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Bio-Dyes, Bio-Mordants and Bio-Finishes: Scientific Analysis for Their Application on Textiles

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Abstract

This chapter deals with testing/characterization and other scientific analyses and process standardization for the application of bio-dyes, bio-mordants, and bio-finishing agents on cotton textiles. Few case studies on selective natural/bio-dyes in terms of Fourier-transform infrared spectroscopy (FTIR), high-performance liquid chromatography (HPLC), ultraviolet–visible (UV–VIS) spectroscopy, and differential scanning calorimetry (DSC) analysis have been discussed. Based on these characterizations, few test protocols have been established for the identification of each natural dye from dyed textiles, as standards of Bureau of Indian Standards (BIS). One such case study on madder is shown. Exemplary case studies on the standardization of extraction, suitable mordanting, and dyeing process variables for the application of specific natural dyes on cotton have also been provided. Few case studies on improving color fastness to washing and sunlight by suitable post-treatment with natural agents have been discussed. Case studies on different post-treatments/simultaneous dyeing and finishing treatments with bio-dyes and bio-finishing agents for improving antibacterial properties and UV protection factor (UPF) have also been explained.

Keywords: bio-mordants/mordants, bio-dyes/natural dyes, bio-finishes/natural finishes, cotton, colour fastness, dyeing process variables, natural antibacterial finish, natural UV-protective finish, madder, tesu

1. Introduction

Natural dyes are the coloring matters derived from natural sources. The production of synthetic dyes involves many chemical reactions with petrochemical-based dye intermediates, which are high energy consuming and deliver hazardous toxic chemicals to the environment [1–5]. This pollution problem of production of synthetic dyes has led many researchers worldwide to reinvestigate the methods of producing eco-friendly natural dyed textile products for future eco-textiles. Natural fiber-based textiles are biochemically processed with enzymes and dyed with natural dyes using bio-mordant and later finished with natural finishing agents in an eco-friendly mode; these whole processing chain and such textile products developed are considered as sustainable [6–8]. A sustainable textile product thus should begin and end its life cycle as smoothly as possible without harming not only human beings but also the flora and fauna of the environment.

The sustainability of textile and clothing consists of a fairly long supply chain, which starts from fiber formation and ends at the apparel production, use and disposal at the end, covering the entire life cycle analysis of textile products, where nearly half of this entire supply chain occupies the said production process life cycle and the rest is left to the consumers in terms of its usage and disposal.

A sustainable textile product can be defined as one that is created, produced, transported, used and disposed of with due consideration to environmental impacts, social aspects and economic implications, thereby satisfying all three pillars of sustainability, and is expected to create the minimum possible or very least environmental and social impacts throughout its entire life cycle. In a specific product life cycle of any textiles, it uses different materials and consumes different forms of energy and many other processing inputs to produce or generate the desirable textile products as desirable outputs in different stages of their manufacture, packaging, despatch, use and final disposal. To make this life cycle sustainable for any textile goods, all these inputs and outputs are to be environment-friendly and eco-safe particularly to the living bodies on earth including humans for the entire life cycle, i.e. it should be noncarcinogenic and has to utilize renewable/ recycled input streams with the least energy consumption.

When synthetic dyes were not known to humankind, dyeing of textiles was dependant on natural colors only. Later, when synthetic dyes were made available at ease and were started their commercial selling at low cost under different classes as ready-made dye powders to use with low cost and processing advantages, large-scale textile manufacturers and even small-scale dyers had been shifted to use more and more of synthetic dyes and pigments. But, with the enhancement of knowledge on environmental concern, people started to search for eco-friendly dyeing approaches as alternatives, as synthetic dyes are made from a non-renewable source of petrochemical base with chances of generating toxic chemicals as the by-product, which are not environment-friendly. Hence, the importance of eco-friendly dyeing of textile goods has started re-examination with the growing interest of consumers towards the use of eco-friendly natural dyed fiber-based textile products, which thus have been revived now needing more and more scientific information and analysis on those.

Moreover, the century-old natural dyeing processes had never died or discarded fully, and it is being practised still in different corners of the world and India is not an exception. Considering the niche market of eco-friendly dyed and finished natural fiber-based or organic textiles, recently, most of the textile dyers-cum-exporters are showing fresh interest for using natural dyes and natural finishing agents for textile dyeing, printing and finishing, if it can bring much more value addition (than using synthetic dyes), as a sustainable textile processing for eco-textile products. Natural dyes in addition of being eco-friendly produce very uncommon, soothing and soft shades in comparison with synthetic dyes [9]. For a successful commercial use of natural dyes for any particular natural fibre-based textiles, there has to be a standardization of process variables [9, 10] for extraction, mordanting and dyeing of that particular fiber-natural dye system with its testing and characterization [11], identification of important ingredients and other scientific analysis and process standardization for application of such bio-/natural dyes, bio-/natural mordants and bio-/natural finishing agents on natural fiber-based textiles. To obtain newer compound shades using a mixture of natural dyes needs a test of compatibility [12, 13]. The scientific determination of the dyeing rate, dyeing kinetics/thermodynamics and other physico-chemical parameters [14] of dyeing of a specific natural dye for specific textiles should be derived to establish appropriate standardized scientific dyeing techniques/procedures with the optimization of

dyeing process variables and to decide the required after-treatment process necessary for obtaining an acceptable color fastness behavior with reproducible and uniform color yield. The status of natural dyeing up to 2001 [4], a comprehensive review on scientific studies on natural dyes up to 2009 [5, 6] including the characterization and scientific analysis for natural dyes, eco-friendly natural dyeing with bio-mordants [15], use of sonicator/ultrasonic assistance [16, 17] in natural dyeing and enzyme-based preparation and natural dyeing of textiles [18] and functional properties of selective natural dyes like UV protection [19, 20] and antibacterial properties [21, 22] are available in the literature.

However, the major problem of natural dyes encountered is their sufficient availability due to difficulty in collection, cost, poor color fastness and standardized methods of their application. Till date, there are limited studies available in the literature on scientific evaluation and testing, characterization, identification of important ingredients and process standardization related to optimization of dyeing process variables, mechanism of dye-mordant-fiber fixation, role of different mordants and mordanting assistants/additives and chemical pre-treatments/post-treatments/modifications for natural dyeing with evaluation of dyeing rate, dyeing kinetics and to develop compound shades (to overcome shade limitations) by use of binary or ternary mixture. Hence, there is a need for precise scientific and technological knowledge and development of systematic scientific methods of dyeing textiles with natural dyes and natural finishing agents.

Natural colorants have the following advantages as compared to synthetic colorants, but natural dyes have some disadvantages too.

The advantages [6–9] of natural colorants and natural finishing agents:

1. **Eco-friendliness:** Natural dyes are less toxic, less polluting, less health hazardous, noncarcinogenic and non-toxic. Most of the natural dyes are considered to be eco-friendly as these are obtained from renewable resources as compared to synthetic dyes (derived from non-renewable petroleum resources and synthesized in an intermediate route involving many chemical hazards).
2. **Soothing to the human eye:** They have harmonizing colors, are gentle, soft and subtle and create a restful effect producing a soothing shade.
3. **Biodegradability:** Unlike non-renewable basic raw materials for synthetic dyes, the natural dyes of plant sources are usually agro-renewable/vegetable-based products and at the same time are biodegradable.
4. **Availability of a wide range of colors:** Natural dyestuff also can produce a wide range of colors by a mix-and-match system. A very small variation in the dyeing technique or the use of different mordants with the same dye or different concentrations of mordants on the same dye can create a variety of new shades.
5. **Functional benefits of natural dyes/finishing agents towards wearers:** Many natural dyes and natural finishing agents can be used as UV-protective and antibacterial materials. Natural textiles dyed with suitable natural colorants and finished with specific natural finishing agents can thus provide protection from UV rays, microbes or even mosquito bites. Natural dyes, e.g. myrobalan, turmeric, madder/manjistha (MJ), Arjuna, safflower, etc., possess a medical curative property as Ayurvedic medicine.

Despite so many advantages, natural dyes have some drawbacks [6–9] too as listed below:

1. Requirement of a longer time: Natural dyes require a longer dyeing time for extraction and purification and also for actual dyeing via mordanting in comparison with time required to apply synthetic dyes on same textiles, for additional step of mordanting. Dye extraction steps require additional time and setup. The exhaustion of most of the natural dyes on textile materials is poor in spite of using the mordant which leaves a large quantity of colorant component in the dye bath after dyeing due to poor exhaustion, which increases the cost of dyeing though natural dyes are eco-safe as compared to dyeing with synthetic dyes.
2. Shade range limitations: It is difficult to obtain all desirable shades from natural dyes, i.e. ranges of shade available from natural dyes and pigments are limited. Out of the required three primary colors—red, green and blue—although there are several sources for reddish and greenish dyes, there is only one major source of the blue natural dye, i.e. from natural indigo. As different natural dyes and pigments are differing in their chemistry and application process, only few natural dyes are compatible to be applied together in a binary/ternary mixture and obviously are noncompatible for producing compound shades.
3. Non-reproducible shade: Due to the difference in proportion of constituents, the variation of these agro-products from one crop season to another in terms of location, species maturity period and consistent shade always cannot be obtained. However, after extraction, by UV spectral analysis, if the dye extract can be diluted to bring it to the same concentration level of colored solution, the reproducibility of shades can be better assured even with the extract of varying concentration of colored extract of such selective natural dyes.
4. Fastness properties: Only a few natural dyes and pigments possess a good rating of the overall color fastness satisfying consumers' needs. As mordants with objectionable metal salts such as Cr, Cu, Sn, etc. are not permitted or allowed under eco-norms of different countries (ecomark scheme of India or OTN-100 norms of the UK, etc.), the overall color fastness rating of natural dyed textiles is sometimes poor to medium only. However, recent approaches of a suitable pre-treatment with natural bio-mordants containing tannic acid residues or pre-treatment with natural cationic agents like acid-extracted soya bean seed waste [23] and post-treatment with chitin (natural cationic agent) or post-treatment with natural UV absorber agents (like orange peel, eucalyptus leaves, etc.) are being used for enhancing the color fastness rating for wash and light to an acceptable level.

The present scenario shows that an approximately 1% share of textiles is only being dyed with natural dyes that are used mostly in the cottage sector by traditional artisans and small-scale textile dyers. The reasons for not using natural dyes in the large-scale textile sector were, however, lack of availability of ready extracted and purified dye powder, lack of standardized dyeing processes with assurance of reproducible and uniform shades and non-warranty of the required level of color fastness to achieve. Natural dye application processes cannot be easily implemented by large-scale textile mills as machine dyers. However, recent effort of people, understanding environmental friendliness of natural dyes and finishes with

growing demands of customers for such eco-friendly products, ready availability of extracted and purified natural dye powder by certain newer natural dye manufacturers along with their recommendation of standardized mordanting and natural dyeing and finishing processes have partly overcome these issues for machine dyeing viable in large-scale textile sector. The natural bio-indigo dyeing on cotton denim [24] to produce bio-denim using natural reducing agents, as developed by Ama Herbal Lab Pvt Ltd, Lucknow and use of earth colour from plant waste developed by Archoma, Mumbai has become a commercial success in India for large scale industry.

However still natural dyeing industry is a labour-intensive industry concentrating in the small-scale sector of handloom textiles and khadi (hand spun and handloom woven) sector in developing countries like many South-East Asian countries providing livelihoods by creating job opportunities for all those engaged in cultivation, extraction and application of these natural dyes on textiles. Cultivation of natural dye plant is also an alternative cash crop to the cultivators. For the promotion of natural dyeing and natural finishing of textiles including the khadi sector, the availability of extracted and purified natural dye and pigment powder as ready soluble colorants has to be assured to promote such eco-friendly natural dyed textiles in the khadi sector. Some work [19] in this endeavor by Mahatma Gandhi Institute for Rural Industrialization (MGIRI), Wardha, Maharashtra, India, is worth mentioning for the cotton khadi sector. As the small-scale khadi and handloom sectors of textiles lack the resources to install and operate expensive effluent treatment plants needed to bring the synthetic dye's effluent within the eco-limits set by regulatory authorities, they will be more benefitted by adopting standardized dyeing methods with natural dyes and natural finishes on specific natural fiber-based textiles, by mitigating its major problems.

To promote natural dyed textiles, there is an essential need of establishing proper identification methods and test protocols with suitable national and international test standards of identifying natural dyes from the dyed textiles followed by establishing proper certification protocols for natural dyes from the natural dyed textiles in the form of natural dye mark protocol, which would definitely improve consumers' confidence and would benefit both producers and users. In this attempt BIS, India, and also ISO/TC-38 have been working on it since 2015, and till date few such test standards are finalized and published [25, 26] by BIS, India, and ISO/TC-38 has framed a special working group—WG-31—on natural materials for textiles for finalizing such global standards for worldwide consumers and producers benefit, so that both large- and small-scale sectors of textile industries can get benefitted.

2. Results and discussion on a few case studies for the application of natural dyes on textiles

2.1 Characterization and testing of natural dyes

2.1.1 Ultraviolet-Visible UV-VIS spectral analysis of aqueous extracted solution of natural dyes

1% aqueous solution of each purified individual natural dye powder was separately prepared and was subjected to a wavelength scan in a UV-VIS absorbance spectrophotometer for 200–700 or 1100 nm wavelength range to identify the predominant lambda maximum with specific peaks in UV region and specific peaks in visible region in order to understand the UV-absorbing nature of the dye.

Absorbance peaks of UV-VIS spectrum of a dilute aqueous solution of few individual purified natural dyes have been shown in **Table 1**.

In the UV-VIS spectrum of each natural dye, if there are predominating sharp peaks in the UV region, the dye has a reasonable UV-absorbing character, indicating that the said particular dye may have a higher UV absorption rate enhancing the UV-fading rate due to its more UV-absorbing character, and hence specific cares and after-treatments with more stronger UV absorber compounds [8, 13] are necessary for improving light fastness of particular dyed textiles, by additional treatment with more stronger UV absorber compounds having preferential UV absorption, leaving the dye with UV absorber character to absorb less UV light.

It may be observed from the wavelength scan of UV-VIS spectrum of tesu extract (**Figure 1**) in an aqueous medium that in the UV region (190–380 nm), there is hardly any preferential absorbance peak in this UV region, but in the extended UV zone, it shows a small broad hump at 250 nm and a small trough at 385 nm along with showing negative absorbance in a particular wavelength (190–250 nm). Thus, there is almost no preferential UV absorption which occurs in tesu colorant (extracted in the aqueous medium), and hence the light fastness of tesu dye is not to be affected much by UV light exposure, showing predominating hue by large peak at λ_{max} -490 nm for tesu.

UV-VIS spectrum of few selective natural dyes and their peaks is shown in **Figure 2** and **Table 1**, which shows that these selective natural dyes (except tesu) show UV-absorbance peaks either at 242–250 nm or at 370–380 nm in UV region, where it is found to be dominating in 242–250 nm in UV zone for babool and marigold, whereas madder (Rubia/manjistha) has no such preferential UV-absorbance peak in 242–370 nm zone except a small but sharp peak at 380/390 nm, which is possibly due to absorbance of the keto or more specifically for

Purified natural dyes	Wavelengths (nm) for major UV-VIS peaks with λ_{max}
a. Marigold (MG)	250, 598 (λ_{max})
b. Babool (BL)	242, 372, 550, 602 (λ_{max})
c. Jackfruit wood (JFW)	250, 540 (λ_{max})
d. Sappanwood (SW)	242, 373, 610 (λ_{max})
e. Red sandalwood (RSW)	250, 370, 540, 602 (λ_{max})
f. Manjistha/madder (MJ)	380, 540, 610 (λ_{max})
g. Tesu (TS)	250 (very small negligible peak), 385 (small trough), 490 (λ_{max})

Table 1. UV-VIS absorbance peaks at different wavelength for few purified natural dyes.

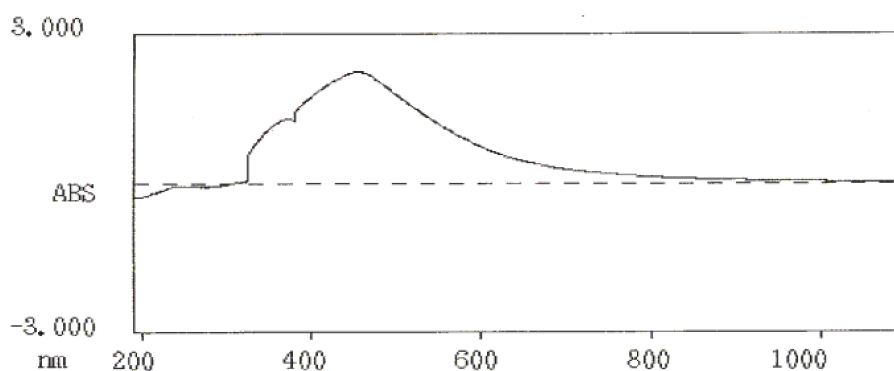


Figure 1. UV-VIS spectra of the extract of color component of tesu as natural dyes.

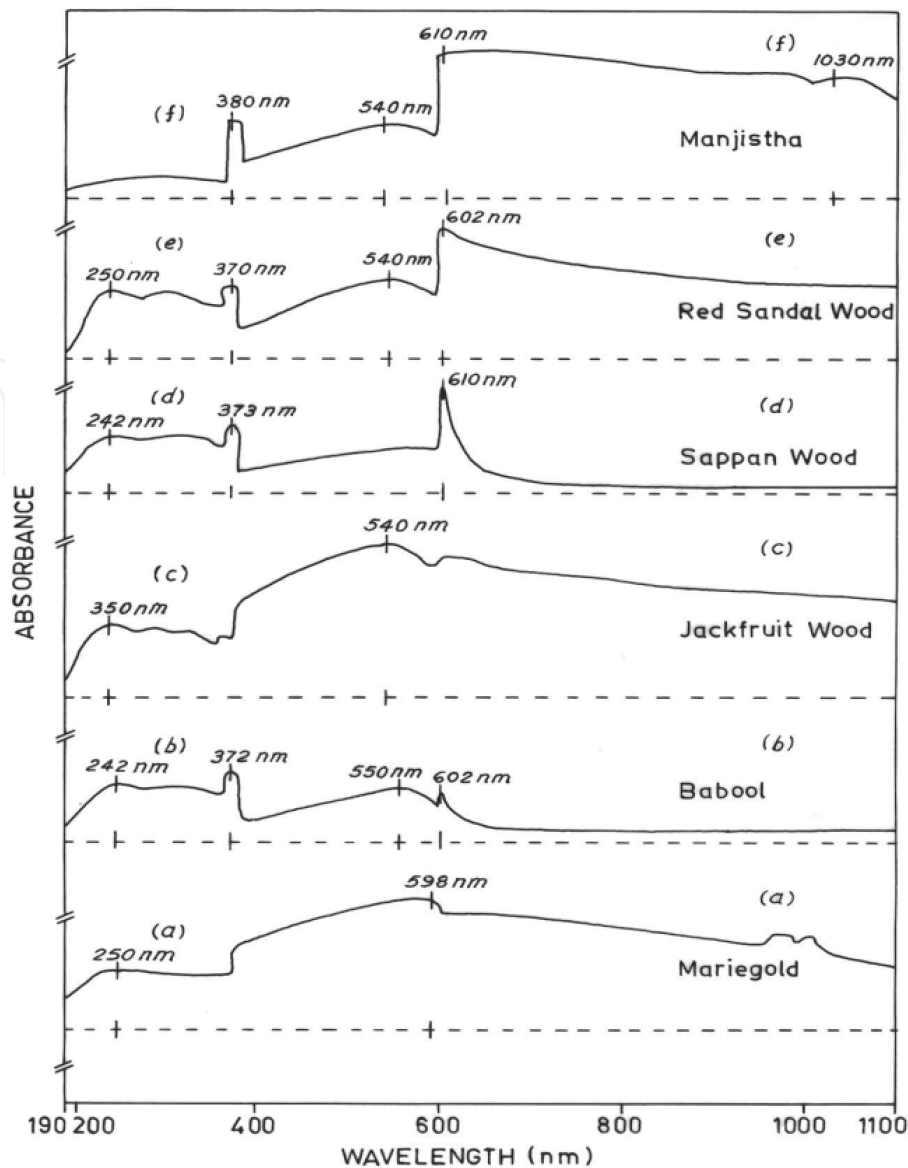


Figure 2.
UV-VIS spectra of the extract of color component of few natural dyes other than tesu (*x*- and *y*-axes: Absorbance values in *y*-axis are -3.0 to $+3.0$ and wavelength values are 190 – 1100 nm).

quinone group in anthraquinone structure present in madder/manjistha (*Rubia*) containing manjisthin, alizarin, etc. [8]. Besides these peaks, the other characteristic peaks in the visible region (400 – 700 nm), in the UV-VIS spectrum of corresponding solutions of the said natural dyes, are the peaks for the predominating hue of the main color component of the corresponding dye. In some cases (as in madder, red sandalwood, babool, etc.), there are more than one or multiple peaks in the visible region that indicates the presence of more than one color component as a mixture which shows multiple peaks at the visible region closely differing from λ_{max} for predominating hues for each of them [8, 11, 13].

2.1.2 Fourier-transform infrared spectroscopy (FTIR) spectral analysis

The purified dye powder was further washed in distilled water followed by washing in 100% acetone before final drying and was then subjected to FTIR spectroscopy in a double-beam spectrophotometer (in Perkin Elmer spectrum-II FTIR spectrophotometer) using a KBr disc technique. The FTIR spectrum for each purified selective natural dye powder has been shown in **Figure 3** for tesu, **Figure 4** [spectra (a)–(e) for red sandalwood, jackfruit wood and madder/manjistha

(Rubia)] and **Figure 5** [spectra (d)–(f) for marigold, babool and sappanwood]. The characteristic FTIR bands/peaks (absorption band, type and mode of vibrations, nature and appearance of bands/peaks along with the description of responsible bonds and associated chemical functionalities) for each of the purified natural dyes observed have been marked with corresponding wave number (cm^{-1}) for each spectrum [8, 11] in **Figures 3–5** and are also tabulated in **Tables 2–4** [8, 11].

The FTIR spectral scan analysis is presented in **Tables 2–4**, which are easy to understand for confirming the type of chemical groups indicating types of bonds present therein in the main color components for each purified natural dye mentioned there. The known chemical structures of the major color components of each of these natural dyes have been reported in the earlier literature [7, 8]. The FTIR bands of each purified natural dye are found to be matching with the earlier reported chemical structures of major color components of each individual natural dye mentioned here.

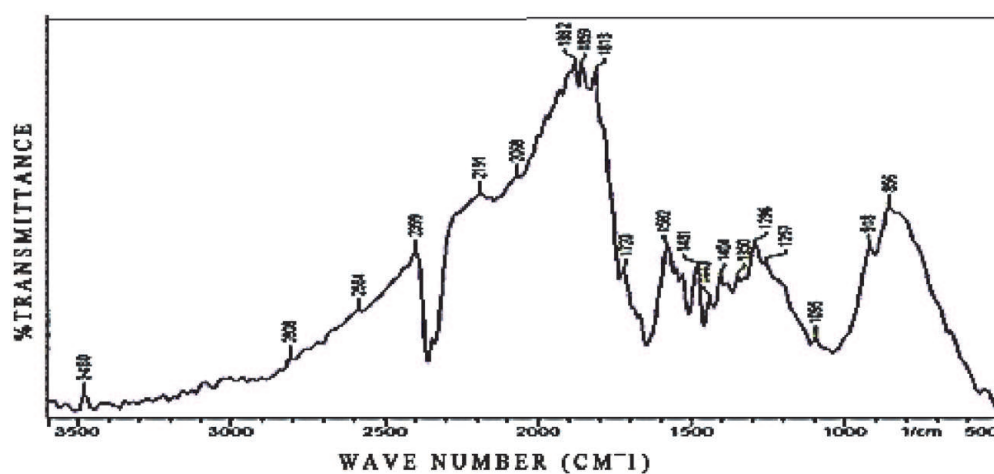


Figure 3.
FTIR spectra of purified tesu as natural dyes (transmittance values are 25–100%).

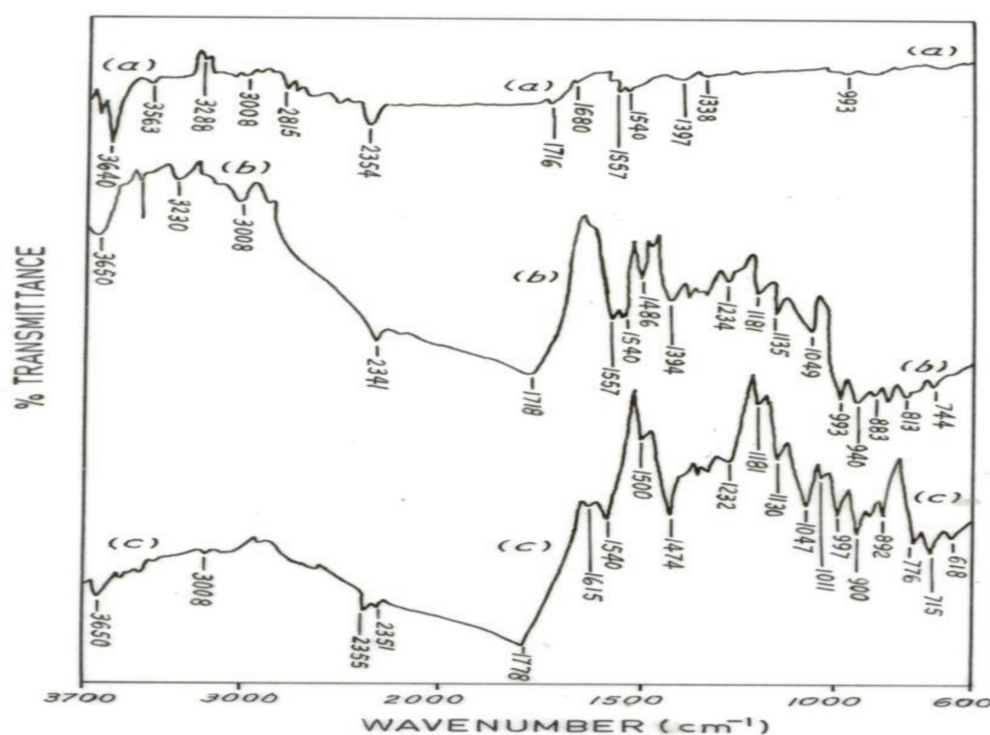


Figure 4.
FTIR spectra of purified natural dyes: (a) red sandalwood, (b) jackfruit wood and (c) manjistha/madder (Rubia) (transmittance values are 25–100%).

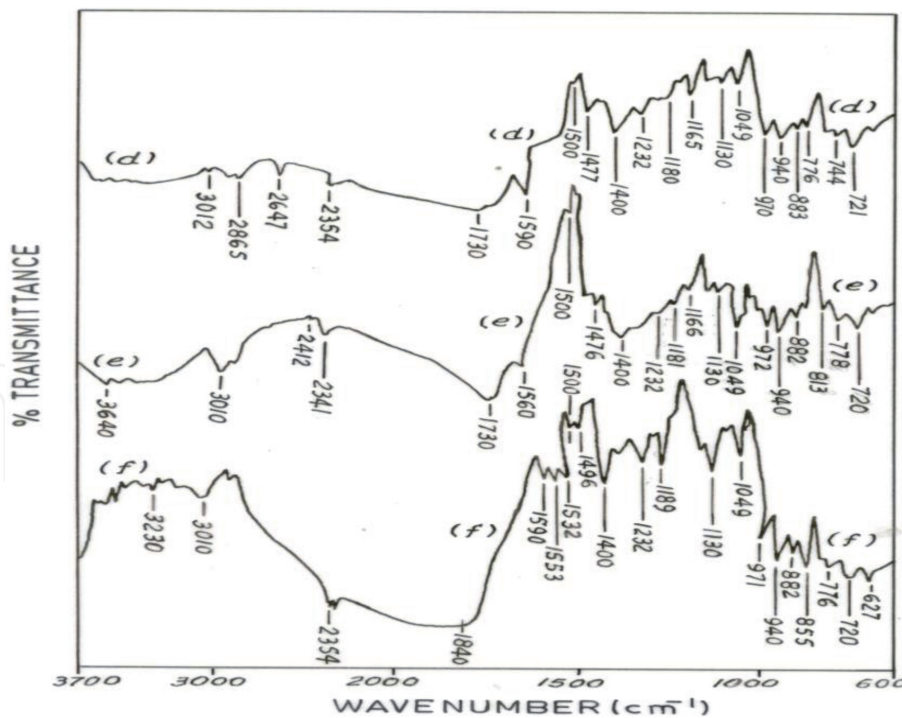


Figure 5. FTIR spectra of purified natural dyes (d) marigold, (e) babool and (f) sappanwood (transmittance values are 25–100%).

Absorption band, wave number in cm^{-1}	Nature of bands/peaks	Bond and its mode of vibration with associated responsible functional groups
For TS (TESU)		
608–668 (avg. 647) and 1350	Small	–OH out-of-plane bending and –OH in-plane bending
1210–1296 (avg. 1257)	Small	–C–O–C and –C=O stretching combination
1376–1487 cm^{-1} (avg. 1381)	Medium	–CH and –CH ₂ bending
1540–1557, 1582, 1589 and 1630	Small and doublet	–C=C stretching in nonconjugated –C=C–
1680–1750	Medium sharp	–C=O stretching attached with aromatic ring structure
2359, 2810 and 3008	Weak but intense	–C–H stretching in aromatic ring
3288 and 3563–3650	Small	–O–H stretching in free –OH of phenolic structure

Table 2. Spectroscopic data for FTIR peaks of a purified extract powder of tesu as natural dyes.

2.1.3 Analysis of DSC thermograms

The purified dye powder for each selective natural dye (except tesu) was further repeatedly washed in distilled water twice followed by washing with ethyl alcohol followed by washing again in 100% acetone and was then subjected to final drying under a vacuum oven. Then 2 mg of each individual dye powder was placed in the aluminium crucible of differential scanning calorimeter (DSC) console (using Shimadzu differential scanning calorimeter Model-DSC-50) and started heating and running it by usual method under flowing nitrogen (N_2 gas flow rate was at

Absorption band, wave number in cm^{-1}	Nature of bands/peaks	Bond and its mode of vibration with associated responsible functional groups
a. For RSW		
993	Small	-C-H deformation in benzene ring
1338-1397	Doublet	-C-O-H bending in primary and secondary alcohol
1540-1557	Small and doublet	-C=C stretching in nonconjugated -C=C
1680	Small	-C=C stretching in nonconjugated -C=C
1716	Small	-C=O quinone to aromatic ring or -C=O stretching in ring ketone in aromatic ester and 6C ring ketone
2354 and 3008	Weak but intense	-C-H stretching in aromatic/benzene ring
2815	Small	-C-H stretching in -O-CH ₃ group
3288	Small	-O-H stretching in bonded H-bonds
3563-3650	Small	-O-H stretching of phenolic -OH
b. For JFW		
744-883	Multiplet	-C-H out-of-plane deformation in benzene ring
940	Weak but intense	-C-O stretching vibration in higher cyclic ether linkages (as present in morol for jackfruit wood)
993	Weak but intense	-C-H deformation in benzene ring
1049	Medium	-C-O stretching in primary or secondary alcohol
1135-1234	Multiplet and sharp	-C-O stretching and -OH in-plane deformation in phenol
1394	Small	-C-H bending in methyl ketone or methyl groups
1486	Sharp but small	-C=C stretching in aromatic ring
1540-1557	Small doublet	-C=C stretching in aromatic ring
1718	Small	-C=O stretching of quinone to aromatic ring or -C=O stretching of ring ketone in aromatic ester and 6C ring ketone
2341	Small but sharp	-C-H stretching in benzene ring
3008	Small	-C-H stretching in aromatic ring
3230	Medium intense	Hydrogen bond -OH stretching in phenolic structure
3563-3650	Weak but intense	-OH stretching for aromatic phenolic -OH groups

Table 3. Spectroscopic data for FTIR bands/peaks of other selective purified natural dyes.

50 cm^3/min), and heating rate was maintained at 10 $^\circ\text{C}/\text{min}$ over a temperature range from ambient (about 28-30 $^\circ\text{C}$) to 490-500 $^\circ\text{C}$ and obtained DSC thermograms are plotted as shown in **Figure 6**.

In each case, the thermal transition temperatures are marked in each thermogram (a) to (f) in **Figure 6**, and the corresponding data on the maximum peak for thermal transition temperatures, nature and appearance of DSC peaks and probable reasons [8, 11] of the observed thermal transitions are tabulated in **Table 5**, except

Absorption band, wave number in cm^{-1}	Nature of bands/peaks	Bond and its mode of vibration with associated responsible functional groups
c. For madder/MJ, also known as Rubia		
618–900	Multiplet	–C–H out-of-plane deformation in benzene ring
997	Sharp	–C–H deformation in benzene ring
1011–1047	Medium	–C–O stretching in primary or secondary alcohol
1130–1232	Very strong	–C–O stretching and –OH in-plane deformation in phenol
1474	Small	–C=C stretching in aromatic ring
1500–1540	Sharp	–C=C stretching in aromatic ring
1615 and 1718	Small and sharp	–C=O stretching in aromatic ring and ring ketone
2355–2351	Doublet	–C–H stretching in –O–CH ₃ group
3008	Small	–C–H stretching in aromatic/benzene ring
3653–3650	Small	–O–H stretching in phenolic –OH groups
d. For MG		
720	Small but intense	–C–H bending in polymethylene (as present in xanthophyll esters present in MG)
744–883	Multiplet and sharp	–C–H out-of-plane deformation in benzene ring
940	Tiny	–C–O stretching vibration in higher cyclic ether linkages
970	Small and sharp	–C–H deformation in aromatic ring
1049	Sharp and intense	–C–O stretching in primary or secondary alcohol
1130–1232	Multiplet	–O–H in-plane deformation in phenols
1390–1477	Sharp	–C=C stretching in aromatic ring
1590	Sharp and intense	–C=C stretching in aromatic ring
1730	Small	–C=C stretching and –C=O stretching in nonconjugated–C=C
2354, 2647	Small	–C–H stretching in –O–CH ₃ or methyl ether
3022–3012	Doublet	–C–H stretching in aromatic ring
e. For BL		
720	Small but intense	–C–H bending in polymethylene (as present in xanthophyll)
778–882	Sharp multiplets	–C–H out-of-plane deformation in benzene ring
940	Sharp	–C–O stretching vibration in higher cyclic ether linkages
972	Small and sharp	–C–H deformation in aromatic ring
1049	Sharp and intense	–C–O stretching in secondary or primary alcohol
1130–1232	Sharp multiplets	–OH in-plane deformation for phenolic structure
1400–1500 and 1500	Multiplet or tiny	–C=C stretching associated with aromatic ring structure

Absorption band, wave number in cm^{-1}	Nature of bands/peaks	Bond and its mode of vibration with associated responsible functional groups
1730	Small	-C=C stretching in nonconjugated structure
2354–2312	Doublet	-C-H stretching in benzene/aromatic ring structure
3640	Small	Vibration of free phenolic -OH groups
f. SW		
627	Small	-C-H out-of-plane deformation in benzene ring
720	Small	-C-H bending in $(\text{CH}_2)_n$, i.e. polymethylene
776–882	Sharp multiplets	-C-H out-of-plane deformation in benzene ring
940	Sharp	-C-O stretching vibration in higher cyclic ether linkages
971	Sharp	-C-H deformation in aromatic ring structure
1049	Sharp	-C-O stretching in primary or secondary alcohol
1130–1232	Sharp multiplets	-OH in-plane deformation phenols
1400–1500	Multiplet	-C=C stretching in aromatic ring
1532–1590	Multiplet	-C=C stretching in aromatic ring
1840	Very small	
2354	Broad trough	-C-H stretching in benzene ring
3010	Small	-C-H stretching in aromatic ring
3230	Small	Hydrogen bonded -OH stretching in phenol

Table 4.

Spectroscopic data for FTIR bands/peaks of selective other purified natural dyes.

tesu, as tesu is considered in the earlier literature to contain normal heat-resistant butein [29] as the color component (hence, there was no need to study the thermal stability of tesu at dyeing temperature zone of 60–100°C).

The frequently asked question (FAQ) for this study arises: why DSC study of natural dyes is necessary? By DSC thermogram analysis, the thermal degradation temperature of any color components present in any natural dye molecules is indicated for heating under nitrogen at different temperature zones, which very well identify and reveal lower-temperature degradable components, if present in that sample. If any lower-temperature degradable components are there in a specific natural dye extracted sample, then its dyeing should be done below that temperature, i.e. dyeing temperature should not exceed above that temperature at all. Otherwise, if one of the color components degrades thermally at dyeing temperature in dye bath, this will cause some loss of color component and less shade depth. To avoid this, it is also essential to study the DSC parameters for natural dyes also. For example, in DSC thermogram—c for red sandalwood—there is an exothermic sharp thermal degradation peak at 82°C, and hence it should not be dyed above 80°C, i.e. preferably dyed below 80°C or preferably at 70°C. Similarly for DSC thermogram—f for madder—there is also an exothermic broader hump for thermal degradation of one of its component starting at 74°C and continuing up to 125°C, indicating that madder dyeing should be done below 74°C, i.e. preferably around 60–65°C only (not at the water boiling temperature).

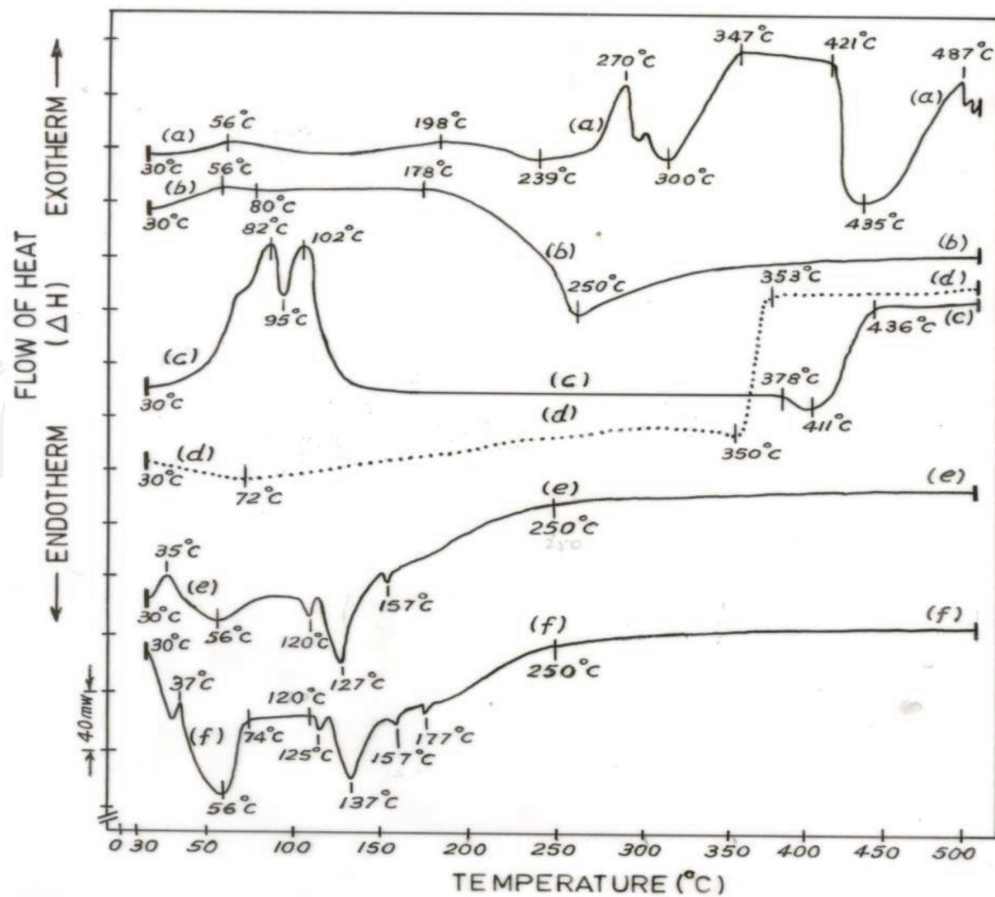


Figure 6.
 DSC thermograms of purified natural dyes: (a) babool, (b) jackfruit wood, (c) red sandalwood, (d) sappanwood, (e) marigold and (f) manjistha/madder (*Rubia*).

2.1.4 Test method for the identification of specific natural dyes from such dyed textiles

A number of test methods developed for different commercially used natural dyes for textiles to test those natural dye powder and natural dyed clothes for the identification of specific natural dyes from such dyed textiles have been adopted by the BIS as IS standards [25, 26], some of which are under favorable consideration of ISO/TC-38 also for global standardization of these test methods as per the ISO format. For example, one such method of test of identification for madder/manjistha (*Rubia*) as natural dye is discussed here to understand the process.

2.1.4.1 Identification of natural madder (*Rubia*) as compared to synthetic alizarin by UV-VIS spectral test

Purified natural and synthetic counterparts of similar two red dyes (madder/*Rubia* known as manjistha containing manjisthin and synthetic alizarin considered being used instead of madder) were taken and weighed separately (0.1 gm) and dissolved in 1000 ml dichloromethane and scanned through UV-VIS spectrophotometer for wavelength scan. For the visible spectrum these two solutions were further diluted five times and were used for UV spectrum study for identification by comparison of the peaks and UV-VIS spectrum with lambda maxima and optical density (OD) values of natural madder (*Rubia*) and synthetic alizarin red colors, as shown in **Figure 7** and **Table 6**.

It is observed that in the visible region (400–700 nm) of the UV-VIS spectrum, characteristic peaks found are at 426 and 491 nm for synthetic alizarin, and

Compound dyes	Thermal transition temperatures, °C	Nature and appearance of DSC peaks	Probable reasons for observed thermal transitions
a. BL	56	Small wide hump (exothermic)	Combined effects of breaking of H-bonds and moisture evaporation
	178	Broader crest (exothermic)	Decomposition of other minor constituents
	239	Broader trough (endothermic)	Decomposition of some other minor constituents
	279	Sharp peak (exothermic)	Thermal decomposition of gallic acid
	300	Deep trough (endothermic)	Decomposition of epicatechin
	347–421	Flat plateau region (exothermic)	No effects
	435	Deep trough (endothermic)	Thermal decomposition of catechin
	487	Small sharp peak (exothermic)	Thermal decomposition of theoflavones or other minor constituents present
b. JFW	56	Small hump (Exothermic)	Combined effects of breaking of H-bonds and moisture evaporation
	80–178	Flat plateau region	No effects
	250	Wide trough (endothermic)	Thermal decomposition of morol
c. RSW	82	Sharp peak (exothermic)	Breaking of strong H-bonds of deoxysantalín
	95	Sharp trough (endothermic)	Thermal decomposition of deoxysantalín
	102	Sharp peak (exothermic)	Breaking of more strong H-bonds of santalín (A and B)
	129–378	Flat plateau region (endothermic)	No effects
	411	Small trough (endothermic)	Thermal decomposition of santalín (A and B)
	436–500	Flat plateau region (exothermic)	No effects
d. SW	72	Small transition (endothermic)	Moisture evaporation
	350	Small trough with sharp transition (endothermic)	Thermal decomposition of brazeline
	353–500	Flat plateau region (exothermic)	No effects
e. MG	35	Tiny peak (exothermic)	Breaking of H-bonds
	56	Medium trough (endothermic)	Moisture evaporation [7]
	120	Small trough (endothermic)	Thermal decomposition of xanthophyll ester
	127	Sharp trough (endothermic)	Thermal decomposition of quectrol (flavanol) [7]

Compound dyes	Thermal transition temperatures, °C	Nature and appearance of DSC peaks	Probable reasons for observed thermal transitions
f. MJ or madder (Rubia)	157	Tiny trough (endothermic)	Decomposition of other minor constituents
	250–500	Flat plateau region (exothermic)	No effects
	37	Tiny peak (exothermic)	Breaking of H-bonds
	56	Deep trough (endothermic)	Moisture evaporation
	74–120	Flat plateau region (exothermic)	No effects
	125	Small and sharp trough (endothermic)	Thermal decomposition of purpuroxanthin
	137	Sharp trough (endothermic)	Thermal decomposition of manjistha
	157	Tiny trough (endothermic)	Thermal decomposition of purpurin
	177	Tiny trough (endothermic)	Thermal decomposition of pseudopurpurin
	250–500	Flat plateau region (exothermic)	No effects

Table 5.
 DSC thermal transition temperatures of extracted and purified natural dyes.

corresponding peaks for natural madder (Rubia) dye containing manjisthin are at 398 nm (OD 0.801) and 426 nm (OD 0.838) as distinguishing characteristic peaks and their optical densities for differentiating natural madder containing manjisthin and synthetic alizarin by UV-VIS spectral analysis as shown in **Figure 7**.

While in the UV region of the UV-VIS spectrum, optical density at same lambda max. Values for peaks in UV region for natural madder (Rubia) and synthetic alizarin dyes are different. In the UV region (200–380/399 nm) of the UV-VIS spectrum, although both shows the lambda max peaks in UV region at same wavelength, i.e. at 250 nm, but their optical densities values at 250 nm for both the red colors are different (corresponding data are provided in **Table 6**).

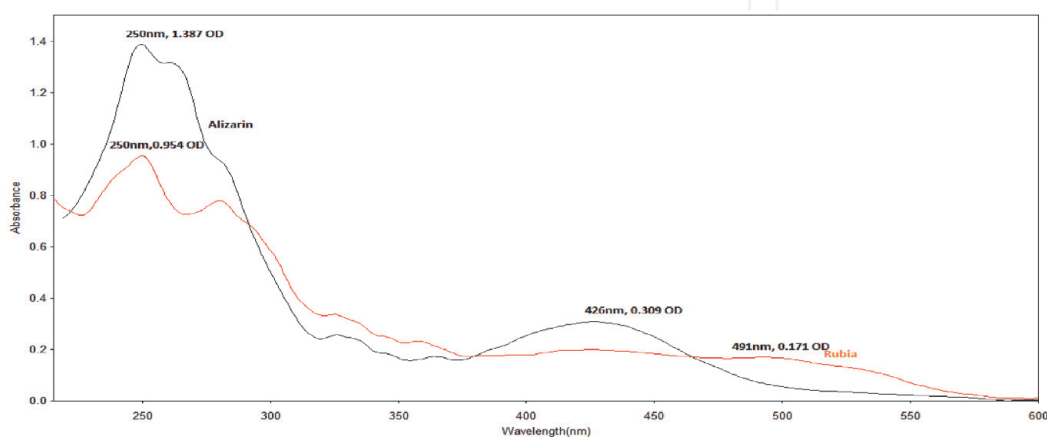


Figure 7.
 UV-VIS spectrum of madder (Rubia) and synthetic alizarin dyes.

Peak shown at nm	In synthetic red alizarin	In natural madder (Rubia)	Comments for distinguishing peaks and lambda max values for identification (describing difference with reason)
	250 nm (1.38 OD) and 426 nm (0.309 OD)	250 nm(OD, 0.954) and 491 nm (OD, 0.171)	The pattern of the peaks and optical density at lambda max values in UV and visible region are very different for the two dye samples as per Figure 7

Table 6.

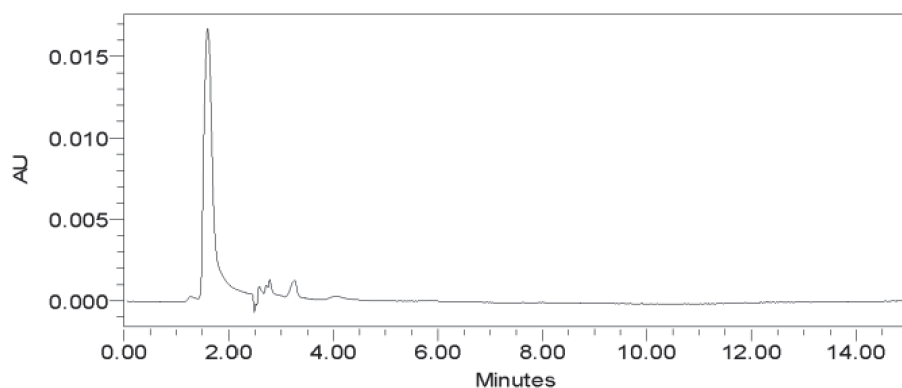
Identification of peaks and lambda max values from UV-VIS spectrum of natural madder (Rubia) and synthetic alizarin.

2.1.4.2 Identification of natural madder (Rubia) dye with synthetic alizarin using high-performance liquid chromatography (HPLC) with UV detector

The purified extracted dye powder of natural madder (i.e. Rubia containing manjisthin) and synthetic alizarin as two different red dye samples were analyzed by HPLC method [27]. Both the natural madder and synthetic alizarin purified and washed dye powder were weighed separately (0.1 g) and were dissolved in 1000 ml of methanol. 1 μ L of the prepared solution of both one by one was injected to the C-18 reverse phase column of HPLC with UV detector and eluted in HPLC column. The base line showed response within a run of 15 min for natural madder (Rubia) and synthetic alizarin. The parameters of this assay were made to be such that a clean peak of the both the samples are observed. Clear observation was made from these two red dye samples as shown in the two chromatographs given in **Figures 8** and **9**, that for synthetic alizarin, one main peak is at 1.6 min and no peak after 3.5 min, while natural madder (Rubia) has main peak at 1.8 min and another peak at 11.3 min, as per data provided in **Table 7**.

Thus, natural madder (Rubia) and synthetic alizarin show clear differences in their characteristic peaks, retention times and peak heights. Natural madder (Rubia) always shows two equivalent peaks as compared to synthetic alizarin which shows three peaks due to un-purified sample of the latter; this is a mark of identification factor between natural madder (Rubia) and synthetic alizarin by HPLC method with a UV detector.

This method of identifying Rubia (madder) as a natural dye to identify from its dyed textiles has been standardized and adopted as Indian standard—IS-17085-2019, January 2019 [25]—and many more such natural dye test standards for the identification [25, 26] of specific natural dyes from dyed textiles are adopted as Indian standards by the BIS.

**Figure 8.**

Chromatogram of synthetic alizarin.

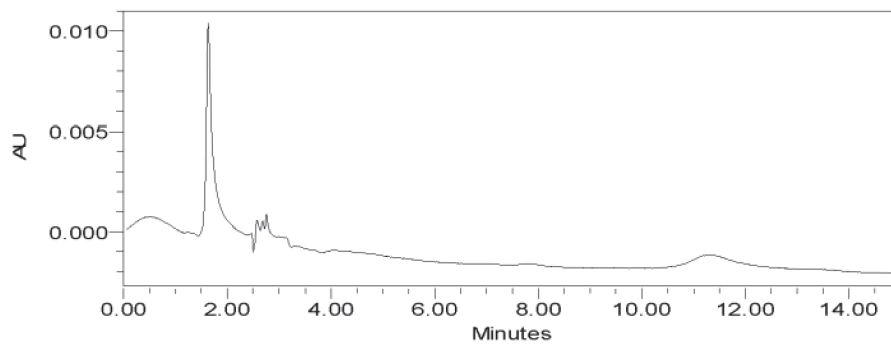


Figure 9.
 Chromatogram of natural madder (*Rubia*) containing natural alizarin.

Peak shown at nm	In synthetic alizarin	In natural <i>Rubia</i>	Comments for distinguishing main peaks and time in min for identification (with reason for differences)
255 nm	One main peak is at 1.6 min and no peak after 3.5 min	1.8 min main peak, small peaks at 2.5 and 11.3 min	One main peak is at 1.6 min and no peak after 3.5 min while natural <i>Rubia</i> has a main peak at 1.8 min and a characteristic peak at 11.3 min

Table 7.
 Chromatogram analysis data of natural madder (*Rubia*) and synthetic alizarin.

2.2 Standardization of extraction, mordanting and dyeing process variables: a specific case study

The study of optimization of extraction conditions, mordanting, and dyeing process variables of few natural dyes on different textiles is available in the literature [6, 10, 28, 29], but the study of dyeing process standardization of madder (*Rubia tinctorum*-Indian madder was obtained from M/s AMA Herbals Lab Pvt Ltd, Lucknow, India) applied on cotton is reported here. In this part of study, initially the optimization of conditions of extraction of madder (manjistha/*Rubia*) as a natural dye/colorant is reported in **Item 2.2.1**. Later, bleached cotton fabrics were dyed after a sequential double natural pre-mordanting [10% myrobalan (harda) + 10% natural potash alum, i.e. 20% overall application of harda + natural Potash alum in 50:50 ratio], and then dyeing process variables (such as mordant concentration, dye concentration/shade %, pH, dyeing temperature, dyeing time, material-to-liquor ratio (MLR) and electrolyte/Salt concentrations) are reported using madder (*Rubia*/manjistha) extract as a natural dye to optimize the dyeing process conditions, and the observed results are discussed in **Item 2.2.2**.

2.2.1 Optimization of aqueous extraction of Indian madder (*Rubia tinctorum*)

For optimizing the extraction conditions, a colored aqueous extract liquor was obtained from madder (*Rubia*) dried powder under differently varying conditions of MLR 1:20–1:60, pH 4–10, extraction time period 15.0–90.0 min and extraction temperature 50–90°C for optimizing the conditions of extractions of color components of madder/*Rubia* (manjisthin and purpurin) from its natural source materials. The optical absorbance or OD values of the filtered aqueous extracts of the madder/*Rubia* were measured at λ_{max} of 540 nm (i.e. maximum absorbance wavelength) using Hitachi-U2000 UV-VIS absorbance spectrophotometer. Results of optical density (color value of dye solution) of aqueous extraction of madder under varying

Extraction variables	OD/absorbance for madder at λ_{\max} 540 nm	Extraction variables	OD/absorbance for madder at λ_{\max} 540 nm
MLR		Temperature (°C)	
1:20	0.238	50	0.198
1:30	0.279	60	0.278
1:40	0.266	70	0.132
1:50	0.252	80	0.164
1:60	0.236	90	0.177
Time (min)		pH	
15	0.241	4	0.192
30	0.273	5	0.281
45	0.188	6	0.188
60	0.173	8	0.193
90	0.182	10	0.205

*Values in bold indicate the optimum values considered while studying the effect of extraction parameters for madder. When one parameter was varied, say for MLR variation of 1:20–1:60, time was 30 min, temp was 60°C, and pH was 5. For time variation of 15–60 min, MLR was 1:30, temp was 60°C, and pH was 5; for temperature variation of 50–90°C, MLR was 1:30, time was 30 min, temp was 60°C, and pH was 5; and for pH variation 4–10, MLR was 1:30, temp was 60°C, and time was 30 min.

Table 8.

OD or absorbance values of aqueous extract of madder (*manjistha/Rubia*) (λ_{\max} of 540 nm) extracted under varying conditions of aqueous extraction*.

conditions have been shown in **Table 8**. The maximum values of OD [30] at λ_{\max} of 540 nm wavelength are identified and marked in bold letters (for corresponding maximum color yield) as shown in **Table 8** and are considered as optimum or best extraction conditions, i.e. MLR at 1:30, pH at 5, extraction temperature at 60°C and extraction time at 30 min.

2.2.2 Study of mordanting and dyeing process variables for dyeing cotton with madder (*Rubia*)

2.2.3 Results of variation of concentrations and type of mordants

Table 9 shows the effect of concentrations and types of mordanting (as single or as double pre-mordanting technique) on surface color depth and other color interaction parameters of cotton fabric dyed with 4% aqueous extract (extract of purified 4% dry powder of madder obtained from M/s AMA Herbals Lab Pvt. Ltd., Lucknow) as colored dye solution used in this natural dyeing. Amongst all the single and double pre-mordanting done (**Table 9**), a combination of 20% overall application of harda and natural potash alum (50:50 ratio), i.e. 10% harda and 10% natural potash alum applied in sequence, satisfies the most desirable required stoichiometric ratio for effective complexing showing maximum surface color strength (K/S value) than that obtained by using either any of the said single pre-mordants or any other double pre-mordants studied for dyeing bleached cotton fabric with madder/*Rubia*. This may be an important fact that myrobalan (harda) acts as a mordanting assistant or dyeing additive, when used in conjunction with metallic salts. Myrobalan (harda) contain chebulinic acid/tannic acid moieties (having mordantable –COOH/–OH groups) in it, which thus is useful for a higher color yield when used along with the metal salts as second mordant forming insoluble metal

Mordant concentration and dye concentration	K/S at λ_{mx}	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔC^*	ΔH^*	BI	MI	CDI	CV % of K/S
(10% harda + 10% potash alum) only mordanted cotton	1.53										
Harda (H) + $KAl_2(SO_4)_2$ (Pa)*, overall 20% application with ratio											
0:100 [harda (H): $KAl_2(SO_4)_2$] + 4% madder	1.66	4.54	-3.70	2.12	1.55	2.59	0.45	22.08	0.95	0.86	1.50
25:75 [harda (H): $KAl_2(SO_4)_2$] + 4% madder	2.53	2.95	2.55	0.47	1.39	1.31	0.67	19.85	0.36	2.46	2.32
50:50 [harda (H): $KAl_2(SO_4)_2$] + 4% madder	3.67	1.49	1.23	0.76	0.36	0.32	0.78	15.22	0.33	3.03	2.05
75:25 [harda (H): $KAl_2(SO_4)_2$] + 4% madder	3.40	3.49	3.05	0.91	1.43	1.66	0.34	16.34	0.48	4.26	4.15
100:0 [harda (H): $KAl_2(SO_4)_2$] + 4% madder	2.05	1.53	1.06	0.13	1.09	1.08	0.19	29.83	0.31	2.78	2.99

*H, harda, and Pa, potash alum.
 Note: K/S, ΔL^* , Δa^* , Δb^* , ΔE^* , ΔH^* , ΔC^* , etc. are all color parameters as per the latest CIE formula [30].

Table 9.
 Effect of different single and double natural bio-mordants on color strength and other colour interaction parameters of cotton fabric dyed with 4% madder extract (λ_{max} of 540 nm).

tannates/chebulinate (containing tannic/chebulinic acids) utilising multiple nos of carboxylates (for chebulinic acid)/multiple -OH groups (having high coordinating power) present in harda/myrobalan helping to enhance more fixation of such natural mordantable/anionizable dye molecules forming giant coordinating complex of fibre-harda-metallic mordant-natural dye to fix with -OH groups of cellulosic (cotton) fibers [19]. But it still has enough free adjacent hydroxyl/carboxylic acid groups to form mordant-dye complex to fix the anionizable/mordantable selective natural dye like madder/Rubia on the said harda and alum double pre-mordanted bleached cotton fibers. However, that is why the application of harda alone containing chebulinic acid is not found to provide sufficient color yield and color fastness for these natural dyes, which however when applied with the combination of metallic salts together (here, it is potash alum containing aluminum) give such an encouraging result on the subsequent dyeing with madder as an anionizable/mordantable natural dye. A similar result and higher color yield of anar peel dyeing on cotton were referred in the earlier literature for use of myrobalan/harda and alum double pre-mordanting [19].

Data on color fastness properties of dyed cotton fabric samples pre-mordanted with varying types of single mordant and different ratio of double pre-mordanted samples (with overall 20–40% mordant application combining Harada and potash alum in 50:50 ratio) subsequently dyed with 4% madder extract has been reported in **Table 10**.

It is evident from the color fastness data in **Table 10** that applications of single mordant and also higher mordant concentration (above overall concentration of 20%) do not show better or higher color fastness to wash. However, light fastness appears to be independent on mordant concentration and is steadily always moderate to good to UV light exposure. Fastness to dry rubbing (crocking fastness) of the dyed samples remains relatively higher, whereas fastness to wet rubbing (crocking)

Mordant concn. Used and dyed with madder (manjistha)	Color fastness				
	Washing		Light	Rubbing	
	LOD	Staining		Dry	Wet
10% harda and dyed with 4% madder	3	4	2/3	4	3
10% $KAl_2(SO_4)_2$ and dyed with 4% madder	3	4	3/4	4	3
10% of harda +10% of $KAl_2(SO_4)_2$ and dyed with 4% madder	3–4	4/5	4	4	4
20% of harda +20% of $KAl_2(SO_4)_2$ and dyed with 4% madder	2/3	4	4	3–4	2/3

Table 10. Effect of different single and double mordants on color fastness properties of madder- (manjistha/Rubia) (λ_{max} of 540 nm) dyed cotton fabric.

becomes a bit lower irrespective of the concentration of harda and natural potash alum (mordant) used.

Moreover, there is little difference in color fastness to washing, light and rubbing for the different single mordants used, but there are some clear differences on color fastness ratings when the double mordanting system with overall 20% application of harda + natural potash alum in 50:50 ratio is used. Amongst the different combinations of double pre-mordanting systems used, 20% overall application of harda and natural potash alum (in 50:50 ratio) applied in sequence shows better color fastness rating amongst all combinations of mordant tried. This may be presumed to be due to some synergistic effects of this particular combination of natural potash alum with harda as a mordanting assistant due to additional coordinating power of chebulinic acid of harda as a mordanting assistant applied, which perhaps facilitates more number of strong and giant bigger complex formation amongst the said fibre (cotton)-mordanting assistants (harda)—metallic mordant (natural alum)—natural dye (madder) system in the presence of both myrobalan (harda) containing chebulinic acid residue and potash alum containing aluminum in combination in equal proportion. This may be noted that the application of 20% harda and 20% potash alum in combination impairs the colour fastness to washing and crocking, and hence 10% harda and 10% potash alum combination applied in sequence as a double mordant is found to be the better option in this case.

2.2.4 Results of variation of different dyeing process variables for uniform dyeing

Results of the effect of different dyeing process variables such as (a) dyeing time in min; (b) dyeing temp in °C; (c) dye bath in pH; (d) dye concentration in %; and (e) salt concentration in % which have been studied to optimize the dyeing conditions for maximum and uniform color yield (in terms of K/S value) for overall application of 20% harda + $KAl_2(SO_4)_2$ in 50:50 ratio pre-mordanted and dyed cotton fabric are shown in **Table 11**. From relevant data in **Table 11**, it is found that when all other variables are kept fixed, with the increase in time of dyeing (15–120 min), the K/S value initially increases up to 60-min dyeing time and then starts decreasing on further increase in dyeing time from 60 to 120 min, whereas there is hardly any change of the K/S value from that obtained in 60-min dyeing time. Thus, the K/S value is maximum for 60-min dyeing time. This may be explained by the possibility of achieving dyeing equilibrium at a medium faster rate for synergistic action of harda and potash alum both as pre-mordanting agents, and hence within 30–60 min, the dye uptake rate may be maximum for a double pre-mordanted cotton with high coordinating capacity of mordantable natural dyes like madder. However, the final dyeing rate depends on the diffusion rate (being the slowest step

in dyeing operation) besides transportation, absorption, diffusion and fixation of any dye like madder/Rubia extract. There are also chances of desorption/breaking of dye-fiber-mordant complex at either higher temperature or higher dyeing time which may lead to a dropping trend above the said 60 min of dyeing time.

For variation of dyeing temperature, on increase of the dyeing temperature (40–95°C), keeping other variables constant, the surface color strength (K/S values) is found to show a slow increase to a small extent from 40 to 65°C whereafter it almost remains same or at par up to 80°C, after which there is a further decrease beyond 80°C up to 95°C. An increase in temperature of dyeing inevitably supplies more energy for the transportation of dye molecules, thus facilitating the higher rate of dye sorption and diffusion up to 65°C, and thereafter this dyeing rate does not alter much even after increasing temperature up to 95°C, i.e. the desorption starts at relatively high temperature above 80°C and maybe one of the components of madder starts degrading above 74°C and the color value, i.e. K/S value, decreases noticeably. However, dyeing of cotton with madder extract at warm conditions, i.e. at 50–65°C, is considered to be best suited and cannot be excluded fully for the decentralized sector for energy-saving purpose.

The corresponding data in **Table 11** show almost a similar level of dye uptake in terms of surface color strength (K/S value) with the variation of dye concentration (keeping other variables constant) for purified madder dye concentration from 3 to 7%, showing a maximum K/S value for 4% dye concentration of purified madder extract. For the variation of pH from 6 to 14 (keeping other variables constant), the surface color strength (K/S value) starts increasing slowly showing a maximum K/S value at pH 12, after which color value further reduces. Thus, pH 12 may be considered optimum, though here pH is to be treated as a critical variable for relatively higher differences of color difference index (CDI) values (showing higher differences of maximum CDI and minimum CDI values amongst the results of varying pH of dye bath). However, considering the corresponding color fastness data, as reflected in **Table 12**, it is further clear that pH 12 renders a better overall balance of all types of color fastness data and shows even sometimes better than that obtained at pH 14. So, pH 12 is considered as the optimum value for this dyeing in this case of cotton fiber-(alum + harda) mordant-dye (madder/Rubia) system. It may be fact that at pH 12, as it is found to be alkaline, there are higher chances of ionization of phenoxy hydroxyl groups of color component of madder/Rubia (containing alizarin, manjisthin and purpurin) and hence provide better chances of complex formation with mordant like natural alum and mordanting assistant like harda forming a giant coordinated complex amongst them for better fixation and higher anchoring by formation of the said fibre-mordanting assistant + mordant-dye system in this case.

Keeping other variables constant, with the variation in MLR from 1:10 to 1:50 (**Table 11**), the K/S value is maximum for MLR at 1:10, and then there is a slow decrease after MLR 1:20, after which the K/S value continues decreasing slowly in small quantum with further increase for MLR at 1:50. Though MLR 1:10 shows the highest K/S value as compared to any other MLR used, MLR 1:20 gives the same value of K/S and better wash and other color fastness results. Hence the optimum MLR may considered to be 1:20 instead of 1:10. From color fastness data in **Table 12**, it is indicated that except wash fastness results for MLR 1:50, all other MLR used show almost medium to good overall color fastness data. However, amongst all these, overall color fastness data for all types of color fastness results are found to be quiet acceptable for MLR 1:10 and 1:20 only. Thus, considering both color yield and color fastness data, MLR 1:20 gives a better balance having a more uniform dyeing and hence may be considered as optimum dyeing conditions with respect to MLR.

Dyeing conditions	K/S at λ_{max}	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔC^*	ΔH^*	BI	MI	CDI
10% harda and 10% KAl (SO₄)₂ pre-mordanted cotton fabric dyed with 4% purified madder dye	1.53	—	—	—	—	—	—	19.85	—	—
Time, min										
15	2.29	2.33	-1.65	0.30	1.62	1.23	1.10	20.34	0.42	2.43
30	2.95	4.46	-3.31	2.94	0.58	2.75	-1.20	18.59	1.04	3.89
60	3.18	9.34	-8.55	-3.28	-1.84	-3.73	0.44	15.13	1.29	1.96
90	2.34	2.45	-1.35	1.36	1.53	1.99	0.48	18.40	0.43	1.69
120	2.19	3.24	-2.91	0.21	1.40	1.04	0.95	16.77	0.44	5.35
Temp °C										
40	2.01	3.76	1.42	0.90	0.05	0.71	0.56	18.25	0.71	4.33
50	2.21	5.65	-4.35	3.60	-0.20	3.06	-1.91	17.73	1.39	4.36
65	3.04	4.22	-3.38	2.20	-1.22	0.95	-2.33	21.38	0.90	3.79
80	2.10	2.05	0.72	0.49	0.59	0.77	0.02	24.89	0.19	4.81
95	1.81	2.66	-2.05	1.69	0.06	1.16	-1.24	22.22	0.57	5.84
pH										
6	2.14	0.88	-0.74	-0.21	0.43	0.14	0.45	19.04	0.14	9.58
8	2.35	1.51	-1.14	0.56	0.81	0.96	0.21	18.28	0.18	4.81
10	2.58	1.12	-1.34	0.37	0.97	0.24	0.38	16.37	0.15	8.24
12	2.96	2.89	-0.30	-0.71	-0.44	-0.81	0.21	18.50	0.27	6.17
14	2.74	2.88	-2.84	0.38	0.36	0.52	0.40	16.16	0.27	4.31
MLR										
1:10	2.82	2.27	-1.74	-0.01	1.45	1.09	0.97	22.70	0.32	5.39
1:20	2.80	2.05	-0.72	0.49	0.59	0.77	0.02	24.89	0.19	4.81
1:30	2.15	3.59	-2.17	2.67	1.02	2.59	-1.23	21.22	0.87	4.10
1:40	2.09	5.01	-4.21	2.58	0.84	2.40	-1.27	21.06	0.93	2.45
1:50	2.22	1.83	-1.66	0.75	0.17	0.67	-0.38	19.61	0.28	2.39
Dye concn.,%										
3	2.60	1.27	0.20	-0.06	1.25	0.65	1.07	16.96	0.23	3.79
4	2.82	5.45	-4.36	3.24	0.38	2.90	-1.50	15.78	1.16	3.44
5	2.57	2.93	-1.81	1.91	1.27	2.30	-0.08	17.55	0.55	2.26
6	2.61	2.19	-1.64	1.33	0.60	1.42	-0.29	17.61	0.52	0.17
7	2.69	4.71	-3.66	2.86	0.77	2.81	-0.95	16.41	0.98	4.23
Salt concn., gpl										
5	3.12	3.31	-2.48	1.94	1.02	2.18	-0.17	13.22	0.70	2.99
10	3.37	4.31	-3.69	2.15	0.63	2.14	-0.66	13.36	0.83	3.24
15	3.22	5.45	-5.01	2.13	0.26	1.93	-0.93	11.74	0.94	4.69
20	3.13	0.75	-0.72	0.19	0.07	0.20	-0.04	12.45	0.11	2.78

*Values in bold indicate the optimum values considered while studying the effect of process variables of dyeing of madder. When one dyeing parameter was varied, other dyeing parameters were kept constant, say for MLR variation of 1:10–1:50, dye (madder) concn. Was 4%, time was 60 min, temp was 65°C, pH was 12, and salt concn. Was 10 gpl; similarly, for time variation of 15–120 min, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, temp was 65°C, pH was 12, and salt concn. Was 10 gpl; for temperature variation of 40–95°C, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, salt concn. Was 10 gpl, and pH was 12, and for pH variation of 6–14, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, salt concn. Was 10 gpl, and temp was 65°C; for salt concn. Variation of 5–20, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, temp was 65°C, and pH was 12. λ_{max} for K/S data of madder was taken as 540 nm from UV-VIS scan in all cases.

Note: K/S, ΔL^* , Δa^* , Δb^* , ΔE^* , ΔH^* , ΔC^* , etc. are all color parameters as per the latest CIE formula [30].

Table 11.

Color strength, brightness index (BI), metamerism index (MI), CDI value and related color parameter for variation of dyeing process variables* for dyeing of 10% Harda and 10% $KAl(SO_4)_2$ pre-mordanted cotton fabric subsequently dyed with 4% madder/Rubia.

The addition of an electrolyte (common salt) to the dyeing liquor expectedly increases the exhaustion of the dyeing case of most of the anionizable dyes. Common salt (electrolyte) is dissolved completely in the aqueous liquor in the dye bath at a specific temperature of dyeing, thereby positive sodium ion is attracted to –ve cellulosic surface in water and neutralizes the –ve charge of cellulose and thereby anionic natural dye ions are able to be attracted to cellulose increasing exhaustion. But excessive amount of electrolyte/salt above a certain limit, causes a retardation effect in the dye absorption vis-à-vis color yield and renders lower color depth. From the relevant data in **Table 11**, a similar trend is observed that with the increase in salt/electrolyte concentration from 5 to 20 gpl, the color yield in terms of K/S value is increased for the application of 5–10% salt concentration and starts decreasing for use above 15% salt concentration. Moreover comparing overall color fastness properties for the corresponding part, the overall round color fastness properties are found best for 10% salt concentrations, and fastness results for use of 15% salt concentration are a bit inferior. Considering all the above matter, the optimum concentration of common salt for dyeing cotton fabric with madder is selected to be 10 gpl.

Thus, the observed optimum conditions of dyeing of the double pre-mordanted with 10% concentration of harda and 10% concentration of natural potash alum in sequence for bleached finer cotton fabric with aqueous extract of purified madder (manjistha/Rubia) are as follows: dyeing time, 60 min; dyeing temperature, 65°C; MLR, 1:20; pH, at 12; dye concentration, 4% (on weight percentage of dried purified color extract powder); and common salt concn., 10 gpl, considered as optimum.

Table 11 also shows the effects of different process variables on K/S values and other latest CIE color measurement parameters [30], including total color difference (ΔE^*), change in hue (ΔH^*), change in chroma (ΔC^*), general MI, BI and CDI values [13]. It is interesting to observe that amongst the varying dyeing conditions (time, temperature, pH, MLR, mordant, dye concentration and salt concentration), the most important and predominating variables are identified as pH of the dye bath, dyeing time and dye concentration. Therefore, for uniform dyeing using madder (manjistha/Rubia) extract for cotton fabric, special care is to be taken for the control of pH, dyeing time and concentration of dye solution of madder (manjistha/rubia).

The said other color parameters like ΔE^* , ΔL^* , Δa^* and Δb^* indicate the variation in color strength and related parameters for varying dyeing conditions in each case, as compared to standard undyed pre-mordanted control cotton fabric. Changes in hue (ΔH^*), in most of the cases, are found to be small negative values (**Table 11**), and in very few cases, there are small positive values, indicating that there is a

Varying dyeing conditions 10% harda + 10% potash alum pre-mordanted cotton fabric dyed with 4% purified madder dye	Overall color fastness properties				
	Washing colour fastness at 50°C		Light	Rubbing	
	Loss of depth	Staining		Dry	Wet
Varying parameters of dyeing					
Time, min					
15	3/4	5	3	4/5	4
30	3/4	4	3	4	4
60	3/4	4/5	3/4	4/5	4
90	2/3	4	4	4/5	4
120	3	4	4	4/5	4
Temp °C					
40	2	4/5	3	4/5	4
50	2/3	4/5	3	4/5	3
65	3/4	5	3/4	5	4/5
80	2/3	5	3	4/5	4
95	1/2	4/5	3/4	4/5	4
pH					
6	2/3	4	3	4/5	3/4
8	2/3	4	3	4/5	3/4
10	1/2	4/5	3	4/5	3/4
12	3/4	4/5	3/4	4/5	3/4
14	2/3	5	3	4/5	3/4
MLR					
1:10	3	4/5	3/4	4/5	4
1:20	3-4	4/5	3/4	4/5	4
1:30	3	4	3	4/5	4
1:40	3	4	3	4	3/4
1:50	2	4/5	3	4/5	4
Dye concn.,%					
3	2	4	3	4	4
4	3-4	5	3/4	4/5	3/4
5	3	4/5	3	4/5	3/4
6	2/3	4/5	3	4/5	3/4
7	2/3	4/5	3/4	4/5	3/4
Salt concn., gpl					
5	3	5	3/4	3	4/5
10	3-4	5	3/4	4/5	4
15	3/4	4/5	3	3/4	4/5
20	2/3	4/5	3	3/4	3

*When one dyeing parameter was varied, other dyeing parameters were kept constant, say for MLR variation of 1:10–1:50, dye (madder) concn. Was 4%, time was 60 min, temp was 65°C, pH was 12, and salt concn. Was 10 gpl; similarly, for time variation of 15–120 min, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, temp was 65°C, pH was 12, and salt concn. Was 10 gpl; for temperature variation of 40–95°C, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, salt concn. Was 10 gpl, and pH was 12, and for pH variation of 6–14, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, salt concn. Was 10 gpl, and temp was 65°C; for salt concn. Variation of 5–20, MLR was 1:20, dye (madder) concn. Was 4%, time was 60 min, temp was 65°C, and pH was 12.

Bold values are optimum results.

Table 12.

Color fastness data against the variation of dyeing process variables* for dyeing 10% Harda +10% potash alum pre-mordanted cotton fabric subsequently dyed with 4% madder/Rubia.

minor change in the predominating hue in each case. However, the maximum ΔH^* value is observed in the case of the variation in temperature from 40 to 95°C which further indicates the high sensitivity of color strength parameter for this particular natural dye for the variation in temperature of dyeing, indicating it as also a critical parameter. The brightness index of dyed products depends on reflectance value of the dye and its orientation along the fiber axis after fixation. However, interestingly it may be noted that at lower pH of 6–10, lower concentration of dye (30–40%) and lower temperature (50–65°C), the reduction in BI values is much lower than that observed in other conditions of dyeing. Expectedly the reduction in brightness index is found to be higher when the application of dye concentration and/or dyeing temperature are higher, due to disorientation of dye molecules during fixation, for either use of higher concentration of dye molecules or higher dyeing temperature. Results of general MI indicates the metamerism effect on the madder- (manjistha/rubia) dyed cotton fabric for different conditions of dyeing. In all these cases, the MI varies from 0.11 to 1.39 (Table 11) and it is observed that these MI data are not much widely dispersed within a particular condition being varied, but varies to a noticeable degree from one condition to other, indicating its potential metamerism nature for varying one condition to the other. Therefore, use of standardization of conditions of dyeing is a must to minimize metamerism for achieving least metamerism dyed products like fibre-mordant-dye system for natural dyeing of cotton with madder/rubia.

Moreover, the ecotoxicology property of madder is available in the literature that the hepato-protective [31] activity of an aqueous-methanol extract of *Rubia cordifolia/Rubia tinctorum* was investigated earlier against acetaminophen and CCL₄-induced damage. Acetaminophen produced 100% mortality at a dose of 1 g/K in mice, while pre-treatment of animals with plant extract reduced the death rate to 30%, proving its ecocompatibility. This is just one example by how after a series of lab experiments, dyeing process parameters are standardized to ensure reproducibility, dye uniformity, etc. and critical dyeing process variables are identified, but for the application of a specific natural dye to any specific textiles, this standardized process parameters are to be made available for each dye-fiber combination separately to the dyers as ready-made guide like synthetic dye application manuals supplied by dye manufacturers or suppliers.

Similarly, it has also been revealed from our earlier lab study that the optimized conditions for dyeing of 15% overall harda + alum (50:50) double pre-mordanted cotton fabric with tesu as natural dye are: dye concentration of 30% (aqueous extract based on the weight of dry powder of natural tesu flower petal (*Butea monosperma* or commonly known as palash or flame of the forest)), pH of 12, MLR of 1:30, time of 60 min for dyeing and 90 min for simultaneous dyeing and finishing and dyeing temperature of 90°C with salt concentration of 10 gpl (though the

detailed study and results of the optimization of conditions of dyeing process variables for tesu as natural dye applied on the said 15% overall application of alum + harda pre-mordanted cotton are not mentioned here considering its duplication).

2.3 Functional finishing to impart/to improve the antibacterial property and UV protection factor (UPF) using natural resource-based finishing agents for tesu-dyed cotton textiles: a specific case study

Few studies on UV-protective and antibacterial characteristics of some natural materials including few natural dye extracts are sparingly reported [32–41]. Hence, an attempt for such natural dyeing-cum-finishing is studied in the present work as reported below.

2.3.1 Antibacterial finish on natural dyed cotton fabric with natural finishing agents

The antibacterial characteristics of many natural resource materials are explored by many researchers [21, 22, 35–41], which include the antibacterial property of eucalyptus, curcumin, banana peel and few natural dyes like catechu, rheum emodi, etc. All the required natural resource materials and tesu as natural dye were obtained from the M/s AMA Herbals Lab Pvt. Ltd., Lucknow, India. A recent accounting of the present status and advanced studies on natural dyeing and natural finishing of textiles including modern techniques of dyeing processes and analyses in different angles have been compiled comprehensively by Vankar [42]. In this part of report, eucalyptus leaf extract has been used as a natural antibacterial agent applied on tesu-dyed cotton. Effects of few different post-treatments on cotton fabric dyed with aqueous extract of 30% (based on the weight of dry powder of natural solid source) tesu flower petal (*Butea monosperma* or commonly known as flame of the forest) with 10% of both aqueous and MeOH extracts of eucalyptus leaves by a pad-dry-cure technique (by a two-dip-two-nip padding process, followed by drying at 100°C for 15 min and curing at 120°C for 3 min) after dyeing or by simultaneous dyeing and finishing process with or without suitable catalyst system (like citric acid, 5 gpl). mainly for improving the antimicrobial properties of tesu-dyed cotton fabric after pre-mordanting with 15% overall harda + alum (50:50) have been discussed.

For simultaneous dyeing and finishing, predetermined percentages of eucalyptus leaf extract along with citric acid were added to the dye bath, and dyeing-cum-finishing was carried out simultaneously at 90°C for 90 min. Relevant results in the change in surface color strength and other related parameters along with fastness properties are tabulated in **Tables 13** and **14**.

In **Table 13**, relevant data indicates that when a post-treatment of eucalyptus leaf extract is carried out in the presence of a suitable catalyst (citric acid) on the above said double pre-mordanted and 30% tesu-dyed cotton fabric by a pad-dry-cure technique, its color strength value is found to be higher as compared to the simultaneous dyeing and finishing technique with the same agents/compounds. Also the fabric samples post-treated with 10% of both aqueous and MeOH extracts of eucalyptus leaves by a pad-dry-cure technique are found to be much yellower and darker in case of similar post-treated fabric produced by the simultaneous natural dyeing and finishing process.

However, taking the color fastness results into consideration, data in **Table 14** indicate that light fastness rating obtained for simultaneous natural dyeing and finishing process is slightly better than the similar sample produced by natural dyeing followed by separate finishing process by a pad-dry-cure technique of separate post-finishing of tesu-dyed cotton fabric using 10% extract of eucalyptus, as

Treatments	K/S	ΔE	ΔL	Δa	Δb	ΔC	ΔH	BI	MI	CDI
Standard bleached cotton control fabric	0.01							92.11	0.91	—
15% overall application of harda + alum (50:50) (no dyeing)	0.16	6.12	-1.15	-0.91	5.85	-0.044	-5.92	44.65	3.43	—
15% harda + alum (50:50) and 30% tesu aqueous extract dyed	2.65	17.77	-4.58	-1.062	17.13	11.20	-13.01	15.93	7.26	2.84
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% harda + alum (50:50) pre-mordanted in sequence										
(10%) Eucalyptus leaf aqueous extract + citric acid (5 gpl)	5.49	15.40	3.18	-0.727	4.31	4.37	11.05	18.61	6.44	5.90
10% Eucalyptus leaf MeOH extract + citric acid (5gpl)	7.49	20.40	3.19	-0.824	4.11	5.33	12.00	19.61	6.75	6.80
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% alum pre-mordanted cotton fabric										
10% Eucalyptus leaf MeOH extract + citric acid (5gpl) (15% alum pre-mordanted)	4.49	14.60	3.00	-0.676	5.36	5.71	11.70	16.33	6.02	4.97
Simultaneous dyeing and finishing with 15% harda + alum (50:50) pre-mordanted cotton fabric with extract of tesu and eucalyptus leaves with citric acid										
Tesu (30%) extract + eucalyptus leaf aqueous extract (10%) + citric acid (5 gpl)	4.85	14.42	2.38	-0.52	3.68	3.72	12.01	17.56	5.61	8.29

Table 13.

Effect of post-treatment with eucalyptus leaf extract by a pad-dry technique and by simultaneous dyeing and finishing technique using a suitable catalyst for natural dyeing and finishing of cotton fabric with tesu extract after pre-mordanting with 15% overall dosage of Harda + alum (50:50).

the natural finishing agent. The washing and rubbing fastness obtained are more or less found to be similar between the two processes. Moderate fastness to washing of only 30% tesu natural dyed cotton can be attributed to the fiber-metal-tannin-dye complex formation between color components of tesu (containing butrin, butein, flavonoids) and alum as a metallic mordant along with harda (containing chebulinic acid) as a mordanting assistant. Darker shades are obtained after 10% eucalyptus extract post-treatment as a finishing treatment on tesu-dyed cotton fabric, which is considered to be due to the addition of active constituents of eucalyptus containing tannins, polyphenols and an active coloring substance called quercetin which has the brightest yellow shade. Hence, in case of post-finishing treatment by a pad-dry-cure technique, the K/S value is found to be higher than that of simultaneous dyeing-finishing treatment owing to the of formation of giant bigger molecule size of complex formed with eucalyptus component in the presence of citric acid used as a catalyst during the finishing process. In case of simultaneous process, a bigger molecular size of citric acid preferably starts crosslinking with cellulose of cotton reducing and preventing an effective fiber-mordant-dye complex formation with the cotton fabric, resulting in a less color yield.

Ten percent eucalyptus post-treatment on 30% aqueous extracted tesu-dyed [after the said double pre-mordanted with 15% overall mordant application with harda and alum (50:50)] and 10% eucalyptus post-treated or finished cotton fabric as well as simultaneous dyeing and finishing (adding 30% tesu and 10% eucalyptus and 5 gpl citric acid and heated at 90°C for 90 min) of the said pre-mordanted

Treatments	Wash fastness		Rubbing fastness	Light fastness
	LOD	Cotton (staining)	Dry	
Variation in dyeing and finishing treatments				
15% harda + alum (50:50) and 30% tesu aqueous extract dyed	4	3–4	4–5	3
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% harda + alum (50:50) pre-mordanted in sequence				
(10%) eucalyptus leaf aqueous extract + citric acid (5 gpl)	4–5	4–5	4	4
10% eucalyptus leaf MeOH extract + citric acid (5gpl)	4–5	4	4	4
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% alum pre-mordanted cotton fabric				
10% eucalyptus leaf MeOH extract + citric acid (5gpl)	3–4	3–4	3	3
Simultaneous dyeing and finishing of cotton fabric dyed with 30% tesu aqueous extract and 10% eucalyptus aqueous extract on 15% harda + alum (50:50) pre-mordanted cotton fabric				
Tesu (30%) extract +10% eucalyptus leaf aqueous extract + citric acid (5 gpl)	4–5	4–5	4	4

Table 14.

Color fastness to washing, rubbing, light after post-treatment of tesu-dyed double pre-mordanted cotton fabric with eucalyptus as well as simultaneous dyeing and finishing.

cotton fabric were subjected to the standard antimicrobial test as per the American Association of Textile Chemists and Colorists (AATCC)-100–2012 method in terms of bacterial reduction (%) as shown in **Table 15**.

As per the results shown in **Table 15**, for both *Klebsiella pneumoniae* and *Staphylococcus aureus* bacteria, there is 99% reduction of bacterial growth on cotton fabric for double pre-mordanted with alum and harda, i.e. after 15% overall application of harda + alum (50:50) only without any dyeing (no dyeing). This can be attributed to the presence of the natural alum (also known as Fitkari) as mordant, which contributes to the prevention of bacterial growth. However, a remarkable increase of bacterium can be observed when mordanted fabrics were subsequently dyed with 30% tesu extract as natural dye, from which it can be concluded that after dyeing with tesu extract, as potash alum is ionized during dyeing and all aluminium present in alum are consumed for complexion of fibre-mordant-dye complex formation and hence, prevention of bacterial growth by alum is reduced and antibacterial property is reduced partly to Gram-positive bacteria (showing results of 68.88% or approx. 69% bacterial reduction only) and reduced fully to Gram-negative bacteria (showing results –No bacterial reduction at all). However, when the said double pre-mordanted and 30% tesu extract-dyed cotton fabric samples is post-treated or finished with 10% aqueous extract of eucalyptus with citric acid catalyst, there is no bacterial reduction against Gram-negative bacteria (showing results—no bacterial reduction at all), but shows 93.01 bacterial reduction against Gram-positive bacteria. While when a similar pre-treated and tesu-dyed sample of cotton fabric is post-treated with 10% MeOH extract (instead of an aqueous extract of eucalyptus leaves as antibacterial natural finishing agents), it shows the highest bacterial reduction results for against both Gram-positive bacteria (showing a bacterial reduction of 99.99%) and Gram-negative bacteria (showing a bacterial reduction of 99.97%).

Simultaneous dyeing and finishing show antibacterial test results in much similar fashion or quite similar to the only pre-mordanted and subsequently 30% tesu-dyed cotton fabric samples, showing there is no reduction in bacterial growth

Treatments	Bacterial reduction (%) as per AATCC-100-2012	
	<i>Klebsiella pneumoniae</i> : ATCC 4352 (Gram-negative bacteria)	<i>Staphylococcus aureus</i> : ATCC 6538 (Gram-positive bacteria)
Standard bleached cotton control fabric	No reduction	No reduction
15% overall application of harda + alum (50:50) (no dyeing)	99.98	99.43
15% [harda + alum (50:50)] and 30% tesu aqueous extract dyed	No reduction	68.88
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% harda + alum (50:50) pre-mordanted in sequence		
10% eucalyptus leaf aqueous extract + citric acid (5 gpl)	No reduction	93.01
10% eucalyptus leaf MeOH extract + citric acid (5 gpl)	99.97	99.99
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% alum pre-mordanted cotton fabric		
10% MeOH extract of eucalyptus + citric acid (5 gpl)	99.79	99.52
Simultaneous dyeing and finishing of cotton fabric dyed with 30% tesu aqueous extract and 10% eucalyptus aqueous extract on 15% harda + alum (50:50) pre-mordanted cotton fabric		
Tesu (30%) extract + eucalyptus leaves aqueous extract (10%) + citric acid (5 gpl)	No reduction	54.02

Table 15.

Results of the antimicrobial test as per AATCC-100-2012 for pre-mordanted 30% tesu extract-dyed and eucalyptus extract finished cotton fabric after pre-mordanted with 15% total application of Harda + alum (50:50).

against Gram-negative bacteria (showing results of no bacterial reduction at all) and antibacterial property is reduced partly to Gram-positive bacteria (showing results of 54.02% or approx. 54% bacterial reduction only). But only 15% alum pre-mordanted (without harda) and 30% tesu extract-dyed cotton fabric sample, post-finishing application of 10% MeOH extract of eucalyptus leaves render it highly antibacterial in nature showing almost at par or similar level of bacterial reduction results that obtained for said 15% application of harda + alum (50:50) same fabric samples dyed with tesu and post finished with 10% MeOH extract of eucalyptus, for both against Gram-positive bacteria (showing bacterial reduction of 99.79%) and Gram-negative bacteria (showing bacterial reduction of 99.52%).

All corresponding pictures of petri plates for the said antimicrobial tests as per AATCC-100-2012 against Gram-negative and Gram-positive bacteria are also given in **Figure 10** with petri plate numbers being 1–7, where 1A–7A are samples incubated for 0 h, 1B–7B are samples incubated for 24 h with Gram-negative bacteria and 1C–7C are samples incubated after 24 h with Gram-positive bacteria, against the corresponding samples; the photographs of petri plates are almost matching with bacterial reduction (%) results shown in **Table 15**, which are self-explanatory.

Hence, in case of simultaneous dyeing and finishing, the antibacterial property results obtained are not fully satisfactory as compared to the said double pre-mordanted and tesu dyed and post-treated/finished with 10% aqueous extract of eucalyptus, but that effect of antibacterial property is highly enhanced if, the same

Pictures of Petri plates of corresponding samples for Antibacterial test as per AATCC-100-2012		
Tested with Bacterial Species--- as mentioned	<i>Klebsiella Pneumoniae</i> ATCC 4352 (A gram negative bacteria)	<i>Staphylococcus aureus</i> ATCC 6538, (A gram positive bacteria)
(A) AT 0 HOURS	(B) After 24 HOURS	(C) After 24 HOURS
 Sample-1A	 Sample-1B	 Sample-1C
(1): Control fabric (Standard bleached cotton control fabric: un-mordanted and undyed) --- no mordanting and no dyeing		
 Sample-2A	 Sample-2B	 Sample-2C
(2): 15 % overall application of Harda+Alum [50:50] treated cotton fabric : (No dyeing)		
 Sample-3A	 Sample-3B	 Sample-3C
(3): 15 % Harda+Alum [50:50] pre-mordanted +30% Tesu dyed cotton fabric		
POST TREATMENT with 10% extract of Eucalyptus leaves on 30 % TESU AQUEOUS EXTRACT DYED COTTON FABRIC - AFTER DOUBLE PRE MORDANTED with 15% Harda + alum (50:50) in sequence or only 15% Alum Single Pre Mordanted.		
 Sample-4A	 Sample-4B	 Sample-4C
(4): Sample Post treated with 10% Eucalyptus extract (Aqueous) + citric acid (5 gpl) on 30% Tesu dyed after 15% total harda + Alum (50:50)Pre-mordanted Cotton Fabric		
 Sample-5A	 Sample-5B	 Sample-5C
(5): Sample Post treated with 10% Eucalyptus extract (in MeOH) + citric acid (5 gpl) on 30% Tesu dyed after 15% total harda + Alum (50:50) Pre-mordanted Cotton Fabric		
 Sample-6A	 Sample-6B	 Sample-6C
(6): Sample Post treated with 10% Eucalyptus extract (in MeOH) + citric acid (5 gpl) on 30% Tesu dyed after 15% Alum Single Pre-mordanted Cotton Fabric		
SIMULTANEOUS DYEING AND FINISHING OF COTTON FABRIC Dyed with 30% TESU Aqueous Extract AND 10% EUCALYPTUS Aqueous Extract on 15% Harda + alum (50:50) pre-mordanted Cotton Fabric		
 Sample-7A	 Sample-7B	 Sample-7C
(7): Sample produced by Simultaneous Dyeing and Finishing with 30% Tesu aqueous extract and with 10% Eucalyptus extract (Aqueous) + citric acid (5 gpl) on 15% t Overall Harda + Alum (50:50) Pre-mordanted Cotton Fabric.		

Figure 10.

Pictures of petri plates for antimicrobial test as per AATCC-100-2012 against gram-negative and gram-positive bacteria.

percentage, i.e. 10% MeOH alcohol-extracted eucalyptus leaves, is applied instead of its aqueous extract. So, in order to improve the fullest/highest bacterial reduction finish with a natural agent, the said double pre-mordanted cotton fabric after dyeing with tesu natural dye, the dyed fabric is to be finished separately by pad a dry-cure technique using 10% MeOH alcoholic extracted eucalyptus leaves for good results in the reduction of bacterial growth for both Gram-positive and Gram-negative bacteria. In case of cotton fabrics dyed with methanol (alcohol) aided extracted eucalyptus leaves post-treatment, they give a very darker color depth/shade as well as excellent antimicrobial finishing properties.

2.3.2 UV-protective finish on natural dyed cotton fabric with natural finishing agent

Few reports are available in the literature on the role of natural dyes and other natural resource materials, when applied on textiles for UV-protective properties [19, 32–34, 43]. Finishing of textiles with vegetable oil is also reported in the literature [44].

But nowadays, UV protection in textiles has become also equally important for the protection of the human skin. Considering this in view, reddening of the skin under any barrier like textiles or other materials can be judged by UPF or sun protection factor (SPF) values. The classification of performance-based UPF value grading/rating is given below.

Performance-related UPF rating and classification	
UP F value	UV protection rating/category
15–24	Good protection
25–40	Very good protection
40–50+	Excellent protection

So, as a case study, UV-protective finish on 30% aqueous extract of tesu-dyed cotton fabric (pre-mordanted with 15% overall application of harda + alum (50:50)) was imparted as a finishing post-treatment by a pad-dry-cure technique with aqueous extract of eucalyptus, MeOH extract of eucalyptus and emulsified coconut oil in the presence of citric acid as a catalyst for finishing with these two types of natural UV absorber for imparting UV-protective finish. Relevant data of UV protection factor values before and after the said treatments are measured as per AATCC-183-2010/2014 and are tabulated in **Table 16**. Double pre-mordanted with 15% overall application of harda + alum (50:50) and 30% tesu aqueous extract-dyed cotton fabric samples are when post treated with both aqueous or alcoholic extract of eucalyptus leaves and also with emulsified coconut oil in presence of citric acid as catalyst (in all the cases), UV protection performance are much enhanced as compared to said double pre-mordanted and tesu-dyed cotton fabric (without any post-treatment). Relevant results of UPF values from **Table 16** indicate that best result, i.e. UPF value of 40, is obtained when the said double pre-mordanted cotton fabrics dyed with tesu extract (as natural dye) is finished with MeOH alcoholic 10% extract of eucalyptus leaves in the presence of citric acid (5 gpl) by a pad-dry-cure technique as compared to UPF value obtained as 30 for post-treatment with equal dosages of emulsified 10% coconut oil in the presence of citric acid (5 gpl) under comparable conditions of treatment. However, when cotton fabrics are subjected to simultaneous dyeing and finishing process with the said two types of natural UV-protective agents (emulsified coconut oil and aqueous extract of eucalyptus leaves applied simultaneously in dye bath), the said enhancement of UPF values for simultaneous dyeing and finishing process are much less showing a UPF values 20 for emulsified coconut oil and UPF value is 25 eucalyptus leaves aqueous extract, i.e. UPF values in case of simultaneous dyeing and finishing treatment are not shown to be as high as it shows by sequential post-treatment process by pad-dry-cure process in both the cases respectively. UPF values of 15–24/25 are considered to be moderate to good protection, and hence UPF values 20 and 25 in these two cases of simultaneous dyeing and finishing using either emulsified coconut oil and eucalyptus leaves aqueous extract as natural finishing agents applied simultaneously in the dye bath can be considered to provide a moderate to good UV protection, but not as

Samples/type of post-treatments with UV absorbers	UPF	UV-A (%)	UV-B (%)
Standard bleached cotton control fabric (un-mordanted and undyed cotton)	5	29.67	22.10
15% overall application of harda + alum (50:50) (no dyeing)	10	19.56	11.01
15% [harda + alum (50:50)] and 30% tesu aqueous extract dyed	12	10.15	7.89
Post-treatment with 10% extract of eucalyptus leaves and 10% coconut oil with citric acid as a catalyst on 30% tesu aqueous extract-dyed cotton after pre-mordanted with 15% harda + alum (50:50) pre-mordanted cotton fabric			
10% coconut oil + citric acid (5 gpl) post-treatment	30	2.76	2.02
10% eucalyptus leaves aqueous extract + citric acid (5 gpl)	25	4.16	3.60
10% eucalyptus leaves alcoholic (MeOH) extract + citric acid (5 gpl)	40	2.08	1.81
Post-treatment with 10% extract of eucalyptus leaves on 30% tesu aqueous extract-dyed cotton after pre-mordanted with only 15% alum single pre-mordanted cotton fabric			
10% eucalyptus leaf alcoholic (MeOH) extract + citric acid (5 gpl)	30	2.66	2.89
10% coconut oil + citric acid (5 gpl)	25	5.37	8.22
Simultaneous dyeing and finishing of cotton fabric dyed with 30% tesu aqueous extract and 10% eucalyptus leaf aqueous extract or 10% coconut oil emulsion on 15% harda + alum (50:50) pre-mordanted cotton fabric			
Tesu (30%) extract + eucalyptus aqueous extract (10%) + citric acid (5 gpl)	25	4.49	4.56
Tesu (30%) + coconut oil (10%) + citric acid (5 gpl)	20	3.94	6.08

Table 16.

Result of UPF test as per AATCC-183-2010 for 15% Harda + alum (50:50) pre-mordanted or only 15% alum pre-mordanted cotton fabric dyed with 30% aqueous extract of tesu and post-treatment with natural UV absorbers (aqueous and alcoholic (MeOH) extract of eucalyptus leaves and coconut oil).

good as the UPF value of 40 obtained for post-treatment with MeOH extracted eucalyptus leaves by a pad-dry-cure process on the said double pre-mordanted with 15% overall application of harda + alum (50:50) and 30% tesu aqueous extract-dyed cotton fabric samples. While without any after-treatment or simultaneous treatment with eucalyptus or coconut oil, 15% overall harda + alum (50:50) and 30% tesu aqueous extract-dyed cotton fabric sample shows a UPF value of 12 only as compared to a UPF value of 5 for the standard bleached control cotton fabric (un-mordanted and undyed).

Thus, according to the data in **Table 16**, cotton samples treated with methanol-extracted eucalyptus leaves post-treatment by a pad-dry-cure system provide an excellent UV protection factor against exposure to ultraviolet rays since their UPF value is 40, which lies in the range of UPF category between 40 and 50.

However, when an emulsified coconut oil is treated in the presence of citric acid, it is hydrolysed forming lauric acid (approx. 46–47% content) and α -tocopherol. So during post curing of cotton fabric treated in the presence of citric acid, the hydrolysed emulsified coconut oil (10%), possibly is attached by reaction of –COOH group of lauric acid with hydroxyl group of cellulose forming ester linkage and possible also helps to attach α -tocopherol forming an ether linkage by reaction between hydroxyl group of α -tocopherol and hydroxyl group of cotton cellulose under heat (curing) and acidic catalyst (citric acid). The attachment of eucalyptus to cotton is not yet referenced in any current research, which needs to be further explored by research in this field. However, from compositional analysis, it is known that essence oil parts of eucalyptus contain volatile chemical constituents in

MeOH extract of the eucalyptus leaf having 1,8-cineole, benzene, nerolidol, limonene, alpha-pinene and beta-pinene, which can participate in crosslinking with cellulosic-OH groups in the presence of citric acid and heat showing a better result for protecting bacterial growth and protection against UV rays also, while any type of extract of eucalyptus contain eucalyptol, alpha-pinene, beta-pinene, alpha-phellandrene, gamma-terpinene, caffeic acid, linaool, geraniol and thymol, which are strongly responsible for reducing and blocking the bacterial growth as well. Thus, the eucalyptus leaves MeOH extract can be used as a natural resource-based multiple finishing agent for textiles.

3. Conclusion

The important scientific and technological aspects of natural dyeing on cotton, jute and silk fabrics in terms of extraction and purification, characterization of purified extracted natural dyes by different scientific and instrumental analyses, case studies on the effect of use of different bio-mordanting on color strength, case studies on the standardization of dyeing process variables for optimizing dyeing conditions to get reproducible shades, etc. have led to the generation of scientific ways and means for practising a precise technological control during such processing with variable natural materials, over the traditional and conventional artisan-based natural dyeing processes of textiles.

Similarly the worldwide current research interest on natural resources has improved knowledge of concern textile dyers and other related persons on the use of plant-based bio-mordants, bio-dyes/natural dyes and natural finishing agents, part of which has ultimately come into practice for its commercial utilization and exploitation for eco-friendliness and environmental advantages. Hence, the above said scientific analyses and case studies presented here in brief with natural resource materials for textile dyeing and finishing, may lead to generate further interest of concern readers towards more and more use of these natural resource materials for textile dyeing and finishing like use of blue natural indigo for creating bio-denim, i.e. natural indigo dyeing by natural reduction process applied on cotton has several environmental safety and advantages. A detailed scientific characterization and index-based ingredient identification of such natural dyes and finishes have been also felt essential to formulate test standards for the identification of natural dyes from such natural dyed textile materials for consumers' protection. All effort towards this goal should be encouraged.

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