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DYEING SILK FABRICS WITH STINK BEAN POD (*PARKIA SPECIOSA* HASSK.) NATURAL DYE IN THE COLOR FASTNESS AND UV PROTECTION

M. MASAE [1,]*, L. SIKONG [2], P. CHOOPOOL[2], P. PITSUWAN[1], W. SRIWITTAYAKUL[3], A. BONBANG[1], N. KIMTHONG[1]

[1]Department of Industrial Engineering, Faculty of Engineering, Rajamangala University of Technology Srivijaya, Songkhla, Thailand
[2]Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla, Thailand
[3]Department of Industrial Technology, Faculty of Engineering, Rajamangala University of Technology Srivijaya, Songkhla, Thailand
*Corresponding Author: susumeme1983@yahoo.com

Abstract

This paper describes natural dye extracted from stink bean pod (*Parkia speciosa Hassk.*) which was dyed on the silk fabric. The mordants as aluminum potassium sulfate, iron chloride, sodium hydroxide and mud were used to dye fabric using three different dyeing methods: pre-mordanting, meta-mordanting and post-mordanting. 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 on silk fabrics were investigated. The chemical functional groups of the dyes were characterized by Fourier transform infrared spectroscopy (FTIR). The results revealed that the dyeing silk fabrics with stink beans pod were fair to good fastness to washing and crocking and very poor to poor light fastness with the exception of samples mordanted with iron chloride. The water and perspiration fastness ratings were fair to good. Silk fabrics mordanted with iron chloride and dyed with stink bean usually showed good UV-protection levels even if undyed. These extracts gave polyphenolic, betalain dye and chlorophyll content. Therefore, it ~~was~~ suggested that stink bean pod has the potential in producing functional dyes that could be imparted into the silk dyeing natural colorant system.

Keywords: Natural dyes, Color fastness, silk, UV protection.

1. Introduction

Nowadays, the interest towards natural dye is growing as our lives are affected by

Nomenclatures

E_λ	The relative erythemal spectral effectiveness
S_λ	The solar spectral irradiance
T_λ	The average spectral transmittance of the specimen

Greek Symbols

Δ_λ	The measured wavelength interval (nm)

Abbreviations

AATC	The American Association of Textile Chemists and Colorists
Al	$AlK(SO_4)_2 \cdot 12H_2O$
Fe	$FeCl_3 \cdot 6H_2O$
Na	NaOH
Un	Undyed
UPF	Ultraviolet protection factor
Wom	With-out mordanting

pollution. Consumers concern about the quality of goods to avoid toxic or allergic reactions. We are leading the development of natural dye coloring.Natural dyes can be obtained from plants, animals and minerals [1]. These natural dyes have been successfully applied to natural fiber fabrics such as cotton [2], wool [3-5], silk [6-7] and flax [8].

Parkia speciosa is known as stink bean or “sator” in Thailand and “petai” in Malaysia as shown in Fig. 1. It bears long and flat beans pod with green seeds. These beans are popular in Southeastern Asia including south of Thailand, Malaysia and Northeastern India. These pods are regarded as waste material during the processing in the food industry. Therefore, it is possible to evaluate this pod as potential novel functional dyes. Stink bean pod is well known for having abundant phenolic, gallic acid, flavonoid and antioxidative contents. These plant materials found broad applications in the areas of foods (e.g., as thickener, gelling agent, emulsifier, coating, fat substitute) and pharmaceuticals (e.g., radical-scavenging agent, diet supplement) [9].

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 [10]. 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 [11]. In general, light colors reflect solar radiation more efficiently than dark ones [12], 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. [13]. Nonetheless, as regards the UV-protection properties of natural dyes, few researches have been performed on natural fabrics [14-16] and most of these concern animal fibers, as reported by Grifoni et al. [17]. Very few studies exist on the UV-protection properties of natural dyes in combination with fabrics made from vegetable fiber [13, 14, 17] because very few natural dyes provide plant fibers with strong colors without the aid of mordants. An ecofriendly natural dyeing can however be achieved by replacing metal mordant with natural mordant, like tannic acid or other vegetable tannins [18], 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 [19]. 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 [20] and light fastness [21], e.g., in cotton fabrics. The evaluation of the level of UV protection properties of natural colors needs to be supported by knowledge of the dyes chemical structure, absorption characteristics in the UV region, interaction and complexation with the pre-mordanted substrate, as well as the ability to block or absorb the hazardous UV rays [17].

The objectives of this study were to study the color fastness and ultraviolet protection properties of silk fabric using an aqueous extraction of stink bean pod as natural dye. Different factors affecting dyeing ability were also examined.

Fig. 1. Stink beans (*Parkia speciosa* Hassk.).

2. Experimental Details

2.1. Materials

Stink bean pod (*Parkia speciosa* Hassk.) was supplied from a market in Songkhla province, Thailand. A commercially scoured and bleached silk fabric (81.4 g m^{-2}, plain weave) was used. Amount of silk, dyeing, mordant and water were used with the weight ratio of 0.50:1.00:0.04:40.00. Four different mordants were used, aluminum potassium sulfate ($AlK(SO_4)_2 \cdot 12H_2O$), Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH) and mud (from Sonkhla lake)**.** The FTIR transmittance spectra of the samples were also analyzed in order to confirm chemical functional groups of the dyed.

2.2. Extraction and Dyeing

The collected stink bean pods were crushed to small pieces before being used for dye extraction. The dye extraction was performed by mixing the plant material and distilled water in the weight ratio of 1:40 and boiling for 2 h. After that, the resulting solution was filtered to remove the residue and the dye solution was separated. Dyeing without a mordant the fabric was dyed at a liquor dye extracted at 50°C for 10 min. and then heated up to 90°C with the dyeing duration of 60 min.

In pre-mordant method, the fabrics were first immersed in an aqueous solution of mordant at the 40°C for 10 min. and then heated up to 80°C with the dyeing duration of 30 min. Pre-mordant fabric was dyed at 50°C for 10 min. and then heated up to 90°C with the dyeing duration of 60 min.

In the meta-mordant dyeing method (i.e. dyeing in the presence of mordant), the fabric were immersed in a dyeing a mordant and the dye extract, and the dyeing at the 50°C temperature, 10 min holding time, and rate of temperature rise at 90°C, and the dyeing duration of 60 min.

In the post-mordant method, dyeing was carried out in the absence of a mordant, followed by mordant for 10 min at the 40°C, and rate of temperature rise at 80°C, and the dyeing duration of 30 min, further processing was the same as described in the pre-mordant method.

2.3. Determination of color fastness

The color fastness to washing, light, crocking, perspiration, and water of the dyed samples were determined according to AATCC Test Method 61-2010, AATCC Test Method 16-2004 Option 3, AATCC Test Method 18-2007, AATCC Test Method 15-2009, and AATCC Test Method 107-2009, respectively.

2.4. UV measurements

The UV protection factor (UPF) was determined on three fabric samples (3x1 cm^2). Each sample was taken from the centre of the fabric, fixed on a common slide frame and placed in a Genesys 10S UV-vis spectrophotometer with thin film holder equipped with an integrating sphere to measure both direct and diffuse transmitted light. Each sample was positioned at right angles to the light beams. 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 Eq. (1):

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

where: E_λ is the relative erythermal 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 UVR 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

3. Results and discussion

3.1. The coloration and fastness of dyed silk fabrics

Figure 2 shows the various colors of silk fabrics dyed with stink bean pod (*Parkia speciosa* Hassk.). The color of the dyed silk fabric was reddish brown. The obtained colors (Fig. 2) show that silk fabrics dyed without mordant had grey color, while those mordant with Iron chloride produced a variety of dark to pale brown color shades. With mud, aluminum potassium sulfate and sodium hydroxide, the color shade was reddish brown and light brown. This may be associated with the change of Iron chloride into a ferric form by reacting with oxygen in the air [22]. Additionally, the betalain dye in the stink bean pod extract combine with sodium hydroxide to form complexes, which also result in a light brown to yellow shade of fabric.

Table 2 shows that the wash fastness ratings of both non-mordant and mordant 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 [23, 24] or (b) the decomposition of the dye itself, resulting in a colorless or a differentially colored compound [24]. 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 3. The color fastness to perspiration in acid conditions of fabrics dyed with and without mordant ranged from 4 to 4-5 (good to very good), as seen in Table 4. The light fastness was very poor to poor (1-2), except for the fabric mordant with Iron chloride, whose rating were fair to good (3-4) depend on the exposure to light time irradiation as shown in Table 5. Color fastness to crocking is found to be in the range of 3-4 to 4-5 (fair to good and good to very good), when subjected to wet and dry rubbing respectively, as seen in Table 6.

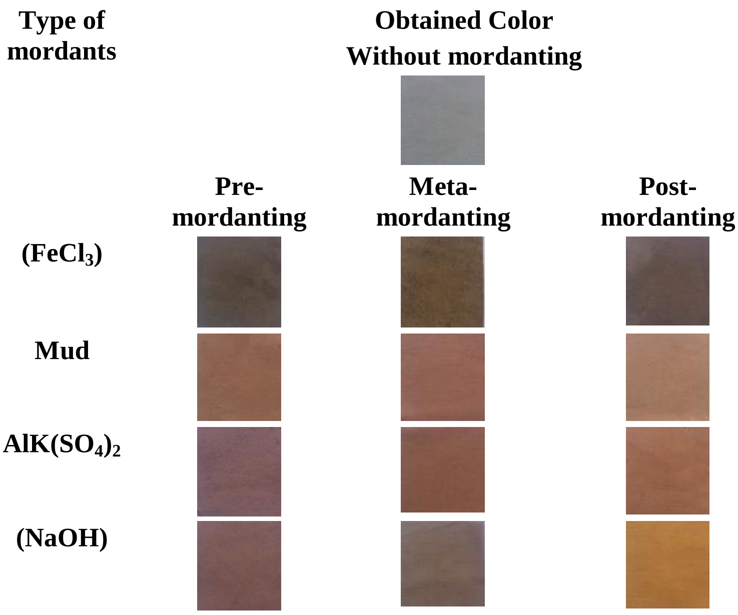


Fig. 2. Various colors of silk fabrics dyed with Stink bean pod (*Parkia speciosa* Hassk.).

Table 2. Colorfastness to washing at 40°C (AATCC Test Method 61-2010).

Fastness	Mordant												
	Wom	Pre-mordanting				Meta-mordanting				Post-mordanting			
		Na	Fe	Mud	Al	Na	Fe	Mud	Al	Na	Fe	Mud	Al
Color change	4.0	4.0	3.5	4.0	4.5	4.0	3.5	4.0	4.5	4.0	3.5	4.0	4.5
Color staining													
ACETATE	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
COTTON	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
NYLON	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
SILK	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
VIACOSE	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
WOOL	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5

Table 3. Colorfastness to water (AATCC Test Method 107-2009).

Fastness	Mordant												
	Wom	Pre-mordanting				Meta-mordanting				Post-mordanting			
		Na	Fe	Mud	Al	Na	Fe	Mud	Al	Na	Fe	Mud	Al
Color change	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
Color staining													
ACETATE	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
COTTON	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
NYLON	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
SILK	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
VIACOSE	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
WOOL	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5

Table 4. Colorfastness to perspiration (AATCC Test Method 15-2009).

Fastness	Mordant												
	Wom	Pre-mordanting				Meta-mordanting				Post-mordanting			
		Na	Fe	Mud	Al	Na	Fe	Mud	Al	Na	Fe	Mud	Al
Color change	4.0	4.0	4.5	4.0	4.0	4.0	4.5	4.0	4.0	4.0	4.5	4.0	4.0
Color staining													
ACETATE	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
COTTON	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
NYLON	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
SILK	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
VIACOSE	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5
WOOL	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5	4.5	5.0	4.5	4.5

Table 5. Colorfastness to light (AATCC Test Method 16-2004 Option 3).

Type of mordants	Color change					
	Pre-mordanting		Meta-mordanting		Post-mordanting	
	20 hr.	40 hr.	20 hr.	40 hr.	20 hr.	40 hr.
Wom	2.5	1.5	2.5	1.5	2.5	1.5
Na	2.5	1.5	2.5	1.5	2.5	1.5
Fe	4.0	3.0	4.0	3.0	4.0	3.0
Mud	2.5	1.5	2.5	1.5	2.5	1.5
Al	2.5	1.5	2.5	1.5	2.5	1.5

Table 6. Colorfastness to crocking (AATCC Test Method 18-2007).

Type of mordants	Color stainning					
	Pre-mordanting		Meta-mordanting		Post-mordanting	
	Dry	Wet	Dry	Wet	Dry	Wet
Wom	4.5	4.0	4.5	4.0	4.5	4.0
Na	4.5	4.0	4.5	4.0	4.5	4.0
Fe	4.5	3.0	4.5	3.0	4.5	3.0
Mud	4.5	4.0	4.5	4.0	4.5	4.0
Al	4.5	4.0	4.5	4.0	4.5	4.0

Note :Wom= Without mordanting, Na=NaOH, Fe = $FeCl_3$, Mud=Mud and Al = $AlK(SO_4)_2$.

Silk fabrics dyed without mordant show grey color. It can be concluded that silk fabric can be successfully dyed with stink bean pod extract due to the tannin content in stink bean pod. Tannin contains phenolic compounds that can form hydrogen bonds with the carboxyl group of protein fibers. Furthermore, there are two other possibilities involved; (a) the anionic charge on the phenolic groups forms an ionic bond with cationics (amino groups) on the protein substrate; and (b) a covalent bond may also form by an interaction between any quinine or semiquinone groups present in the tannin and suitable reactive groups on the silk fiber.

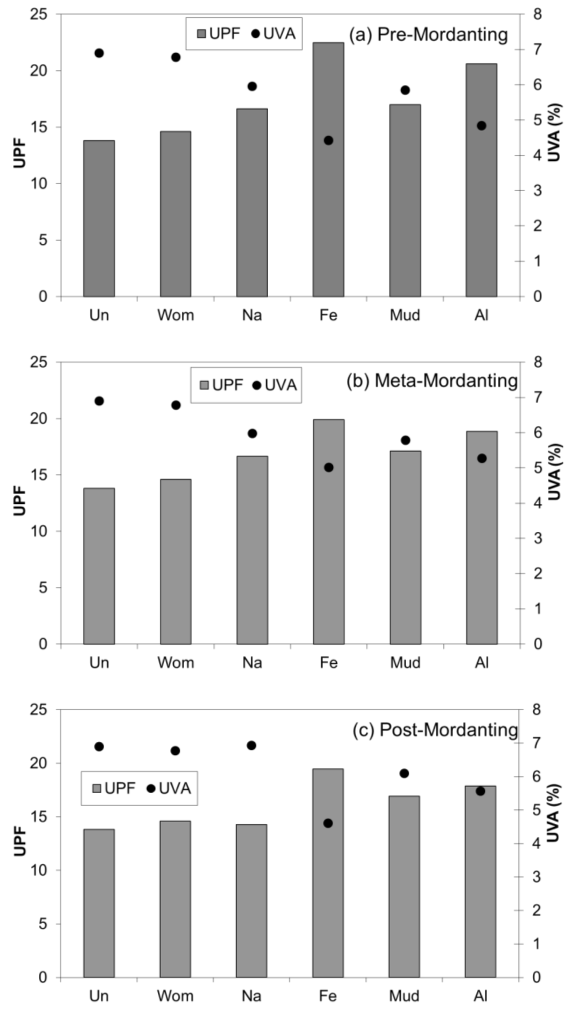
Group-I (sodium), these metal ions did not exhibit any tendency to from coordinate complexes. They can form only ionic bonds with the stink bean pod dye. Light fastness properties of stink bean pod dye with sodium ions were poor due to the weak bonding formation between the dye molecule and the fiber.

Group-II (aluminum), these metals formed weak coordination complexes with the dye. They tended to form quite strong bonds with the dye but not with the fiber. They blocked the dye and reduced its interaction with the fiber. The ionic bonding of aluminum with the fiber was weak.

Group-III (silicon and iron), it always found SiO_2 in mud. These metals are well known for the ability to from coordinate complex, and in this study both readily chelated with the dye, as the coordination number of silicon and iron are 4 and 6, respectively. Some co-ordination sites remained un-occupied when they interacted with the fiber, amino group, attached with wool fiber occupied these sites. Thus these metals formed a binary, complex with the fiber with dye. Such a strong coordination tendency enhanced the interaction between the fiber and the dye, resulting in the high dye uptake [25].

3.2. Transmittance and UPF measurements

The results obtained by Grifoni et al. [17] and Feng et al. [26] 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. Apart from pre-mordanting, meta-mordanting and post-mordanting, in which 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 mordant 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 stink beans pod of (*Parkia speciosa* Hassk.) are phenolic, gallic acid, flavonoid, tannin and antioxidant contents [9]. As already stated by many authors [9], tannins absorb UV radiation with efficiency similar to carotenes and anthocyanins, and provide the same protection from UV radiation damage that accessory pigments do. Similar behavior was also shown in Fig. 3. However the UPF value of stink beans pod with $FeCl_3$, Mud 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. In apparel silk fabrics no relevant differences in UPF were detected among different dyeing process (pre-, meta- and post-mordanting) (Fig. 3).



Note: Un= Undyed, Wom= Without mordanting, Na=NaOH, Fe = $FeCl_3$, Mud=Mud and Al = $AlK(SO_4)_2$.

Fig. 3. UPF (bars) and UVA transmittance (black dots) for dyed silk fabrics mordant (a) pre-mordanting (b) meta-mordanting and (c) post-mordanting. 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. 3), 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 [27]. Nevertheless high UPF do not necessarily imply low transmission in UVA wavelengths, as already found by Gambichler et al. [12, 28] and Grifoni et al. [17].

In this study, for example, $FeCl_4$, Mud and $AlK(SO_4)_2$ dyed that had UPF corresponding to good protection, showed UVA transmittance values slightly in range 4.2-6.7%. Polyphenols and tannins in fiber act as absorbing UVR radiation that has high energy. It can convert UVR energy into thermal energy for fabrics. They react with radical or oxygen by UVR. A possible photochemistry reaction of the natural dyes could occur as explained in Fig. 3.

The cleavage of H-O bonds could occur in the reaction, during absorbing a sufficient energy UVR. Therefore, it can be proposed that the cleavage of hydrogen bonds in the molecules of the natural dyes contributes to their capacity to absorb UVR [26].

3.3. FTIR analysis

The band frequencies of the spectra obtained with their assignment are given in Table 7. The FTIR spectrum of the stink bean pod dyed with different mordant consisted of eight main groups of absorption bands in the wavelength range of 400-4000 cm^{-1} (Fig. 4). The intense band detected in the 3300-3500 cm^{-1} and 1300 cm^{-1} regions 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.

A comparison of the IR spectrum of dyed with mud and $AlK(SO_4)_2$ disappear the peaks at 2900-3000 cm^{-1}. It could be concluded that mechanisms are ion exchange and/or complex reaction between the metal ion (Al^{3+} in $AlK(SO_4)_2$ and Al_2O_3 in mud) and the chlorophyll molecule [29]. The bands in the region of 400-800 cm^{-1} and 1310-1390 cm^{-1} can be assigned to the polyphenols and aromatic compound/phenols respectively. 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}) and C-O-C stretching bands (800, 1016-1060, 1130-1230 cm^{-1}), which are typical of aromatic molecules. The peaks at 1040-1100 cm^{-1} and 1380 cm^{-1} are attributed mainly due to C-C and C-N vibrations of the tetra pyrrole ring of chlorophyll [9, 30].

Stink bean pod dyed with all mordant showed that the intensity of the carbon-carbon bonds in the phenolic groups absorbed in the region of 1040-1100 cm^{-1} [29]. Indeed, in aqueous metal mordant liberated blocks the tetra pyrrole ring of chlorophyll (C-N) interaction.

Table 7. FTIR analysis of dyed (stink beans pod) by using different mordant with major peak frequency (cm^{-1}) and assignment.

Assignment and Vibrating group	Range/cm^{-1}	Samples				
		Stink bean pod dye	Dyed with NaOH	Dyed with $FeCl_3$	Dyed with Mud	Dyed with $AlK(SO_4)_2$
O-H (ethanol)	3300-3500, 1300	/	/	/	/	/
O-H ethanol (betalain dye)	3270-3400	/	/	/	/	/
C-H (chlorophyll)	2900-3000	/	/	/	-	-
C-NTetra pyrrole ring of chlorophyll	1230	/	-	-	-	-
C-C	1040-1100	-	/	/	/	/
Polyphenols	400-800	/	/	/	/	/
Aromatic compound/ Phenols	1310-1390	/	/	/	/	/
C=O (carboxylic)	1600-1630	/	/	/	/	/
C-O-C	800,1016-1060, 1130-1230	/	/	/	/	/

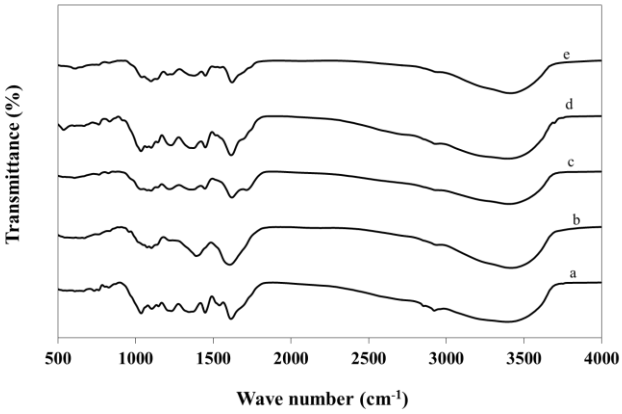


Fig. 4. FTIR spectrum of (a) dye (stink bean pod); (b) dyed with NaOH; (c) dyed with $FeCl_3$; (d) dyed with mud and (e) dyed with $AlK(SO_4)_2$.

4. Conclusion

This study has been demonstrated for the first time that natural colorant can be extracted from stink bean pod (*Parkia speciosa* Hassk.) by traditional extraction method applied to silk fabric. It was found that dyed samples present interesting color fastness and ultraviolet protection properties. Further improvement in color yield was observed with different types mordanting. The following conclusions are arrived at:

- Each mordant gave different color shades from medium to dark brown for Iron chloride, to significantly paler and darker shades for mud and aluminum potassium sulfate, and from light brown to yellow for sodium hydroxide.
- All stink bean pods dyed silk fabric exhibited fair to good fastness to washing and crocking, very poor to poor light fastness with the exception of samples mordant with Iron chloride. The water and perspiration fastness ratings were fair to good.
- In this study the mordant affected the UV-protection properties of all silk fabrics. A very good protection level was reached by mordanted silk with Iron chloride and dyed in stink bean pod.
- According to dyeing process of stink bean pod natural dye, the process of pre-mordant dyeing was considered to be the most suitable process because it has the ability to improve the UV-protection of the dyed silk samples.

- This result indicates that stink bean pod contains high polyphenolic, betalain dye and chlorophyll contents. These colorants might be alternative sources to synthetic dyes.

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