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EFFECT OF BRASI-COLOR DYE ON UV PROTECTION OF BAMBOO KNITTED FABRICS

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Abstract: *Even natural dyes have several limitations such as high sensitivity to washing, light, pH, and low color strength and seasonal variation, their use is largely encouraged due to their renewability and multi-functional properties. In this study, 100% bamboo knitted fabric was dyed with Brasi-Color, a dyestuff extracted from brazilwood. The UV-VIS spectra demonstrate the presence of brazilin at pH 4 and of brazilein at pH 7 and 10. The molecular structure of the brazilein is changed at higher pH, due to deprotonation at the OH group of C3. The dyeing parameters and their effect on the dye exhaustion were investigated to optimize the dyeing method and to evaluate the ultraviolet protection factor (UPF). The optimal value was selected based on the highest degree of exhaustion, the dyeing uniformity and the highest color intensity. The maximum degree of exhaustion was achieved for 0.05% dye concentration, pH 7, 90 minutes dyeing at 90^{0}C. Even mean UPF, UVA and UVB transmission largely depends on process dyeing parameters, all the fabrics demonstrate an excellent UV protective effect (UPF >50+) and a very low transmission on both UVA and UVB region, being able to protect the human body against the harmful effects of UV rays.*

Key words*: Natural dye, brazilwood, UPF, UV-VIS spectra, exhaustion degree*

1. INTRODUCTION

Brazilin is the red pigment obtained from the heartwood of the tree Ceasalpinia sappan Linn. [1], used to dye textiles and prepare pigments and inks. Brazilin is colorless or pale yellow due separation of the two chromophores existing on the molecule. Under the influence of oxygen and light, brazilin is converted to brazilein due to the oxidation of one hydroxyl group to a carbonyl group. In brazilein, the quinone structure is conjugated with aromatic ring, acting as a chromophore absorbing at higher wavelengths. As all the natural dyes, brazilein is very sensitive to oxygen, temperature, pH, which modifies its chromophores. Therefore, it is necessary to optimize the dyeing process to avoid or minimize the photooxidation and to stabilize the fabric color.

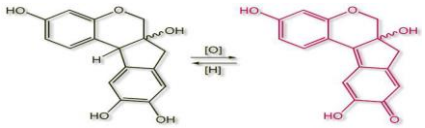


Fig. 1: *Brazilin (reduced form) and brazilein (oxidised form) [2]*

As studies [3] have demonstrated, brazilin and brazilein have anti-inflammatory, anti-bacterial, antineoplastic, antioxidant and UV protective effects [4]. The overexposure to UV rays may lead to keratosis and premature aging of the skin, cataracts and blindness, skin cancers [5]. The dyed clothes represent one of the most effective ways to protect the human body against the harmful effects of UV radiation. In this paper, a systemic approach of dyeing parameters of bamboo with dyes extracted from brazilwood was assessed to select the fabrics with high degree of UV protection.

2. MATERIALS AND METHODS

2.1. Materials

100% bamboo knitted fabric, 222g/m^2, 0.762mm thick, fabricated in INCDTP. Brasi-Color: dyestuff extracts of brazilwood, kindly provided by NIG Nahrungs - Ingenieurtechnik GmbH, Austria; Chemicals: CH_3COOH and Na_2CO_3 used for adjusting the pH.

2.2. Optimization of bamboo dyeing parameters

Optimization of dyeing parameters was performed to evaluate the appropiate conditions for the dyeing of bamboo fabric with Brasi-Color. It was considered as the optimal value, the value at which the highest degree of exhaustion was obtained and the fabric was uniformly dyed. In each optimization experiment, the values of the parameter to be optimized was varied while maintaining all other parameters constant, and the optimal value from the previous experiment was further used.

2.3. Characterization

The dyebath exhaustion was assessed by recording the absorbance of dyebath solutions before and after dyeing using UV- VIS- NIR spectrophotometer (Lambda 950, Perkin- Elmer, USA). The percentage of exhaustion was calculated with the equation (1):

$$E\% = 100 \times (A_i - A_f)/A_f \quad \textbf{(1)}$$

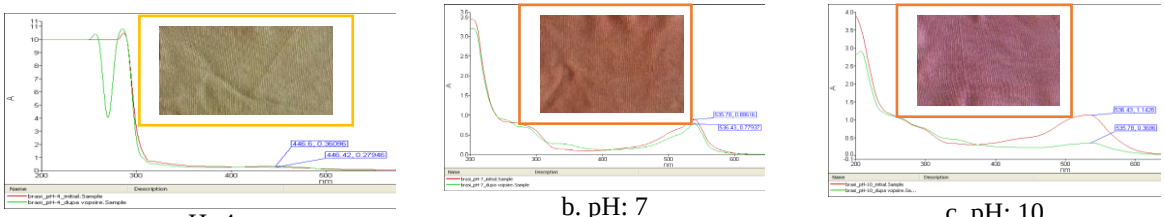
where, A_i and A_f are the concentrations of the dye bath before and after dyeing. The ultraviolet protection factor (UPF) of each dyed fabrics were measured on Carry 50 spectrophotometer (Varian, Australia) fitted with a specific accessory and dedicated software, according to AS/NZS 4399:1996 standard. Depending of UPF rating, the fabrics are classified as providing moderate (UPF 10 – 19), high (UPF 20 – 29), very high (UPF 30 – 49) and maximum (UPF > 50) protection [6].

3. EXPERIMENTAL

3.1. pH optimization

The bamboo fabrics were dyed with 0.1% Brasi Color at different pH(4, 7, 10) maintaining constant the temperature (80^{0}C), the dyeing time (60min.) and ratio M: L = 1: 60. The UV-Vis spectra were recorded on diluted solutions, dilution factor of 3:1 at pH 4 and 30:1 for pH 7 and 10. The optimal pH was considered that pH at which the highest degree of exhaustion was obtained, and the fabric has the highest color intensity and uniformity by visual evaluation.

The color, UV-VIS spectra and the degree of exhaustion are shown in the Figure 2 and Table 1.



a. pH: 4 b. pH: 7 c. pH: 10

Fig. 2: *The appearance of dyed fabrics and UV-VIS spectra of the Brasi Color dyeing baths: a. pH: 4; b. pH: 7; c. pH: 10; red line: initial dye bath, green line: dye bath after bamboo knit dyeing*

The studies [7] assigned to aqueous solution of brazilein, three major absorption bands at 446 nm (band I), 541 nm (band II) and 276 nm (band III). Band I was associated with the absorption of the cinnamoyl system, and band III with the absorption of benzoyl ring. At pH 4, the maximum absorption occurs at 446 nm (Fig. 2a), the acidic species, AH, displaying a faint yellow color. The peak at 446 nm is considered typical for the identification of brasilein [2] while the maximum absorption at 292 nm is characteristics for brazilin which, shows electronic transition shifted in blue region due to the sp3 carbon atom at C9[8]. A red shift of the maximum wavelength is recorded as the pH increases due to the changes in molecular structure of the brazilein were deprotonation at the OH group of C3 takes place [9]. At pH 7 (Fig. 2b) and 10 (Fig. 2c), the peak is shifted to 536nm (anionic form A^-), the absorption of the orange and violet solutions being largely intensified.

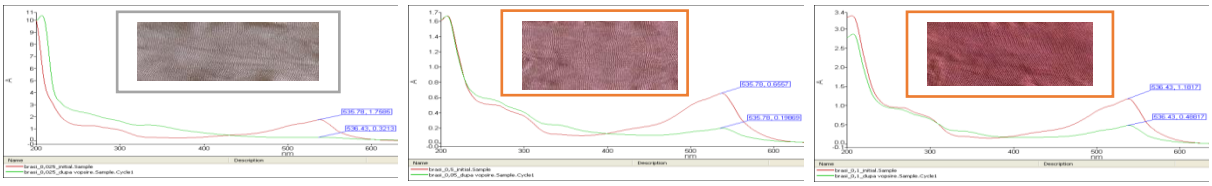
Table 1: *The exhaustion degree of 0.1% Brasi- Color solution at different pH*

pH	λ, nm	A_i	A_f	E, %	Color
4	446.5	0.28	0.36	-28.57	yellow
7	536	0.88	0.77	12.5	red-orange
10	540	1.14	0.37	67.54	move

The degree of exhaustion ((Table 1) increases with increases of the pH value of the dyeing bath from pH 4 to 10. The highest exhaustion degree is obtained at pH 10, but the uniformity and color intensity are higher at pH 7. More than that, as bamboo fabric is very sensitive at alkaline conditions, we have chosen pH 7 for the following experiments.

3.2. Optimization of the Brasi-Color concentration

The bamboo fabrics were dyed with different concentrations of Brasi Color, maintaining constant the former parameters. The UV-Vis spectra were recorded on diluted solutions, using a dilution factor of 6:1 for 0.025% Brasi-Color and 30:1 for 0.05% and 0.1% dye (Fig. 3 and Table 2).



0.025% BrasiColor 0.05% BrasiColor 0.1% BrasiColor

Fig. 3: *UV-Vis spectra of BrasiColor solutions before and after dyeing, pH 7*
Where: red: before dyeing; green: after dyeing

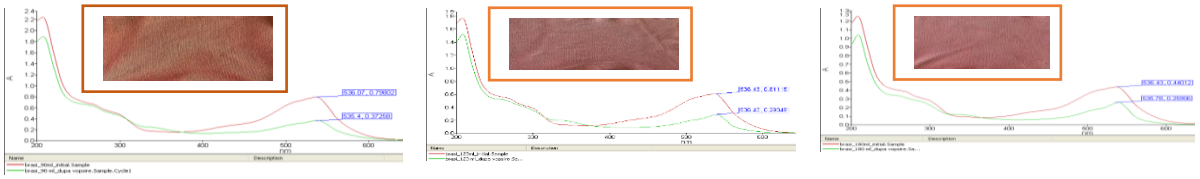
Table 2: *The exhaustion degree of Brasi Color dyebaths at different concentrations*

λ, nm	Dye concentration, %	A_i	A_f	E, %	Color
536	0.025	1.76	0.32	81.82	lavender
536	0.05	0.66	0.19	71.21	move
536	0.1	1.18	0.49	58.47	ruby

Increasing the dye concentration causes color intensification. The highest exhaustion degree is obtained at 0.025% dye concentration but the dyeing is relatively uneven and the color intensity is reduced. Therefore, 0.05% was chosen as the optimal dye concentration.

3.3. Optimization ratio textile material:dye solution

The bamboo fabrics were dyed at different ratio M:L maintaining constant the former parametrs. The effect of ratio material: dye solution on color intensity and degree of exhaustion of Brasi-Color of bamboo fabric is displayed in the Figure 4 and Table 3. The UV-VIS spectra were recorded on the initial and final dye solution with a dilution factor = 30:1.



a. **1:30** b. **1:40** c. **1:60**

Fig. 4: *UV-VIS spectra of dyeing baths: a. 1:30; b. 1:40; c. 1:60*

Table 3: *The exhaustion degree of Brasi-Color baths at different M:L ratio*

λ, nm	M:L	A_i	A_f	E, %
536	1:30	0.79	0.37	53.16
536	1:40	0.61	0.29	52.46
536	1:60	0.44	0.26	40.91

A wide variation shades is noticed at different M:L ratios determinated by the susceptibility to photo-oxidation and the inhomogeneity of the dye composition, which may consist of multiple components with different solubilities highly depending on solvent polarity, degree of polymerization of phenolics, interaction with other constituents and formation of insoluble complexes [10]. As the results show the highest degree of exhaustion was obtained at a ratio of 1:30 but the shade is very non-uniform. Consequently, a M:L of 1:40 was chosen for the next trial.

3.4. Optimization of dyeing time

The bamboo fabrics were dyed at for different durations under former constant dyeing parameters. The diluted solutions (DF = 30:1) of dye baths were recorded initially and after 45, 60 and 90 minutes of dyeing (Figure 5 and Table 4).

Table 4: *The exhausting degree of Brasicolor dyebaths at different dyeing time*

λ, nm	Time, min.	Ai	Af	E, %
536	45	0.49	0.38	22.45
536	60	0.49	0.33	32.65
536	90	0.49	0.28	**42.85**

As the dyeing time increases, the dye diffuses inside the fabrics until the dyeing equilibrium state is reached. As the results show, the maximum degree of exhaustion is attained after dyeing for 90minutes. Resuming, the optimum parameters to dye the cotton fabric are: pH 7, dyeing temperature: 80^0C, the BrasiColor concentration: 0.05% reported to the weight of fabric, fabric: dye solution = 1:40.

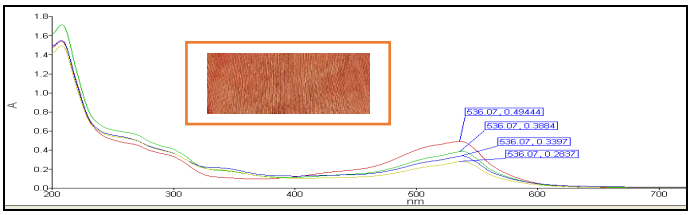


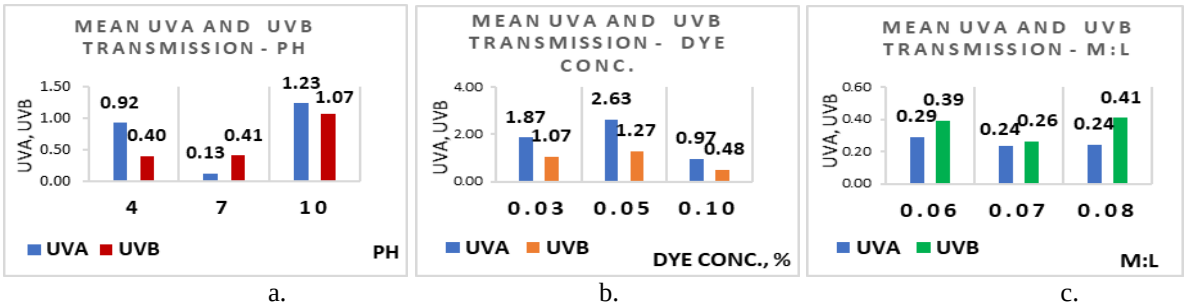
Fig. 5: *UV-VIS spectra of initial (red line) dye solutions and after 45 minutes (green line), 60 minutes (blue line), 90 minutes (yellow line)*

3.5. Ultraviolet protection factor (UPF) of dyed samples

UV protection provided by textile materials depends on various factors such as yarns type, fabric construction, porosity, density, moisture, type and concentration of applied dye. The results for each of the fabrics dyed in different conditions are displayed in the Table 5 and Figure 6.

Table 5: *UPF of the bamboo knit dyed with Brasi Color*

	Undyed knit	**Bamboo knit dyed with Brasi Color**									
		pH			**Dye concentration, %**			**M:L ratio**			**Time**
UPF values		pH 4	pH 7	pH 10	0.025	0.05	0.1	1:30	1:40	1:60	120min
Mean UPF	13.861	172.21	204.42	85.68	84.16	70.10	178.11	224.56	347.14	213.59	154.37
Mean UVA Transmission	9.623	0.924	0.129	1.232	1.868	2.633	0.966	0.289	0.237	0.244	0.717
Mean UVB Transmission	6.515	0.396	0.406	1.071	1.065	1.274	0.484	0.394	0.263	0.408	0.556
UPF calculate	13.204	144.76	173.52	66.62	71.95	54.84	148.25	194.28	288.83	191.71	143.05
UPF rating	**10**	**50+**	**50+**	**50+**	**50+**	**50**	**50+**	**50+**	**50+**	**50+**	**50+**



a. b. c.

Fig. 6: *Correlation of mean UVA and UVB transmission with dyeing parameters: a: UVA/UVB – pH; b. UVA/UVB –dye conc; c: UVA/UVB – material/dye solution ratio*

To minimize the harmful of ultraviolet radiation it is important that fabrics let to pass a minimum amount of UV rays, especially in the UV-B region. All the fabrics dyed at different pH have a low UV transmittance and a very high UPF value, being classified as excellent. Even mean UPF, UVA and UVB transmission largely depends on pH of dyeing, the lowest transmission of UVA rays is provided by the fabric dyed at pH 7. In the case of fabrics dyed at different

concentrations, the relative erythemal spectral efficiency is higher in the UV-B region compared to the UV-A region, responsible for the most UV harmful effects. Even at very low dye concentration (0.025%), the knitted fabric ensures an excellent protection (UPF 50). At 0.1% concentration, mean UVA transmission is 0.966 and UVB of 0.484, which is 2-3 times lower than that of the fabric dyed with the lowest dye concentrations. The mean UPF depends also, on the material: dyes solution ratio, the highest values being recorded for 1:40 ratio. As it is obviously from the UPF values, all the dyed fabrics are classified as having excellent UV protection (UPF values 50+). The best relative erythemal spectral effectiveness in the UV-B region is provided by the fabric dyed at the ratio 1:40.

4. CONCLUSIONS

Dyeing with natural dyes by the exhaust method is a difficult task due to non-homogeneity of dye composition and the large variation of color shade and intensity over a range of dyeing variables. The results of this study showed that simultaneous maximum exhaustion and intense color uniformity is not possible to be acquired in the case of natural dyes. Due to their strong absorption in UV domain, the dyed textile materials provide an excellent protection to UV radiation.

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