Silk fabrics Dyed with Archidendron jiringa pod - the Application of Color and UV Protective Properties

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Received 7 December 2017; Revised 28 March 2018; Accepted 2 April 2018

Abstract

Archidendron jiringa pod (AJP) has been extracted. Its dye ability of silk fabric has been studied together with its colorfastness and UV protection properties. The mordants such as aluminum potassium sulfate, ferrous chloride and sodium hydroxide were used to dye fabric. The color fastness to washing, water, perspiration, light and crocking of the dyed samples was determined according to AATCC test methods. In this study the UV protection properties were investigated on silk fabrics. The chemical functional groups of the dyes were characterized by using Fourier transform infrared spectroscopy (FTIR). Silk fabrics mordanted with ferrous chloride and dyed with AJP usually showed good UV protection levels even if undyed. These extracts yielded polyphenols, betalain dye, chlorophyll, carboxylic and djenkol acid contents. Therefore, it was suggested that AJP has the potential in producing functional dyes that could be imparted into the silk dyeing natural colourant system.

KEYWORDS: Natural dyes; Colour fastness; Silk; UV protection

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Introduction

Nowadays, the interest towards natural dye is growing as our lives are affected by pollution. Costumers concern more about the quality of goods to avoid toxic or allergic reactions. The production process together with the use of material and ethical problems may affect consumer’s decision. The growth of natural dye for textile development is steady [1]. Natural dyes can be obtained from plants, animals and minerals [2]. These natural dyes have been successfully applied to natural fiber fabrics such as cotton [3], wool [4], silk [5] and flax [6].

Djenkol Bean is known as common name “niang” in Thailand, “djenkol” in Indonesia, “krakos” in Cambodia, “jering” in Malaysia. Scientific name are *Archidendron jiringa* (Jack) I. C. Nielsen. The AJP has a broad, round shape and reddish color. The beans grow in large, dark purple pods (3 – 9 beans/pod) on the djenkol tree, which grows to 25 m (82 ft) in height. These beans resemble a large, flattened horse chestnut, and the crushed bean emits a faint sulfurous odor. Djenkol beans are a local delicacy in Indonesia, Malaysia, southern Thailand, and Myanmar. The beans are commercially available in markets during most of the year and are consumed raw, roasted, or fried. The djenkol bean contains the sulfur-containing amino acid, djenkol acid (CAS RN: 498-59-9, $C_{11}H_{23}N_3S_3O_6$) in the range of about 0.3 – 1.3 [7]. These pods are regarded as waste material during the processing in the food industry and the functional properties of this raw material. Therefore, it is possible to evaluate this pod as potential novel functional dyes. AJP is well known for having abundant gallic acid, tannic acid, ellagic acid and rutin contents. These AJP have broad applications in the areas of medicinal herbs and dietary plants potential use for cancer prevention and pharmaceuticals [8].

Overexposure to solar UV radiation has been identified as causing an increased incidence in skin problems such as sunburn, premature aging, allergies and skin cancers [9]. In order to avoid or limit these health risks, it is important to reduce the UV ray exposure with clothing, accessories and shade structures made of protective materials. Textiles have been shown to provide UV blocking properties but these characteristics depend on fiber type, fabric construction and nature of finishing chemicals. Dyed fabrics are more protective than undyed ones and the protection level rises with the increase in dye concentration [10]. In general, light colours reflect solar radiation more efficiently than dark ones [11], but part of the radiation penetrates more easily through the fabric thanks to multiple scattering. Moreover, most of the studies on this topic concern synthetic dyes. The high compatibility with the environment of naturally dyed textiles and their lower toxicity and allergic reaction have been arousing growing interest in the last 15 years and, for this reason, many studies have focused on the multifunctional properties of dyeing plants extracts, as shown by Islam et al. [12]. Nonetheless, as regards the UV protection properties of natural dyes, few researches have been performed on natural fabrics [13] and most of these concern animal fibres, as reported by Grifoni et al. [14]. Very few studies exist on the UV protection properties of natural dyes in combination with fabrics made of vegetable fiber maybe because very few natural dyes provide vegetable fibers with strong colours without the aid of mordants [13, 14]. An ecofriendly natural dyeing can however be achieved by replacing metal mordant with natural mordant, like tannic acid or other vegetable tannins [15], even if metal mordants such as potassium alum and aluminium sulphate can also be used in ecofriendly natural dyeing as their environmental toxicity is almost nil [16]. Tannins are water soluble phenolic compounds that have been used on textiles for several hundred years both as a pre-treatment and post-treatment factor to increase wash fastness [17] and light fastness [18], e.g. in cotton fabrics. The evaluation of the level of UV protection properties of natural colours needs to be supported by knowledge of the dyes chemical structure, absorption characteristics in the UV region, interaction and complexation with the premordanted substrate, as well as the ability to block or absorb the hazardous UV rays [14].

The objectives of this study were to explore the potential of AJP by investigating of dyeing, color fastness and ultraviolet protection properties of silk fabric using an aqueous extract of AJP as a natural dye. Different factors affecting dyeing ability were examined.

Materials and Methods

Extraction and dyeing

AJP were collected in July at Songkhla province, Thailand. A commercially scoured and bleached silk fabric (81.4 g m^{-2}, plain weave) was used, the method of pre-mordant dyeing was considered to be the most suitable for this study because it has the ability to improve the colorfastness of the dyed samples [19]. Amount of silk, dyeing, mordant and water were used with the weight ratio of 0.50:1.00:0.04:40.00. Three different mordants were used, potash alum ($AlK(SO_4)_2{\cdot}12H_2O$), ferrous chloride ($FeCl_3{\cdot}6H_2O$, 96% Ajax Finechem) and sodium hydroxide (NaOH, 99% Merck). The UV-vis spectra values of dye in the solution form were measured by UV-vis Spectrometer with integrating sphere attachment (Genesys 10S UV-vis spectrophotometer). The FTIR transmittance spectra of the samples were also analyzed in order to confirm chemical functional groups of the dyed.

Determination of color fastness

The color fastness to washing, perspiration, and water of the dyed samples were determined according to AATCC Test Method 61-2010, AATCC Test Method 15-2009, and AATCC Test Method 107-2009, respectively.

UV measurements

The UV protection factor (UPF) was determined on three fabric samples (3×1 cm^2). Each sample was taken of the fabric, fixed on a common slide frame and placed in UV-vis spectrophotometer. Transmission measurements were made in the 280 – 400 nm range with a 1 nm step (AATCC Test Method 183-2004). UPF was calculated according to Equation (1):

$$UPF = \frac{\sum_{280}^{400} E_\lambda S_\lambda \Delta_\lambda}{\sum_{280}^{400} E_\lambda S_\lambda T_\lambda \Delta_\lambda} \quad (1)$$

where: E_λ is the relative erythemal spectral effectiveness, S_λ is the solar spectral irradiance, T_λ is the average spectral transmittance of the specimen (measured) and Δ_λ is the measured wavelength interval (nm). UPF values higher than 40 were reported as 40 corresponding to the highest UV-protection category (excellent protection, Table 1).

Table 1 UPF categories with relative transmittance and protection level

UPF range	Protection category	Effective UVB_{eryt} transmission (%)
< 15	Insufficient protection	> 6.7
15 – 24	Good protection	6.7 – 4.2
25 – 39	Very good protection	4.1 – 2.6
40 – 50, 50+	Excellent protection	≤ 2.5

Results and Discussion

The coloration and fastness of dyed silk fabrics

The silk fabrics colors with AJP dyed with various mordants are shown in Fig. 1 (a) – (d). The obtained colors show that silk fabrics dyed without mordant had dark brown color, while those mordanted with ferrous chloride and aluminum potassium sulfate produced of dark purple color shades. With sodium hydroxide, the color brown shade. This may be associated with the change of ferrous chloride into a ferric form by reacting with oxygen in the air [20]. Additionally, the betalain dye in the AJP extract combine with sodium hydroxide to form complexes, which also result in brown shade of silk fabric.

The intensity of the extracted liquor samples was measured in terms of the level of absorption on a UV-visible spectrophotometer. From Fig. 1(e) it was found that the wavelength of maximum absorption for the extracted liquor was at 278 nm. This was the wavelength selected for UV-visible spectrophotometric measurements. Fig. 1(e) shows that the maximum absorption values of the extracted AJP dyed with ferrous chloride, aluminum potassium sulfate and sodium hydroxide were found in the 250 – 350 nm wavelength range, which is similar to the absorption range for gallic acid Fig. 1(e) [19]. Higher absorbance values indicate that the color of dye solution intensifies with increasing pH [2]. It is proposed that AJP dyed with sodium hydroxide might be able to high pH.

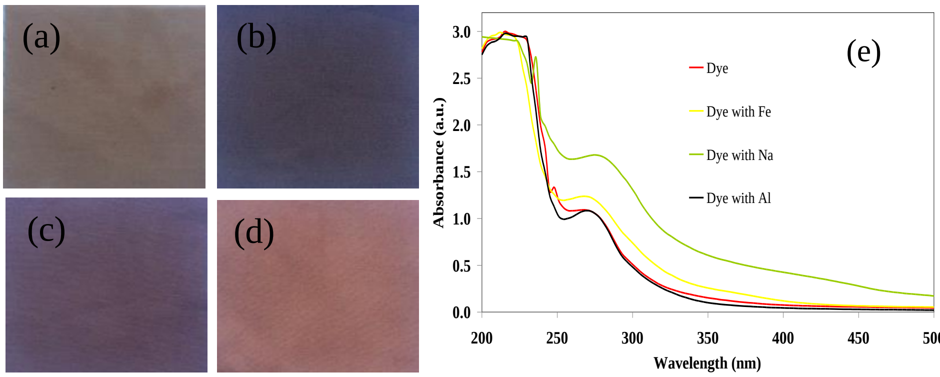


Fig. 1 Silk fabrics colors with AJP dyed with various mordants (a) Without mordanting, (b) $FeCl_3$, (c) Al $K(SO_4)_2$, (d) NaOH and (e) UV-Visible absorption spectrum of extracted AJP liquor at different mordants.

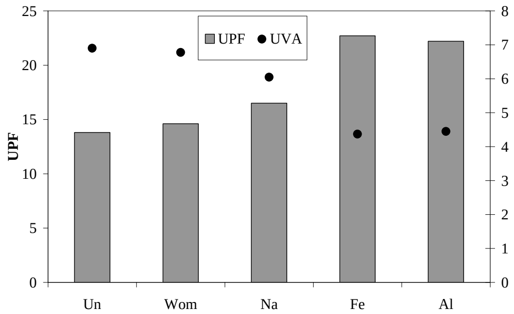
Table 2 shows that the wash fastness ratings of both with-out mordanted and mordanted dyed samples were fair to good (3 – 4), whose rating was good to very good (4 – 5). This drastic color change may be attributed to (a) the ionization of the hydroxyl groups in the dye molecules under the alkaline condition of the standard detergent solution [21] or (b) the decomposition of the dye itself, resulting in a colorless or a differentially colored compound [21]. The ratings obtained for color fastness to water in terms of the degree of color change and color staining were good to very good (4 to 4 – 5), as shown in Table 2. The color fastness to perspiration in acid conditions of fabrics dyed with and without mordants ranged from 4 to 4 – 5 (good to very good), as seen in Table 2.

Table 2 Colorfastness to washing, water and perspiration.

Fastness	washing at 40 °C				water				perspiration			
	Without Mordant	NaOH	$FeCl_3$	$AlK(SO_4)_2$	Without Mordant	NaOH	$FeCl_3$	$AlK(SO_4)_2$	Without Mordant	NaOH	$FeCl_3$	$AlK(SO_4)_2$
Color change	4.0	4.0	3.5	3.5	4.5	4.5	5.0	4.5	4.0	4.0	4.5	4.0
Color staining												
Acetate	4.5	4.5	4.5	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5
Cotton	3.5	3.5	3.5	3.5	4.5	4.5	4.5	4.5	4.5	4.5	5.0	4.5
Nylon	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	5.0	4.5
Silk	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	5.0	4.5
Viscose rayon	4.0	4.0	4.0	4.0	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5
Wool	4.5	4.5	4.0	4.0	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5

Transmittance and UPF measurements

The results were reported by Grifoni et al. and Feng et al. [14, 22]. In similar experiments in which the mordants used during the dyeing process did not show any UV-absorbing capacity, in the present experiment the first mordanting markedly affected the UV-protection properties of all silk fabrics. The UPF value remains lower than 15 (the minimum protection level as defined in Table 1). The protection category of all other silk fabrics moved from no protection to good protection for $FeCl_3$ and $AlK(SO_4)_2$ were used as mordant. The different effect of mordanting in this experiment in comparison with those previously mentioned was ascribable to the use of natural mordant containing tannins. Indeed, the main constituents of the djenkol beans pod are gallic acid, tannic acid, ellagic acid and rutin contents [8]. As already stated by many authors [8], tannins absorb UV radiation with an efficiency similar to carotenes and anthocyanins, and provide the same protection from UV damage that accessory pigments do. Similar behavior was also shown in Fig. 3, however the UPF value of AJP with $FeCl_3$, NaOH and $AlK(SO_4)_2$ dyed silk fabric slightly exceeded the threshold of 15, corresponding to a good UV protection, even if the UPF variability was high.



Note: Un = Undyed, Wom = With-out mordanting, Na = NaOH, Fe = $FeCl_3$, Mud = Mud and Al = $AlK(SO_4)_2$.

Fig. 2 UPF (bars) and UVA transmittance (black dots) for dyed silk fabrics mordanted. Bars and dots are means of three measurements.

Generally, in all the cases in which UPF reached at least the good protection level UVA transmittance was also in range 4.2 – 6.7% (Fig. 2), which the American Association of Textile Chemists and Colorists (AATCC).

The threshold above which photosensitive skin disorders, like chronic actinic dermatitis and solar urticarial can be aggravated [23]. Nevertheless high UPF do not necessarily imply low transmission in UVA wavelengths, as already found by Gambichler et al. [11, 19, 24]. In this study, for example, $FeCl_3$, NaOH and $AlK(SO_4)_2$ with AJP dyed that had UPF corresponding to good protection, showed UVA transmittance values slightly in range 4.2 – 6.7 %.

FTIR analysis

The band frequencies of the spectra obtained with their assignment are given in Fig.3. The FTIR spectra of the AJP dye consisted of six main groups of absorption bands in the wavelength range of 400 – 4000 cm^{-1} (Fig. 3). The intense band detected in the 3300 – 3500 cm^{-1} region and 1300 cm^{-1} originated from compounds with –OH groups such as water and ethanol, which are major compounds in these samples, The bands in the region of 3270 – 3400 cm^{-1} were assigned to the O-H ethanol (Betalain dye) and region 2900 – 3000 cm^{-1} can be assigned to the C-H (chlorophyll) was useful in this work. The bands in the region of 400 – 800 cm^{-1} can be assigned to the polyphenols. These wavelengths are part of the fingerprint region and include infrared typical absorption of phenolic molecules such as the stretching band of carboxylic (C=O) groups (1600 – 1630 cm^{-1}). The peaks at 1380 cm^{-1} are attributed mainly due to C-N vibrations [25]. Betalains are water-soluble nitrogen-containing pigments [26], which comprise the red-violet betacyanins and the yellow betaxanthins [26]. They are ammonium conjugates of betalamic acid with cyclo-DOPA and aminoacids or amines, respectively [27], whose chromophore is a 1,7-diazaheptamethinium system [28], represent one of the most important natural pigment classes.

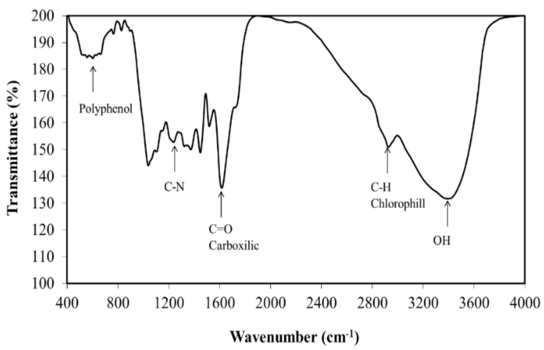


Fig. 3 FTIR spectra of AJP dye.

Conclusion

The purpose of this study was to investigate the colorfastness and UV protection properties of silk fabrics dyed with AJP natural dyes. It was found that dyed samples present interesting color fastness and ultraviolet protection properties. Further improvement in color yield was observed with different types of mordanting. Each mordant yielded different color shades from dark brown to dark purple for ferrous chloride and aluminum potassium sulfate, and color shade is brown for sodium hydroxide. AJP dyed silk fabric exhibited fair to good and good to very good fastness to washing. The water and perspiration fastness ratings were good to very good. In this study the mordanting affected the UV-protection properties of all silk fabrics. A very good protection level was reached by silk mordanted with ferrous chloride and dyed with AJP. This result indicates that AJP contains high polyphenolic, betalain dye, chlorophyll and djenkol acid content. These colorants might be alternative sources to synthetic dyes.

Acknowledgements

This work was supported by the Higher Education Research Promotion and National Research University project of Thailand, Office of the Higher Education Commission. We would like also to acknowledge the Faculty of Engineering, Rajamangala University of Technology Srivijaya, Songkhl and Materials Engineering Research Center (MERC), Faculty of Engineering, Prince of Songkla University for their facility supports.

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