Fibers and Polymers 2018, Vol.19, No.1, 41-54
DOI 10.1007/s12221-018-7315-4

ISSN 1229-9197 (print version)
ISSN 1875-0052 (electronic version)

Application of *Sterculia Foetida* Fruit Shell Waste Biomolecules on Silk for Aesthetic and Wellness Properties

M. D. Teli* and Pintu Pandit*

Department of Fibres & Textile Processing Technology, Institute of Chemical Technology, University under Section-3 of UGC Act, 1956, Matunga, Mumbai-400019, India

(Received March 30, 2017; Revised November 8, 2017; Accepted November 11, 2017)

Abstract: There has been growing interest in the use of bioresource waste for natural dyeing and finishing. This paper discusses dye extraction from the novel source fruit shell waste of *Sterculia foetida* and its application on mulberry silk fabric to confer aesthetic coloration and wellness properties such as ultra-violet (UV) protection and antibacterial properties. Treated fabrics showed a substantial increase in color depth and adequate wash, light, and rubbing fastness properties for dyed silk fabrics with and without mordanting. Pre- and post-mordanting of silk fabrics were carried out using mordants such as alum, harda (myrobalan), and copper sulfate. UV-visible spectrophotometric analysis of fruit shell extract (FSE) at different pHs and FSE with three different mordants at neutral pH was used to understand the phenomena of dye-fiber interaction. The treated fabrics characterised by ATR-FTIR, SEM-EDS, and XRD analysis indicate the nature of dye fiber interaction justifying the multifunctional properties. The treated fabric also showed very good ultraviolet protection property and antibacterial properties both against *S. aureus* and *E. coli* bacteria even after ten washes. The results indicate that *Sterculia foetida* fruit shell extract offers an excellent potential as coloration, antibacterial, and ultraviolet protective agent for mulberry silk fabric.

Keywords: *Sterculia foetida* fruit shell, Silk dyeing, Antibacterial, UV protection, FTIR, XRD

Introduction

Various plant materials which can be rich and varied sources of dyestuff have income-generating potential when such plants are harvested to supplement the rural economy in many of the world's developing countries. Recently increasing awareness is observed about water pollution as well as health risks involved in using some of the synthetic dyes. It has resulted in growing interest in the use of natural resource-based biomolecules for ecofriendly sustainable products. Present day's consumers are more conscious about eco-friendliness of products as well as processes, which couple with the tougher government legislation, and make sustainability as a thrust area in all the new generation functional textiles. Textile companies all over the world are also showing a keen interest in natural dyeing and finishing to reestablish the technology in their production line. Among them, antimicrobial textiles have a significant share in the market as far as the hygienic and healthy lifestyle requirements are concerned. During last few decades, a range of synthetic antimicrobial chemicals like triclosan, metallic salts, quaternary ammonium-based products, etc. have been developed and widely used as finishing agents for making antimicrobial textile. However, these products are known to have significant limitations such as the toxic side effects, effluent problems, water pollution, etc.

In accordance with the sustainability parameters, natural products are being used by many researchers for functional finishes giving value-added textile materials. A lot of plant sources like tamarind seed coat, flower waste from the temple, Emblica Officinalis G. fruit (amla) etc. have been utilized for natural dyeing [1,2]. Soybean seed waste treatment on cotton muslin and chitosan treatment on cotton for cationizing-cum finishing of cotton to increase the dye uptake of natural or synthetic anionic types were also reported by a group of researchers [3-5]. Natural products derived from plants do not affect the ecological balance as the residual material is easily degradable and thus it is a good alternative for control and maintenance of the ecosystem. Ultraviolet protection from the textile material has also been reported through the application of different plant biomolecule sources such as manjistha, babool, annatto, ratan jot, *sterculia foetida* fruit shell extract, coconut shell extract, coconut leaf extract, roasted peanut skin, etc. on the substrate [6-12]. Herbal products such as tea plant oil, tulsi leaf, aloe vera, *sterculia foetida* fruit shell extract, coconut shell extract, coconut leaf extract, chitosan, madder, logwood, cutch, chelidonium plants, etc. [7,10,13-16] have been used to get the natural antibacterial effect. Recently researchers have also used biomolecules such as coconut shell extract, banana pseudostem sap, *delonix regia* stem shell waste, etc, for imparting multifunctional properties to the textile materials [7,8,14,17,18]. However, most of the researches done so far indicate that the natural finishes suffered from poor wash durability and thus with an increase in the number of washing cycles, the efficacy of such multifunctional natural finish decreased.

Addressing this very issue, a natural waste *Sterculia foetida* fruit shell extract has been investigated in the present

*Corresponding author: mdt9pub@gmail.com
*Corresponding author: pintupanditict@gmail.com

work, with a view to overcome the fastness limitations along with imparting multifunctional properties. The *Sterculia foetida* is a tropical tree, belonging to the *Sterculiaceae* family which has 2000 types of species. Species distribution of *Sterculia foetida* as documented in agroforest tree database describes the native range to be Australia, Bangladesh, Djibouti, Eritrea, Ethiopia, India, Indonesia, Kenya, Malaysia, Myanmar, Oman, Pakistan, Philippines, Somalia, Sri Lanka, Tanzania, Thailand, Uganda, and Yemen. These species are also called "Java almond" and the seeds are eaten raw, roasted, or fried. It was formerly placed in the family Sterculiaceae; however, DNA cladistical analysis showed that it belongs to the mallow family (Malvaceae) [19]. It is a wild plant and well adapted to tropical and sub-tropical areas with an average life span of more than 100 years. Many studies have been successfully carried out for the preparation of biodiesel from *Sterculia foetida* seed oil. The resultant biodiesel was also evaluated for physico-chemical properties by researchers [20,21]. The seeds have a pleasant taste and are sometimes eaten as roasted or fried. Seed can also be used as an adulterant for cocoa and oils from seeds have been used in local culinary and traditional medicine [19]. The leaves contain up to 2.66 % calcium and are also a good source of protein and phosphorus, meeting the nutritional requirement of ruminants. The kernel meal contains about 31 % crude protein. The plant leaves are also used as herbal medicine as an aperient, diuretic and as an insect repellent [22]. Moreover, the alcoholic extract of the leaves has been found to play a significant role in anti-inflammatory and central nervous (CNS) depressant activity [23]. Fiber obtained from the bark is used as cord, pulpwood, fire wood, charcoal, and timber yields gum or glue which is used in bookbinding. Study of *Sterculia foetida* gum showed that it could be a good polymer candidate for the formulation of different ocular dosage forms like solution or viscous solution drops, nanoparticles, nanosuspension, micro or nanoemulsion, lotion, gels, hydro gels, in-situ forming gels, ointments, films, mini tablets, etc. [19]. The open segments of fully ripe *Sterculia foetida* fruit look a lot like woody, valentine-heart-shaped bowls which have been used for our research as waste material. However, as per the best of our knowledge, no work has been reported on *Sterculia foetida* fruit shell extract as a natural colorant with a possibility of imparting multifunctional properties to mulberry silk fabric which is preferred by ladies for their garments, especially in summer season.

Experimental

Materials

A 100 % mulberry plain woven bleached silk fabric having 44 ends/cm and 40 picks/cm with an areal density of 40 g/m^2 was used in this work. The plant specimen, *Sterculia foetida* fruit shell were collected from the campus of Institute of Chemical Technology, India. *Sterculia foetida* fruit shells were cut into small pieces first and then ground into fine powder. Alum, harda (myrobalan), and copper sulfate were used as mordants. For antibacterial testing, gram-positive bacteria *Staphylococcus aureus* (*S. aureus*) (AATCC 25923) and gram-negative bacteria *Escherichia coli* (*E. coli*) (AATCC 25922) were procured from KEM Hospital, Mumbai, India.

Extraction of *Sterculia Foetida* Fruit Shell

The oven dried *Sterculia foetida* fruit shell was ground to a fine powder in the blender and then was used as the raw material for dye extraction. Refluxing technique was used for extraction. The extract was then centrifuged for 20 min at 4000 rpm to get insoluble particles settled. The supernatant liquor was used for dyeing in laboratory rota dyer machine (R. B. electronic and Engineering Pvt. Ltd., India).

Phytochemical Analysis

Chemical tests for the identification and screening of bioactive chemical constituents in the fruit shell extract (FSE) were carried out with the extracts using the standard procedure [14]. For each test of saponin, phenol, tannin, terpenoid, flavonoids, and glycoside, 2 m*l* of FSE was used for analysis. Other chemicals used are acetic acid (assay 99 %), chloroform (assay 99.5 %), hydrochloric acid (assay 35-37 %), sulfuric acid (assay 99.8 %), ferric chloride hexahydrate (assay 98 %), and ethanol (all chemicals were procured from SDFCL, India). Zinc dust (A.W. 65.37) was obtained from RFCL Limited, India.

Ultra Violet (UV)-Visible Spectrophotometer Analysis

UV-visible spectrophotometer analysis of fruit shell extract (FSE) in distilled water at a concentration of 75 μg/m*l* was done by scanning from 340 to 700 nm wavelength using a UV-1800 spectrophotometer from Shimadzu.

High-Performance Liquid Chromatographic (HPLC) Analysis of FSE

Analysis of *Sterculia foetida* fruit shell extract (FSE) was performed by liquid chromatography using a JASCO PU - 4180 HPLC apparatus equipped with two pumps, a UV-VIS Module, a Rheodyne injector 20 μ*l* loop with ODS2 Waters Spherisorb column (250 mm×4.60 mm, 5 μm particle size). The extract from *Sterculia foetida* fruit shell, used for dyeing, was diluted 20 times with distilled water. 20 μ*l* volume was injected with a microliter Hamilton syringe. Chromatograms were obtained and analyzed using the chromNav software software. The mobile phase consisted of a binary mixture of methanol: water (40:60 v/v) adjusted to pH 2.8 with phosphoric acid [24] at an isocratic flow rate of 1.0 m*l*/min. The absorbance was monitored at λ=280 nm and 300 nm.

Dyeing Procedure

Three different mordants (alum 10 %, copper sulfate 5 %, and harda 10 %) were used for dyeing as both pre and post-mordanting agent. The mordanting and dyeing was carried out in a laboratory rota dyer machine with programmable time and temperature control. The required amount of dye was taken according to the dyeing shade of 10, 20, 30 (%) respectively on the weight of fabric at pH 7. Material to liquor ratio of 1:30 was maintained, and dyeing was carried out at 90 °C for 1 h dyeing time.

Evaluation of Dyed Samples

Evaluation of dyed samples was done by determination of *K/S* and L^*, a^*, b^* values using a computer color matching system. Color depth of the samples was evaluated measuring the reflectance values, using a Spectra Scan 5100+ computer matching system. The relative color strength (in terms of *K/S* value) of the fruit shell extract dyed silk fabrics was measured using the Kubelka-Munk equation:

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

where K is the absorption coefficient, S is the scattering coefficient, and R is the reflectance of the dyed fabric at the wavelength of maximum absorption.

Color Fastness Properties

The dyed fabric was subjected to washing fastness test using ISO 105 C10: 2006 (no. B), test method (ISO method II) where in the composite sample was treated in soap solution of 5 g/*l* at material to liquor ratio 1:50 at 50±2 °C for 45 min in a wash fastness tester, followed by washing and drying. Similarly, light fastness and rubbing fastness of the FSE treated fabric samples were also assessed according to ISO 105-B02:2013 and ISO 105-X 12:2002 methods, respectively [25,26].

Wash Durability Test

Wash durability for FSE treated silk fabric was carried out with 1.5 g/*l* AATCC detergent for 45 min at 50 °C with 50 steel balls in a launder-o-meter which is according to AATCC 61 2A method equivalent to five home washing cycles [18]. The wash durability of antibacterial and ultraviolet protection properties of the treated fabric for up to ten wash cycles was also determined in similar fashion as per AATCC 61 2A method.

Antibacterial Activity

The antibacterial activity of the dyed silk was quantitatively evaluated against *E. coli* (AATCC 25922) and *S. aureus* (AATCC 25923), according to the AATCC 100 test method. Colonies of bacteria recovered on the agar plate were counted, and the reduction of bacteria (R) % was calculated by the following equation:

$$R(\%) = \frac{(B-A)}{B} \times 100$$

where A is the number of bacterial colonies from treated specimen after inoculation over 24 h of the contact period and B is the number of bacterial colonies from untreated specimen after inoculation at zero contact time.

Ultraviolet Protection Factor (UPF) Analysis

The UPF values of the untreated and treated silk fabric with the fruit shell extract were measured using a Shimadzu UV-2600 in the range of 280 to 400 nm. The UPF value of each fabric was determined from the total spectral transmittance based on AS/NZS 4399:1996 method.

Attenuated Total Reflection (ATR), Fourier Transform Infrared (FTIR) Analysis

The IR spectra of the untreated and treated silk fabrics were recorded using a Pike miracle ATR module with diamond/ZnSe crystal on an FTIR spectrometer (Shimadzu 8400S, Japan) by recording 32 scans in % transmittance mode in the range of 700-4000 cm^{-1}.

Scanning Electron Microscope (SEM) Analysis

The surface morphology of the untreated and *Sterculia foetida* fruit shell extract treated silk fabrics with three different mordants was analysed using a SEM (Model - Philips-XL30).

Energy Dispersive X-ray Spectroscopic (EDS) Analysis

EDS analysis was carried out using a field emission gun scanning electron microscope (FEG-SEM, JEOL, JSM-7600F) on pure fruit shell extract (FSE), untreated silk, and FSE treated silk samples to determine elements present and their respective weight percentage. Specimen size of 5×5 mm^2 was used. The conductive agent used was of platinum sputter coated for 600 s. The beam voltage of 15 kV and a working distance of 15 mm for examining the sample were maintained.

X-ray Diffraction (XRD) Analysis

XRD measurement of the untreated and FSE treated silk samples was carried out on a Shimadzu 6100 model equipped with CuKα radiation (λ=1.54 Å) in the 2θ angle ranging from 10 to 35 ° with 0.02 ° step interval. Generator voltage was kept at 40 kV and generator current was 30 mA. The sample in the form of chopped fibers was prepared and placed on the stub.

Results and Discussion

Phytochemical Analysis

Sterculia foetida fruit shell extract (FSE) was placed in a test tube and shaken a few times vigorously. The formation

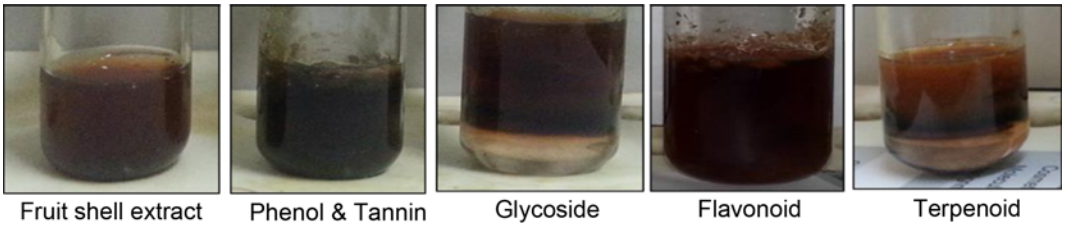


Figure 1. Phytochemical analysis of *Sterculia foetida* fruit shell extract.

of stable foam was taken as an indication of the presence of saponin. Two milliliters of 2 % solution of ferric chloride ($FeCl_3$) was mixed with FSE. A blue-green or black coloration indicated the presence of phenols and tannins. FSE was mixed with 2 m*l* of chloroform followed by careful addition of 2 m*l* of concentrated sulfuric acid and then shaken gently. A reddish brown coloration of the interphase was formed which confirmed the presence of terpenoid (Salkowski's test). The extract was then mixed with zinc dust and concentrated hydrochloric acid was added to it dropwise. It gave red color after few minutes indicating the presence of flavonoids (zinc-hydrochloride reduction test). FSE was mixed with 2 m*l* of glacial acetic acid containing two drops of 2 % $FeCl_3$. The mixture was then added to another tube containing 2 m*l* of concentrated sulfuric acid. The presence of brown ring at the interphase indicated the presence of glycosides. The summarized phytochemical screening of chemical constituents of FSE has been used in this study on a qualitative basis. The results revealed the presence of a number of active compounds in FSEs. All the tests showed the presence of phenols, tannin, saponin, terpenoid, glycoside, and flavonoid as illustrated in Figure 1.

UV-Visible Spectrophotometric Analysis of Fruit Shell Extract (FSE) in the Presence of Different Mordants

UV-visible spectrophotometric analysis of FSE is shown in Figure 2. The measurement was done on solutions with FSE, mordant, and FSE and mordant together as observed in the spectral scale of absorbance magnitude. Anthocyanins absorb strongly in the visible and UV spectral range, with maximum absorbance falling in the region of 465-560 nm and 280-320 nm. Their UV absorbing capacity varies depending

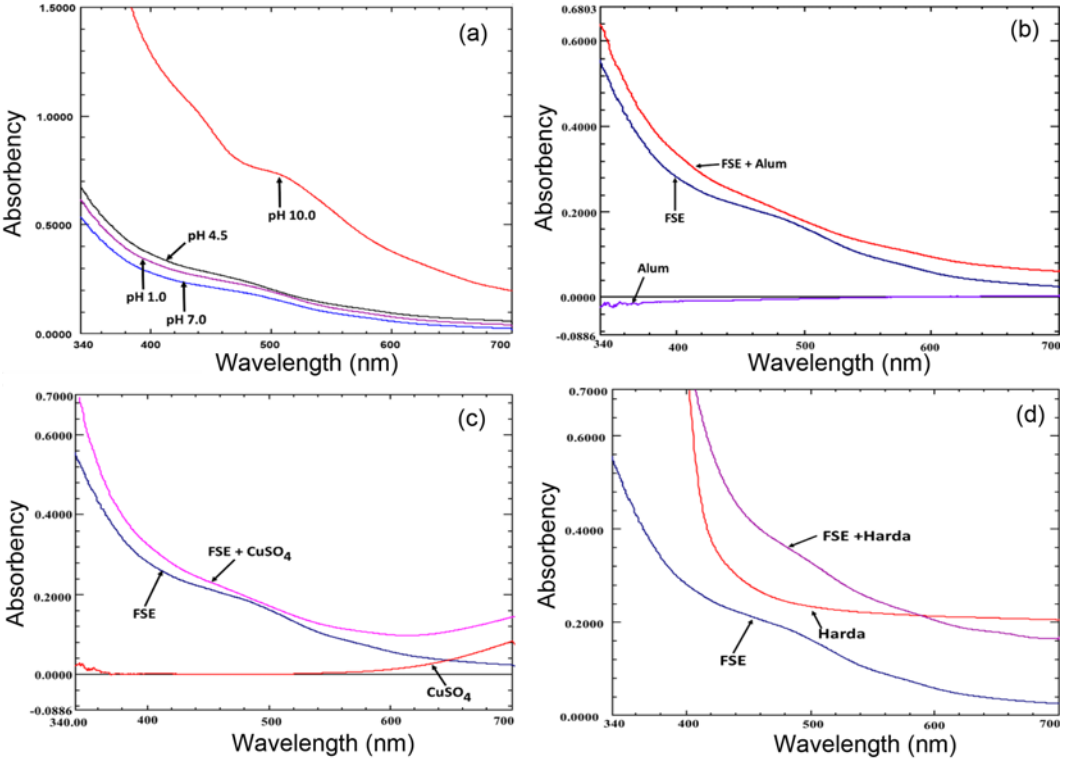
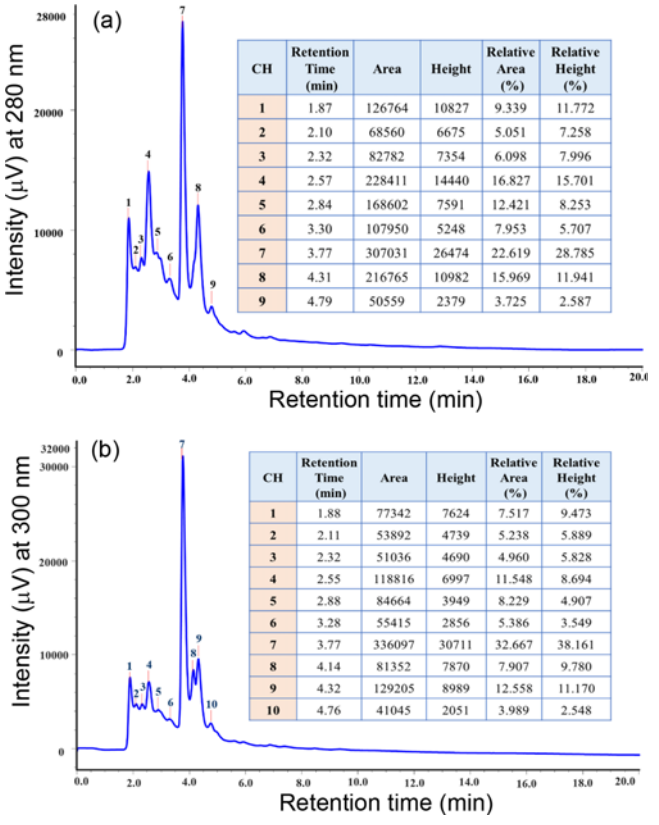


Figure 2. UV-visible spectra of fruit shell extract (FSE) (a) in different pHs, (b) with alum as mordant, (c) with copper sulfate as mordant, and (d) with harda as mordant.

on their specific aglycones, sugar conjugation, and acylation configurations. Anthocyanins are present mostly as fewer hemiketals under mildly acidic conditions, as in the case of FSE. At pH 4.5 and 7, a band with absorbance maxima at 324 nm, undergoes a bathochromic shift to 366 nm at pH 10. At pH 4.5 and 7, the two other band maxima at 416-420 nm and at 505 nm collapse to a slight band maxima at 505 nm on the increase to pH 10, while increasing in magnitude. As the pH is raised, kinetic and thermodynamic competition occurs between the hydration reaction of the flavylium cation and the proton transfer reactions related to the acidic hydroxyl groups of the aglycone [27].

At neutral pH, in the presence of mordants, the FSE complexes with harda, alum and $CuSO_4$ to give overall intensified absorbance, when compared at the same concentrations of FSE and mordants. Harda maximizes the absorbance by almost tripling in magnitude, while alum and $CuSO_4$ give an increased absorbance of the FSE ($CuSO_4$>alum), around 50 % more than FSE alone. Complexation of FSE occurs in the order alum<$CuSO_4$<<Harda. Cupric ions have a greater hydration sphere than the aluminum ion, to allow for greater interaction with FSE dye, while the tannin phenolic compounds and coumarin quinonoid in harda and the anthocyanins and tannins in FSE interact by π-π stacking to give intense action



(a)

CH	Retention Time (min)	Area	Height	Relative Area (%)	Relative Height (%)
1	1.87	126764	10827	9.339	11.772
2	2.10	68560	6675	5.051	7.258
3	2.32	82782	7354	6.098	7.996
4	2.57	228411	14440	16.827	15.701
5	2.84	168602	7591	12.421	8.253
6	3.30	107950	5248	7.953	5.707
7	3.77	307031	26474	22.619	28.785
8	4.31	216765	10982	15.969	11.941
9	4.79	50559	2379	3.725	2.587

(b)

CH	Retention Time (min)	Area	Height	Relative Area (%)	Relative Height (%)
1	1.88	77342	7624	7.517	9.473
2	2.11	53892	4739	5.238	5.889
3	2.32	51036	4690	4.960	5.828
4	2.55	118816	6997	11.548	8.694
5	2.88	84664	3949	8.229	4.907
6	3.28	55415	2856	5.386	3.549
7	3.77	336097	30711	32.667	38.161
8	4.14	81352	7870	7.907	9.780
9	4.32	129205	8989	12.558	11.170
10	4.76	41045	2051	3.989	2.548

Figure 3. HPLC analysis of reversed-phase chromatograms of fruit shell extract (FSE) at (a) 280 nm and (b) 300 nm with corresponding peak tables.

than harda or FSE alone. This may explain the UV-vis spectra shown in Figure 2.

High-Performance Liquid Chromatographic (HPLC) Analysis of FSE

High-performance liquid chromatography is probably the most widely used analytical technique for characterizing the polyphenolic compounds [28]. The results in Figure 3 and attached table showed that almost 9 compounds were detectable at the UV wavelength of 280 nm and this number increased to 10, when detected at 300 nm. Detection is due to the polyphenolic class of compounds [29,30] present in the fruit shell extract obtained by reflux boiling of dried powder in water. It was seen that gallic acid and catechins were detectable at 280 nm and hydroxy-cinnamic acids at 300 nm [30]; the comparison of UV absorbance spectra of phenols derived from lignin, showed that syringyl, *p*-hydroxy, *o*-hydroxy (catechol), and vanillyl phenols absorbed around 280 nm, while the cinnamyl-phenol absorbed at 300 nm [31]. This explains the difference in the two HPLC chromatograms of the FSE peaks at 4.14 min in the chromatogram (b) being cinnamyl phenolic compound while the rest of the peaks, may be of catechin and gallic acid derived substances. The hydroxybenzoic acids occur in plants mainly as glycosides, whereas hydroxycinnamic acids are bound to cell wall polymers, or they occur as simple esters [30] as observed in FSE.

Natural Dyeing with Sterculia Foetida Fruit Shell Extracts on Silk Fabric

It was observed from the Table 1 that *K/S* values increased with increase in dye concentration as well as mordant. The efficacy of mordant in enhancing the *K/S* values of the dyeing was found to be in the following order: Harda> $CuSO_4$>Alum>without mordanting. The results show that there was a decrease in brightness (L^*) values for harda and copper sulfate compared to alum and only fruit shell extract dyed sample. When harda and copper sulfate mordant were used, L^* values decreased, and hence deeper tone was obtained. In the case of alum mordant, there was no significant change in yellowness (b^*) value, where as b^* value increased in the case of copper sulfate and harda as mordant, for all the fabrics dyed with fruit shell extract.

The highest *K/S* value in case of harda and copper sulfate dyed sample with fruit shell extract was thus due to decreased values of L^* and relatively enhanced values of b^*. From a^* and b^* values it can be concluded that fruit shell extract in combination with copper sulfate and harda mordant when used onto silk fabrics, it produced good improvement in coloration and their values (a^* and b^*) were positive and thus showed shift in their tones resulting in beautiful colors as compared to the dyeing obtained without using mordant. Copper sulfate and alum mordants are well known for their ability to form coordination complexes and to readily chelate

Table 1. *K/S* values and color co-ordinates of dyed silk fabric with and without mordanting

Type of mordants	FSE dye conc., (%) o.w.f.	*K/S*	L^*	a^*	b^*
Without mordant	10	0.71	72.54	7.23	11.96
	20	1.38	72.62	9.09	13.35
	30	1.79	72.95	9.33	13.71

		Pre-mordanting				Post-mordanting			
		K/S	L^*	a^*	b^*	*K/S*	L^*	a^*	b^*
Alum (10 %)	10	0.62	74.46	6.53	14.11	0.76	75.45	5.13	15.10
	20	1.41	74.21	5.46	14.27	1.73	74.47	7.61	14.68
	30	1.89	75.09	7.43	16.54	2.04	73.94	8.14	14.73
Copper sulfate (5 %)	10	1.80	68.37	3.98	17.75	2.23	67.92	4.43	17.36
	20	4.67	68.47	6.66	18.83	4.87	68.74	7.27	19.51
	30	5.19	67.49	8.97	19.01	5.85	68.32	7.32	19.17
Harda (10 %)	10	4.31	54.51	10.29	25.26	5.37	56.38	11.43	27.19
	20	5.33	55.85	10.03	26.24	5.56	59.92	8.17	28.37
	30	5.48	56.96	8.35	26.56	5.94	61.49	6.37	30.14

Note: FSE=fruit shell extract; L^*: lightness (0=black, 100=white); a^*: red-green co-ordinates (positive values=red, negative values=green); b^*: yellow-blue coordinates (positive values=yellow, negative values=blue).

with the dye. The coloring substance of *Sterculia foetida* fruit shell contains natural tannins and polyphenols, varying from 4 % to 5 %. Thus, dyeing of silk fabric with *Sterculia foetida* fruit extract may be attributed to the tannin richness [32]. Dyeing was fast for dimethyl formamide (DMF) boil [33], indicating that some level of dye fixation must be through a covalent bond which may also form through an interaction between quinone or semiquinone groups present in the tannins and suitable reactive groups on the silk fiber [34].

Assessment of Fastness Properties of the Dyed Silk Fabric

The fastness ratings of silk fabric dyed without mordant and dyed with three different mordants are presented in

Table 2. Fastness properties of without and with mordanting of silk fabric

Dyeing parameters		Washing fastness		Light fastness		Rubbing fastness			
Type of mordants	FSE dye conc., % o.w.f.					Dry		Wet	
Without mordant	10	4		5-6		5		5	
	20	4		6		5		5	
	30	4-5		6		5		5	
Types of mordants	FSE dye conc., % o.w.f.	Pre Mordanting	Post Mordanting	Pre Mordanting	Post Mordanting	Pre		Post	
						Mordanting			
						Dry	Wet	Dry	Wet
Alum (10%)	10	4	4	5-6	5-6	5	5	5	5
	20	4-5	4-5	5-6	6	5	5	5	5
	30	4-5	4-5	6	6	5	5	5	5
Copper sulfate (5%)	10	4-5	4-5	6	6	5	5	5	5
	20	4-5	4-5	6	6	5	5	5	5
	30	4-5	4-5	6	6	5	4-5	5	5
Harda (10%)	10	4	4	5-6	5-6	5	5	5	5
	20	4-5	4-5	5-6	5-6	5	5	5	5
	30	4-5	4-5	5-6	5-6	5	4-5	5	4-5

FSE: Fruit shell extract.

Table 2. These results indicate that the washing fastness of the silk fabrics dyed with *Sterculia foetida* fruit shell was good to very good (4 to 4-5) and the light fastness was of the grade good to very good (5 to 5-6). The color fastness to rubbing the silk fabric dyed without or with three different mordants was found to be in the range of 4-5 to 5, i.e. very good to excellent. The dyed sample washed with boiling water for 10 min and subsequently treated with DMF showed no bleeding. This clearly indicates that dye fixed during exhaust dyeing is not just mechanically held by hydrogen bonding or Van der Waal forces, but may be held by the formation of metal chelates in the presence of tannin, which was present to a significant extent in *Sterculia foetida* fruit shell extract. The tannins having phenolic structure, contribute to the formation of metal chelate with different mordants. Hence, after mordanting, these tannins are insoluble in water, ultimately improving washing fastness [34]. Also, the presence of some dye in the form of covalent bonding with functional groups in silk is also not ruled out due to the possibility of quinone or semiquinone present in tannins. This further explains excellent wash and rubbing fastness properties. Natural dyes are substantive and require a mordant to fix to the fabric and prevent from either fading with exposure to light or washing out. These methods have different effects on the shade obtained after dyeing and also on the fastness properties. Alum is a white powder that is safe for hands and easy to use which produces bright shades and relatively good light fastness. Copper sulfate provides good color fastness to light. It is, therefore, necessary to choose a proper mordanting method to get the desired shade and fastness properties. The further work relating to antibacterial and UV protective properties was carried out by using silk dyed with 30 % shade depth.

Antibacterial Test of Sterculia Foetida Fruit Shell Extract on Silk Fabric

The quantitative analysis of the percent reduction in Gram-positive (G+, *S. aureus*) and Gram-negative (G-, *E. coli*) bacteria was done for silk fabric dyed with only fruit shell extract (no mordant) of *Sterculia foetida* and in presence of three different mordants such as alum, copper sulfate, and harda and results are given in Table 3. The results clearly indicate that the silk fabric dyed with *Sterculia foetida* fruit shell extract inherently showed excellent antibacterial properties both against *S. aureus* and *E. coli* as shown in Figure 4. The percent reduction in bacteria increased on the application of different mordants. To test the wash durability, the antibacterial activity of post-mordanted and without mordanted dyed silk fabrics were tested after five and ten washes using 30 % shade depth.

From the Table 3, it can be seen that the highest colonies reduction (%) was observed in the case of copper sulfate mordant followed by harda and alum mordants against *E. coli.* After five and ten washes this level of colonies reduction percentage gradually decreased. Compared to *E. coli* excellent results were obtained for *S. aureus* without and

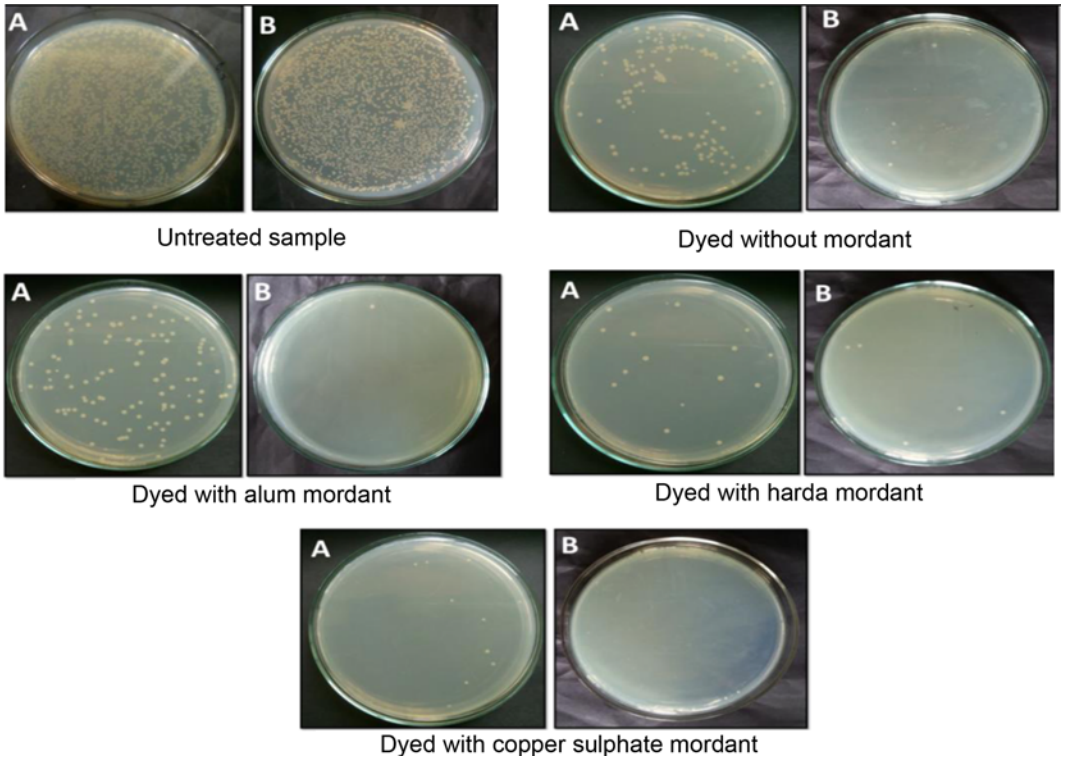


Figure 4. Antibacterial activity of *Sterculia foetida* fruit shell extract; (A) *E. coli* and (B) *S. aureus* on the untreated and treated silk samples.

Table 3. Reduction percentage of *E. coli* and *S. aureus* on dyed silk fabric

Silk fabric	*E. coli* (G-)			*S. aureus* (G+)		
	Colonies reduction (%)			Colonies reduction (%)		
	Initial (no wash)	After five washes	After ten washes	Initial (no wash)	After five washes	After ten washes
FSE without mordant	97.45	94.51	82.63	99.91	99.82	93.87
FSE with alum	98.64	95.83	91.62	100	99.90	95.20
FSE with Harda	99.82	98.02	88.77	99.9	99.73	94.67
FSE with copper sulfate	99.90	99.60	97.63	100	100	97.33

FES: fruit shell extract; *E.coli*: Escherichia coli; *S. aureus*: *Staphylococcus aureus*.

with three different mordants. As seen in all the cases after five washes, still overall reductions in colony growth was more than 99 % for *S. aureus* while for *E. coli*, it ranged from 94.51 % to 99.6 %. Moreover, the reduction percentage in colonies against *S. aureus* was still very good even after ten washes in the range of 93.87 % to 97.33 % which is far better than *E. coli* reduction percentage which was in the range of 82.63 % to 97.63 %. It is evident from this data that a component in *Sterculia foetida* fruit shell extract has strong antibacterial activity without and also in presence of three selected mordants.

The fruit shell extract, when applied with harda and copper sulfate mordant at the same percentage of shade, gave much higher *K/S* values than that of alum and without mordant dyed silk fabric. *K/S* value is due to the greater coloring matter in the dyed silk fabric, and thus more percentage reduction in antibacterial activity is expected. Moreover, the observed antibacterial property of the treated silk fabric might be due to the tannins, present in *Sterculia foetida* fruit shell which was found to be 4.71 % and these polyphenolic compounds that bind to proline residues in silk have been shown to have antibacterial activity. The presence of flavonoids in the extract, as well as terpenoid and saponin, was also detected in fruit shell extract, out of which terpenoid act as an antibacterial agent against both *S. aureus* and *E. coli* whereas saponins which are glycosides provide inhibitory effects on *S. aureus* bacteria. The EDS analysis also showed that Sterculia *foetida* fruit shell extract contains metal ions such as sodium, silicon, magnesium, calcium, potassium along with silicon and chlorine atoms which might be responsible for getting good antibacterial property even after ten washes for without and with three different mordant dyed silk fabric.

Ultra-Violet (UV) Protection Property

UV radiation is one of the major causes of degradation of textile materials due to its very large surface to volume ratio. Even though silk has poor swelling properties, it's very fine nature and a greater number of fibers in the cross-section of yarn results in higher swelling due to capillary absorption, and in turn less UV transmittance. Depending upon the type of dye or pigment, the absorptive groups present in the dyestuff, depth after dyeing, the uniformity, and additives, the UV protection abilities of the textile materials are considerably influenced. Dyes extracted from various natural resources also show the ultra-violet protection factor (UPF) within the range of 15-45 depending on the mordant used [35].

UPF of untreated silk fabric which showed 3.25 has no protective abilities and it allows transmission of solar radiation. There is an improvement of UPF rating of silk fabric after dyeing with fruit shell extract both without mordant and with harda and copper sulfate mordants, whereas there was not much improvement in silk fabric after mordanting with alum. Analysis of results in Table 4 reveals that mordanting of silk fabric with harda and copper sulfate showed good UPF rating even after ten washes. Up to ten washes of dyed silk fabric with mordants showed slight decrease in UPF value due to washing-off of dye-mordant complex. However, these values were of the order of "good" (15-24 UPF) category. Maximum UV protection was found in the case of fabric mordanted with harda. Improvement of

Table 4. Ultra-violet protection value of silk fabric dyed with fruit shell extract

Sample	Ultraviolet protection factor (UPF), 290-400 nm		
	Initial (no wash)	After five washes	After ten washes
FSE dyed without mordant	22.89	21.69	19.94
FSE dyed with copper sulfate mordant	22.64	21.17	20.93
FSE dyed with alum mordant	16.74	15.51	13.50
FSE dyed with harda mordant	31.64	29.96	25.36

FSE: fruit shell extract.

UV protection is mainly attributed to the synergistic effect of mordant and *Sterculia foetida* fruit shell extract as a natural dye. Deep dyeing due to the presence of tannin also helps to increase UPF rating. Moreover, "good to very good" UPF rating after dyeing with *Sterculia foetida* fruit shell might be due to coated layer on the dyed silk fabric as shown in SEM image (Figure 6). EDS analysis also shows the presence of an elemental peak of silicon, magnesium, calcium, potassium, sulfur, phosphorus, and chlorine on dyed silk fabric with fruit shell extract without any use of mordant which also support the ultraviolet protection of silk fabric.

ATR-FTIR Analysis

FTIR spectral analysis was performed for understanding the functional groups present in the untreated silk, treated silk fabric and *Sterculia foetida* fruit shell extract and results are shown in Figure 5. Concerning the FTIR spectra of the dried fruit shell extract, it showed a broad peak at 3265 cm^{-1}, indicating the presence of exchangeable protons, likely from alcohol, amine, or carboxylic acid group, most probably the -OH stretching of hydroxyl moiety of carboxylic acid in gallic acid-based tannins [36]. The IR absorption bands observed at 1040-1090 cm^{-1} might be assigned to antisymmetric stretching modes of the phosphate group (PO_4^{-3}) present in inorganic salts [35]. Moreover, for the dried *Sterculia foetida* fruit shell extract from Figure 5(c), it shows the peak at 1037 cm^{-1} and 1249 cm^{-1}, may be due to C-O stretching of phenolic compounds, such as lignin. The additional peak at 1604 cm^{-1} could be stretching vibration of -C=C in aromatic groups. When this compound was used to treat the silk fabric, the hydroxyl (-OH) group of the phenol might have engaged in the hydrogen bond formation, broadening the -N-H stretching band of amide group of original silk β-sheet structure in treated silk fabric (b). Both untreated (a) and fruit shell extract treated silk fabric (b) showed a peak at 3282 cm^{-1}, assigned to the -N-H stretching vibration. However, peak area is more for the treated silk as illustrated in Figure 5(b) as compared to the untreated silk. As far as the *Sterculia foetida* fruit shell extract treated silk fabric is concerned, the peak corresponding to N-H stretching at 3282 cm^{-1}, C=O (amide I band indicative of β-sheet) at 1625 cm^{-1} and N-H deformation (amide II) at 1512 cm^{-1} increased in the treated sample compared to the untreated silk fabric. The increasing absorbance at 1548 cm^{-1} and 1016 cm^{-1} in the treated compared to control silk indicates the presence of the greater number of precursor helical structures and random coils in secondary structure perturbed from the normal β-sheet structure. Peaks at 1130 cm^{-1} indicative of -CH_2OH polyphenols and tannins at 1733 cm^{-1} are observed only in the treated silk spectra.

SEM-EDS Analysis

SEM micrograph of silk fabrics in Figure 6 shows the fiber surface of the untreated and three different mordants treated dyed silk fabric. As shown in Figure 6(a), the untreated silk fabric had a bright, smooth surface, with no surface imperfections and irregularity. Mordant with alum-treated silk fabric as shown in Figure 6(b) reveals that the surface of the material has less deposition of a coated layer with the solution of the *Sterculia foetida* fruit shell extract. With copper sulfate mordant as shown in Figure 6(c), the treated silk fabric surface is found to have more deposition as a coated layer on silk surface as compared to alum. Mordant harda as shown in Figure 6(d) showed the maximum deposition of the coated layer as compared to alum and copper sulfate. Moreover, it also showed rougher and irregular surface than that of the untreated silk fabric. This herbal surface coating might have helped in increasing Ultraviolet protective as well as the antibacterial properties of the silk fabric.

Elemental peaks of *Sterculia foetida* fruit shell extract, untreated and treated silk fabric are shown in Figure 7 with its atomic and weight percentages are reported in Table 5. *Sterculia foetida* fruit shell extract showed several elemental peaks as illustrated in Figure 7(a). These correspond to carbon, oxygen, magnesium, silicon, sodium, calcium,

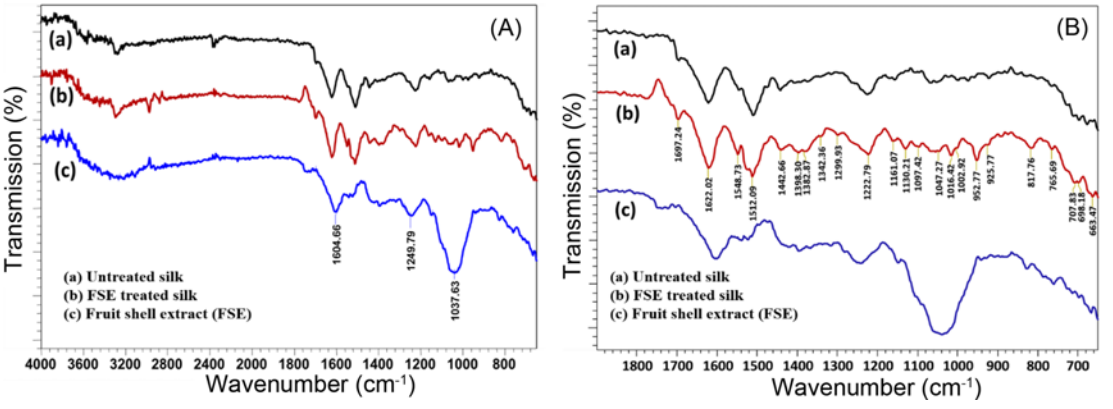


Figure 5. ATR- FTIR images of (a) untreated, (b) treated silk fabric without mordant, and (c) *Sterculia foetida* fruit shell extract.

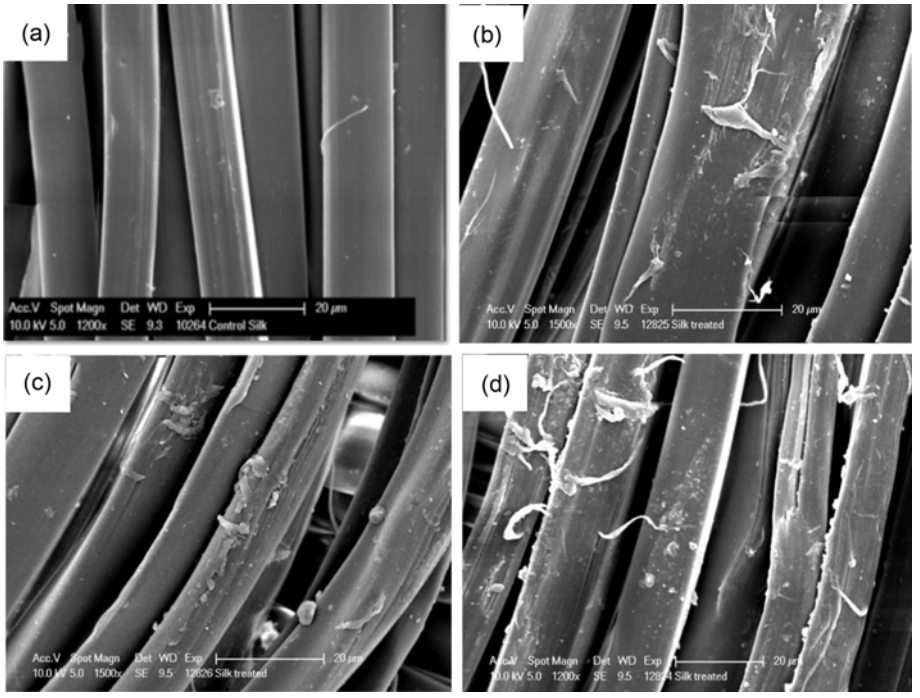


Figure 6. SEM images of (a) untreated, (b) alum, (c) copper sulfate, and (d) harda treated silks.

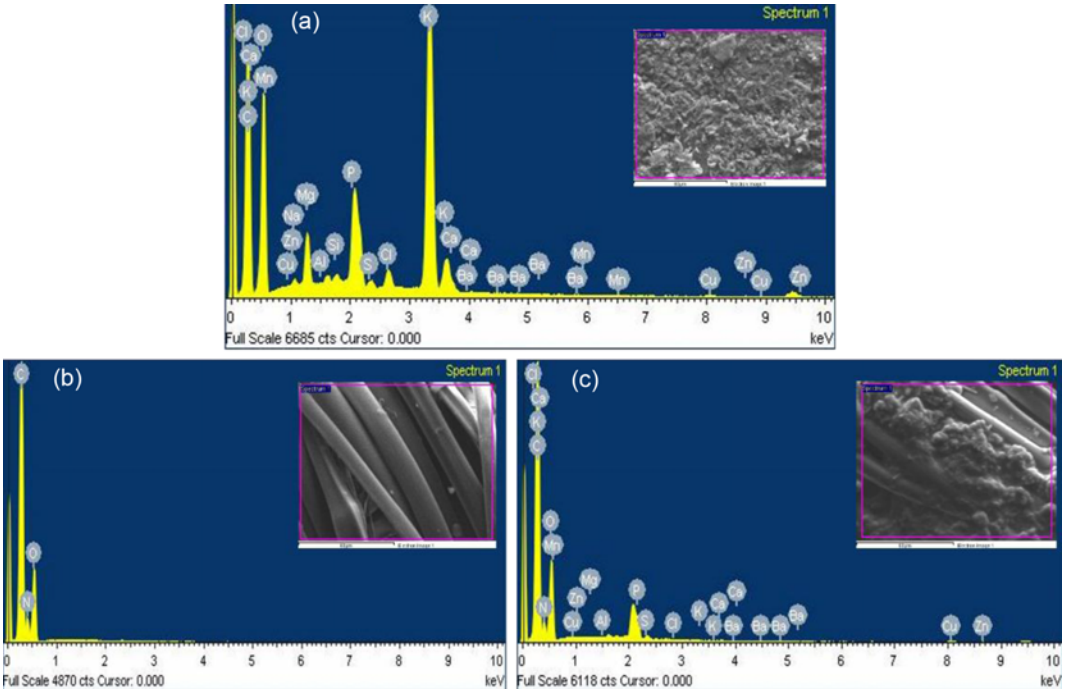


Figure 7. EDS analysis of (a) fruit shell extract, (b) untreated, and (c) treated silk fabrics without mordant.

potassium, sulfur, phosphorus, and chlorine. As expected, the untreated silk sample showed only the presence of carbon, nitrogen, and oxygen atom as the technique could not detect hydrogen atom as shown in Figure 7(b). The elements present in the dried fruit shell extract as well as treated extract solution on silk sample as illustrated in figure 7(c) might be in the form of either metal oxide or metal chloride. It has been found that fruit shell extract treated silk fabric contained atomic percentages of potassium, silicon, magnesium, phosphorus, calcium, sulfur, and chlorine of

Table 5. Quantification of elements present in *Sterculia foetida* fruit shell extract, untreated and treated silk fabric

Elements	*Sterculia foetida* fruit shell extract (a)		Untreated silk (b)		*Sterculia foetida* fruit shell extract treated silk (c)	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
Carbon (C)	21.96	33.18	44.87	50.66	44.90	51.46
Nitrogen (N)	0.00	0.00	21.73	21.03	12.44	12.23
Oxygen (O)	44.01	49.01	33.40	28.31	36.93	33.73
Sulfur (S)	0.59	0.33	0.00	0.00	0.62	0.27
Sodium (Na)	0.38	0.30	0.00	0.00	1.14	0.71
Silicon (Si)	0.41	0.26	0.00	0.00	0.17	0.09
Magnesium (Mg)	2.54	1.90	0.00	0.00	0.28	0.17
Phosphorus (P)	0.81	0.47	0.00	0.00	0.30	0.13
Chlorine (Cl)	1.32	0.67	0.00	0.00	0.60	0.25
Potassium (K)	26.96	12.51	0.00	0.00	1.63	0.60
Calcium (Ca)	1.02	0.46	0.00	0.00	0.99	0.36

1.63, 0.17,0.28, 0.30, 0.99, 0.62, and 0.60, respectively, which might be responsible for the good antibacterial and UV protection properties of the without and with mordanted and dyed silk fabric.

X-ray Diffraction (XRD) Analysis of Silk

XRD analysis of fruit shell extract dyed silk compared to untreated silk was carried out for the purpose of determining the change in secondary structure of silk [38,39] as shown in Figure 8. Bombyx mori silk contains the fibrous protein fibroin which has been known to adopt polymorphic structures namely silk I (α-form, type II β-turn) structure dominated by α-helix and random coil structures, and silk II (antiparallel β-pleated sheet) [40,41], and silk III, a trigonal structure - a threefold helical chain conformation identified for fibroin at an air-water interface [42]. For silk, the Bragg reflections at 19.8° and 24.2°, which correspond to the (210) and (002) planes of the protein β-sheet structure respectively,

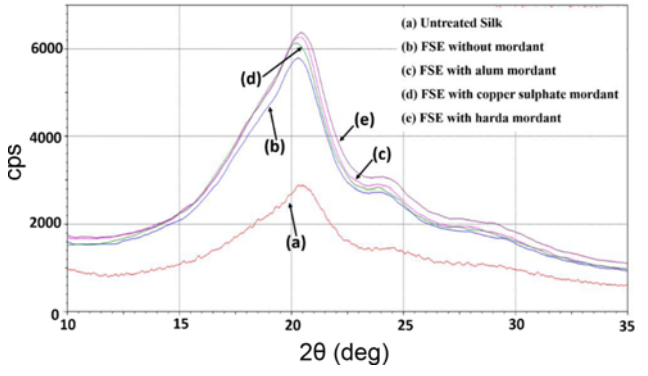


Figure 8. X-ray diffraction (XRD) analysis plots of (a) untreated silk and fruit shell extract treated silk (b) without mordant, (c) with alum mordant, (d) with copper sulfate mordant, and (e) with harda mordant.

are seen [43].

For the treated silk, data shows (refer to Table 6) similar diffraction peaks of the 2θ angles, consistent with those of the typical silk protein, though the protein β-sheet structure is perturbed on dyeing with and without mordants, to indicate partial change to silk I forms, i.e., ordered structure composed of α-helix and random coil forms, along with lowered crystallinity [27]. This effect is maximum when dyed without mordant, giving the lowest crystallinity of the silk samples. The samples show crystallinity in the following order: untreated silk > silk dyed with $CuSO_4$ mordant > silk dyed with alum mordant > silk dyed with harda mordant > silk dyed without mordant. The metallic salt mordant dyed silk show different peaks characteristic for (β-sheet) forms, while the harda mordanted dyed silk does not show the characteristic 2θ angle for (201) plane.

Mechanism of Imparted Multifunctional Properties of Silk Fabric

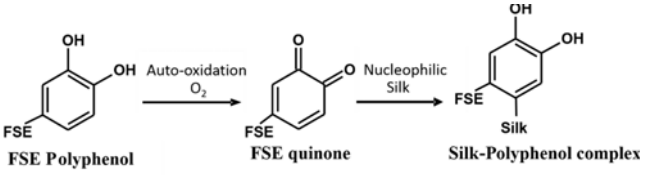
FSE treated silk fabric showed coloration which may be attributed to the presence of phenols, tannin, and other phytochemical groups present which are responsible for the formation of coloration on silk fabric alone as well as with three different mordants. Anthocyanins (a component of FSE) belong to the group of flavonoid natural dyes and contain three to six hydroxyl groups that can be methylated. There might be the electrostatic interaction of the anionic silk and cationic anthocyanins in FSE. During dyeing of the polypeptide chains of silk fibers, dye anions and metal cations have a strong attraction towards positively charged amino and negatively charged carboxyl groups, respectively. Hence, they enter the fiber and form ionic bonding between dye and fiber, between the metal ion and fiber and finally between the dye and metal ions. The dye-metal chelates thus produced also form coordinate bonds with the uncharged

Table 6. Comparison of XRD data with untreated and treated silk [44-46]

Sample	2 theta (2θ)	*d*-spacing (Å)	Conformation	Crystallinity (%)
Untreated silk	19.28	4.599	Silk I	25.797
	19.58	4.53	Silk I	
	20.82	4.263 (201) plane	Silk II (β-sheet)	
	24.46	3.63 (002) plane	Silk II (β-sheet)	
FSE dyed silk without mordant	16.04	5.52	Silk 1	24.21
	18.0	4.92	Silk I	
	20.28	4.37 (201) plane	Silk II (β-sheet)	
	23.96	3.71 (002) plane	Silk II (β-sheet)	
	27.96	3.88	Silk I	
	29.42	3.03	Silk I	
FSE dyed silk with alum Mordant	16.7	5.30	Silk II (β-sheet)	24.73
	18.0	4.91	Silk I	
	20.38	4.35 (201) plane	Silk II (β-sheet)	
	23.8	3.73 (002) plane	Silk II (β-sheet)	
	25.88	3.44	Silk I	
	28.22	3.16	Random coil [23]	
	29.48	3.027	Silk I	
FSE dyed silk with $CuSO_4$ mordant	17.02	5.20	Silk II (β-sheet) [24]	23.86
	18.84	4.706	Silk II (β-sheet) [24]	
	20.22	4.39 (201) plane	Silk II (β-sheet)	
	23.92	3.72 (002) plane	Silk II (β-sheet)	
	25.84	3.45	Silk I	
	29.82	2.99	Silk I	
FSE dyed silk with harda mordant	17.52	5.06	Silk I	23.43
	19.91	4.46	Silk I	
	24.04	3.70 (002) plane	Silk II (β-sheet)	
	25.58	3.48	Silk I	
	27.92	3.19	Random Coil [25]	
	29.08	3.07	Silk I	

FSE: Fruit shell extract.

amine (-NH_2) groups of silk.



Considering the stoichiometry of dye fiber molecules, one molecule of dye can form a bond with one site of fiber molecule. But one molecule of mordant can form bonds with two or more molecules of dyes. As a result, when the mordant molecule binds on to fiber it holds two molecules of dye with it. Therefore, using mordant, the color yield was increased [47]. This is also due to the color enhancement by photophysical π-π interactions, as shown in the UV-visible spectral studies. ATR-FTIR and XRD data analysis confirm the changes in silk secondary structure, on dyeing in presence and absence of mordants. However, natural dyes in general with few expectations are non-substantive, and hence it must be used in conjunction with mordants. Different positive metal ions (potassium, magnesium, calcium) present in the FSE (as observed from EDS analysis), the presence of tannin, terpenoid, saponin bio-molecules jointly may rupture the negatively charged bacterial cell wall, finally killing the bacteria and provide antibacterial property. Moreover, good UPF property after treatment of FSE might be due to a coated layer which contains different metal oxides on the dyed silk fabric as shown in SEM and EDS analysis. Polyphenols (phytochemical analysis) and anthocyanins (UV-visible spectroscopy analysis) have been reported as potential effective agents to prevent ultraviolet radiation.

Conclusion

Sterculia foetida fruit shell extract can be successfully employed as a natural colorant for dyeing of silk fabric. Silk fabric showed higher color depth in terms of enhanced *K/S* values on post mordanting with harda (myrobalan) as compared to those without mordanting. The silk fabric showed progressive increase in *K/S* values as the mordant was varied from alum<$CuSO_4$<harda. When *Sterculia*

foetida fruit shell extract was used as a natural dye, the dyed silk fabric showed very good antibacterial activity against *S. aureus* and *E. coli* bacteria. On using additional mordant, the treated fabric showed very good wash durability, even after ten washes. *Sterculia foetida* fruit shell extract also showed "good to very good" rating for Ultra-violet protection, even after ten washes. Hence, it could be concluded that *Sterculia foetida* fruit shell extract shows promising potential to be used as an industrial colorant to silk textile while simultaneously imparting antibacterial and ultra-violet protection properties.

Acknowledgements

One of the authors Mr. Pintu Pandit is indebted to University Grants Commission - Basic Scientific Research (UGC-BSR) having award letter number F.25-1/2014-15 (BSR)/No. F.5-65/2007(BSR), for the Ph. D. Tech. scholarship support from the Govt. of India during the study period.

References

1. K. H. Prabhu, M. D. Teli, and N. G. Waghmare, *Fiber. Polym.*, **12**, 753 (2011).
2. M. D. Teli, J. Sheikh, and M. Kamble, *Text. Light Ind. Sci. Technol.*, **2**, 78 (2013).
3. A. K. Samanta, T. R. Kar, A. Mukhopadhyay, D. Shome, and A. Konar, *Text. Res. J.*, **86**, 2179 (2016).
4. K. Singha, S. Maity, and M. Singha, *Int. J. Text. Sci.*, **1**, 69 (2012).
5. M. A. R. Bhuiyan, A. Shaid, and M. A. Khan, *Chem. Mater. Eng.*, **2**, 96 (2014).
6. S. N. Chattopadhyay, N. C. Pan, A. K. Roy, S. Saxena, and A. Khan, *J. Text. Inst*., **104**, 808 (2013).
7. M. D. Teli and P. Pandit, *J. Ind. Text*. doi:10.1177/1528083717725113 (2017).
8. M. D. Teli and P. Pandit, *ACS Sustain. Chem. Eng.*, **5**, 8323 (2017).
9. M. D. Teli and P. Pandit, *J. Nat. Fibers*, http://dx.doi.org/10.1080/15440478.2017.1328327 (2017).
10. M. D. Teli, M. R. Sahoo, and P. Pandit, *Int. Res. J. Eng. Technol.*, **4**, 1310 (2017).
11. M. D. Teli, P. Pandit, and P. Ugale, *J. Text. Assoc.*, **77**, 27 (2016).
12. R. Pandey, S. Patel, P. Pandit, S. Nachimuthu, and S. Jose, *J. Clean. Prod.*, doi:10.1016/j.jclepro.2017.10.268 (2017).
13. M. Joshi, S. W. Ali, R. Purwar, and S. Rajendran, *Indian J. Fibre Text. Res.,* **34**, 295 (2009).
14. M. D. Teli and P. Pandit, *J. Ind. Text*. doi:1528083717725113 (2017).
15. M. M. Kamel, H. M. Helmy, H. M. Meshaly, and A. Abou-Okeil, *J. Text. Sci. Eng.*, **5**, 1 (2015).
16. M. D. Teli and P. Pandit, *J. Text. Assoc.*, **76**, 293 (2017).
17. S. Basak, K. K. Samanta, S. K. Chattopadhyay, P. Pandit, and S. Maiti, *Colour. Technol.*, **132**, 135 (2016).
18. M. D. Teli and P. Pandit, *Fiber. Polym.*, **18**, 1679 (2017).
19. Y. G. Prakash, V. Gopal, and L. Kaviarasan, *Int. J. Pharm. Rev. Res.*, **2**, 93 (2012).
20. P. Sivakumar, K. S. Parthiban, P. Sivakumar, M. Vinoba, and S. Renganathan, *Ind. Eng. Chem. Res.*, **51**, 8992 (2012).
21. C. H. Bindhu, J. R. C. Reddy, B. Rao, T. Ravinder, P. P. Chakrabarti, M. S. L. Karuna, and R. B. N. Prasad, *J. Am. Oil Chem. Soc.*, **89**, 891 (2012).
22. R. N. Chopra, S. L. Nayar, and I. C. Chopra, "Glossary of Indian Medicinal Plants", New Delhi: Council of Scientific and Industrial Research, 1956.
23. D. G. Naik, A. M. Mujumdar, R. J. Waghole, A. V. Misar, S. W. A. Bligh, A. Bashall, and J. Crowder, *Planta Med.*, **70**, 68 (2004).
24. V. Kuntić, N. Pejić, B. Ivković, Z. Vujić, K. Ilić, S. Mićić, and V. Vukojević, *J. Pharm. Biomed. Anal.*, **43**, 718 (2007).
25. M. D. Teli, K. K. Samanta, P. Pandit, S. Basak, and S. K. Chattopadhyay, *Fiber. Polym.*, **16**, 2375 (2015).
26. M. D. Teli, K. K. Samanta, P. Pandit, S. Basak, and S. K. Chattopadhyay, *Indian J. Nat. Fiber*, **1**, 1 (2014).
27. B. A. Bohm, "Introduction to Flavonoids", Harwood Academic Publishers, 1998.
28. A. M. Gómez-Caravaca, M. Gómez-Romero, D. Arráez-Román, A. Segura-Carretero, and A. Fernández-Gutiérrez, *J. Pharm. Biomed. Anal*., **41**, 1220 (2006).
29. K. Bouzid, F. T. Benali, R. Chadli, M. Bouzouina, A. Bouzid, A. Benchohra, and M. M. Dif, *Eur. J. Mol. Biotechnol*., **6**, 160 (2014).
30. S. H. Haekkinen, S. O. Kaérenlampi, I. M. Heinonen, H. M. Mykkänen, and A. R. Toerroenen, *J. Sci. Food Agric*., **77**, 543 (1998).
31. J. M. Lobbes, H. P. Fitznar, and G. Kattner, *Anal. Chem.*, **71**, 3008 (1999).
32. E. Conde, E. Cadahia, and M. C. García-Vallejo, *Phytochem. Anal*., **8**, 186 (1997).
33. M. D. Teli, S. P. Pandian, and U. V. Vyas, *Indian J. Fibre Text. Res*., **15**, 18 (1990).
34. B. J. Agarwal and B. H. Patel, *Man Made Text. India*, **45**, 237 (2002).
35. D. Saravanan, S. N. Sree Lakshmi, K. Senthil Raja, and N. S. Vasanthi, *Indian J. Fibre Text. Res*., **38**, 156 (2013).
36. A. Ricci, K. J. Olejar, G. P. Parpinello, P. A. Kilmartin, and A. Versari, *Appl. Spectrosc. Rev*., **50**, 407 (2015).
37. F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).
38. Y. Hu, Q. Zhang, R. You, L. Wang, and M. Li, *Adv. Mater. Sci. Eng.*, **2012**, Article ID 185905 (2012).
39. E. Kamalha, Y. Zheng, and Y. Zeng, *Res. Rev. BioSciences,* **7**, 76 (2013).
40. Q. Lu, X. Hu, X. Wang, J. A. Kluge, S. Lu, P. Cebe, and D. L. Kaplan, *Acta Biomater.*, **6**, 1380 (2010).
41. L. F. Drummy, B. L. Farmer, and R. R. Naik, *Soft Matter*, **3**, 877 (2007).
42. R. F. P. Pereira, M. M. Silva, and V. de Zea Bermudez,

Macromol. Mater. Eng., **300**, 1171 (2015).
43. J. Yao, D. Xiao, X. Chen, P. Zhou, T. Yu, and Z. Shao, *Macromolecules*, **36**, 7508 (2003).
44. G. M. Nogueira, A. C. D. Rodas, C. A. P. Leite, C. Giles, O. Z. Higa, B. Polakiewicz, and M. M. Beppu, *Bioresour. Technol.*, **101**, 8446 (2010).
45. G. Freddi, Y. Gotoh, T. Mori, I. Tsutsui, and M. Tsukada, *J. Appl. Polym. Sci*., **52**, 775 (1994).
46. M. A. de Moraes, G. M. Nogueira, R. F. Weska, and M. M. Beppu, *Polymers*, **2**, 719 (2010).
47. M. G. Uddin, *J. Text.*, **2014**, Article ID 405626 (2014).