APPLYING BI–FUNCTIONAL DYEING AND UV PROTECTION ON PROTEIN TEXTILE MATERIALS WITH WASTE FROM USED TEABAGS AND MANGOSTEEN HULLS

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Received: 30 December 2016; Accepted for publication: 3 March 2017

ABSTRACT

This paper presents the connection among three factors of the eco–friendly approach and products: natural textile materials, natural dyes and utilization of waste. The silk and wool materials were chosen as they are both protein fibers that have natural dyes affinity. The dyes were extracted from wastes (mangosteen hulls and used tea–bags) with optimal conditions found during our experiments: 80 °C for 120 min with a 15 % w/v citric acid solution in a 1:10 ratio of mangosteen flakes to solvent and 100 °C for 60 min in a 1:20 ratio of spent tea powder to solvent. The silk dyeing and wool dyeing were carried out at separately proper temperature, time and concentrations. The effect on dyeing of mordant types with different salt–metals mordanting methods and mordant techniques – pre–mordanting, simultaneous mordanting and post–mordanting were undertaken. The K/S values were used for determining the fixation of dyes on textile materials as it reflects the surface luster shade of the dyeing products. The results helped to estimate the influence of dyeing processes on protein materials where low temperature (< 90 °C) and post–mordanting methods exhibited good effects. The UPF values above 29 measured on dye fabric proved the excellent UV protection, even with non–mordant dyeing.

Keywords: natural dyes, waste, UV protection, protein, textiles.

1. INTRODUCTION

Natural dyes have been well known for their use in coloring of food substrate, leather as well as natural protein fibers like wool and silk. They seemed to be replaced by synthetic dyes since 19th century with more reasonable prices, wider range of colors and applications, and better color–wash and light fastness. However, a reviving interest in dyeing textiles with natural dyes has risen in recent years due to their advantages in biodegradability, renewability, compatibility with the environment and low allergic reaction [1]. Natural dyeing of different textiles and leather has been continued, mainly in the sector for special and green products, along with synthetic dyes in large scale sectors for textile and apparel [2]. The advantages of eco–friendly natural dyes have become more significant importance nowadays due to the trend of using green materials and cleaner production. The consumers have become more concerned about the health and environmental impact of synthetic dyes in manufacturing. Some famous clothing and accessories retailer in Europe had strict policy to ban harmful toxins and eradicate all releases of hazardous chemicals throughout its entire supply chain and products. A number of traditional printing and dyeing pattern was encouraged to switch to natural dyes to improve their export market in Europe. Despite the limitation of color compared to synthetic dyes, natural dyes can supply a certain range of colors and shades and can be obtained from various parts of plants, including roots, bark, leaves, flowers, and fruits [3]. Colors in the ranges of red, browns and oranges were found earliest, and then followed by blues, yellows and rarely green appearing. In this study, we utilized the used teabags and the hulls of mangosteen for dyes extraction as they are all waste and can be collected from the daily market. Those natural dyes were also proved that they offer same or more protection than synthetic dyes from UV radiation [4–6]. Dyeing was applied on protein based materials (silk fabric). Their protectiveness depends on types of dyes, dye concentration, UV–absorbing properties and textile materials. Those tannins–based dyes (the galls of Quercus infectoria) together with flavonoid, anthocyanin in the compound exibited UV–protection capacity [5, 6]. UV radiation transmittance of fabrics was measured by a spectroradiometer. Transmittance measurements were used to calculate the ultraviolet protection factor (UPF). Our results showed that fabric dyed with extraction from used–tea bag and mangosteen hulls obtained a good to very good UV protection according to international standard (UPF from 29 to 46 with dyes from mangosteen hulls extracts and UPF 26 to 42 with dyes from used ted bag extracts). This demonstrated a feasible application of using natural colorants as bi–functional dyeing and UV protective treatment on noble textile products.

2. MATERIALS AND METHODS

2.1. Fabric

The commercial 100 % silk fabrics, plain weave, weight 45.45 g/m^2, warp density 68 threads cm^{-1}, weft density 44 threads cm^{-1}, scoured and bleached (supplied by Toan Thinh Silk Co. Ltd. Vietnam) were used. Samples were prepared with the size of 21 cm × 21 cm each corresponding to 2 gram.

2.2. Dye extraction from hulls of mangosteen and used tea–bags

Mangosteen hulls were purchased from Lai Thieu market in Binh Duong, Vietnam. The used tea–bags were collected from commercial Lipton tea–bags. The hulls of mangosteen were dried under sunlight at least 24 h and crushed by a mechanical crushing machine to obtain mangosteen hulls coarse powder. The used tea–bags were dried under sunlight 24 h. Those were the raw materials for dyes extraction. The crushed hulls of mangosteen (100 g) were extracted with 1 L of distilled water at 80 °C for 2 h. The used tea–bags (50 g) were extracted with 1 L of distilled water at 100 °C for 1 h. They were then filtered 2 times by filter paper to obtain dyeing solution.

2.3. Mordants

These laboratory–grade mordants were used: aluminium potassium sulphate ($AlK(SO_4)_2.12H_2O$), ferrous sulfate ($FeSO_4.7H_2O$), and copper(II) sulphate pentahydrate ($CuSO_4.5H_2O$) supplied by AR, China. Mordanting concentration is 5 w/v%.

2.4. Dyeing

The dyeing processes were carried out in a DP–NTN experimental dyeing machine Ø42 mm from Dai Phuoc, Vietnam and a drying machine (China) was used for the drying of the dyed fabrics. To study the effect of dye concentration on the dyeing process, four concentrations of hulls of mangosteen extracted dye were chosen: 25, 50, 75 and 100 v/v%. The similar concentrations were applied for used tea–bags extracted dye solution. The concentration 75% of hulls of mangosteen extracted dye solution was chosen to investigate the effect of different mordants, different mordanting methods, temperature (50 °C, 70 °C, 90 °C), and time (30 min, 60 min, 90 min) on the dyeing process. The concentration 100% of used tea–bags extracted dye solution was chosen to investigate the effect of different mordants, temperature (60 °C, 80 °C, 100 °C), and time (30 min, 60 min, 90 min). Liquor ratio of dyeing was 1:40. After dyeing, the samples were washed with deionized water to remove any unfixed dye and dried at 60 °C.

2.5. Color measurement and fastness testing

CIE L*a*b* values were measured using spectrophotometer (Datacolor 3890). The color strength of the dyed samples was evaluated using the K/S values generated by the spectrophotometer (Datacolor 3890). K/S is a function of color depth and is calculated by the Kubelka–Munk equation, K/S = (1 – R)2/2R, where R is representative of surface reflectance, K is light absorption coefficient, and S is the light scattering coefficient. The color fastness to washing and rubbing of the dyed samples was determined according to ISO 105–C06 A1S: 1994 and ISO 105–X12: 2001 by Testex instrument, respectively. The tests were implemented at Textile-Dyeing Laboratory of Thanh Cong Textile Garment Investment Trading Joint Stock Company (TCG), Vietnam.

2.6. Evaluation of UPF

The transmittance and UPF values of the original silk fabrics and silk fabrics dyed with extracts were measured using a Shimadzu UV3101 PC according to AATCC 183–2014. Fabrics with a UPF value in the range of 15–24 are defined as providing “good UV protection”, 25–39 as “very good UV protection”, and 40 or greater as “excellent UV protection” according to ASTM D 6603–2007. There is no rating assigned if the UPF value is fewer than 15. The tests were implemented at Vietnam Textile Research Institute, Hanoi, Vietnam.

3. EXPERIMENTAL RESULTS

3.1. Optimization of dyeing conditions with K/S and color hue changes

The optimization of dyeing conditions with used–teabag extracts was investigated with the changes of main dyeing factors (temperature, time, dye concentrations, mordant). Those had great effects on the color strength, shades and fastness of the fabrics. Temperature and time are important factors due to the sensitivity of fiber and dye to those factors. According to previous research on natural silk dyeing, we selected 80 °C, pH 4 and 60 min dyeing time as standard dyeing condition [1] to evaluate the influence of mordant on dye color. Figure 1 (left) showed tendency of highest K/S values for iron sulfate silk mordant, then copper sulfate salt. The fabrics dyed without mordant gave the yellow–brown shade while the fabrics dyed with aluminum potassium sulfate and copper (II) sulfate gave the yellow–dark brown shade. Dyeing with iron (II) sulfate mordant gave fabrics the duller and darker shade. Due to the co–existence of iron (II) sulfate and iron (III) sulfate on fiber, the spectra were overlapped leading to the great change on wavelength and to the change of darker color on fabric. However, at 400 nm wave length, copper sulfate salt exhibited the most effectiveness on color strength of fabric. In this case, copper sulfate salt is preferred to iron sulfate salt, as it also maintain the original color than iron sulfate salt. Figure 1 (right) with copper sulfate salt mordant guides to the fact that both simultaneous and pre – mordanting are suitable, where post–mordanting process gave negative influence on dyeing. After dyeing the fiber, the mordant can give color surprises or perk up uninteresting colors. This is especially suitable for copper and iron mordanting. Alum tends to slightly remove some of the dye if carelessly used as a post–mordant [1].

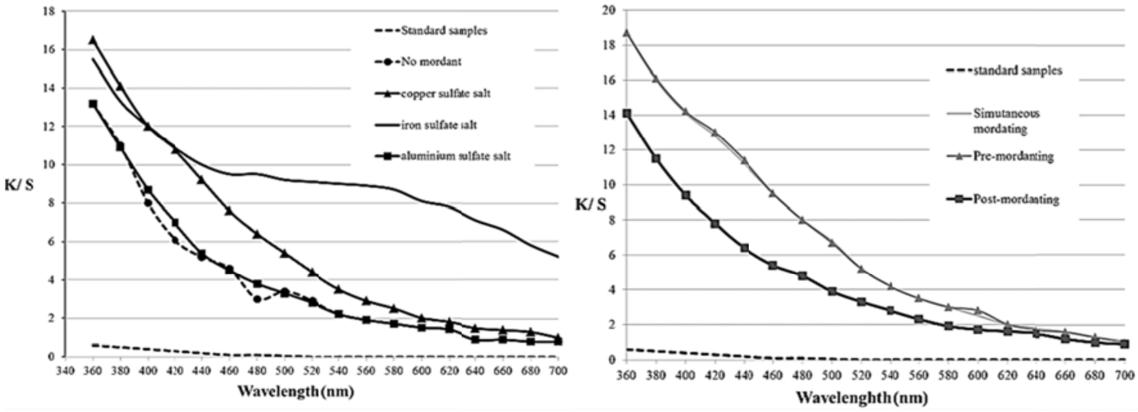

Figure 1. Effect of types of mordant (top) and mordant techniques (bottom) on silk dyed fabric with used tea bag extracts.

Figure 2 (left) showed that the K/S value of dyed silk fabric increased following the temperature and obtained best results at 100 °C at all visible wavelength. However, 80 °C is still considered to be the temperature for silk dyeing as protein fibers are sensitive to temperature and steam. The period of 90 min dyeing reached its best K/S values. The similar curves were recorded for periods of 60 min and 30 min, where silk fabric has not yet obtained plateau values of K/S.

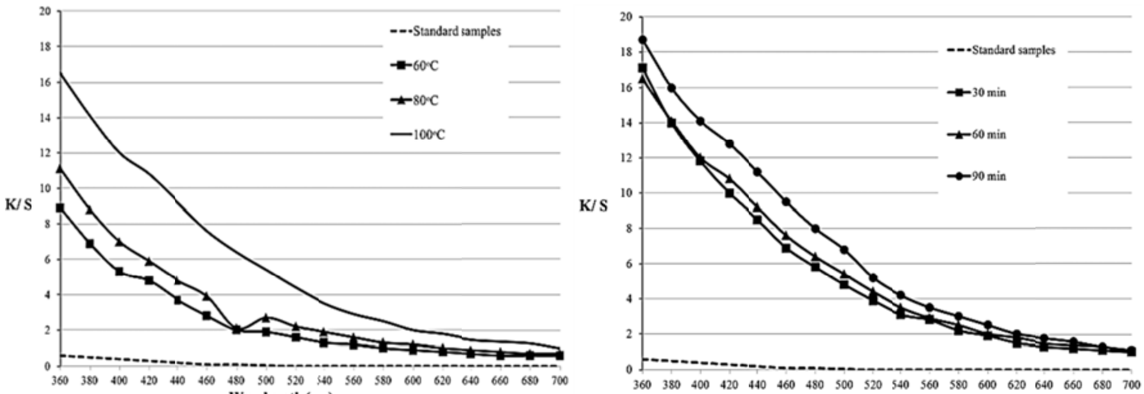

Figure 2. Effect of temperature (top) and dyed time (bottom) on silk dyed fabric with used tea bag extracts.

The K/S curves were also used to estimate the appropriate dye concentration on color. The optimization of silk fabric dyed with used tea–bags extract are: copper sulfate salt mordant, simultaneous or pre mordanting, 100 °C, 90 min and 100 v/v% concentration.

The similar method was applied to investigate the optimal dyeing condition for silk fabric dyed with mangosteen hulls extracts. The concentration of 75 v/v% was chosen to investigate the effect of different mordants, different mordanting methods, temperature and time on the dyeing process. The Lab color space values were additionally used together with K/S at 400 nm wavelength, as it is nearest to the ultraviolet zone and is typically the wavelength with the lowest %R value (the highest K/S value). As shown in Table 1, the K/S values gradually increased from 50 °C (1.9) to 90 °C (4.8). The dyes molecular were more active at high temperature and increase the dye absorbance on silk fabric. The differences of ΔE values between bank and dyed samples also demonstrate this comment.

Table 1. Effect of temperature on silk dyed fabric with mangosteen hulls extracts.

Temperature	L	a	b	C	ΔE	K/S
50 °C	72.39	1.79	26.13	26.19	17.31	1.9
70 °C	68.65	3.66	29.22	29.45	22.49	2.7
90 °C	60.57	7.31	29.63	30.52	30.38	4.8

Table 2. Effect of dyeing time on silk dyed fabric with mangosteen hulls extracts.

Temperature	L	a	b	C	ΔE	K/S
30 min	64.48	5.20	27.29	27.78	25.38	4.0
60 min	60.57	7.31	29.63	30.52	30.38	4.8
90 min	58.24	7.62	28.68	29.67	32.06	5.4

The increasing tendency of K/S values following the increasing of temperature was reported in Table 2. The highest K/S value obtained at 90 min dyeing time (5.4) together with highest ΔE values (32.06) proved the most effective dyeing time at 90 min.

Table 3 describes the effect of mordants on silk dyed fabric with mangosteen hulls extracts. The highest K/S (9.9) value obtained with $CuSO_4.5H_2O$ mordant, highest ΔE value (45.30) obtained with $FeSO_4.7H_2O$. However, iron sulfate salt changes the color tone to grey and dark grey while copper and aluminum sulfate salt maintains brown yellow to dark yellow tone. It can be explained by the action of Fe^{2+} to tannin in water to form Fe^{2+} tarat which possess blue black and convert to black during oxidization. On the other hand, $CuSO_4.5H_2O$ and $KAl(SO_4)_2.12H_2O$ gave brown–yellow tone as they have no compound with dyeing extracts.

Table 3. Effect of mordant on silk dyed fabric with mangosteen hulls extracts.

Temperature	L	a	b	C	ΔE	K/S
No mordant	60.57	7.31	29.63	30.52	30.38	4.8
$KAl(SO4)_2.12H_2O$	61.12	5.19	29.84	30.29	29.32	5.6
$FeSO_4.7H_2O$	40.69	0.63	12.95	12.97	45.30	7.9
$CuSO_4.5H_2O$	49.34	7.81	30.99	31.96	40.76	9.9

3.2. Assessment of color fastness to of silk fabric dyed with used tea bags and mangosteen hulls extracts

The color difference of silk fabrics dyed with used tea bags and mangosteen hulls extracts to washing and rubbing were evaluated, the color fastness to washing and rubbing of the dyed samples obtained the rating from 4–5, where the fastness rating goes step–wise from no visual change (5, best rating) to a large visual change (1, worst rating).

Table 4. Color fastness to rubbing of silk fabric dyed with used teabags and mangosteen hulls extracts at different mordant at dry condition and warp direction.

Mordant	Mangosteen hulls extract	Used tea bag extracts
Non	3–4	2
Iron sulfate salt	3–4	2–3
Copper sulfate salt	3–4	3–4
Aluminum sulfate salts	4	3–4

The fabric dyed with mangosteen hulls extracts exhibited better color fastness to rubbing than ones dyed with used tea bags extracts (Table 4). The results of 3–4 to 4 color fastness are common good to textile usages, especially with natural dyes [1]. In this study, even the absence of mordant, the color fastness to rubbing still showed the good values. The color fastness to washing is even better with 4–5 rating and after certain washing cycles as shown in Table 5. Tannin in both dyes has phenolic structure which can form metal complex with different mordant. The tannin is not dissolved in water leading to the good rating as shown in Table 4 and Table 5.

Table 5. Color fastness to washing of silk fabric dyed with used teabags and mangosteen hulls extracts at different mordant at dry condition and warp direction.

Mordant	Change in color		Staining to cotton	
	Mangosteen hulls extract	Used tea bag extracts	Mangosteen hulls extract	Used tea bag extracts
Non	4–5	4–5	4–5	4–5
Iron sulfate salt	4–5	4–5	4–5	4–5
Copper sulfate salt	4–5	3–4	4–5	4–5
Aluminum sulfate salts	4–5	3–4	4–5	4–5

3.3 UPF of silk fabric dyed with used tea bags and mangosteen hulls extracts

The samples with best color strength and color fastness to washing, rubbing were selected to measure the UPF values. The value % T(UVA) describes the average transmittance in the UVA region (315–400 nm). Table 6 describes UPF values of silk fabric dyed with mangosteen hulls extracts, where the UPF values achieved from "very good" (25–39) to "excellent" (> 40) ultraviolet protection standard. The mordant plays an important role in the UV protective property of silk fabrics due to the lower UPF values of non–mordant dyed fabric.

Table 6. UPF values of silk fabric dyed with mangosteen hulls extracts (90 °C, 60 min, 75 v/v%, O1–non–mordant, O2– mordant $KAl(SO_4)_2.12H_2O$, O3– mordant $FeSO_4.7H_2O$, O4–mordant $CuSO_4.5H_2O$.

Samples	UPF	% UV–A radiation Blocked	% UV–b radiation Blocked
O1	29.4	95.1	97.0
O2	38.2	96.4	97.5
O3	35.7	96.6	97.3
O4	46.5	97.2	97.9

It can be concluded from Figure 3 that all dyed samples with used tea bag extract had a significantly higher UPF value than the undyed reference samples, hence offering higher protection against harmful UV radiation than the undyed reference samples. Sample 2 exhibited excellent UV protection (41.7). This is interesting results in this study, as even at low content of dyes extracted only from used tea–bag instead of from full leaves or fresh tea bag, the dyes concentration is still enough to bring good UV protection to silk fabric, especially with non–mordant dyeing.

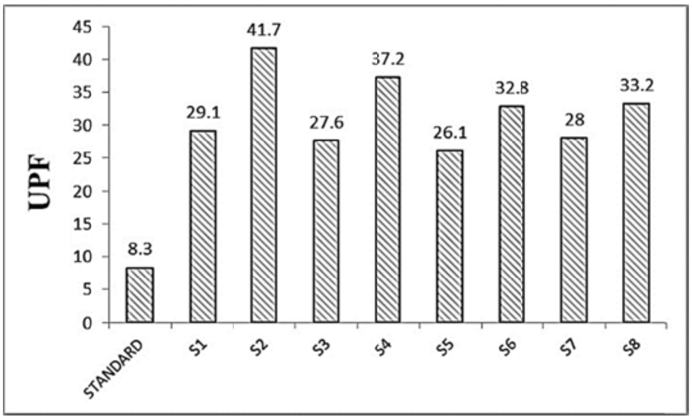

Figure 3. UPF values of silk fabric dyed with used teabag extracts with 100 v/v% concentration (S1 to S4 at 100 °C and 60 min, S5 to S8 at 80 °C and 60 min, S1 and S5 without mordant, S2 and S6 mordant $CuSO_4.5H_2O$, S3 and S7 mordant $FeSO_4.7H_2O$, S4 and S8 mordant $KAl(SO_4)_2.12H_2O$.

4. CONCLUSIONS

It can be stated from this study that the dye solution extracted from mangosteen hulls and used tea–bags can provided silk fabric with good to excellent sun protective property proved by UPF values. The K/S values were used to evaluate the influence of dyeing conditions (temperature, time, pH and dye concentrations, mordants). Optimal dyeing condition for dyeing was found for mangosteen hull extract dyeing (90 °C, 60 min, pre–mordanting with copper sulfate salt, 75 v/v% concentration at extract ratio of 1:20 g/L) and used teabag extract dyeing (100 °C, 90 min, pre–mordanting with copper sulfate salt, 100% v/v concentration at extract ratio of 1:20 g/L). Color strength and shade are improved with metallic sulfate salt mordants, where color can maitain in good condition even after washing test (rating of 4–5) and rubbing test (rating of 3–4). The results demonstrated that the UPF values of all selected samples with good color strenght and fastness achieved from very good to exellent ultraviolet protection standard. The mordant plays an important role in the UV protective property of silk fabrics due to the low UPF values of non–mordant dyed fabric. In particular, the utilization of used teabag and mangosteen hulls in this study contribute to the environmental protection and materials saving.

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