C^*	h^o
Diospyros Kaki	Nil	0.4808	93.15	0.15	12.08	12.09	89.29
	10 % A	3.2171	77.43	3.55	19.03	19.35	79.43
	10 % A+0.5 % Cu	2.4308	71.32	4.31	14.93	15.54	73.88
Dioscorea Cirrhosa	Nil	2.0215	65.88	16.91	29.09	33.65	59.83
	10 % A	3.2878	70.75	13.15	25.23	28.45	62.48
	10 % A+0.5 % Cu	4.1519	58.96	9.43	22.45	24.35	67.23
Millettia	Nil	2.4744	63.37	16.79	29.84	34.24	60.63
	10 % A	3.8346	59.96	9.28	22.16	24.02	67.28
	10 % A+0.5 % Cu	5.3108	56.69	7.13	22.56	23.66	72.46
Ecliptae	Nil	3.2186	71.82	4.88	19.68	20.27	76.08
	10 % A	9.7199	55.01	7.07	23.18	24.23	73.03
	10 % A+0.5 % Cu	9.1752	51.19	5.07	20.92	21.53	76.37
Macrocarpa Nucuma	Nil	1.8257	67.77	1.85	12.79	12.93	81.75
	10 % A	3.4232	66.75	4.66	17.69	18.30	75.26
	10 % A+0.5 % Cu	3.4402	61.03	3.31	15.62	15.97	78.04

A: *Emblica officinalis G.* (Amla), Cu: Copper sulfate.

Table 6. Color characteristics of silk fabrics treated with DI water-extracted natural dyes with and without mordants

Natural dye	Mordant	*K/S* value	Color coordinates				
			L^*	a^*	b^*	C^*	h^o
Diospyros Kaki	Nil	2.2310	90.18	1.59	18.41	18.48	85.06
	10 % A	6.5077	66.44	7.27	28.63	29.54	75.75
	10 % A+0.5 %Cu	7.2472	58.49	9.16	27.24	28.74	71.41
Dioscorea Cirrhosa	Nil	1.8714	80.16	9.70	26.34	28.07	69.78
	10 % A	5.0506	70.76	11.58	31.74	33.79	69.96
	10 % A+0.5 %Cu	7.4266	52.35	11.54	27.17	29.52	66.99
Millettia	Nil	0.9399	76.89	10.94	28.70	30.71	69.12
	10 % A	6.0371	69.88	8.65	32.23	33.37	74.98
	10 % A+0.5 % Cu	8.1933	53.52	10.31	28.36	30.18	70.02
Ecliptae	Nil	7.1148	72.69	2.93	30.49	30.63	84.52
	10 % A	8.4399	59.03	8.28	29.42	30.57	74.28
	10 % A+0.5 % Cu	9.2877	48.25	8.31	25.91	27.21	72.22
Macrocarpa Nucuma	Nil	2.8301	69.98	-0.44	10.55	10.56	92.40
	10 % A	6.8538	67.61	6.65	28.52	29.28	76.88
	10 % A+0.5 % Cu	7.1825	54.64	5.96	23.70	24.44	75.89

A: *Emblica officinalis G.* (Amla), Cu: Copper sulfate.

Similar phenomena can be observed for cotton and silk fabrics treated using DI water-extracted natural dyes with and without mordanting, as shown in Tables 5 and 6, respectively. Again the pre-dyeing process increased the *K/S* value of both cotton and silk fabrics regardless whether one or two mordants were used. However, the differences in *K/S* values obtained using the natural mordant alone and those using both natural and metal mordants were less marked. For cotton fabrics treated with DI water-extracted diospyros kaki and ecliptae, pre-dyeing with both mordants even attained a lower *K/S* value than using the natural mordant alone. In contrast, all silk fabrics showed higher *K/S* values when pre-dyed with both mordants, indicating the efficacy of metal mordant in enhancing color strength of silk fabrics [15]. Insoluble metal tannates were formed between copper sulfate and tannin from *Emblica officinalis G*, which also enhanced color fixation [12].

Overall, the *K/S* values were higher in silk than in cotton fabrics, indicating greater color strength in pre-mordanted silk treated with DI water-extracted dyes. The difference is attributed to silk being a protein fiber and having more functional groups than cotton. As a result, silk has greater affinity for natural dyes, which in turn enhances the fixation of natural colorants on fabrics. This finding is consistent with that reported by Prabhu *et al.* [12].

Regarding the colorimetric data reported in Tables 3-6, the L^* values of pre-mordanted cotton and silk fabrics treated with ethanol- and DI water-extracted natural dyes were lower than those without mordanting. In other words, brightness of the dyed cotton and silk fabrics decreased, again evidencing the darkening in color of fabrics by pre-mordanting. Moreover, using natural mordant alone effected a greater change in L^* value than using both natural and metal mordants, revealing the efficacy of tannin in enhancing color strength.

Variations in color characteristics (a^*, b^*, C^*, and h^o) shown in Tables 3-6 reveal that pre-mordanting changed the hue of cotton and silk fabrics, creating attractive colors and demonstrating good dyeing effect. Different color characteristics were produced by plant dyes extracted using different solvents and when applied on different fabrics. As shown in Tables 3 and 4, the color characteristics of cotton fabrics treated with ethanol-extracted diospyros kaki are located in the second quadrant of the CIE $L^*a^*b^*$ color space while those of silk fabrics are in the first quadrant. On the other hand, the color characteristics of cotton and silk fabrics treated with ethanol-extracted ecliptae are in the second quadrant while those treated with ethanol-extracted dioscorea cirrhosa, millettia, and macrocarpa nucuma are all in the first quadrant. As shown in Tables 5 and 6, the color characteristics of cotton and silk fabrics treated with the five DI water-extracted natural dyes are all in the first quadrant.

Ultraviolet Protection Factor (UPF)

Tables 7 and 8 list the UPF of cotton and silk fabrics treated with natural dyes extracted using ethanol and DI water, respectively. As can be seen, untreated fabrics showed poor or no protection against UVR. In contrast, treatment with natural dyes increased the UPF of both cotton and silk fabrics, indicating better or improved protection against UVR. As seen in Table 7, dyeing with ethanol-extracted dioscorea cirrhosa, millettia, ecliptae, and macrocarpa nucuma led to significant increase in UPF of cotton fabrics, endowing them with "Very Good" protection against UVR (UPF ranging from 26.31 to 39.82). In contrast, natural dyes extracted using ethanol had little impact on UPF of silk fabrics. On the other hand, the increase in UPF of fabrics treated with DI water-extracted natural dyes was even more significant (UPF ranging from 20.69 to 65.77). As seen in Table 8, treatment with DI water-extracted dioscorea cirrhosa, millettia and ecliptae increased the UPF rating of cotton fabrics to "Excellent" as compared with "Very Good"

Table 7. UPF of cotton and silk fabrics treated with ethanol-extracted natural dyes

Natural dye	Fabric	UV protection class	UPF (AS/NZS 4399)	Average UVA Transmittance (%)	Average UVB Transmittance (%)
Undyed	Cotton	No class	2.53	41.8	37.32
	Silk	No class	1.84	60.14	42.89
Diospyros Kaki	Cotton	No class	12.17	12.65	7.51
	Silk	No class	2.25	50.96	35.08
Dioscorea Cirrhosa	Cotton	Very good	33.36	4.35	2.65
	Silk	No class	3.79	33.01	20.63
Millettia	Cotton	Very good	39.82	3.63	2.26
	Silk	No class	6.33	23.2	12.51
Ecliptae	Cotton	Very good	31.75	2.3	3.32
	Silk	No class	13.86	5.74	7.15
Macrocarpa Nucuma	Cotton	Very good	26.31	4.77	3.46
	Silk	No class	6.9	20.84	11.49

Table 8. UPF of cotton and silk fabrics treated with DI water-extracted natural dyes

Natural dye	Fabric	UV protection class	UPF (AS/NZS 4399)	Average UVA Transmittance (%)	Average UVB Transmittance (%)
Undyed	Cotton	No class	2.53	41.8	37.32
	Silk	No class	1.84	60.14	42.89
Diospyros Kaki	Cotton	No class	7.5	14.2	12.65
	Silk	No class	8.36	14.41	9.96
Dioscorea Cirrhosa	Cotton	Excellent	65.77	2.22	1.34
	Silk	No class	10.05	14.21	7.98
Millettia	Cotton	Excellent	55.87	2.45	1.64
	Silk	Good	20.69	10.33	3.69
Ecliptae	Cotton	Excellent	42.33	2.36	2.41
	Silk	Very good	34.87	3.09	2.86
Macrocarpa Nucuma	Cotton	Very good	26.98	4.63	3.38
	Silk	No class	10.42	14.01	7.88

Table 9. UPF of cotton and silk fabrics pre-dyed with *Emblica officinalis G.* and treated with ethanol-extracted natural dyes

Natural dye	Fabric	UV protection class	UPF (AS/NZS 4399)	Average UVA Transmittance (%)	Average UVB Transmittance (%)
Diospyros Kaki	Cotton	Excellent	95.54	2.22	0.87
	Silk	Excellent	40.17	5.17	2.14
Dioscorea Cirrhosa	Cotton	Excellent	359.34	0.39	0.25
	Silk	Excellent	40.1	6.74	1.95
Millettia	Cotton	Excellent	134.39	0.9	0.72
	Silk	Excellent	55.45	3.31	1.63
Ecliptae	Cotton	Excellent	208.88	0.52	0.47
	Silk	Excellent	75.39	1.57	1.31
Macrocarpa Nucuma	Cotton	Excellent	181.28	0.82	0.51
	Silk	Very good	28.99	5.11	3.3

Table 10. UPF of cotton and silk fabrics pre-dyed with *Emblica officinalis G.* and treated with DI water-extracted natural dyes

Natural dye	Fabric	UV Protection class	UPF (AS/NZS 4399)	Average UVA Transmittance (%)	Average UVB Transmittance (%)
Diospyros Kaki	Cotton	Excellent	68.73	2.69	1.24
	Silk	Excellent	55.62	3.31	0.63
Dioscorea Cirrhosa	Cotton	Excellent	110.79	1.27	0.81
	Silk	Excellent	76.1	2.93	1.14
Millettia	Cotton	Excellent	118.86	1.62	0.72
	Silk	Excellent	81.19	2.13	1.15
Ecliptae	Cotton	Excellent	127.85	0.89	0.77
	Silk	Excellent	52.19	2.08	1.92
Macrocarpa Nucuma	Cotton	Excellent	63.92	2.36	1.4
	Silk	Excellent	53.9	2.48	1.81

in their counterparts treated with ethanol-extracted dyes. Of note is that silk fabrics treated with DI water-extracted ecliptae showed enhancement in UVR protection of "Very Good" UPF rating while those treated with ethanol-extracted ecliptae revealed little change in UPF.

Taken together, these results reveal that treatment with natural dyes after mordanting can increase UPF and the enhancement in UVR protection is greater and more significant in cotton fabrics than in silk fabrics, and in fabrics treated with DI water-extracted natural dyes than in those treated with ethanol-extracted ones. Among the five natural dyes, diospyros kaki showed the least impact on UPF of both cotton and silk fabrics; DI water-extracted dioscorea cirrhosa attained the highest UPF of 65.77 in cotton fabrics while DI water-extracted ecliptae achieved the highest UPF of 34.87 in silk fabrics.

The impact of mordanting on UPF enhancement is evidenced by the results shown in Tables 9 and 10. As can be seen, significantly better UVR protection is observed in both cotton and silk fabrics treated with ethanol- and DI water-extracted natural dyes. Almost all treated fabrics reached the highest UPF rating of "Excellent", with UPF of 359 in cotton fabrics pre-dyed with *Emblica officinalis G.*, followed by treatment with ethanol-extracted dioscorea cirrhosa. It is interesting to note combining pre-dyeing with natural mordant and treatment with natural pigment increased the effectiveness of ethanol-extracted natural dyes in enhancing UVR protection.

Conclusion

Results obtained from dyeing cotton and silk fabrics with natural pigments extracted from five plants using ethanol and DI water with and without mordanting revealed the following. *Emblica officinalis G.* had the highest total phenol content, followed by dioscorea cirrhosa. The presence of abundant phenolic groups in the natural dyes and mordant makes them effective colorants for fabrics. Cotton and silk fabrics dyed using ecliptae without pre-mordanting had the highest *K/S* values. Silk fabrics had higher *K/S* values than cotton fabrics, indicating greater color strength in pre-mordanted silk treated with DI water-extracted dyes. Natural mordant used before treatment with natural dyes contribute to significant enhancement in color strength, and *Emblica officinalis G.* alone could darken the color of cotton and silk fabrics dyed with plant pigment. Moreover, treatment with natural dyes after mordanting can increase UPF and the enhancement in UVR protection is greater and more significant in cotton fabrics than in silk fabrics, and in fabrics treated with DI water-extracted natural dyes than in those treated with ethanol-extracted ones. In summary, pre-dyeing with natural mordant followed by treatment with natural dyes extracted using environmentally-friendly solvents can enhance significantly color strength and UPF, offering directions for manufacturing textiles without environmental hazards but with good appearance and health benefits.

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