Chapter

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 a 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.

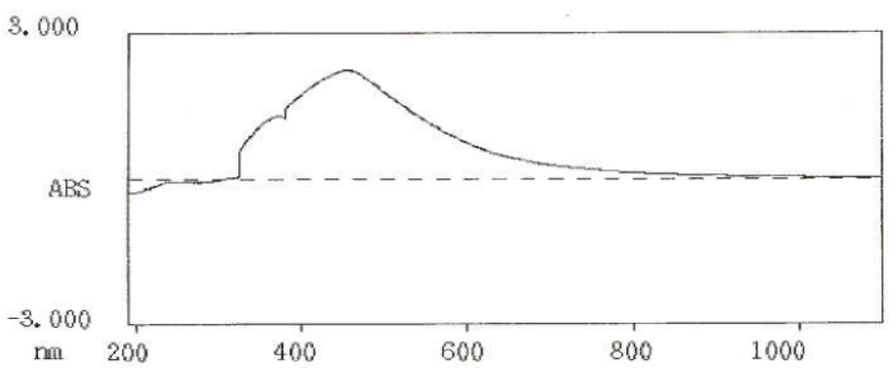

Figure 1.
UV-VIS spectra of the extract of color component of tesu as natural dyes.

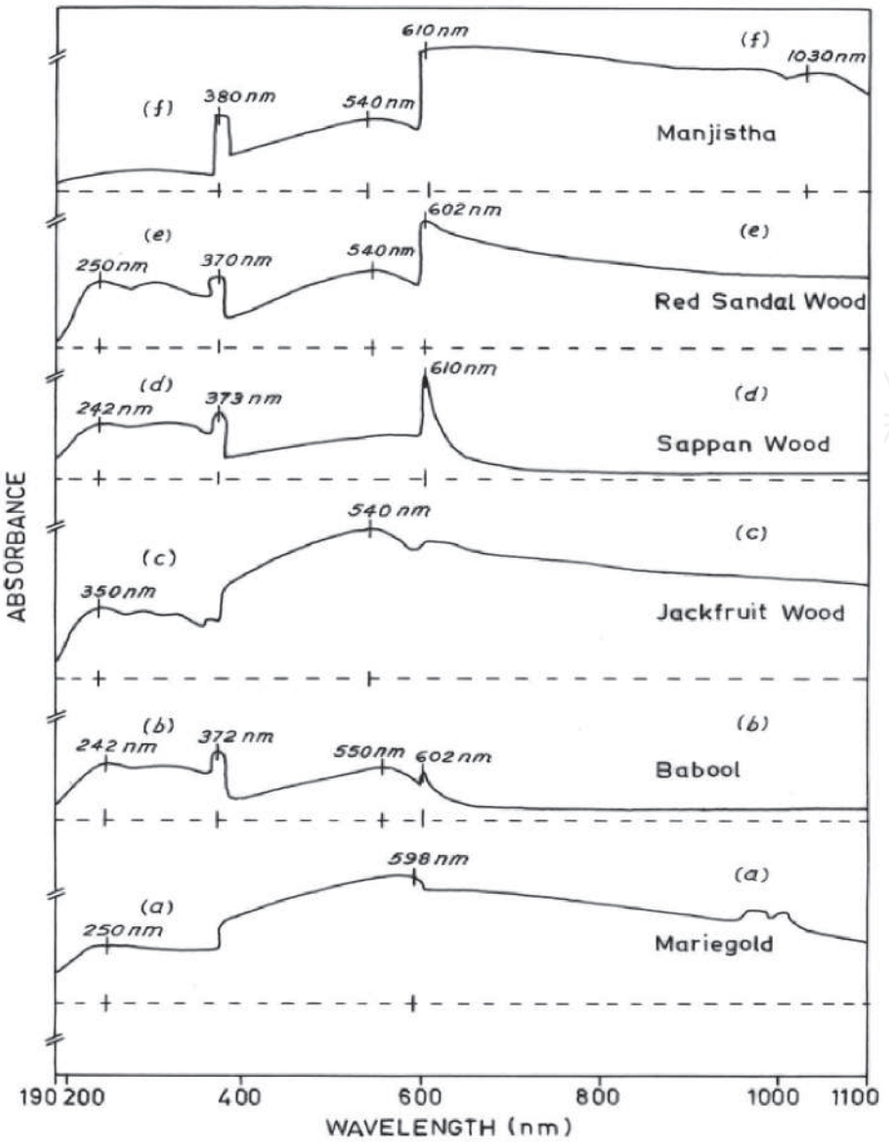

Figure 2.
UV-VIS spectra of the extract of color component of few natural dyes other than tesu (x- and y-axes: Absorbance values in y-axis are −3.0 to +3.0 and wavelength values are 190–1100 nm).

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 made 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.

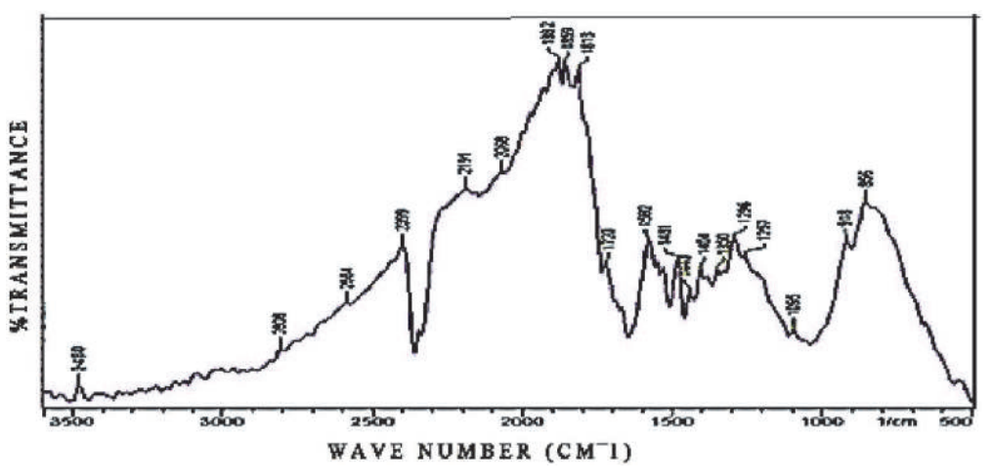

Figure 3.
FTIR spectra of purified tesu as natural dyes (transmittance values are 25–100%).

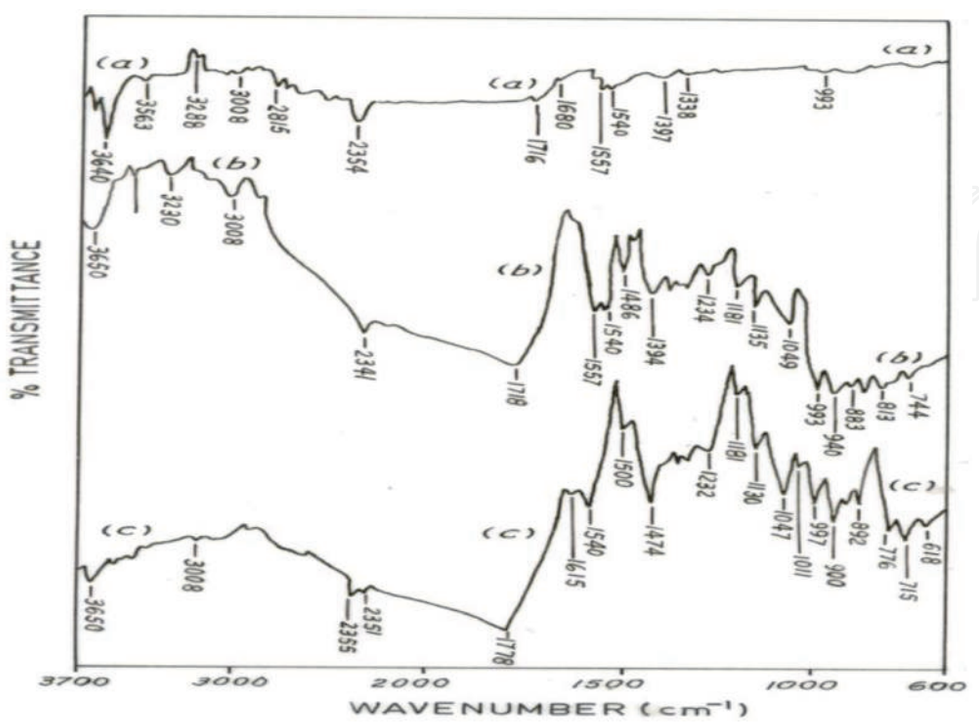

Figure 4.
FTIR spectra of purified natural dyes: (a) red sandalwood, (b) jackfruit wood and (c) manjistha/madder (Rubia) (transmittance values are 25–100%).

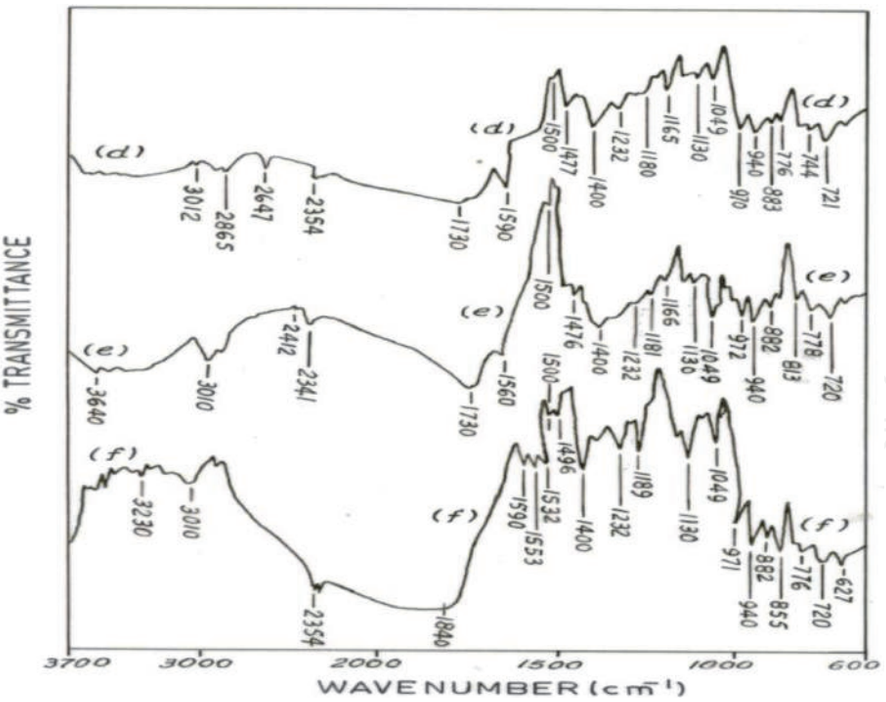

Figure 5.
FTIR spectra of purified natural dyes (d) marigold, (e) babool and (f) sappanwood (transmittance values are 25–100%).

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 °C/min over a temperature range from ambient (about 28–30°C) to 490–500°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 $(CH_2)_n$, 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).

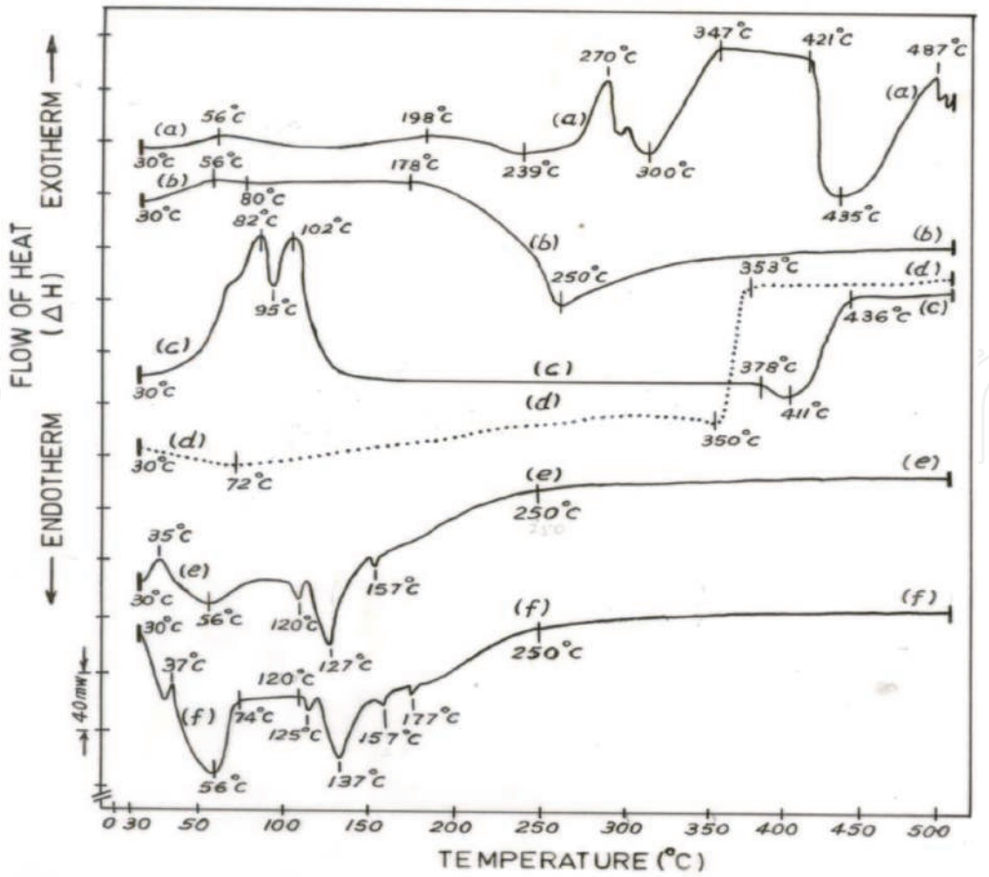

Figure 6.
DSC thermograms of purified natural dyes: (a) babool, (b) jackfruit wood, (c) red sandalwood, (d) sappanwood, (e) marigold and (f) manjistha/madder (Rubia).

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 deoxysantalin
	95	Sharp trough (endothermic)	Thermal decomposition of deoxysantalin
	102	Sharp peak (exothermic)	Breaking of more strong H-bonds of santalin (A and B)
	129–378	Flat plateau region (endothermic)	No effects
	411	Small trough (endothermic)	Thermal decomposition of santalin (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
	157	Tiny trough (endothermic)	Decomposition of other minor constituents
	250–500	Flat plateau region (exothermic)	No effects
f. MJ or madder (Rubia)	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**).

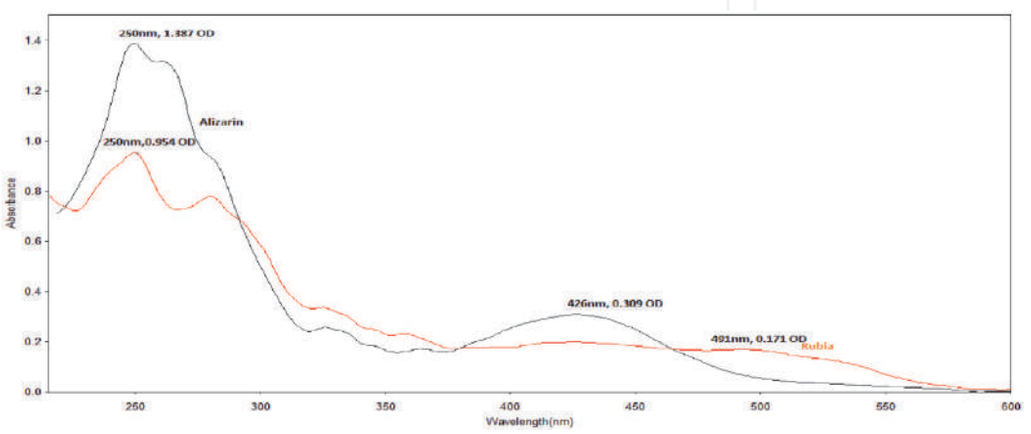

Figure 7.
UV-VIS spectrum of madder (Rubia) and synthetic alizarin dyes.

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 μL 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.

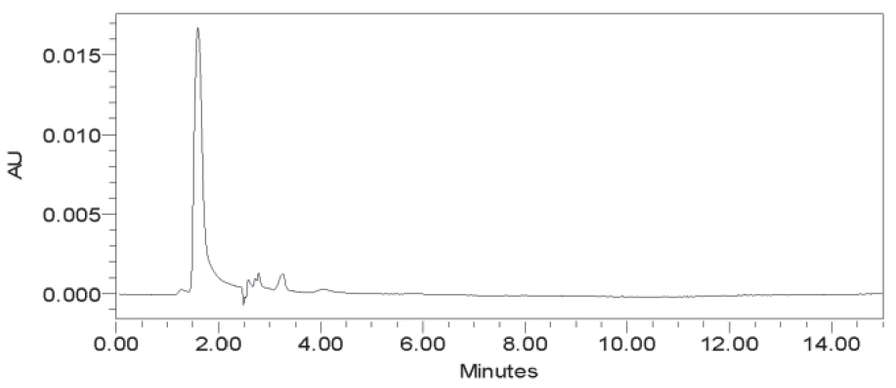

Figure 8.
Chromatogram of synthetic alizarin.

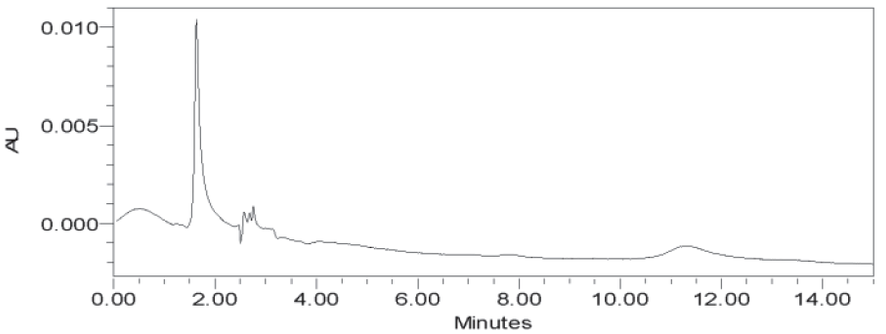

Figure 9.
Chromatogram of natural madder (Rubia) containing natural alizarin.

Peak shown at nm	In synthetic alizarin	In natural Rubia	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 Rubia 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, *p*H 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 $\lambda_{max.}$ 540 nm	Extraction variables	OD/absorbance for madder at $\lambda_{max.}$ 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 λmx	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 λmax	ΔE*	ΔL*	Δa*	Δb*	ΔC*	ΔH*	BI	MI	CDI
10% harda and 10% KAl $(SO_4)_2$ 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
***p*H**										
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	−.093	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
***p*H**					
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 metameric 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 metameric 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 metameric 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 CCL_4-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
Variation in dyeing and finishing treatments	**LOD**	**Cotton (staining)**	**Dry**	
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**	
Variation in dyeing and finishing treatments	***Klebsiella pneumoniae*: ATCC 4352 (Gram-negative bacteria)**	***Staphylococcus aureus*: 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

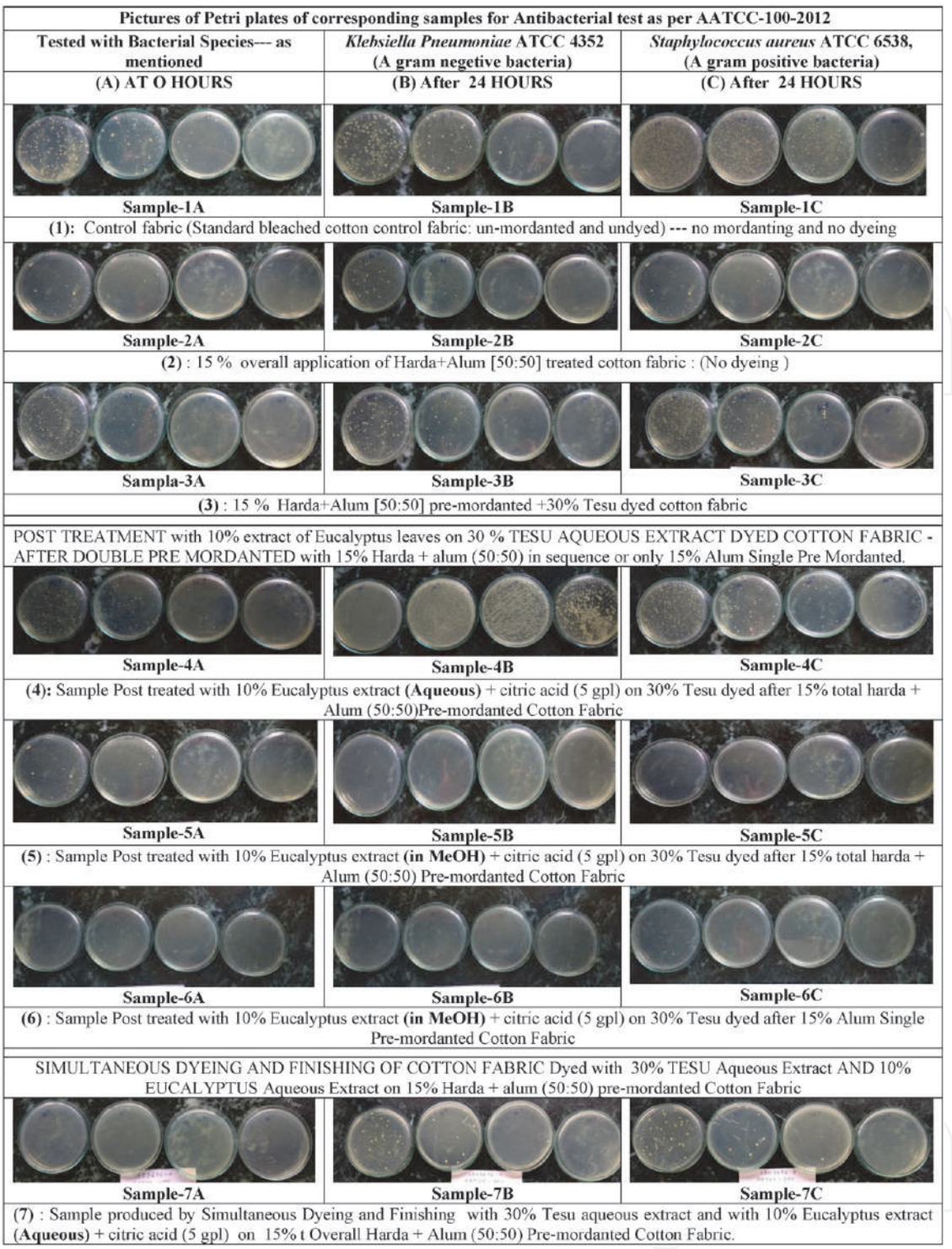

Figure 10.
Pictures of petri plates for antimicrobial test as per AATCC-100-2012 against gram-negative and gram-positive bacteria.

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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Chapter

Fundamentals of Natural Dyes and Its Application on Textile Substrates

Virendra Kumar Gupta

Abstract

The meticulous environmental standards in textiles and garments imposed by countries cautious about nature and health protection are reviving interest in the application of natural dyes in dyeing of textile materials. The toxic and allergic reactions of synthetic dyes are compelling the people to think about natural dyes. Natural dyes are renewable source of colouring materials. Besides textiles it has application in colouration of foods, medicine and in handicraft items. Though natural dyes are ecofriendly, protective to skin and pleasing colour to eyes, they are having very poor bonding with textile fibre materials, which necessitate mordanting with metallic mordants, some of which are not eco friendly, for fixation of natural dyes on textile fibres. So the supremacy of natural dyes is somewhat subdued. This necessitates newer research on application of natural dyes on different natural fibres for completely eco friendly textiles. The fundamentals of natural dyes chemistry and some of the important research work are therefore discussed in this review article.

Keywords: colour fastness, dyeing, extraction of natural dyes, natural dyes

1. Introduction

After the advent of mauveine by Henry Perkin in 1856 and subsequent commercialization of synthetic dyes had replaced natural dyes, and since then consumption and application of natural dyes for textiles got reduced substantially. In present scenario environmental consciousness of people about natural products, renewable nature of materials, less environmental damage and sustainability of the natural products has further revived the use of natural dyes in dyeing of textile materials. Natural dyes are having some inherent advantages:

- No health hazard
- Easy extraction and purification
- No effluent generation
- Very high sustainability
- Mild dyeing conditions

- Renewable sources

There are some technical issues and disadvantages related to the application of natural dyes which reduced its applications that are:

- Mostly applicable to natural fibres (cotton, linen, wool and silk)
- Poor colour fastness properties
- Poor reproducibility of shades
- No standard colour recipes and methods available.
- Use of metallic mordants, some of which are not eco friendly.

Hill [1] had given his views that research work with natural dyes is inadequate, and there is need of significant research work to explore the potentials of natural dyes before its important application to textile substrate.

In India initially Alps Industries Ghaziabad (Uttar Pradesh, India) and later Ama Herbals, Lucknow, and Bio Dye Goa done extensive work for industrial research and production of natural dyes and natural dyed textiles. Textile-based handicraft industries in many countries engaged local people to dye textile yarn with natural dyes and weave them to produce specialty fabrics. Printing of textile fabrics with natural dyes in India are specially done in Rajasthan and Madhya Pradesh.

Turkish carpets are recognised for their beauty made with natural dyes. The major importers of natural dyes are the USA and the EU. In the EU the major importers of natural dyes are France, Germany, Italy and the UK. Natural dyes have many advantages [2] like non toxicity, eco friendliness, pleasing shade to eye and having special aroma or freshness of shade [3]; however, natural dyes have some disadvantages to showing poor colour reproducibility, poor or inconsistent composition, average washing fastness [4] and lesser availability in different regions, which are of great concern against its revival. Moreover natural dyes are not having any standard established dyeing [5] method. The final shade depends on the type of mordant used in dyeing. Natural dyes are used in the dyeing of cotton [6, 7], linen [8], wool [9, 10], silk [11, 12], nylon and polyester [13, 14] fabrics. The natural dyes can be classified in different ways such as based on origin/source type, type of hue, chemical structure [15, 16] and colour components. The classification of natural dyes based on origin/source is given below:

- Vegetable origin
- Animal origin
- Mineral origin

For vegetable origin of natural dyes, the best source of natural dyes are the different parts of plants and trees. Most natural dyes are extracted from different parts of plants and trees. Natural dyes and pigments are taken from the following parts of plants/trees:

- Seed
- Root

- Stem
- Barks
- Leaves
- Flowers

Natural dyes are having wide application in the colouration of most of the natural fibres, e.g. cotton, linen, wool and silk fibre, and to some extant for nylon and polyester synthetic fibre. However, the major issues for natural dyed textiles are reproducibility of shade, non availability of well-defined standard procedure for application and poor lasting performance of shade under water and light exposure. To achieve good colour fastness to washing and light are also a challenge to the dyer. Several researchers had proposed different dyeing methods and process parameters, but still these information are inadequate, so this calls for the need of research to develop some standard dye extraction technique and standardisation of whole process of natural dyeing on textiles. Here there are examples of few important natural dyes [17] which are widely used in the dyeing of textile materials, described below.

1.1 Jack fruits (*Artocarpus heterophyllus* Lam)

It is a very popular fruit of south India and other parts of India. The wood of the tree is cut into small chips and crushed into dust powder and then subsequently boiled in water to extract the dye. After mordanting treatment of dyed fabrics, yellow to brown shades are obtained. The cotton and jute fabrics are dyed by this dye. It belongs to the family of Moraceae. The dye consists of morin as colouring molecule (**Figure 1**).

1.2 Turmeric (*Curcuma longa*)

The dye is obtained from the root of the plant. The turmeric root is dried, crushed in powder form and boiled with water to extract the dye. It can be used in the dyeing of cotton, wool, and silk. Proper mordanting treatment improves colour fastness to wash. The brilliant yellow shade is obtained after dyeing with turmeric natural dye. Turmeric is a rich source of phenolic compounds known as curcuminoids. The colouring ingredients in turmeric are called curcumin. Curcumin is diarylheptanoid existing in keto-enol form. Turmeric is a member of *Curcuma* botanical group (**Figure 2**).

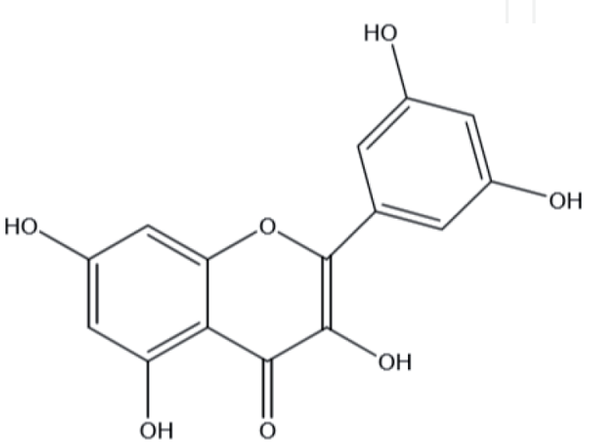

Figure 1.
Molecular structure of morin (3,5,7,2',4'pentahydroxy-flavone).

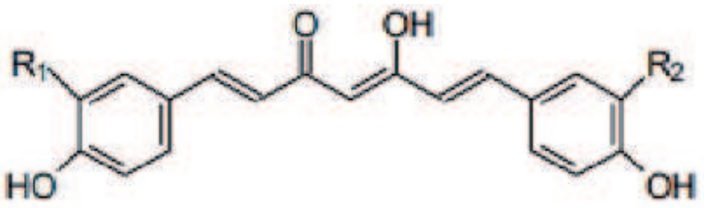

Figure 2.
Molecular structure of curcumin (diarylheptanoid).

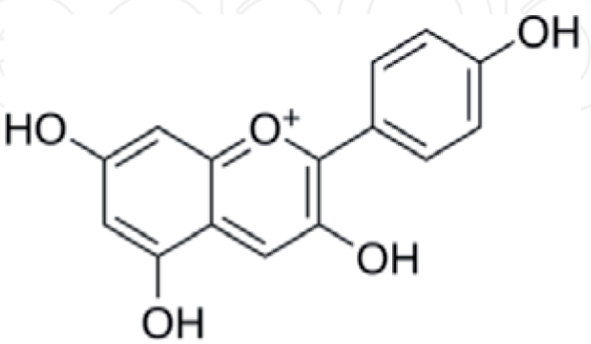

Figure 3.
Molecular structure of pelargonidin (5,5,7,4 tetrahydroxy antocyanidol).

1.3 Onion (*Allium cepa*)

The papery skin of onion is the main source of the dye. Onion skin is boiled to extract the colour and subsequently can be dyed with or without mordanting the fabric. The resulting colour is from orange to brown. It contains colouring pigments called pelargonidin (5,5,7,4 tetrahydroxy antocyanidol). The amount of colouring pigment present varies from 2.0 to 2.25% (**Figure 3**).

1.4 Hina (*Lawsonia inermis* L)

It is the leaf of the plant that is traditionally used in making the coloured design on the hands of women. The leaf of the plant is dried, crushed and subsequently boiled with water to extract the dye from leaf. The mordanted fabric gives colour from brown to mustard yellow. This is the dispersed dye type colour; hence, polyester and nylon can be dyed by hina. However, it stains wool and silk giving a lighter brown colour. Hina is commonly known as lawsone. The chief constituent of hina leaves is hennotannic acid; it is a red orange pigment. Chemically hennotannic acid is 2-hydroxy-1,4-naphthoquinone. The colouring molecules have strong substantivity for protein fibre (**Figure 4**).

1.5 Indigo (*Indigofera tinctoria*)

It is the seed of the plant. The full matured plant has 0.4% colour on weight of the plant. The plants are steeped in the water until the fermentation start. When the hydrolysis of glucoside is completed, the liquor is separated from the plant debris. The extract is aerated which converts indoxyl to indigotin which separates out as a precipitate. The shade of natural indigo is difficult to reproduce exactly. The variety of blue shade on cotton can be obtained by the application of natural Indigo. It is kind of vat dye and hence need reductive vatting with liquid jiggery and citric acid or dithionate.

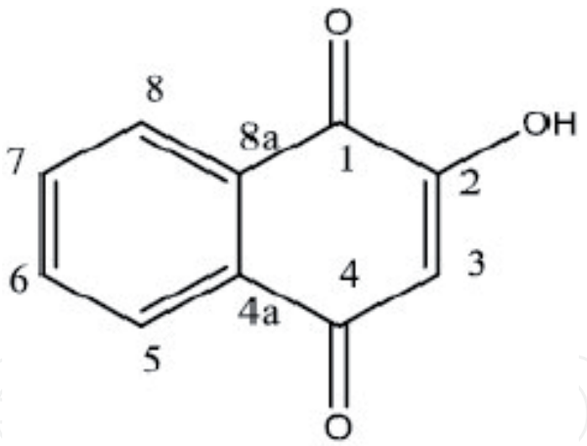

Figure 4.
Molecular structure of lawsone (2-hydroxyl-1,4-naphthoquinone).

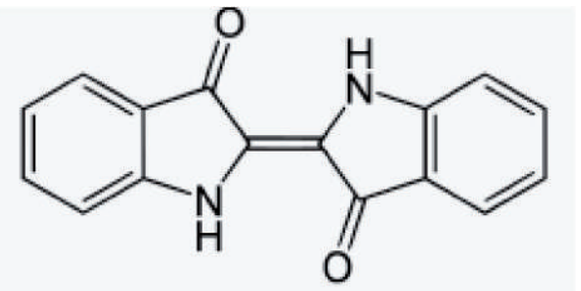

Figure 5.
Molecular structure of natural indigo.

The precursor to indigo is indican which is a colourless water-soluble compound. Indican hydrolyzes in water and releases β-D-glucose and indoxyl. The oxidation of indoxyl resulted in indigotin. The average yield of indican from an indigo plant is 0.2–0.8%. Indigo is also present in molluscs. The molluscs contain mixture of indigo and 6,6′-dibromo indigo (red), which together produce a colour known as Tyrian purple. During dyeing due to air exposure, dibromo indigo is converted into indigo blue, and the mixture produces royal blue colour (**Figure 5**).

1.6 Madder or manjistha or *Rubia* (*Rubia tinctorum*)

The dye is obtained from the root of the plant. The root is scrubbed, dried in sunlight and finally boiled in the water to extract the dye in solution. The dye has red colour. The cotton, silk and wool fibre can be dyed with madder at a temperature of 100°C for time period of 60 min, and subsequently dye solution is cooled. Bright red shade is produced on wool and silk and red violet colour on cotton. This is a mordantable type of acid dye having phenolic (-OH) groups. The colouring matter in madder is alizarin of the antharaquinone group. The root of the plant contains several polyphenolic compounds, which are 1,3-dihydroxyanthraquinone, 1,4-dihydroxyanthraquinone, 1,2,4-trihydroxyanthraquinone and 1,2-dihydroxyanthraquinone (**Figures 6** and 7).

1.7 Tea waste (*Camellia sinensis*)

India is one of the biggest consumer of tea. The left over waste of tea is collectable in large quantity. The extract of tea waste can be used as a natural dye in combination with different mordants, which can produce yellowish brown to brown

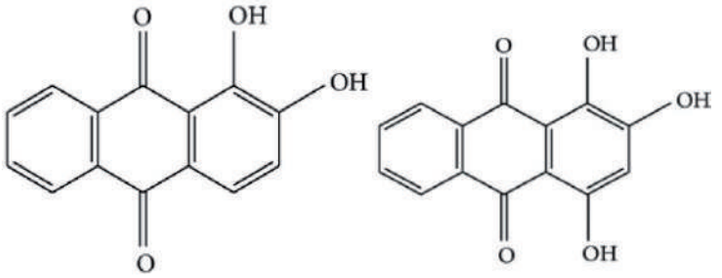

Figure 6.
Molecular structure of alizarin and purpurin.

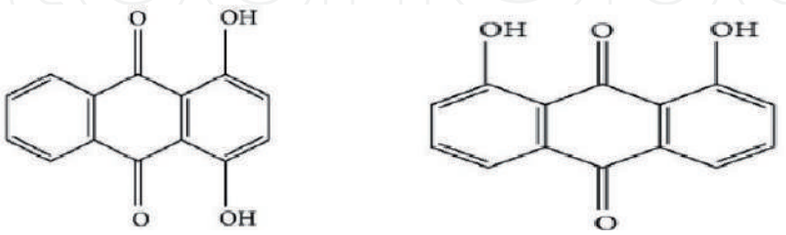

Figure 7.
Molecular structure of 1,4-dihydroxyanthraquinone and 1,8-dihydroxyanthaquinone.

shade. This is a mordantable dye. Flavonoids, flavonols and phenolic acids are the main colouring components in waste of the tea. Polyphenols, which are mostly flavonols, are known as catechins with epicatechin and its derivatives.

1.8 Safflower (*Carthamus tinctorius*)

The safflower petals are soaked in distilled water and subsequently boiled with water for more than 2 h, and it is repeated two times. The solution is filtered and the filtrate is vacuum dried. The obtained powder is having strength of 20–30%. In dyeing it produces cherry red to yellowish red shade. Safflower contains natural pigment called carthamine. The biosynthesis of carthamine takes place by chalcone (2,4,6,4-tetrahydroxy chalcone) with two glucose molecules and that resulted in the formation of safflor A and safflor B (**Figure 8**).

1.9 Sappan wood (*Caesalpinia sappan*)

Aqueous extraction is used to extract the dye from sappan wood. Alkali extraction can also be used. It produces bright red colour. It produces an orange colour in combination with turmeric and maroon shade with catechu. The sappan wood tree is found in India, Malaysia and the Philippines. The colouring pigment is similar to logwood. The same dye is also present in Brazil wood.

1.10 Logwood (*Haematoxylon compechianum*)

The dye is extracted from the stem of the tree. The stems are broken into small pieces and steepened in cold water for several hours followed by boiling. The extracted dye solution is strained. The logwood natural dye is used to produce black shade on the wool. The logwood trees are found in Mexico, Central America and the Caribbean islands. It is also known as compeachy wood. The colouring matter in logwood natural dye is haematoxylin, which after oxidation forms haematein during isolation (**Figures 9** and **10**).

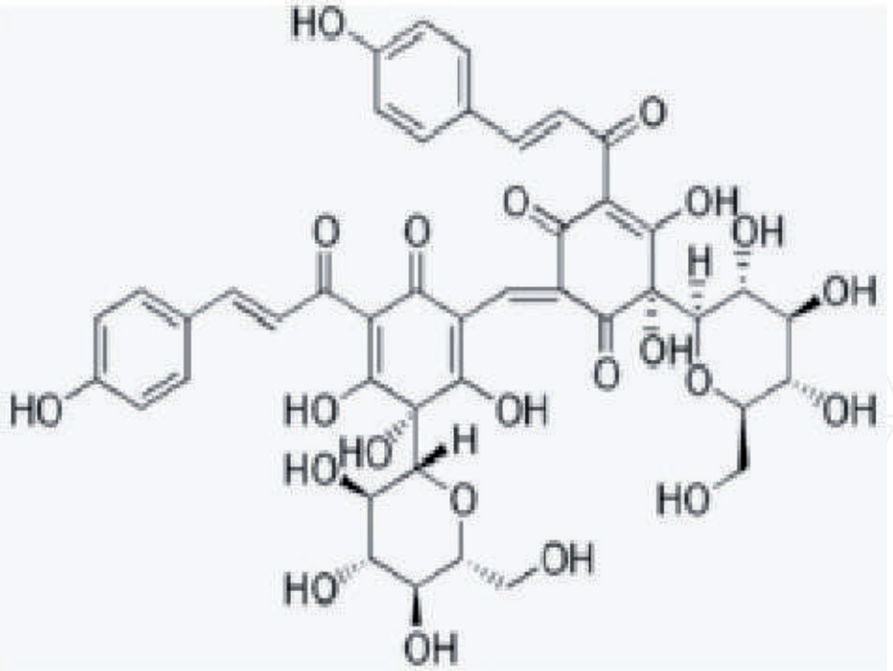

Figure 8.
Molecular structure of carthamine (safflower).

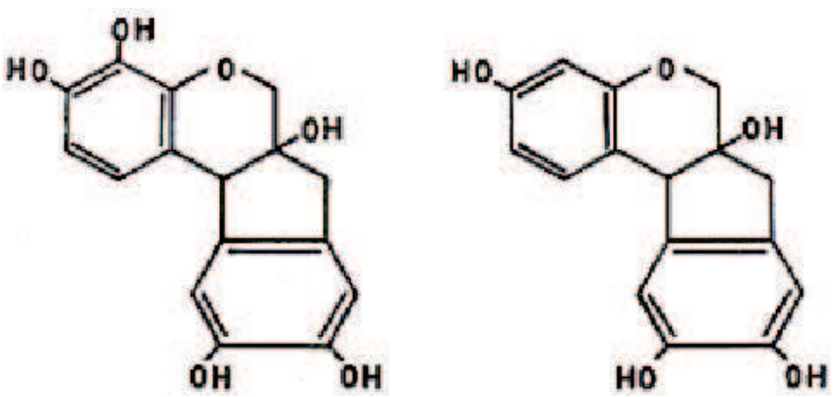

Figure 9.
Molecular structure of haematoxylin and brazilin.

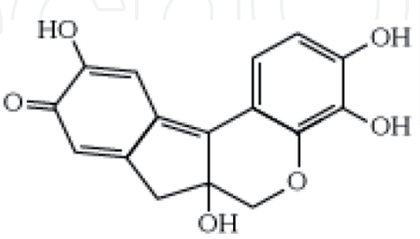

Figure 10.
Molecular structure of haematein.

1.11 Saffron (*Crocus sativus*)

The dye is extracted from the stigma of flower, which is boiled in water, and the colour is extracted. It imparts a bright yellow colour to the textile material. The wool, silk and cotton can be dyed with saffron. Alum mordant produces orange yellow shade which is also called saffron yellow. This is also used as food colouring. Saffron is a perennial plant which belongs to the Iridaceae family. The aqueous

extract of saffron petals contains 12% colourant. The colouring matter of saffron contains phenolic compounds, flavonoids and anthocyanins. Anthocyanidins (pelargonidin) is responsible for the colour in saffron petals. The oxidation of anthocyanidins produces flavonol (**Figure 11**).

1.12 Pomegranate rind (*Punica granatum*)

Rind of pomegranate fruit waste is used as a natural dye. Pomegranate fruit is rich in natural tannins. The anar peel produces a yellow colour dye. This natural dye is used in dyeing of wool, silk and cotton fibre. The colouring molecule in pomegranate rind is flavogallol which is called granatonine. It exists in alkaloid form (N-methyl granatonine). The pomegranate rind is rich in tannin content; therefore, it is also used as tanning material (**Figure 12**).

1.13 Lac insect (*Laccifer Lacca* Kerr)

It is a resinous protective secretion from the insect lac which work as a pest on a number of plants. Lac dye can be obtained by extracting stick lac (shellac) with water and sodium carbonate solution and precipitating with lime. Lac contains a water-soluble red dye. It produces scarlet to crimson red shade after dyeing. The lac dye is obtained from an insect named as coccus lacca. Resin which produced by insect is called stick lac. The lac dye contains laccaic acid A and B which are responsible for the colour of the dye. The amount of colouring matter (laccaic acid) is 0.5 to 0.75% on the weight of the resin (**Figures 13** and **14**).

1.14 Cochineal (*Dactylopius coccus*)

Cochineal is obtained from an insect. It produces beautiful crimson, scarlet and pink colour on cotton, wool and silk. After mordanting with alum, chromium, iron and copper; the colour from purple to grey are produced. Cochineal is a scale insect

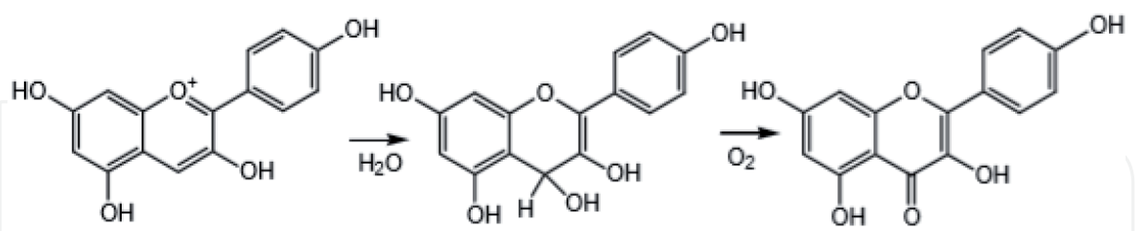

Figure 11.
Molecular structure of pelargonidin (anthocyanidin) purple and kaempferol (flavonol) yellow.

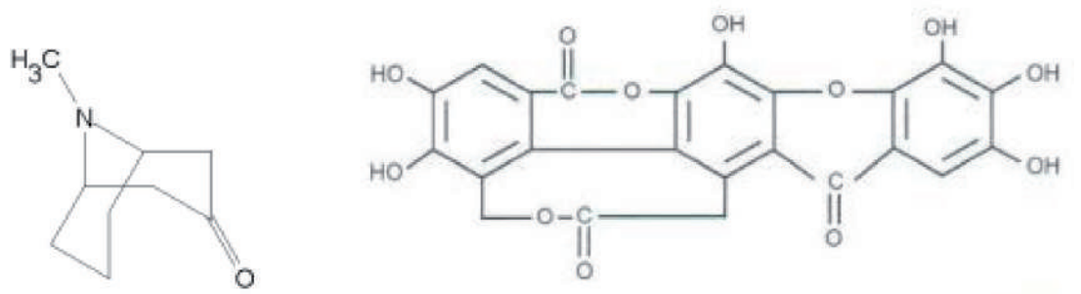

Figure 12.
Chemical structure of granatonine.

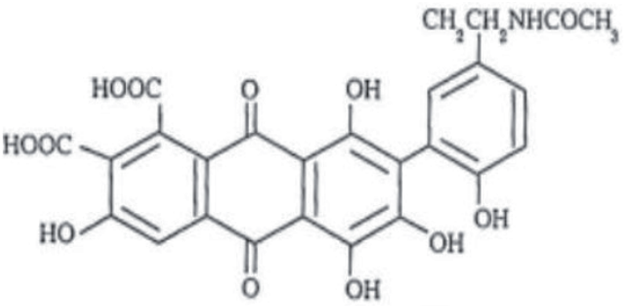

Figure 13.
Chemical structure of laccaic acid A.

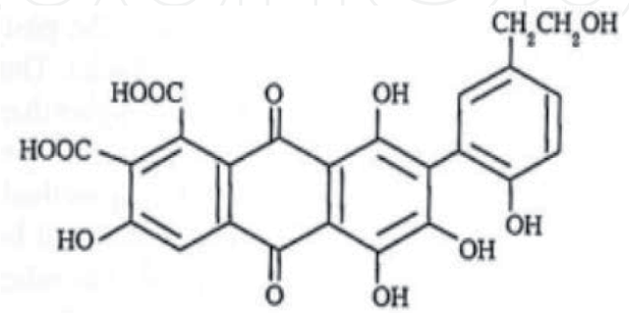

Figure 14.
Chemical structure of laccaic acid B.

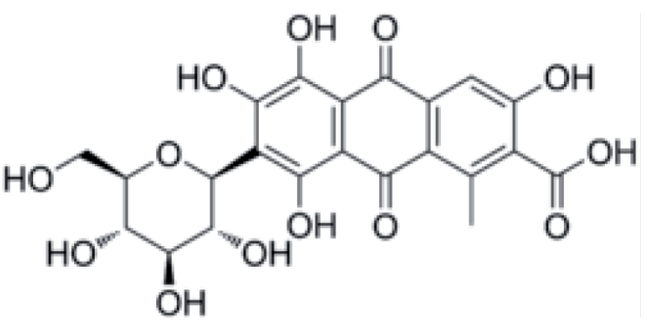

Figure 15.
Chemical structure of carminic acid.

from which natural colourant carmine is derived. Carminic acid is extracted from female cochineal insects. The body of insect is 19–22% carminic acid (**Figure 15**).

1.15 Mineral sources

Some kinds of mineral ores, red clay and ball clay can yield light colours along with mineral salts. But colour composition is not constant and depends on source.

2. Classification of natural dyes

2.1 By chemical constitution

2.1.1 Indigoid class

Two important dyes in this class are indigo blue and Tyrian purple. It occurs as glucoside indicant in the plant. Another blue dye is woad having the same

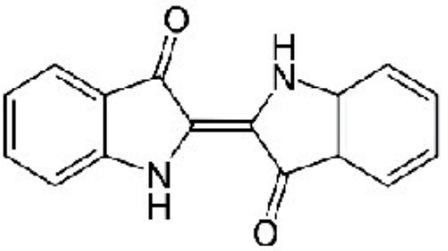

Figure 16.
Indigoid structure.

chemical class. The chemical structure which belongs to indigoid class is shown in **Figure 16**.

2.1.2 Anthraquinone class

Dyes that belong to this class are having anthraquinone structure and obtained from plant and insect. The red shade is specific to this class. Madder, lac, kermes and cochineal are some of the examples. The general chemical structure of this class is shown in **Figure 17**.

2.1.3 Alpha naphthoquinone

The dyes are having alpha naphthoquinone structure such as 2-hydroxy 1-4-naphthoquinone. Hina, lawsone and juglone are examples of this class. The chemical structure of this class is shown in **Figure 18**.

2.1.4 Flavones

The dyes are having yellow shade. The natural dye weld belongs to this category. Most of the dyes are derivatives of hydroxyl and methoxy substituted flavones or isoflavones. The chemical structure of this class of dye is shown in **Figure 19**.

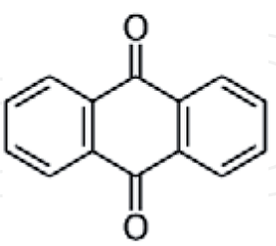

Figure 17.
Anthraquinoid structure.

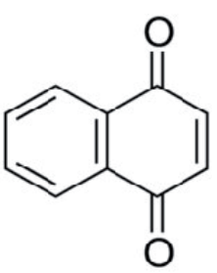

Figure 18.
Naphthoquinone structure.

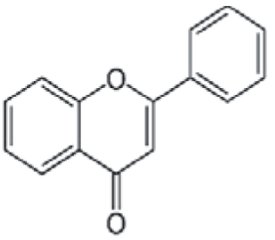

Figure 19.
Flavones structure.

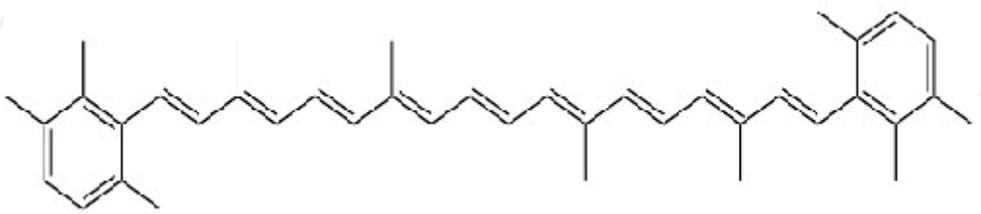

Figure 20.
Carotenoid structure.

2.1.5 Carotenoids

The natural dyes saffron and annatto belong to this class. The dye structure of this class has long-chain conjugated double bonds. The chemical structure of this class is as shown in **Figure 20**.

2.1.6 Dihydropyrans

The dyes which belong to this category are logwood and sappan wood. Logwood, a natural dye, produces dark black shade on silk, wool and cotton.

2.1.7 Anthocyanidins

The natural dye carajurin belongs to this category. The blue and orange shades are obtained from this class.

2.2 Chemistry of natural dyes

Different natural colourants contain different chromophoric and auxochromic groups. Depending on the presence of a particular group in the dye structure, the chemistry of the dyes can be explained in terms of their chromophoric groups. The different dye structures and chromophoric groups are as explained.

2.2.1 Quinoid-based structure

The quinoid-based dye structure can be overviewed as three chemical structures (a) benzoquinone, (b) naphthoquinone and (c) anthraquinone. The natural colourant carthamine belongs to benzoquinone group, and juglone and lawsone are having naphthoquinone structure. Alizarine dye possesses anthraquinone structure.

2.2.1.1 Benzoquinone dyes

In this dye structure the л electron system is small, and the dye contains another unsaturated group in conjugation to л electron system (**Figure 21**). The red colourant

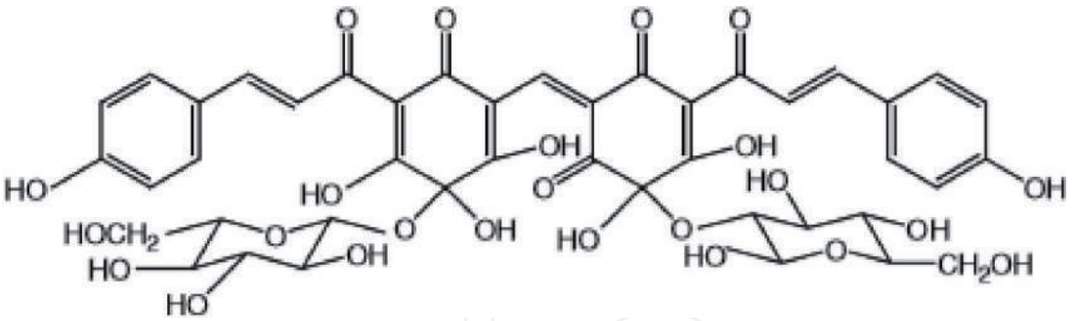

Figure 21.
Structure of carthamine.

carthamine is present in safflower (Natural Red 26). Safflower (*Carthamus tinctorius*) is a subtropical plant and cultivated in India, China, North and South America and Europe. In dyeing, the water-soluble yellow dye (safflor yellow) is extracted [18] by cold water, and then red safflorcamin is extracted by diluted sodium carbonate solution. After the neutralisation of extracted solution, it can be used in dyeing of wool, silk and cotton.

2.2.1.2 Naphthoquinone dyes

Lawsone and juglon natural dye belongs to this category. Lawsone is extracted from hina plant; the leaves also contain flavonoid colourants lutcolin. It is cultivated in countries like India, Africa and Australia. Naphthoquinone is present in glycosidic [19, 20] form named as Hennosid A, B and C. The quantitative analysis of lawsone can be performed by high-performance liquid chromatography on reverse-phase C_{18} column. Chloroform extracted hina leaves were analysed by high-performance thin layer chromatography (**Figures 22** and **23**).

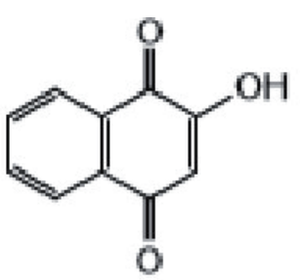

Figure 22.
Lawsone (2-hydroxy, 1,4 naphthalene).

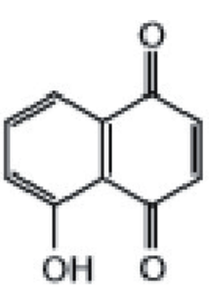

Figure 23.
Juglone (5-hydroxy, 1,4 naphthoquinone).

2.2.1.2.1 Lawsone

Lawsone form 1:2 complex with Fe(II) and Mn (II) and useful in dyeing of wool and silk fibre. The better dye uptake is obtained at pH 3.0. Agarwal et al. [21] studied the effect of different mordants and different mordanting methods to get the different shades. Hina can be used for dyeing of cotton, polyester, polyamide and cellulose triacetate as the structure of dye molecules are similar to disperse dyes [22–24].

2.2.1.2.2 Juglone

Juglone is representative of natural dye with naphthoquinone structure. The dyestuff is extracted from different part of nut trees. Juglone is present as a glycoside form in trees and plants. Wool dyed with juglone are having good resistance with moths and insects. Mordanting treatment further enhances the fastness properties. Dyeing of textile materials with aqueous walnut extract yields brown shade. Wide range of textile fibre, e.g. wool, silk, nylon and polyester, can be dyed with juglone.

2.2.1.3 Antharaquinone

It possess biggest group of anthraquinone dyes. Rhubarb (CI Natural Yellow 23) is extracted from the root of the plant. The extracted dye contains emodin, chrysophenol, aloe emodin and pyscion (**Figure 24**). Rhubarb extract is used in dyeing of wool fibre [25]. It produces yellow to orange shade after mordanting with alum. The mordanting treatment improves light fastness of dyed materials.

Natural dye alizarin, pseudo purpurin and purpurin (**Figure 25**) belongs to plant of Rubiaceae family and has an anthraquinone structure [26]. The dye is obtained from the root of plant.

Madder (C.I Natural Red 8) natural dye produces red colourant; the cultivation of madder is done as a source material for red colour in Europe, Asia and Northern and Southern America. The dyestuff is extracted from the dried roots of the plant. The roots of the plant contain 2–3.0% of di- and tri-hydroxyl anthraquinone glucosides.

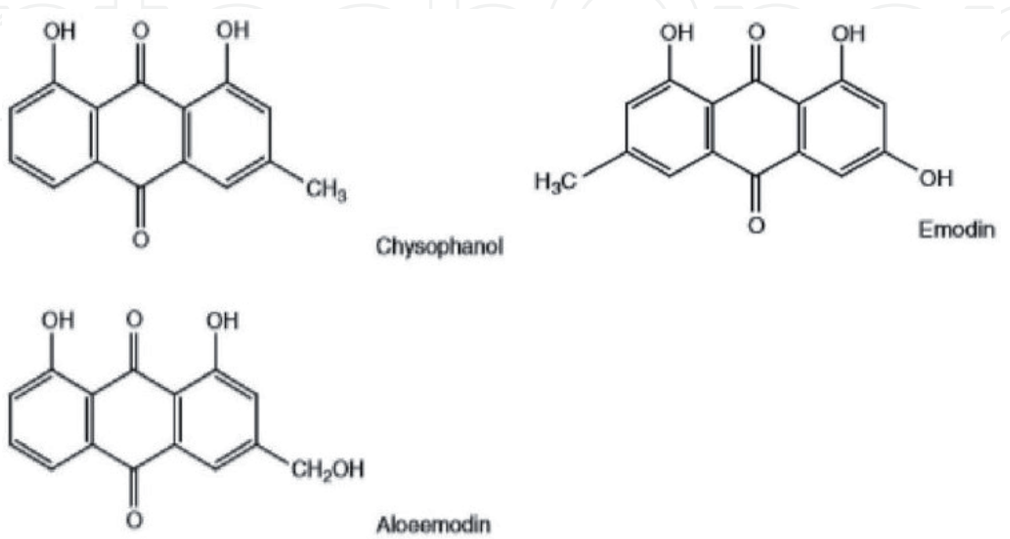

Figure 24.
Different representative structurers of anthraquinone group-based dye molecules.

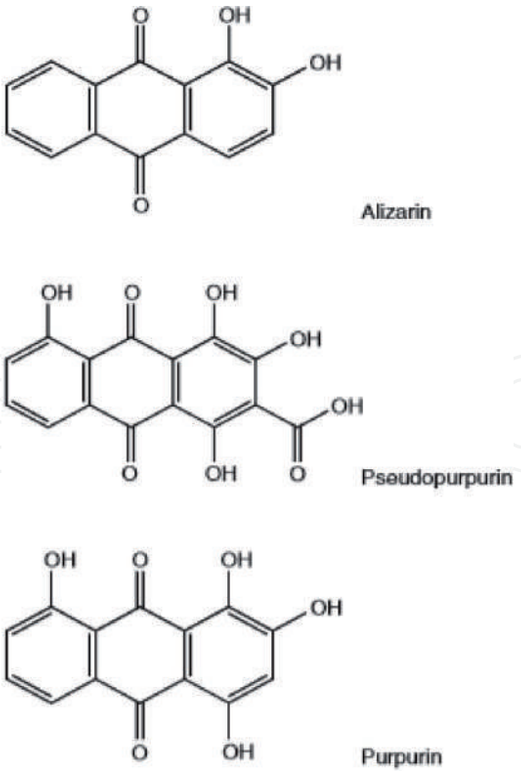

Figure 25.
Structures of alizarin, pseudo purpurin and purpurin.

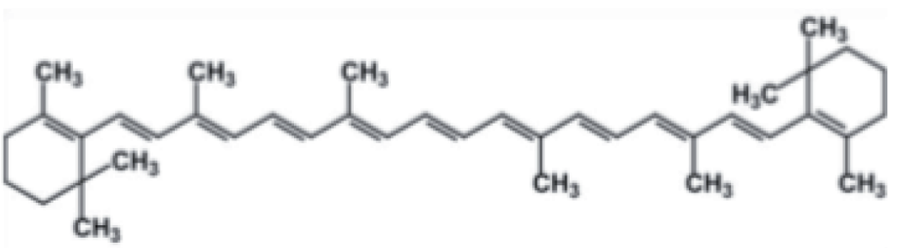

Figure 26.
Structure of β-carotene.

2.2.2 Carotenoids

Carotenoids are red, yellow and orange pigments present in plants and animals [17]. It has a polyisoprenoid structure with a series of centrally located conjugated bonds. The bright colours of many fruits and vegetables are due to carotenoids. Carotenoids are polyisoprenoid structure (**Figure 26**) which contain conjugated double bonds, which acts as chromophore and responsible for characteristic absorption spectra. Carotenoids are divided into two parts:

a. Hydrocarbon carotenoid

b. Oxygen containing called xanthophylls

Structural changes by hydrogenation, double bond migration, isomerization and chain lengthening and shortening resulted in many carotenoid structure. Carotenoids possess strong UV light resistance, and β carotene (**Figure 26**) is a typical structure generally found in natural colourants.

2.2.2.1 Pyron dyes

Pyron dyes contain flavonoids and anthocyanins having structure as shown in **Figures 27** and **28**. The pyron structure is bound to various sugars by glycosidic bonds [17]. Flavonoids are classified as flavonols, flavones, anthocyanidins, isoflavones, flavon-3,4-diols and coumarins. Yellow flavones and flavonols are used as vegetable dyes. The valuable and very popular flavonoid is yellow quercetin which possess several bio effect.

2.2.2.2 Anthocyanins

Anthocyanins are found in fruits and vegetables; some are grape wine, sweet and sour cherries, red cabbage, hibiscus and different varieties of oranges. There are more than 500 varieties of anthocyanins that produces red, pink, violet and orange colours. There are some important anthocyanins which are cyaniding, delphinidin, pelargonidin, malvidin, peonidin and petunidin. Many plants besides anthocyanins also contain quercetin and chlorophylls, and the resulted colour is a mixture of all these.

2.2.3 Dyes from lichens and mushrooms

Violet and purple colours were generally obtained from molluscs and shellfish, and they were source of dyestuff from ancient to the beginning of the Middle Ages. Royale purple and Tyrian purple were the name of the colour obtained originally from molluscs [27]. Lichens and mushrooms are source of natural dyes, and they produce violet and purple colours. Lichens are found in coastal areas and were easier to collect. The dyeing methods with lichens are easy; however, disadvantage associated with lichens is poor light fastness. Therefore, the dyeing of lichens are limited to cheap quality fabrics. Fungi are also used for dyeing of textiles.

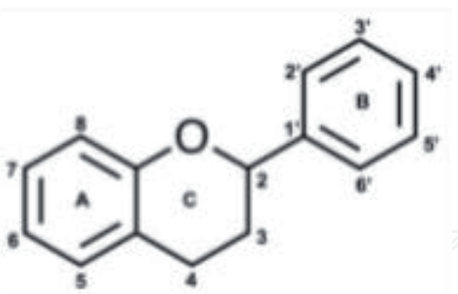

Figure 27.
Structure of anthocyanins.

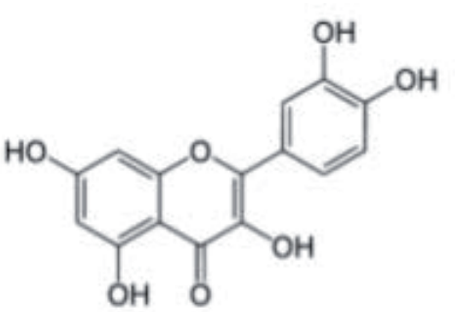

Figure 28.
Structure of quercetin.

In America and India, red colour is obtained from fungus *Echinodontium tinctorium*. In Italy and France, fungi obtained from Polyporales were used to dye the wool.

The colourants in lichens and fungi are benzoquinone derivatives, especially terphenylquinone. Some of these species possess compounds such as *Sarcodon*, *Phellodon*, *Hydnellum* and *Thelephora* [28, 29]. Orchil and litmus are the colourants that are responsible for the colour in lichens. The lichens' colour are produced through pre-compounds of orchil and litmus by consecutive enzymatic, hydrolysation, decarboxylation and oxidation [30] reactions, respectively. Then some pre-compounds are lecanoric acid, atranorin and gyrophoric acid which take part in the formation of orchil and litmus as shown in **Figure 29**.

In the past, the extraction of colourants from lichens were performed by keeping the lichens in water with ammonia for several days. The reaction occurred through enzymatic hydrolysis in which non coloured compounds such as lecanoric acid are converted into orcinol by hydrolysis and decarboxylation. Orcinol after oxidation forms purple orceins or litmus. The colour of both litmus and orchil depend on the pH of the solution [30]. In acidic pH dyestuff forms red cation, and in basic pH, it forms bluish violet anion. The lichens which belong to species *Parmelia*, *Xanthoria parietina*, *Ochrolechia tartarea* and *Lasallia pustulata* are capable to produce yellowish, brownish and reddish brown colours in dyeing of wool with lichens [31]. The dyeing is done by boiling the wool with lichen solution either premordanted or without mordanted wool in presence of ammonia.

The mushrooms which belongs to species *Sarcodon*, *Phellodon* and *Hydlnellum* contain terphenylquinone compounds as a main colourants which produce blue

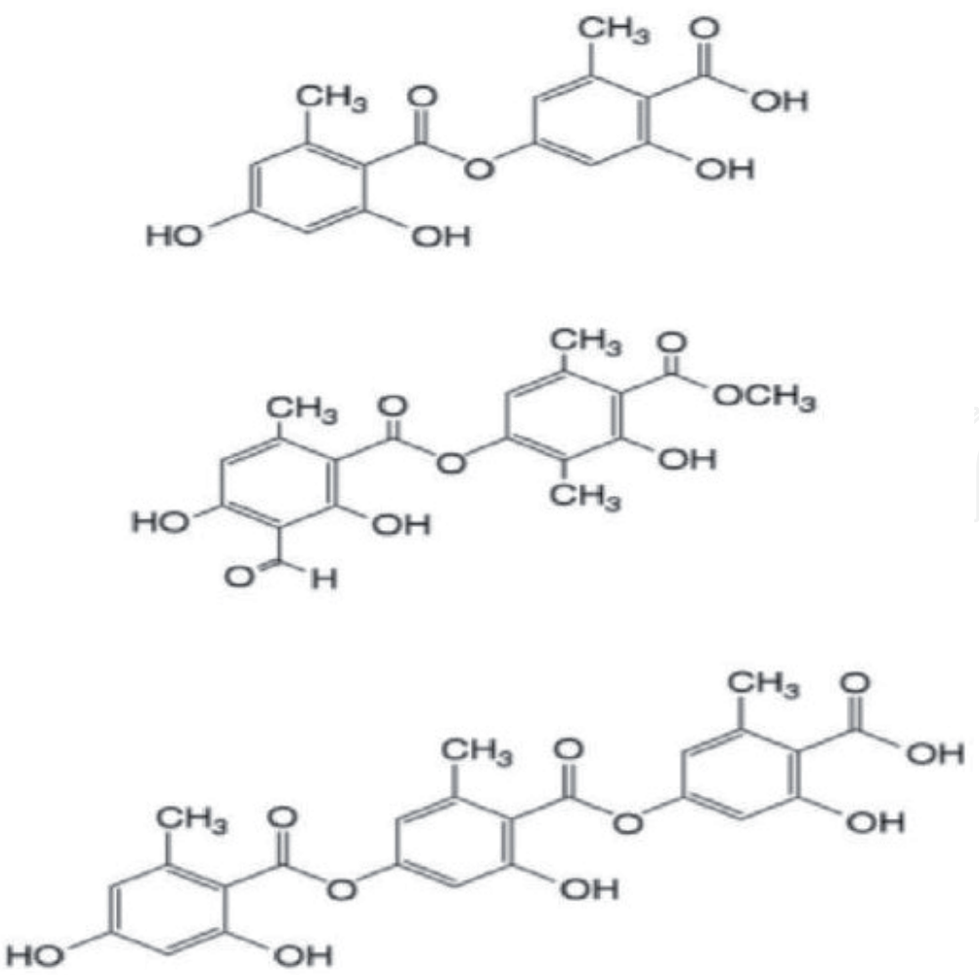

Figure 29.
Structures of different colourants occurring in fungi and lichens.

colour in mushrooms. They are benzoquinone derivatives. The *Cortinarius* species mushrooms are richly coloured in brown, red, olive green and violet. They are anthraquinone derivatives.

2.2.4 Tannins

Tannins are polymeric polyphenols with typical aromatic ring structure with hydroxyl constituents and have relatively high molecular weight. In plants two different groups of tannins are found, (a) hydrolysable tannins and (b) proanthocyanidins (condensed tannin) [32, 33]. Tannins are present in plant cell and are concentrated in epidermal tissues. Tannins are found in wood, leaves, buds, stems, florals and roots [34]. The hydrolysable tannins are concentrated in the roots of several plants. The plants are the source of different variety of tannins. The three major tannins (hydrolysable tannins) are grouped as gallotannins [35] or ellagitannins and which are gallic acid or ellagic acids. The most widespread gallotannins are pentagalloyl glucose. Ellagitannins are esters of hexahydroxydiphenic acids. Gallic acid and hexahydroxydiphenic acid occur together in some hydrolysable tannins [36].

Condensed tannins are polymers of 15-carbon polyhydroxyflavan-3-ol monomer units such as (−) epicatechin or (+) catechin. The complex chemical nature of tannins makes the biosynthesis and polymerisation a difficult task; however, there are some established pathways for bio synthesis. The precursor for biosynthesis of hydrolysable tannins is shikimic acid. The direct aromatization of 3-dehydroshikimic acid produces gallic acid, which upon esterification forms polyol.

The bio synthesis of condensed tannins occurs through two different ways (a) by phenylpropanoid and (b) by polyketide. The polyketide pathway takes malonyl moieties for aromatic ring formation in flavonoid biosynthesis. The phenylpropanoid pathway takes aromatic amino acid, L-phenylalanine, which is non-oxidatively deaminated to E-cinnamate by phenylalanine ammonia-lyase.

2.3 By hue or colour produced

The classification of natural dyes are also done according to the hue of the colour. Some important natural dyes giving primary and secondary colours are:

a. Red: Colour index has 32 red natural dyes. The prominent members are maddar, manjistha, Brazil wood, *Morinda*, cochineal and lac dyes.

b. Blue: There are four natural blue dyes. Some prominent colours are indigo, Kumbh and flowers of Japanese Tsuykusa. Natural indigo blue is known from very ancient time to dye cotton and wool.

c. Yellow: There are 28 yellow natural dyes available which are used in dyeing of wool, silk and cotton. Prominent examples are barberry, tesu flowers, Kamala, turmeric and marigold.

d. Green: Plants that yield green natural colour are very rare; they are made by mixing yellow and blue primary colours. Woad and Indigo produce green colour.

e. Black and brown: There are six black natural dyes. Cutch is used to produce brown shade; for getting black shade lac, carbon and caramel are used.

f. Orange: Natural dyes which produce red and yellow colour are used to produce orange shade. Barbeny and annatto are the examples of orange colour.

2.4 Application based classification

a. Vat dyes: Indigo is a water-insoluble dye, and before application it is solubilised in water. The solubilisation of natural indigo is done with the help of sodium hydrosulphite and sodium hydroxide. After solubilisation, it is applied on cellulosic fibre, and after dyeing the development of colour is done by oxidation with hydrogen peroxide. Indigo dye is the representative of indigoid class of vat dyes

b. Direct dyes: The natural dyes which are water soluble and have a long and planar molecular structure and presence of conjugated (single and double bonds) bonds can be applied by direct dyeing method. The dye molecules may contain amino, hydroxyl and sulphonic groups. Turmeric, Harda, pomegranate rind and annatto can be applied by direct dyeing method. Common salt is used to get better exhaustion of dyes. The dyeing temperature is kept at 100°C

c. Acid dyes: The dye molecules possess sulphonic or carboxylic groups in their structure, which produce affinity for wool and silk fibre. The dyeing is done at acidic pH of 4.5–5.5. After dyeing the fastness improvement is done with tannic acid. The dyeing of wool and silk with saffron is done by acid dyeing method. The presence of common salt in dye bath produces levelling effect

d. Basic dyes: The dye molecules produce coloured cation after dissolution in the water at acidic pH. The dye molecules contain $–NH_2$ groups and react with –COOH groups of wool and silk. The dye bath pH is kept 4–5 by adding acetic acid

3. Extraction of natural dyes

The amount of natural dyes present in natural products are very less [11, 37]. They need specific technique to remove dye from their original source. Here there are some methods which are suitable for extraction of natural dyes from their source materials [28]; the different extraction methods are as follows:

3.1 Aqueous extraction

In this method, the dye containing materials are broken into small pieces or powdered and then soaked in water overnight. It is boiled and filtered to remove non-dye materials. Sometimes trickling filters are also used to remove fine impurities. The disadvantages of this technique are that during boiling, some of the dye decompose. Therefore, those dyes which do not decompose at boiling temperature are suitable by this method. The molecules should be water soluble.

3.2 Acid and alkali extraction

Most of the natural dyes are glycosides; they can be extracted under acidic or alkaline conditions. Acidic hydrolysis method is used in extraction of tesu natural dye from tesu flower. Alkaline solution are suitable for those dyes which contain phenolic groups in their structure. Dyes from annatto seeds can

be extracted by this method. The extraction of lac dye from lac insect and red dye from safflower is also done by this method.

3.3 Ultrasonic microwave extraction

Microwave and ultrasonic waves are helpful in extraction of natural dyes. This technique is having several advantages over aqueous extraction. In this technique less quantity of solvent (water) is required in extraction. The treatment is done at lower temperature and less time as compared to aqueous extraction. Ultrasonic and microwaves are sent in aqueous solution of natural dye, which accelerate the extraction process.

3.4 By fermentation

In the presence of bio enzymes the fermentation of natural colour bearing substances becomes faster, and the extraction of natural dyes takes place. Indigo extraction is the best example of fermentation method of extraction. Enzymes break glucoside indican into glucose and indoxyl by the indimulsin enzyme. Amatto natural dye extraction is also done by enzyme method. Cellulose, amylose and pectinase are having application in the natural dye extraction from the bark, stem and roots.

3.5 Solvent extraction

There is use of organic solvents such as acetone, petroleum, ether, chloroform and ethanol in the extraction of natural dyes. It is a very viable technique as compared to aqueous extraction. The yield of dye is good, and the quantity of water requirement is less. The extraction is done at lower temperature.

4. Characterisation of natural dyes

For successful commercial use of natural dyes, there is need of standardized dyeing technique for which characterisation of natural dyes is essential.

4.1 UV-visible spectroscopy

It is useful in characterising the colour in terms of the wavelength of maximum absorption and dominating hue. The application of UV-characterization is to identify the ability of dye molecules to absorb UV wavelength and fading characteristics of dyes. Some researchers [38] had done UV analysis of natural dyes. Mathur et al. [9] studied UV spectra of neem bark, and it has two absorption maxima at 275 and 374 nm. Beat sugar [39] shows their absorption bands at 220, 270 and 530 nm. Gulrajani et al. [40] studied the absorption bands of ratanjot and observed that at acidic pH, the absorption occurs at 520–525 nm, and in alkaline pH, it occur at 610–615 nm. Red sandal [41] wood shows strong absorption peak at 288 nm and maximum absorption at 504 and 474 nm in methanol solution at pH 10. *Gomphrena globosa* flower has peak at 533 nm. The dye does not have difference in peak value at pH 4 and 7 in visible region; however it shifted towards 554 nm [42]. Bhuyan et al. studied the dye absorption extracted from *Mimusops elengi* and *Terminalia arjun* and concluded that dye absorbed by the fibre varies from 21.94 to 27.46% and from 5.18 to 10.78%, respectively, depending on bath concentration [43–45]. He also reported absorption of colour extracted from the roots of *Morinda angustifolia* Roxb using benzene extract. The colour shows absorption at 446, 299, 291, 265.5 and 232 nm.

Name of the dye	Wavelength of maximum absorption
Neem bark extraction	275 and 374 nm
Beet sugar	220, 280 and 530 nm
Ratanjot at acidic pH	520 and 525 nm
Alkaline pH	570, 610 and 615 nm
Red sandal wood	288 nm

The value of the wavelength of the maximum absorption for a particular dye depends on the chemical constitution of the dye molecules which is variable and depends on the growth environment of a particular natural dye. The characterisation of a particular dye is helpful in deciding the hue of the dye.

4.2 Chromatographic technique

Thin layer chromatography is used to identify different colour components in natural dyes. Koren [46] analysed insect dye, madder and indigoid. Guinot [47] analysed plants containing flavonoids colour compounds. Balakina [48] analysed quantitatively and qualitatively red dyes such as alizarin, purpurin and carminic acid by high-performance liquid chromatography. Mc Goven [49] et al. identified the dyes stripped from wool fibre by HPLC with C18 column. Szostek [50] et al. studied the retention of carminic acid, indigotin, corcetin, gambogic acid, alizarin, flavonoid, anthraquinone and purpurin. He studied examination of faded dyes through emission and absorption spectra by non destructive method. Cristea [51] et al. had reported quantitative analysis of weld by HPLC and informed that after 15 min. Extraction in methanol/water mixture, 0.448% luteolin, 0.357% luteolin 7-glucoside and 0.233% luteolin 3′7 diglucoside were obtained. Son et al. [52] reported analysis of longer dyeing time in indigo dyeing and their effect on structural change in dye molecules through HPLC analysis. The derivative spectroscopy and HPLC were used to analyse annatto dyestuff; the sample preparation involved extraction with acetone in the presence of HCl and removal of water by evaporation with ethanol. The residue was dissolved in chloroform and acetic acid mixture for derivatives spectroscopy or with acetone for HPLC.

5. Theory of dyeing

Natural dyes are very suitable for dyeing of protein fibres as compared to cellulosic fibres. Synthetic fibres which contain polar groups such as nylon, acrylic and viscose are also accessible to natural dyes. Natural dyes are thermo unstable and have poor chemical stability, which make the natural dyes unfit for dyeing at high temperature and pressure. The presence of hydrogen bond and Van der Waals force of attraction play important role in the fixation of natural dyes on the fibre. Natural dyes are having poor exhaustion value due to subdued affinity for fibre materials, so to increase the exhaustion of dyes, common salt/Glauber's salt are added in the dye bath. The isotherm of the natural dyes sorption obeys Nernst isotherm [17, 53, 54].

Natural dyes are having poor affinity and substantivity [55, 56] for cellulosic fibres such as cotton and viscose. The absence of reactive groups in fibres and dyes does not allow for bond formation, so they need mordanting treatment to fix the dye on fibre surface. Protein fibres are having bond-forming groups in fibre structure, and the presence of carboxylic groups in natural dyes provides opportunity for

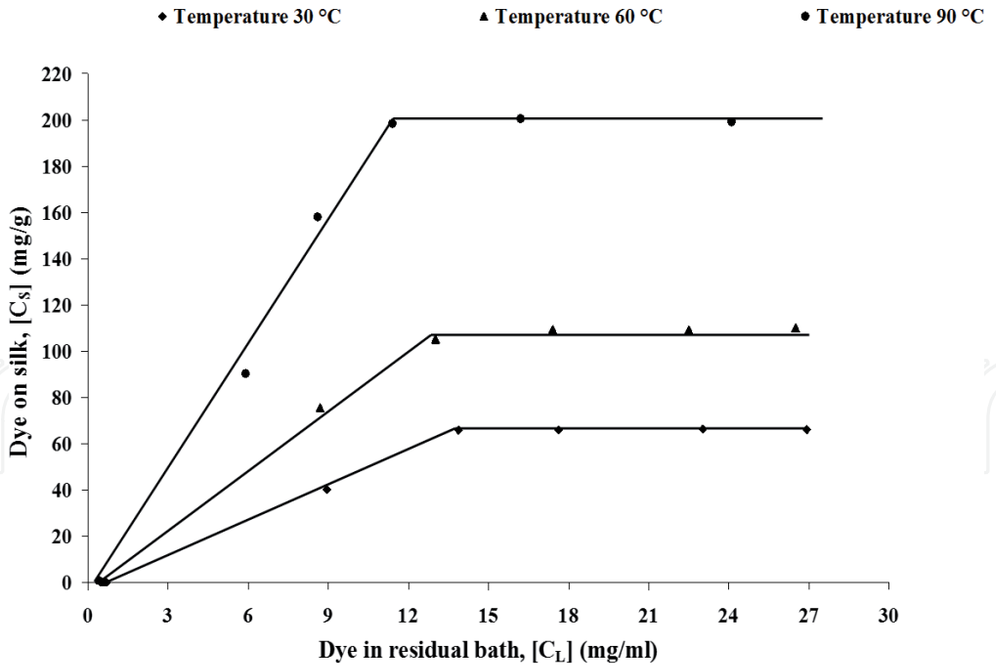

Figure 30.
Sorption isotherm of dyeing of silk fabric (without mordant) with eucalyptus leaves extract at three different temperature 30, 60 and 90°C [17].

bonding and gets bonded with fibre and shows good fastness properties. Natural dyes are having smaller molecular size, and they are not having conjugated linear structure [57]. Therefore, natural dyes are having inferior exhaustion behaviour. Sometimes salt sodium chloride is also used to improve the dye exhaustion % (**Figure 30**).

6. Application of natural dyes

Different researchers had proposed different methods of dyeing of natural and synthetic fibres with natural dyes. The dyeing of textile substrates depends on dyeing parameters which are fibre structure, temperature, time and pH of the dye bath and dye molecule characteristics. The fastness properties of dyes on textile substrates depend on bonding of dyes with fibre. Since natural dyes are lacking in the presence of active groups to make bonds with textile fibres, the fastness properties are not very good. The cellulosic fibres are difficult to dye with natural dyes as they have poor affinity and substantivity. The lack of bonding of natural dyes with cellulosic fibre requires mordanting treatment. Protein fibres have ionic groups and get bonded with natural dyes possessing ionic groups in dye structure.

The dyeing of proteins fibre can be done by exhaust method of dyeing. The dyeing process parameters in wool and silk dying is pH at 4.5–5.5 and dyeing temperature 80–90°C. The exhaustion % of dyes in dyeing is very poor. The longer liquor ratio may be preferred because of poor solubilities of natural dyes in water. Stainless steel-made dyeing machines are suitable in dyeing of wool and silk.

Since natural dyes are having poor affinity for cellulosic fibre and due to poor exhaustion, mordanting treatment [29, 58] is done to fix the dyes on cellulosic fibre. The dyeing of cellulosic fibre can be done at temperature of 80–90°C.The exhaustion of dyes can be increased by adding exhausting agents, sodium chloride or Glauber's salt in dye bath. Most of the dyeing is done at neutral pH. Dyeing of cotton with natural indigo is done at alkaline pH in the presence of sodium hydrosulphite in a container made of stainless steel. The copper container gives deeper

shade in dyeing of cellulosic fibre. The mordanting treatment improves the washing fastness of dyed samples. There are three methods of mordanting [44, 45].

6.1 Conventional method of dyeing

In the state of Maharashtra, Gujrat and Rajasthan [59], the people follow conventional method of dyeing of cotton fabric with natural dyes which may be explained with the following process sequences. The fabric is pretreated before dyeing to get the absorbency. The grey fabrics are given dunging treatment followed by washing. The bleaching treatment is given to make the fabric white, after that it is steamed and stepped into alkaline solution, and finally rinsing and washing treatment is given. After thorough pretreatment the fabric is soaked into solution of harda/myrobolan and dried. The dried fabric is premordanted with alum and subsequently dipped into natural dye solution at boiling temperature. After dyeing the fabric is given washing and rinsing treatment and dried in the sun light. Water is sprayed on the fabric to brighten the shade. The process is repeated 2 to 4 days. The dyeing method differs from place to place. Here are some examples:

6.1.1 In Bengal

The commonly used natural dyes are haldi, babul, madder, pomegranate rind and marigold [59]. In the dyeing of fabric with sappan wood, the fabric is dipped in aqueous extract of sappan wood with or without alum solution and boiled for 2–3 hours. In the dyeing of Indian madder, the madder is extracted either from the stem or root and boiled with water to extract the natural colourants. The pretreated fabric is boiled with dye extract solution. Mordanting treatment may be given either before dyeing or after dyeing with alum solution.

6.1.2 In Orissa

The sappan wood chips are boiled with alum and turmeric and after boiling it was cooled. In cooled solution of dye, the fabric materials are kept for 3–4 h. It is a premordanting process. At some places the cold solution of natural dye is taken with sufficient quantity of water, and the fabric is dipped in cold solution for 24 h and finally boiled for 2 h.

6.1.3 In Uttar Pradesh

The application of natural indigo on cotton fabric is done by two methods which are called Khari Mat and Mitha Mat.

6.1.4 Khari Mat

In Khari Mat's process to dissolve natural indigo, 40 gallon of water is taken in an earthen vessel, and in that water there are addition of 2.0 lbs. indigo, 2.0 lbs. of lime, 2 lbs. of sajji mati and 1.0 ounce of gur (molasses). After 24 h of fermentation, the indigo dye became water soluble. The indigo dye solution is ready for dyeing. This technique is successful in hot weather.

6.1.5 Mitha Mat

In this technique, the solubilisation of natural indigo is done by taking 60 gallon of water; in that water there are addition of 4 lb. of lime, and after 1 day again

4 lb. of lime is added. After 4–5 days natural indigo dye became fully soluble. During application this mitha vat is added with old mitha vat with continuous string. The fabric is dyed in the dissolved indigo dye solution at temperature of 50–60°C.

6.2 Dyeing of cotton fabric with natural dyes

There is a standard recipe-based dyeing process for dyeing of cotton fibre/yarn/fabric. The important pretreatments before dyeing are desizing (acid desizing or enzyme desizing), scouring (sodium hydroxide and auxiliaries) and bleaching with hydrogen peroxide (H_2O_2). The fully pretreated fabric free from all impurities and absorbent is premordanted (single or double mordanting, in single either harda or aluminium sulphate in double taking both consecutively) with aluminium sulphate. After mordanting the mordanted fabric is passed through aqueous solution of natural dyes. The dyeing parameters will be:

- Dyeing time = 60–120 min. (depends on depth % of shade)
- Temperature of dyeing = 70–100°C
- M:L ratio of the bath = 1:20–1:30
- Amount of dye in bath = 10–50% (on weight of the material)
- Concentration of common salt = 5–20 g/l
- pH of the dye bath = 10–11

After dyeing, soaping treatment is given to remove any residual/unreacted dyes and auxiliary chemicals from the surface of the fabric. An after treatment with natural dye, fixing agent may be desirable.

6.3 Dyeing of protein fibres

Wool and silk are protein fibre; both fibres have complex chemical structure and susceptible to alkali treatment. Alkaline pH of aqueous solution damage the fibre. At isoelectric pH of 5.0, the wool is neutral and the silk is slightly positive. The wool and silk can be dyed with natural dyes through premordanting or after mordanting. Mordanting is done with tannin-rich natural source chemical like harda or metal salt aluminium sulphate or ferrous sulphate.

In premordanting, the fabric is treated with either harda or metal salt aluminium sulphate (single or double) with 5–20% (on weight of the material) mordant concentration at temperature of 80–90°C for 30–40 min. The M:L ratio is kept 1:5–1:20. After mordanting, drying treatment may be given and subsequently dipped in dye bath containing aqueous natural dye solution. The following dyeing parameters were maintained:

- The pH of the dye bath = 4–5
- Temperature of dyeing = 80–90°C.
- Time of dyeing = 50–60 min.

- M:L ratio of the bath = 1:20–1:30
- Amount of dye in bath = 10–50% (on weight of the material)

After dyeing, soaping treatment is given to remove any residual/unreacted dyes and auxiliary chemicals from the surface of the fabric. An after treatment with natural dye fixing agent may be desirable.

6.4 Dyeing of synthetic fibres

Different synthetic fibres like nylon, polyester and acrylic can be dyed with natural dyes like onion skin extract, babool bark extract and hina. The dyeing can be done either by padding (cold pad batch) method or exhaust method with or without mordanting. Dyeing is carried out at acidic pH. High-temperature high-pressure dyeing gives better results in terms of colour strength than other dyeing methods.

6.5 Fixation of natural dyes

Natural dyes are having poor affinity and substantivity for textile materials. The bonding groups are not present in natural dyes, due to that most of the natural dyes are having poor washing fastness. The fixation of natural dyes on textile materials can be done with the help of mordanting agents. Mordanting agents are dyeing auxiliaries and are salts (chlorides and sulphates) of heavy metals. The heavy metals Al, Cr, Cu and Sn are having vacant d orbitals and easily make coordinate bonds with natural dyes and fibre-active sites. The formed complex has bathochromic and hyperchromic shift. There are different types of mordanting agents such as metallic mordants, tannins and tannic acid and oil mordants. The different heavy metal salts work as complexing agent and chelate with natural dye colourants. Some metallic salts are toxic in nature, but even after that, they are having application in fixation of natural dyes. The different mordanting agents are:

a. Most controversial are lead salts and chromates (potassium, sodium, ammonium dichromate).

b. The salt $SnCl_2$ also works as mordant. It is water soluble, having reducing agent properties. It is toxic in nature.

c. Copper sulphate ($CuSO_45H_2O$) and ferrous sulphate ($FeSO_47\ H_2O$) molecules are also used as a mordant. They are good chelating agents.

d. Tannins are poly phenolic compounds and able to form complexes with metals and bind with organic substances such as proteins, alkaloids and carbohydrates. The tannins are also called bio mordants. Tannins can be used either alone or in association with metal salts. The phenolic groups of tannins can form effective bonds with fibre and natural dye molecules.

6.5.1 Metallic mordants

Metal salts of aluminium, chromium, iron and copper are used as a mordants. The important mordants are potassium dichromate, ferrous sulphate, copper sulphate, stannous chloride and stannic chloride.

6.5.2 Tannins and tannic acid

Tannins are obtained from the excretions of bark and other parts, e.g. leaves and fruits of the plant. Extractions are either used directly or in concentrated form. Large number of tannin containing substances are employed as a mordant in textile fibre dyeing.

6.5.3 Oil mordants

Oil mordants are used in dyeing of madder. Oil mordants make a complex with alum used in mordanting treatment. Metal atom combined with carboxylic groups of oil and bound metal then makes bond with the dye molecules, and in this way, superior wash fastness can be achieved.

6.6 Mordanting process

a. Premordanting: In premordanting process, mordanting is done before dyeing; subsequently the fabric is dyed with natural dye in aqueous media. It is a two-bath process in which the first bath is used for mordanting of fabric and in the second bath, dyeing is done with natural dyes. Dyeing and mordanting are done at the same temperature of 60–70°C. the mordants are complexing agents, and if they are taken in the same bath, they may react to each other, and precipitation of dyes may occur. That deteriorate fastness properties of dyed fabrics

b. Metamordanting: In metamordanting treatment, the mordant chemicals are added with natural dye in the same dye bath; dyeing and mordanting take place simultaneously. The mordanting and dyeing temperature are 80–90°C

c. After mordanting: In after mordanting treatment [53, 54], the dyeing of fabric is done first; after that in the same bath mordanting compounds are added. The temperature of chroming is 80–90°C. after chroming, the temperature is dropped to 60°C, and goods are run for 15 minutes after that liquor is drained

The application of natural dyes on cellulosic materials are done by the pad-dry-washing and pad-dry-steaming-washing method. High-temperature curing is not suggested as dye molecules are susceptible to decompose. Fibre and yarn dyeing can also be done with natural dyes similar to synthetic dye application.

7. Fastness properties of natural dyes

The quality parameters in dyeing is fastness properties. Several test methods are described to access the colour fastness. The fastness properties give idea about the quality of dyeing. In natural dyes, the fastness properties are strongly related to substrate type and mordant used for dyestuff fixation. Besides the dyestuff itself, there are many factors such as water, chemicals, temperature, humidity, light, pretreatments, after treatments, dyestuff distribution in fibre and fixation of dyestuff affect the fastness properties. In natural dyeing the colour and fastness of natural dyes need special attention for careful selection of materials and process. Natural dyes were in use up to end of the nineteenth century. At that time the dyeing with natural dyes were at peak with excellent fastness properties; however, after commercialization of synthetic dyes in the nineteenth century, the proficiency

in natural dyeing started to decrease. The different fastness properties of dyes show the resistance of dyes towards different external environment in which fabric containing dyes are exposed. The fastness properties of dyes depend on the structure of dyes, exposure on the environment and fastness improvers and type of mordant used. There is need to explore some natural after treatment agents to improve the light and washing fastness.

7.1 Light fastness

The light fastness of natural dyes is poor to medium. The poor light fastness is due to chromophoric change in dye structure after absorption of light. The chromophoric groups are not very strong to dissipate the energy absorbed through resonance. Cook [60] had reported a comprehensive review on light fastness improvement of dyed textile fibres. He studied the use of tannin related after treatments on mordantable dyes to be used in cotton dyeing for improving light and wash fastness, and his findings were useful in improving fastness properties of natural dyed fabrics. Natural dyes have poor light stability as compared to synthetic dyes. Padfield and Landi [61] observed the light fastness of wool dyed with nine natural dyes such as:

a. Yellow dyes (old fustic and Persian berries), light fastness rating 1–2

b. Reds (cochineal with tin mordent, alizarin with alum mordant, lac with tin mordant), rating 3–4

c. Blue (indigo depends on mordants), rating 4–5 and 5–6

d. Black (logwood), rating 4–5

Mordants highly influence the light fastness of natural dyes. Turmeric, fustic and marigold dyes faded more than any other yellow dyes; however, the application of tin and alum mordants causes more fading than chrome, iron and copper. This shows the dependency of fastness properties of natural dyes on the type of mordants. Samanta et al. [62] reported the light fastness improvement in natural dyes applied on jute fabric by 1% benzotriazole. The biggest challenge in natural dyeing for colour fastness is related with light fastness. The choice of suitable mordent will improve the light stability except some iron salts which lead to shift in the resulting colour. Textile auxiliaries also improve fastness properties. To improve the light stability of natural dyes, Lee [63] commended an UV absorber on protein fibre. Oda [18] suggest singlet oxygen quenchers to improve the light fastness rating. Mussak [64] discussed light-induced photo degradation process of natural dyes. Several attempts were made to improve the light fastness of different textile fabrics dyed with natural dyes out of which some are [65–67]:

a. Effect of various additives on photo fading of carthamin in cellulose acetate film.

b. Critical examination of fading process of natural dyes to reproduce original colour of the fabric after fading.

c. The rate of photo fading effect is effectively suppressed in the presence of nickel hydroxyl-arylsulphonate. The addition of UV absorbers in bath has small effect in reducing photo fading effect.

7.2 Washing fastness

The washing fastness of natural dyes is poor to medium. The bonding of dye with fibre is very poor, and due to that dyes are not very fast with detergent solutions. Duff et al. [29] studied the effect of alkalinity of washing solution in washing of natural dyes dyed fabrics. The alkaline pH of the detergent solution changes the colour value in terms of the hue and value. Logwood and indigo are having good fastness value as compared to others. The mordanting treatment improves the washing fastness of dyes. Samanta et al. [68] reported some improvement in washing fastness by use of fixing agent.

7.3 Rubbing fastness

The rubbing fastness of most of the natural dyes are moderate to good. Samanta et al. [8, 58] reported that jackfruit wood, manjistha, red sandal wood, babool and marigold having good rubbing fastness on jute and cotton fabric.

8. Advantages of natural dyes

8.1 UV-protective fabrics

UV-protected fabrics are required to protect the skin and body of the human being from sunburns, tannings, premature skin burns and skin ageing. Researchers had done the work on to produce fabrics which had sun-protecting effect by the application of natural dyes in dyeing. Sarkar [69] evaluated ultraviolet protection factor (UPF) value of cotton fabric dyed with madder, indigo and cochineal with reference to fabric parameters. Grifani [70, 71] studied the effect of natural dyes on cotton, flax, hemp and ramie and got good results. Metallic mordants [72] have potential to improve the UPF value of wool, silk and cotton. Orange peel extract natural dye applied on wool increased the UPF value of dyed wool fabric considerably.

8.2 Insect proof

Cellulosic materials and woollen are susceptible to moth and fungus attack in humid and warm conditions. Koto et al. [73] studied the effect of natural dyes on wool. The anthraquinone-based natural dyes cochineal, indigo and madder are able to produce insect proof and repellent fabric when used as a dyes in dyeing of wool.

9. Summary and conclusions

- Natural dyes due to its unique character of natural origin are known as eco-friendly dyestuff; however the bonding of dye molecules with fibre-active sites are very poor, and they need some bridging chemicals to anchor the dye molecules with fibre, and mordanting agents are helpful in bridging the dye molecules with fibre. The synthetic mordanting agents are not very eco friendly, and some are toxic which depress the efficacy of natural dyes and sometime become matter of debate.

- Natural dye does not have any shade card to match the samples or reproducing the shade. So there is need of collection of spectral data of natural dyes so that any shade can be reproduced.

- There is need of awareness about natural dyes dyed fabric in people so that it can be popular in big way. and due to that demand and consumption of natural dyed fabric will increase.
- Natural dyes are costly as compared to synthetic dyes. So some research work should be done to reduce the cost of production.
- Big production houses, technical institutions and research houses should organised workshops and symposia to spread the advantages of natural dyes.
- The government should promote the production of natural dyes by giving financial incentives to small manufactures of natural dyes.
- There must be some very strong research and development work to improve the quality of natural dyes in terms of low cost, use of natural mordent and widespread applications.

Acknowledgements

I am very thankful to Prof. A.K. Samanta for inspiring me and giving very excellent suggestions for preparing this review paper. I am very thankful to the editor for his remarkable patience and monitoring.

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Chapter

A Review on Application of Natural Dyes on Textile Fabrics and Its Revival Strategy

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Abstract

A comprehensive review on application of natural dyes on textiles and earlier research findings has been discussed in this chapter. Moreover, recently the consumers have become very much conscious about the environment, renaissance of eco-friendly products and process like dyeing textiles with natural dyes, which has thus become also important now. Thus, revival of natural dye application on textiles and summary of earlier researches on standardization of its method of extraction, mordanting, dyeing process variables and even natural finishing, etc. have been elaborated in this review. Characterization of natural dyes and chemistry of its dyeing, etc. are equally important and hence are discussed here critically. Thus this part has become a unique readymade comprehensive chapter for information on chemistry and application of natural dyes on textiles and its revival strategy.

Keywords: natural dyes, natural pigments, extraction, mordanting, natural dyeing methods, characterization of natural dyes, revival of natural dyeing and textiles

1. Introduction

Natural dyes are known to be used since historic times for coloring food substrate, leather, as well as common textile fibers like cotton, wool and silk. However due to the advent of synthetic dyes and their good fastness properties in comparison to natural dyes, the use of natural dyes have suffered drastically. In the present scenario there has been a rise in concern of eco-friendliness and sustainability of the products used by the consumers for which natural dyes are again starting to experience slight rise in popularity. A study has been conducted by Samanta and Agarwal [1] which reports the characterization as well as chemical/biochemical analysis of various natural dyes available, the different types of mordants as well as different mordanting techniques, the different conventional and non-conventional method of natural dyeing of textiles. The different natural dyes used for the study are madder, henna, held, indigo and others such as annatto pulp, *Rubia tinctorum*. Different methods of extraction are employed such as aqueous extraction, non-aqueous method as well as by acid and alkali. Different types of mordant and method of mordanting significantly affect the rate of fading. For cotton the best mordant combinations used in this study are harda and tartaric acid, followed by tannic acid and harda. Double mordanting is employed by using harda and aluminum sulphate. The various process variables to be considered for dyeing with and extraction of

natural dyes are concentrations of dye source material, extraction time, dyeing time, mordant concentration, pH and concentration of salt used.

Another study conducted by Daberao et al. [2] gives us a concept about dyeing with palash or tesu flower petal (*Butea monosperma*) *as* natural dye sources. The dyes were extracted from *Butea monosperma* or in other terms flame of the forest and they were applied on 100% cotton. A different method of extraction by boiling was employed and alum was used as mordant. The fabric was then tested for all color fastness tests. The cotton sample was scoured and bleached for better color uptake. The washing fastness results were observed where the natural dye having not too much affinity with the fiber but by the application of mordant could withstand at least five washes. Also wet rubbing fastness of the dye was found to be poorer in the experimental results. However it was observed that *Butea monosperma* has good perspiration fastness since it is unreactive to acidic and alkaline perspiration.

The use of natural dyes has further started to be increased substantially over the current years for its slow but growing revival phase at present, due to people's concern over reducing environmental pollution and hence to avoid chemically more hazardous synthetic dyes and intermediates. Day by day in export market, demands for natural dyed natural textiles are being increased. Different institutions/organizations and Govt. have started multifold revival strategies for increasing the use of natural dyes as not only as an employment opportunity for several NGOs, weaver and dyers society, designers, industries, small scale cottage industries, etc. but mainly for adopting green technology dyeing. The handicraft industry in India uses local talents to dye yarns and fabrics with natural compounds, where several products are famous worldwide like Kalamkari print. Different countries other than India like Turkey, Korea, Mexico, several countries of Africa have embraced the uses of natural dyes. A study has been conducted by Gulrajni [3] to understand the scope of natural dyes and its present status in the world in addition to different application techniques, extraction of different natural dyes as well as varying mordanting techniques. Different problems associated with such natural dyeing are also highlighted there.

The Tharu tribes of the Devipatan [4] division have found a new source of natural dyeing from the local leaves and stems of *Jatropha curcas L.* The dyes are extracted by simple boiling the leaves in water and then evaporating the extract to dryness. The extract obtained is of yellowish olive syrupy color and when applied to the cotton fabrics the different shades of tan and brown color are obtained.

Another state in our country, Manipur has been considered to be a source of a natural dye namely extracts from *Strobilanthus flaccidifolius* for uses in handicrafts, handlooms, fine arts, etc. Other tribes of Manipur like the Meitei community have been using species like *Parkia javanica*, *Melastoma malabathricum*, *Pasania pachyphylla*, *Solanum incidum*, *Bixa orellana*, *Tectona grandis*, etc. these plants are combined with other plants for extraction and then dye is prepared by indigenous sources. This study is a report by Potsangbam et al. [5] of the dyes extracted from the above sources, the method of extraction as well as their application.

Now from the forest of Chhattisgarh, different dye yielding plants have been identified and collected. A study was conducted by Tiwari and Bharat [6] on the diversity of dye-yielding plants of Chhattisgarh, the indigenous method of dye extraction and ethnic uses of dyes. These colors are being used by tribal folks of this region for different purposes such as ornamentation, cosmetics, decorating houses and coloring home utensils made up of mud.

From the state of Goa [7] natural dye-yielding plants like *Cassia fistula*, *Garcinia indica*, *Tectona grandis* are obtained and studied where Goa is said to house more than 3000 different species of flowering plants. Natural dyes were extracted from

various parts of plant like fruits, seeds, bark, flowers, roots, etc. The extraction processes are studied and dyes of different shades are obtained. This study can also encourage the small scale industries to use natural dyes from these sources to be applied on cotton and silk fabrics.

A report by Gaur [8] shows the extensive description of survey, collection of botanical information and review of relevant literature on the vegetable dye yielding resources of Uttarakhand Himalayas. Of which, very little known dye yielding plants are considered like *Acacia nilotica*, *Agrimonia pilosa*, *Careya arboraea*, *Averrhoa carambola*, etc. Different extraction processes for each plant are carried out and subsequently dyeing is done by using different mordants. Some of these plants also have high medicinal values and has no toxicity.

1.1 Sources of different natural dyes and their characterization

Various natural products are being used for dyeing these days in order to fulfill the demand of consumers for sustainable environment. The reviews below are for the various natural dyes used on textile materials.

Bechtold et al. [9] have studied on the quality of Canadian golden rod plant material as a natural dye. Aqueous solutions of the material containing the extracted flavonoid dyes were characterized by means of direct photometry, absorbance after addition of $FeCl_2$ is measured, total phenolics (TPH) in the extract and dyeing on wool yarn are analyzed where only relatively small differences in color depth and shade were noted amongst the major parts of the different materials collected.

A study on natural dye henna was conducted by Rahman Bhuiyan et al. [10]. Henna is a red-orange pigment that has long been used for the coloration of skin and hair as well as textile materials. A large number of studies were carried out on extraction as well as application of henna dye in textile fibers and the standardization and simplification of dyeing techniques were determined. Due to burgeoning environmental conditions and growing awareness on sustainability there has been a renewed interest in expanding the scope and applications in the coloration of textile fibers with some successes and promises. Henna shows an acidic nature due to the presence of polar groups, which promotes its use in the textile dyeing process.

Dyeing of natural dye extracted from *Liriope platyphylla* fruit on silk fabrics have been studied by Huang et al. [11]. From which it has been observed that the total phenolic content (1109.13 ± 69.02 mg), total flavonoid content (530.60 ± 89.44 mg), and total anthocyanin content (492.26 ± 77.79 mg) were measured in 100 g fresh weight of *L. platyphylla* fruits. A broad variation in color shade and color depth has been achieved with mixtures of different combinations of dye extracts and metal mordants. Purple, blue, and pale green were main color shades obtained when dyed with the extracts. The fastness of dyed silk fabrics against light, washing, and rubbing were noted to be acceptable with at least a gray scale rating of 3.

A study has been conducted on orange peel by Hou et al. [12]. Orange peel is an easily available agricultural byproduct and it is cheap as well as abundant. The variation in effects of dyeing methods and conditions, including pH value, temperature, time and concentration of OP extracts on the colors of the dyed wool fabrics, were studied. Eco-friendly mordants of aluminum and iron were used. The optimum dyeing conditions were noted which included dyeing temperature of 100°C, dyeing time of 120 min, pH of 3 for direct dyeing and pH 7–9 for one-bath mordant dyeing. Good colourfastness to washing with soap, good colourfastness to rubbing and acceptable colourfastness to light were displayed by the tested specimen.

Hibiscus is a major source material for natural dyeing. It belongs to the family Malvaceae. Aqueous extracts of these flowers have shown good fastness properties according to the study conducted by Shanker and Vankar [13]. The dye has been

found to have a good scope in the commercial dyeing of cotton, silk for garment industry and wool yarn for carpet industry. In the present study dyeing with hibiscus has been shown to give good dyeing results. The material is pretreated with 2–4% metal mordants, keeping M:L ratio as 1:40 on weight of the fabric to plant extract. The dye is cheap and has good commercial value if dyed with cotton, wool and silk.

Another natural material has been found by Vankar et al. [14] to be a good source of natural dyeing which is *Mahonia napaulensis DC*., common name taming, from the family Berberidaceae. The natural dye is from the stem and has been used by the tribes of Arunachal Pradesh. The fastness properties for dyed cotton, silk fabrics and wool yarn were show to increase substantially when pretreated with metal mordant (2% w/w with respect to the fabric).

An attempt has been made by Kamel et al. [15] in dyeing of wool fabrics using lac as a natural dye in both conventional and ultrasonic techniques. The dye extraction was compared between conventional method and ultrasonic technique and the data were evaluated. Accordingly the effects of dye bath pH, salt concentration, ultrasonic power, dyeing time and temperature were compared. The result of fastness properties obtained was fair to good.

Montazer and Parvinzadeh [16] have dyed wool with marigold as a source of yellow color. At first the wool yarns were premordanted with alum, dyed with marigold and then treated with different percentages of ammonia solutions. After washing with standard soap after color hue alters and there has been no effect of ammonia after treatment on washing fastness however the samples show lower light fastness.

A study on the dyeing properties of woolen yarns using gallnut extract as a natural dye was conducted by Shahid et al. [17]. A conclusion that gallnut extract can be applied on woolen yarn with or without mordants to produce bright ivory to light brownish yellow color with good fastness properties against light, washing and rubbing was obtained from the test.

Natural dyes have been slowly garnering popularity all over the world. So a study was carried out by Mirjalili et al. [18] by extraction of dyes from weld using soxhlet apparatus. The natural dyes were extracted and isolated and the colored substance obtained was used for dyeing of wool fiber. Finally a comparison was made with the synthetic colorants on the color fastness tests. It can be concluded from the study that weld can be used as a non-toxic dye. Good fastness properties were obtained from this natural extract.

An attempt has been made to dye the wool fabric with Limoniastrum monopetalum stems by Bouzidi et al. [19]. Extraction parameters were optimized. The optimization of extraction results obtained were dye concentration of 60 g/l, a temperature of 90°C and time duration of 100 min. The best results were obtained of pH 2, dyeing temperature of 100°C, and time duration of 60 min. Metal mordants were used in this process. The extract has ample natural tannin and polyphenol compounds which are considered as mordants since they have the ability to fix the dyes in bath to the fabric.

Indigo carmine is another renewable resource based blue dye which can be used to color protein fibers. Komboonchoo and Bechtold [20] have worked on use indigo carmine in combination with other natural dyes in a one-bath procedure as a hybrid dyeing concept. Optimum dyeing parameters of pH in the range of 4–5 and temperature between 40 and 60°C were obtained.

A new concept of few natural dyes as dye sensitized solar cell (DSC) was brought forth by Hao et al. [21–24]. Amongst all these photochromatic natural dye-extracts, black rice extract dye shows best results, perhaps due to high interaction between carbonyl [—C═O] and hydroxyl [—OH] groups of anthocyanin present

in such dyes. Because of the simple preparation technique, these are considered as widely available and low/cheap cost natural dyes as photo sensitized color of natural dyes, having photo-sensitized solar cell type character. Other materials like achiote seeds, rosella, blue pea flowers, spinach and ipomoea were also reported for such natural dyes having in built photo-sensitized solar cell in it.

Cochineal is an insect species of scientific name *Dactylopius coccus.* Carminic acid is the natural colorant obtained from the dried female body of such insects. This finds application in cosmetics, foods, pharmaceutical sectors as well as textile and plastic industries. The study has been conducted by Borges et al. [25] and the study on the newer process of extraction will be discussed in the extraction methods section.

A study of natural eco-friendly dye extracted from *Plumeria rubra* is carried out by Vettumperumal et al. [26]. Due to the existence of highly delocalized systems absorption spectrum shows a broad absorption in the range of 292–590 nm. This plant also encourages usage of waste lands, afforestation of wasteland and provides consequent additional source of income to rural population.

Rubia tinctorum is commonly known as madder produces anthraquinone pigments in its roots, one of them being alizarin (1,2 dihydroxy anthraquinone) which has been used for dyeing textiles since ancient times. Angelini et al. [27] has evaluated four madder genotypes for their agronomic characteristics as well as for their industrial value and to assess its value as a new industrial dye crop. Industrial assays demonstrated good performance when using dry powder 30% of the weight of material to be dyed for dyeing cotton, wool and silk yarns. Resistance to fading appears to be fairly good for dyed wool when using madder.

Different coloring plants from New Caledonia were considered for research by Toussirot et al. [28] amongst which *Hubera nitidissima*, an Annonaceae, showed an intense yellow color on fibers. Color was extracted from the leaves of the said plant on linen, silk and wool. The color fastness results were obtained where it was concluded that *H. nitidissima* appears as an excellent source of light-fast yellow dye with interesting antioxidant properties. These days natural dye extracted from mangrove bark was also used as a dyeing material.

1.2 Application of natural dyes on different textiles

Punrattanasin et al. [29] applied selectively extracted few natural dyes to a silk fabric by an exhaustion dyeing process where aluminum potassium sulfate, ferrous sulfate, copper sulfate, and stannous chloride were used as mordants. Dyeing was carried out in three different stages of the fabric-premordanted, meta-mordanting and post-mordanting. Color fastness values of each were reported. Dyeing conditions were optimized as dyeing temperature of 90°C, dyeing time—60 min and dye bath pH of 3 was fixed to be optimum. In this work, natural silk textiles were dyed with and without mordants using $SnCl_2$, KAl SO_4, $FeSO_4$ and $CuSO_4$ providing varying degree of color/tone/shade, where $FeSO_4$ produced darker and blackish brown shade, $CuSO_4$ produced lighter to pale reddish brown shade, both showing poorer washing fastness but very good water soaking, perspiration, light and rubbing fastness.

The various physical tests were done and tensile strength, tearing strength and stiffness of the fabrics before and after dyeing were also compared.

Shukla et al. [30] has reported dyeing of woolen textiles with extract of *acacia pennata* plants. The color was extracted from barks of the said plant and applied on wool. *Acacia pennata* is a thorny shrub found throughout India and Burma. Experiments were carried out where acacia pennata was used in conjunction with banana stem. When compared without banana stem it was observed that dye

fastness without the banana stem was poorer than when stem was used. It was concluded that banana stem acted as a good mordant thus eliminating the use of metallic, carcinogenic mordants.

An attempt has been made by Gulrajni et al. [31] to dye nylon and polyester with annatto. Annatto also known as *Bixa orellana* has a color component namely carotenoid dye bixin. It has been observed that both of these fibers show good affinity for this dye but moderate fastness to washing and poor light fastness.

An attempt has been carried out by Gulrajni et al. [32] to extract dyes from ratanjot also known as *Arnebia nobilis* for application on cotton, wool, silk, nylon, polyester and acrylic. The process conditions such as pH and temperature were recorded. It has been noted that dye exhibits acute sensitivity to pH in terms of solubility and color and is found to be thermally stable upto 80°C. The different colors shown by various fabrics were noted such as pink color for polyester, blue for nylon and other substrates acquiring a purple hue under similar dyeing conditions.

A study by Gulrajni et al. [33] on the kinetics and thermodynamics of dye extracted from *Arnebia nobilis* on woolen textiles was reported. Physicochemical and dyeing kinetics parameters of this natural dyeing using aqueous extract of *Arnebia nobilis* applied on woolen textiles were reported as compared to the same for other natural colorants like juglone, lawsone and *Rheum emodi*, etc. The results showed here that anthraquinonoid based these natural colors do not form desired coordinated complex with wool and rather are absorbed on wool substrate by partition mechanism following Nernst isotherm like absorption of disperse dye on polyester.

Chakraborty and Chavan [34] reviewed on dyeing of cotton denim with Indigo, which gives the information on the newer application techniques of indigo dyes applicable for natural indigo. Since indigo has negative affinity for cotton conventional methods cannot be applied. The details of indigo reduction, solubilization and dye application has been studied in this reference.

Deo et al. [35] had attempted dyeing of ecru denim with onion extract as natural color using Potash-alum in combination with harda and tartaric acid as mordants. Any of the single mordant did not produced desired shade. Amongst combined mordants used, Potash-alum + harda combination was found to be better than potash-alum + tartaric acid for producing desired depth of shade, but potash alum + tartaric acid (5%:5%, that is, 1:1 combination of each 5% application) post mordanting showed best overall color fastness results.

A study has been carried out by Samanta et al. [36] on standardizing dyeing process variables for its application on bleached jute fabric with aqueous extract of tesu (Palash flower petal). It is observed that higher amount of pre-mordanting with 20% myrobolan (Harda containing chebulinic acid) followed by 20% aluminum sulphate in sequence and dyeing at pH −11.0 produced optimum color yield and all round good color fastness. Improvement in wash and light fastness was also achieved with suitable chemical post-treatment using suitable agents.

Gray jute fabric bleached with hydrogen peroxide in conventional method was mordanted with different concentrations of ferrous sulphate and dyed separately with natural dyes extracted from deodara leaf (*Cedrus deodara* L.), jackfruit leaf (*Artocarpus integrifolia* L.) and eucalyptus leaf (*Eucalyptus globulus* L.). Pan et al. [37] have observed the interdependency of color yield and color fastness properties on dosages, that is, concentrations of mordants ($FeSO_4$) used, higher iron-mordant concentration lead to higher color yield, darker color and better overall good color fastness. But they have not studied loss of strength of due to mordanting and which is essentially needed to be assessed also.

Narayana Swamy et al. [38] have studied the use of *madhuca longfolia* as a dye source. The dried leaves of the said plant are taken as dye source for silk dyeing. The optimum conditions under which the dye has been extracted are pH of 10,

time (60 min) and temperature (95°C). Varying range of shades is obtained using different methods with or without using mordants. The dyed samples have been evaluated for color measurements and standard wash, light and rub fastness tests. Eco-friendliness of the dye has been kept into account. The dyed samples are also tested for antimicrobial activity against Gram-positive and Gram-negative bacteria. The dyed silk fabrics show acceptable fastness properties and the results show that *Madhuca longifolia* leaves are promising as a natural colorant, which can thus open new doors towards environment friendly products.

An attempt has been made to color silk using barberry, a cationic type natural dye by Pruthi et al. [39] Barberry bark also known as *Berberis aristata* DC. was used for dyeing of degummed pure silk yarn using four selected mordants; alum, chrome, copper sulphate and ferrous sulphate in different ratio, that is, 1:1, 1:3 and 3:1. Optimized results was obtained for aqueous extraction of barberry as 60 min time, 8% dye source material and optimized dyeing conditions were observed to be pH-of dye bath-4.0, dyeing time-45 min for standard mordanting with chrome + ferrous sulphate (1:3) and chrome + copper sulphate (3:1) produced the higher degree of color fastness properties. Varying shade percentages and color tone were obtained by using varying degree/percentages of different combination of mordants.

Das et al. [40] have worked on the application of *Bixa orellana* on protein textiles viz. on wool and silk. Seeds of annatto have been extracted first and then have been employed on silk and wool in absence and presence of magnesium sulphate, aluminum sulphate and ferrous sulphate. Effective colouration has been achieved at pH 4.5 commonly in the absence and presence of such inorganic salts. Color uptake for wool is found to be more than that for silk under all the conditions studied. When both the substrates are treated with such salt prior to application of annatto there has been significant increase in color uptake. Colored protein fibers, in general, produce light and wash fastness ratings of 2–3. Ferrous sulphate in turn, improves color fastness properties and color retention on washing of wool and silk fibers.

Another study has been conducted by Das et al. [41] on the application of *Punica granatum* on wool and silk textiles. *Punica granatum* also commonly known as pomegranate rind was used on wool and silk fabric in the presence and absence of environment-friendly mordanting agents. Both the dyeing of silk and wool with pomegranate solution is found to be effectively accomplished at pH 4.0. With the application of ferrous sulphate and aluminum sulphate during pre- and post-mordanting has shown improvement in the color uptake, light fastness and color retention on repeated washing. The use of such mordants, however, does not show any improvement in wash fastness property of dyed substrates.

An application of *Terminalia bellerica* fruit extract dyeing on woolen textile under different conditions of pH, concentrations of natural coloring matter, time of extraction/durations and temperatures were studied by El-Zawahry and Kamel [42]. The results evaluated were mainly surface color strength and color depth. The study shows that optimum color yield was obtained using following extraction and dyeing conditions:

Extraction: source coloring matter—5%, temperature of extraction bath—near boil, that is, 90–100°C at pH—7 (neutral).

Mordanting: (i) potassium dichromate + lactic acid-application 0.5 gpl, and (ii) chromic chloride + lactic acid-application −0.5 gpl,

Dyeing: time—60 min and temperature—near boil (95°C),

Shade obtained: moss green with mordanting system (i) as above, mustard yellow with mordant system (ii) as above and muster brown with both copper acetate and ferrous sulphate or ferric chloride as mordant. Thus for such natural dyes-color tone and shade depth are much dependant on type of mordant and its concentration

used. Overall color fastness results to washing, to acid or alkaline human perspirations and rubbing/crocking fastness were found to be almost the same for said premordanted and dyed wool fabrics. In case of light fastness, longer the duration of exposure to light, darker the shade and better light fastness were obtained. There has been no change of color strength and fastness properties despite of use of standing dye bath (50 g T.b. fruits/100 ml water) for 8 times.

A new approach of dyeing was undertaken by Naz et al. [43] where Eucalyptus (*Eucalyptus camaldulensis*) bark powder (without any further treatment/irradiation) using gamma ray irradiated natural colorant of dry powder of eucalyptus leaf extract, for producing natural colored textiles of soothing brown color with improved color fastness by required pre and/or post mordanting. Thus, when this fabric was therefore dyed in this case using gamma ray irradiated powder of eucalyptus dry leaf, it showed noticeable improved overall color fastness properties.

A paper was presented by Ferda Eser et al. [44] on dyeing of polyester and polyester/viscose blends dyed with walnut shell extracts. Different extraction conditions were considered such as material—liquor (M:L) ratio, extraction temperature, extraction time and pH in order to obtain highest color depth. Optimal extraction of natural dyes from walnut shells (*Juglans regia*) was obtained at temperature—80°C, time of extraction—75 min using MLR as 1:30 at pH 2. For dyeing polyester and polyester/viscose blends with said extract of wall nut shell using $AlKHSO_4$ or $AlK(SO_4)_2$ or $FeSO_4$ for separate mordanting for 90 min time and subsequent dyeing was studied and found that pre mordanting with $FeSO_4$ offers best dyeing results with good color depth and overall good color fastness, which can be used for future applications for ecofriendly dyeing of polyester and its blended textiles.

A detailed study was carried out by Samanta and Agarwal [45, 46] on dyeing of jute and cotton fabrics with binary mixtures of jackfruit wood along with other natural dyes in combination for producing compound shades after study of their compatibility. Conventionally hydrogen peroxide bleached jute and cotton fabrics were taken and was pre-mordanted with 10–20% harda (myrobolan) followed by 10–20% $Al_2(SO_4)_3$ or $FeSO_4$ salt in sequence as sequential double mordanting as a most prospective mordanting system for subsequent dyeing with aqueous extract of jack fruit wood. Study of dyeing process variables showed that optimum dyeing results were obtained for 90 min dyeing time, 70–90°C dyeing temperature, 11.0 pH, 1:30 material-to-liquor ratio, 20–30% mordants concentration, 30–40% source dye concentration, and 15 gpl common salt. In conventional method, for test of compatibility of these selected binary pairs of natural dyes, in order to obtain progressive depth of shade, two sets of five different samples were produced and tested after dyeing with 1:1 mixture of two dyes at 1% fixed shade depth with varying time and temperature profile in one set as well as by varying total concentrations of the binary pairs of dyes (using varying shade depth with 1:1 equal proportion of mixture of two dyes) keeping time and temperature fixed for second set were obtained and their color parameters of K/S vs. DL and DC Vs. DL were compared to judge compatibility by graphical comparison method. However, in this work, a newer method of compatibility rating procedure with calculation of Color Difference Index data (a newly defined useful color difference parameter) was described and adopted here for easy determination of compatibility rating between two dyes of any binary pairs of selective natural dyes used for applying that binary mixture of natural dyes in the same dye bath for compound shade. Moreover, they have shown methods of improving color fastness to washing by using separate post treatment with cationic agents like CTAB (n-cetyl-N-trimethyl ammonium bromide), or cetrimide, etc. Similarly separate post treatment with 1% benztriozale as an UV absorber had also shown an improvement in light fastness results.

Another attempt of dyeing ratanjot on nylon and polyster was studied by Gulrajni et al. [47] where the observed results indicated that this dye has a good substantivity for both nylon and polyester fibers, probably due to less polar structure of this dye and Nernst partition isotherm of absorption of this dye on these two fibers. However, deep color shade and better fastness to light and washing was obtained.

Sagarika Devi et al. [48] have studied about *Alternaria alternata* for textile dyeing and printing where reddish brown natural pigments which was obtained after extraction of colors from dry mycelium of *Alternaria alternata* in methanol solvent media. At pH −6, this Fungus produce the said extractable colored pigment, which can be applied on cotton for light color with medium grades of color fastness results using pigment dyeing process. This natural color is antibacterial and antifungal as evidenced in this work by AATCC100 test method for both gram positive and gram negative bacteria species for test, showing its antimicrobial nature.

Ke [49] studied the dyeing properties of natural dye extracted from *Rhizoma coptidis* on acrylic fibers. Acrylic fiber was dyed with *Rhizoma coptidis* aqueous solution and its dyeability was studied in terms of the thermodynamic and kinetic properties and dyeing process conditions. This study showed that effect of dyeing temperature is positive, that is, color yield and dye diffusion rate increases with increase of dyeing temperature up to a limit, indicating dyeing temperature and mordant concentration as important critical variables in such dyeing of acrylic with extract of *Rhizoma coptidis*. Color fastness to washing and rubbing are found to be grade—4.

Haque et al. [50] extracted ubiadin dye from *Swietenia mahagoni* and studied its dyeing characteristics onto silk fabric using metallic mordants. Metallic mordants such as $MgCl_2$ and $FeSO_4$ were used and dyeing properties were evaluated. $FeSO_4$ as compared to that of $MgCl_2$ showed good result for color yield and color fastness results.

Mahale et al. [51] studied about natural dyeing of Silk yarn skeins using extract of *Acalypha wilkesiana* leaves using varying concentrations of mordants like potash alum, potassium dichromate, copper sulphate and ferrous sulphate. Potassium dichromate and copper sulphate are not ecofriendly mordant. Potash alum though gives good fastness but considering color yield and fastness both, $FeSO_4$ offers best results of color yield and color fastness.

A study was conducted by Poorniammal et al. [52] for natural dyeing with extracted and purified natural fungal pigment from *Thermomyces* sp. to apply on different textile fabrics to optimize and dyeing process parameters for silk, cotton and woolen fabrics. This extracted pigment color obtained from *Thermomyces* sp. indicated good affinity towards silk fabrics than others, with good light fastness (rating 4), color fastness to washing (rating 4–5) and color fastness to rubbing (rating 3–4). The optimum conditions for dyeing was found to be dyeing temperature—30°C, dyeing pH—3, myrobalan mordant—5%, and dyeing time—20 min duration were suggested. The pigment also gave a reasonable extent of bacteria reduction in such silk dyed sample against *Salmonella typhi* (51.05%).

An attempt is made by Onial et al. [53] on utilization of *Terminalia chebula* Retz. fruits pericarp as a source of natural dye for textile applications. *Terminalia chebula* Retz. of Family-Combretaceae, trade name-Myrobalan fruits pericarp powder was taken for the utilization as a dye. The dried fruits constitute one of the most important vegetable tanning materials and have been used in India for a long time. This fruit pericarp thus can be used as a raw material for natural dyeing.

Das et al. [54] made an attempt to dye wool and silk with *Rheum emodi*. Silk and woolen fabrics, which were dyed with colorant extracted from *Rheum emodi* in the absence and presence of metallic mordants such as magnesium sulphate, aluminum sulphate and ferrous sulphate for producing shades of different colors, ranging from yellow to olive green. Study of dyeing isotherms and kinetics of dyeing process indicated that this dyeing mechanism do not follow coordinated complex formation

amongst fiber-mordant-dye, rather follow Nernst type isotherm showing pattern of partition mechanism, for this anthraquinonoid-based colorant where the dye molecules are adsorbed by silk and woolen fabrics as a disperse dye.

However, rate of dyeing is found to be higher for silk than that of wool and that color depth is increased by use of both aluminum sulphate or ferrous sulphate as mordant and considering color fastness test results, the later, that is, ferrous sulphate as mordant is found to be superior (offering wash fastness grade as 3 to 4 or 4) than use of same dosages of aluminum sulphate.

Thus ferrous sulphate is preferred as mordant for obtaining an improvement in the color fastness properties and color retention on washing of both wool and silk fabrics further.

Goodarzian and Ekrami [55] used brown dry rind of pomegranate as dyestuff. Extraction was carried out by solvent extraction method. Woolen fabrics were dyed with both raw and extracted dyestuffs using variations of concentrations. Spectrophotometric evaluations as well as colorimetric studies were carried out to compare the color strength of raw and extracted dye stuff on woolen fabric. It was concluded that color strength of extracted dye from pomegranate rind was more than raw dye stuff.

As mentioned by Garfield and Mauve [56], 'Mauviene' was the first synthetic dye synthesized by William Perkin in 1856. Like every scientific invention with man-made materials, advantages and disadvantages coexist, and the synthesis of synthetic-dyes is no exception. With the present growing global concern for environment protection and use of eco-friendly and bio-degradable materials, the trend of application of natural dyes have once again gained the momentum and for growing concern of consumers on eco friendliness of textile products, application of natural dyes on textiles is slowly being revived again.

Advantages of natural dyes over synthetic are manifolds [57] as they are eco-friendly, safe for body contact and are harmonized as reported by Brian [58]. Many scientists have also suggested and reported the medicinal and antibacterial importance of natural dyes [59, 60]. Yellow dye from rhizome of turmeric has been reported to be traditionally used in medicine as an anti-inflammatory drug [61]. Most of the natural dyes are proved to be non-toxic and eco-friendly, although there are some exceptions.

The natural dyes are the colorants extracted from the vegetables matters, minerals or insects [62]. Although most of the natural dyes have poor to moderate light fastness and the synthetic dyes represent a full range of colors with light fastness properties ranging from moderate to excellent [63], the use of natural dyes on textiles have been reported by many scientists. Dyeing of cotton with leaf-extract of Beilschmiedia fagifolia was reported by Vankar et al. [64], who has used sonicator method to dye cotton with aqueous extracts of *B. fagifolia*. The authors have reported that pre-treatment of cotton with 1–2% metal mordant and dyeing with 5% plant extract produced optimum results with good fastness properties.

In another report, Shah and Datta [65] used floral dye extracted from marigold flower to dye cotton fabrics. Gahlot et al. [66] used colorants extracted from Jatropha integarrima flowers for dyeing of cotton, wool and silk. Dyeing of silk with Onosma echiodes (Goldendrop) was reported by Sidhu and Grewal [67]. Mahale et al. [68] dyed cotton with Arecanut palm extract. Ultrasonic dyeing of cotton and silk with *Nerium oleander* flower has also been carried out [69]. Purohit et al. [70] reported use of natural color from waste leaves of Arotocarpus beterophyllus on different textile substrates like cotton and silk to get standard reproducible shades of golden yellow color.

The application of natural dyes such as turmeric, madder, catechu, Indian rhubarb, henna, and tea and pomegranate rind on manmade fiber nylon has been reported by

Teli et al. [71]. Some studies have also been conducted on application of Lac dyes [72] on different fibers. Application of a natural dye, annatto, on mulberry silk was carried out by Javali et al. [73]. Some studies [74–76] on natural dyeing of silk textiles have been reported in literature for use of Indian madder, *Spathodea campanulata* and lac dyes as natural sources. Patel et al. [77], have reported environmental-friendly and cost-effective method to create various shades on silk with few natural dyes.

There are many historic books documenting the literature on the use of natural dyes or natural dyed materials (textiles, candles, food, furrs, etc.) dating to as far back as the eighteenth century. The significant literary document on natural coloring matter was made available for the first time by Perkin and Everest [78].

Sahid and Mohammad [79], and Mayer and Cook [80] have also reviewed details of chemistry asnd application of natural dyes and more recent report on the structures of quinonoids natural colorants is described in Thomson's book [81]. Recent reviews in this area also include work undertaken by Parris [82] and Hofenk de Graaff [83] the latter includes information on fastness properties and history of use. Studies in the analysis of natural colorants in textiles are a fascinating subject which started as early as 1930s.

Recently, Samanta et al. [84–86] have described thermodynamic analysis of rate of dyeing, half dyeing time, enthalpy, free energy, etc. as a physico-chemical parameter of dyeing jute with red sandal wood, jackfruit wood and tesu as natural dyes.

The analysis of mass spectrometry of textile fibers dyed with indigo has been reported by McGovern [87]. However, Wong [88] was not able to detect 6,6-dibromoindigotin by direct analysis, but only after it had been separated by reductive extraction with sodium hydrosulphite.

Thin layer chromatography (TLC) was used by many workers to identify natural dyes in textiles [82]. Dyes detected were insect dyes and vegetable dyes viz., yellow, red and blue colors. Koren [89] also analyzed the madder and indigoid dyes by HPLC. Guinot et al. [90] also used TLC chromatography analysis to carry out a preliminary evaluation of plants containing flavonoids (flavonols, flavones, flavanones, chalcones/aurones, anthocynanins), hydroxycinnamic acids, tannins and anthraquinones, which are the phylo-compounds (color compounds) found in the plants.

Physicochemical dyeing parameters of red sandal wood as natural dyes and its compatibility with other dyes were analyzed by Samanta and Agarwal et al. [91, 92]. Neem bark [93] colorant showed two absorption maxima at 275 and 374 μm; while beet sugar showed three absorption bands at 220, 280 and 530 μm as per study undertaken by Mathur [93]. The visible spectra of ratanjot [47] in methanol solution was observed at both acidic and alkaline pH by Gulrajani et al. [47]. *Gomphrena globosa* flower colorant showed one major peak at 533 μm. The dye did not show much difference in the visible spectrum at pH 4 and 7; however the peak shifted to 554 μm as reported by Shanker and Vankar [94].

Bhuyan [95] observed the amount of dye absorption for extract of *Mimusops elengi* and *Terminalia arjun* varies from 21.94 to 27.46% and 5.18 to 10.78%, respectively, for the said two dye sources. The color components isolated from most of the barks contain flavonoid moiety. Samanta et al. [96, 97] postulated a new index called color difference index (CDI) value which can be calculated by an empirical formula postulated by them and which made determining dye compatibility easier and simpler for a binary mixture, that is, between a pair of natural dyes.

Identification of dyes in historic textiles though chromatographic and spectrophotometric methods as well as by sensitive color reactions was highlighted by Blanc et al. [98], who studied the retention of carminic acid, indigotin, corcetin, gambogic acid, alizarin flavanoid, anthraquinone and purpurin, etc.

A non-destructive method was reported for identifying faded dyes on textiles fabrics through examination of their emission and excitation spectra. Zin and Moe [99] purified and characterized extracted natural agents and colors from mango bark for application in protein fibers like wool.

Walker and Needles [100] carried out the separation and identification of natural dyes from wool fibers using reverse phase HPLC using a C-18 column. Two quaternary solvent systems and one binary solvent system were reported to be used to obtain chromatograms of by the HPLC analysis of plant and insect based red anthroquinonoid and molluscan type blue and red purple indigoid dyes [89]. This method enables the elution process for the determination of different chemical functionality and class of dyes and significantly shortens the time of test. Son et al. [101] reported HPLC analysis of indigo highlighting the structural changes of indigo component, attributing a decrease/increase in color strength with variation of dyeing time.

Balakina [63] also investigated/analyzed the quantitative and qualitative analysis of red dyes such as alizarin, purpurin, carminic acid, etc. by HPLC. High Performance Liquid Chromatography (HPLC) has been also used by several workers to identify synthetic as well as natural dyes.

Jain and Vashanta [102] characterized antimicrobial activity after eco-friendly dyeing with arcea nut using natural mordant/mordanting additives like myrobolan, lodhra and pomegranate rind and found that pomegranate rind renders best antibacterial activity and Lodhar renders highest color fastness to wash amongst all the moderating additives used.

Mondhe and Rao [103] made an attempt to prepare azo-alkyd dyes by the reduction of nitro alkyds, followed by diazotization of amino alkyds and coupling with different phenol compounds present in *Jatropha curcas* seed oil by using IR spectra.

The toxicity [104, 105] data also provide evidence about the adverse effect to human and environment. Of primary concern are the acute toxicity, irritation effects on the skin and the eye and sensitization potential besides environmental pollution in the society. Furthermore, possible long-term effects such mutagenic, carcinogenic or reproductive toxicity is best judged by LD50 test. The crude methanolic extracts of stem and roots stem, leaves, fruit, seeds of *Artocarpus Hetrophyllus* [106] exhibited good rating of antibacterial activity. The butanol fractions of the same root bark and fruit were also found to be the most active.

Mishra and Patni [107] extracted tannins from gall leaf from oak plant (i.e., oak galls containing gallic acid and tannic acid and helps in better dye fixation) from Himalayan region and dyed cotton, woolen and silk textiles with different metallic mordants and obtained better color fast fabrics, which are skin friendly too. The main reason of revival of natural dyes for textiles are its environmental friendliness and skin friendliness too.

1.3 Natural dyes cum natural antimicrobial finishing agents

A study was conducted by Mari Selvam et al. [108] to investigate the antibacterial and antifungal effects of such dyed textiles dyed with Turmeric, Terminalli, Guava and Henna. The results obtained indicated that at a dose level of 50 μl of Terminalli dye was able to inhibit the growth of all the fungi tested. The absorbance rate of natural dyes was analyzed by UV Spectrophotometer. The absorbance rate obtained were high in Terminalli (2.266) and turmeric (2.255). Hence from this study it was concluded that natural dyes were bound with traditional products to give good color and good antimicrobial activity against isolated fungal pathogens.

Another study carried out by Rajni Singh et al. [109] on antimicrobial activity of some natural dyes like *Acacia catechu*, *Kerria lacca*, *Quercus infectoria*, *Rubia*

cordifolia and *Rumex maritimus*, which gives us an idea about to determine their minimum inhibitory concentration (MIC), which was found to be varying from 5 to 40 mg. So, such dyed textile material with these dyes must up take above MIC concentration for effective antimicrobial action in such natural dyed textiles.

Curcumin, a common natural dye used for fabric and food colorations was used by Han and Yang [110] to dye woolen fabric to obtain dyeing and antimicrobial finishing simultaneously showing relation amongst bacterial reduction percentage and dye (curcumin) concentration, and microbial inhibition rate and surface color strength (K/S value). However, durability of antimicrobial action for different nos. of washing cycle after laundering and after exposure to UV light/sun light are also very important criteria, which were also critically discussed in this work.

Shafat Ahmad Khan et al. [111] attempted a work to investigate the antimicrobial action of *Rheum emodi* L. as a potential antibacterial natural dye and they dyed wool yarns with extract of *Rheum emodi* L. as purified dye applying dye concentration of 5–10% with or without mordants like ferrous sulphate, stannous chloride and natural alum for subsequent antimicrobial test against *E. coli* and *S. aureus* following AATCC100 test method. Test results of such *Rheum emodi* natural dyed woolen yarn samples indicated 90% bacterial reduction percentage as well as very high fungal protection showing very effective antimicrobial properties.

Shahid-ul-Islam et al. [112] have studied the use of *Tectona grandis* L. leaves extract plant colorants for dyeing woolen fabrics for simultaneous dyeing and antimicrobial finishing with natural dye cum natural antimicrobial finishing agent. This study indicated that the dyeing woolen yarn with extract of *Tectona grandis* L. is suitable for dyeing cum multifunctional finishing to impart simultaneous dyeing and antioxidant and antibacterial finishing properties to woolen based textile fabrics.

Fatemeh Shahmoradi Ghaheh et al. [113] have found that pre-treatment with aluminum sulphate as pre mordanting and followed by subsequent dyeing with selective natural dyes extracted from green tea leaf, madder route, turmeric route, saffron petals, and henna as natural dye cum natural antimicrobial agents provide moderate to good antibacterial finishing property on woolen fabrics and also led to good durability of the said antimicrobial action even after five cycles of laundering and above 300 min exposure to UV light/sun light.

Mohd Ibrahim Khan et al. [114] have conducted a study on antimicrobial activity of catechu itself and catechu extract dyed woolen yarn. The results indicated to show more than 90% antibacterial reduction as per standard test method. Observed antimicrobial inhibition character indicate that catechu may be a promising natural antimicrobial finishing agent for developing bioactive and antimicrobial dyed textile materials for today's need.

A number of recent studies on simultaneous natural colouration and antimicrobial finishing of different textiles using selective natural dyes/natural agents applied alone or in combination were investigated by several authors as mentioned below for detailed study and further references:

Prusty et al. [115] have studied about simultaneous natural coloring and antibacterial finishing of few natural colorants on silk.

Similarly Gupta and Laha [116] have worked on simultaneous natural dyeing and antimicrobial finishing of cotton fabric using natural tannin-rich extract of *Quercus infectoria* (QI) plant in combination with alum, copper and ferrous sulphate as mordants showing good antimicrobial activity at 12% concentration (owf), inhibiting the bacterial reduction around 45–60% for ferrous sulphate and bacterial reduction increases to 70–90% when mordanted with alum or copper sulphate making it suitable for anti-odor agent for use in medical, sports and home textiles.

Chen and Chang [117] have applied extract of onion skin on plasma pretreated cotton fabric to obtain simultaneous coloring and antimicrobial finishing effect

where the plasma-pre-treated cotton samples subsequent dyed/grafted with extract of onion skin showed measurable inhibition zone against *S. aureus* around 1.1–0.8 cm inhibition for 10 min grafting time with onion skin extract and 0.7–0.5 cm inhibition zone for 30 min grafting time of onion skin extract.

Joshi et al. [118] have reported a comprehensive review on natural product based bioactive agents such as chitosan, natural dyes, neem extract and other herbal products for antimicrobial finishing of textile substrates which is useful for further study.

1.4 Natural dyes cum natural UV protective finishing agents

A study has been conducted by Salah [119] about antibacterial and UV property of Egyptian cotton fabrics treated with aqueous extract from waste peel of banana fruits after its extraction in 1% NaOH solution.

Chattopadhyay et al. [120] have worked on developing natural dyed jute fabric with improved color yield and UV protection characteristics using harda (myrobolan) as bio mordant (though it is not truly a mordant, it is rather a mordanting assistant having high coordinating power for promoting fiber-mordant-dye complex formation using several —OH and —COOH groups of chebulinic acid present in it) and pomegranate rind extract as natural dye as well as UV protective agent using ecofriendly ferrous sulphate and potash alum as mordants. Very good ultraviolet (UV) protection ratings were achieved in case of dyeing of jute fabric with pomegranate rind. However, Jute fabric treated with manjistha, annatto, ratanjot and baboolas natural dyes cum natural UV protective finishing agents, applied after pre-mordanting with sequential pretreatment with Harda extract as biomordant and Alum as metallic but natural eco-friendly chemical mordant. Observed results indicated that UV protection properties of the said selective natural dyes cum natural UV protective finishing agents applied on bleached jute fabric follows the following order of UV protective performances: babool > annatto > manjistha > ratanjot.

Hou et al. [12] has used in their study waste orange peel as agricultural bye product for obtaining concurrent natural coloring and UV protective finishing on textiles for potential strong UV absorbance character of orange peel applied on woolen fabrics. The results was encouraging and optimum conditions of this concurrent natural coloring and UV protective finishing of woolen textiles is: optimum temperature of 100°C, optimum time—120 min, dyeing cum finshing bath pH—3 for following dyeing cum finishing without mordant and pH is 7–9 for simultaneous mordanting, dyeing and finishing in one bath using aluminum sulphate or ferrous sulphate, that is, iron as metallic eco-friendly mordant, showing great potential of orange peel extract as useful for this purpose.

Grifoni et al. [121] have shown in their reports that UV protection property not only depends on the surface finishing agents applied whether natural or synthetic, but also depend much on fabric construction, type of fibers, type of natural or synthetic dyes and finishes used (absorption criteria of dyes and finishing agents in UV zone). In this study, they measured UPF value of different types of textile apparels, hats, canopy type shade structure made of textiles with varying fabric construction for vegetable and natural fibers based product and finally dyed with different natural dyes cum natural finishing agents using tannin based natural mordants for obtaining maximum level of safest UV protection from sunlight radiation.

Feng et al. [122] have conducted a study on the UV protective properties of hats and clothing against solar ultraviolet radiation and found that *Rheum emodi* and *L. erythrorhizon* shows equally good and comparable UV-absorption protection character as compared to the common known standard UV-absorber compounds like benzophenone and benztriazole, etc.

Sinnur et al. [123] have reported a study on natural colouration and UV protective finishing using aqueous extract of pomegranate rind, that is, commonly known as anar peel. Besides optimization of conditions of natural color extraction from dried anar peel powder, effect of different single and double mordants in different proportions and concentrations on color yield and optimization of dyeing process variables as well as measurement of UV protective action of such dyed cotton khadi fabric with extract of anar peels (pomegranate rind, i.e., *Punica granatum* L.) as a natural colorant has been reported recently as an encouraging work.

The analysis of mass spectroscopy of cellulosic textile fibers dyed with indigo has been reported as a method of its identification, which may be the basis and can be used as a finger print for identifying natural indigo with TLC and UV VIS spectroscopic results in combination. Similarly for assuring any textiles being only dyed with natural dye, need its identification method. Very recently BIS has published two national IS standards on identifying natural Indigo and madder (IS 17084-2019 for natural indigo and IS 17084-2019 for madder) for test and identification of these two natural dyes from such a natural dyed textiles.

2. Conclusions

Thus, still there are many gaps in standardizing dyeing conditions for specific fiber-mordant-dye combinations and there is still need of required scientific and industrial research on the effects of different ecofriendly chemical mordants and bio mordants (tannin based natural compounds) and mordanting assistants (gallic acid or chebulinic acid based natural compounds) for finally standardization/optimization of dyeing process variables for obtaining uniform and repeatability of shades to produce with natural colors. Another side of utilizing antibacterial/antifungal and UV protective action or deodourizing action of selective natural dyes by detailed scientific study of the effects of different after-treating compounds antibacterial/UV absorbers compounds for improving its uses as high valued textiles. Similarly study of different natural and ecofriendly chemical dye fixatives for improving color fastness to Washing and effects of UV absorber compounds on exposure of such natural dyed textiles to the exposure to sun-light/UV light can be improved by suitable after-treatment with UV absorbers. For improving rubbing fastness of such natural dyed textiles, after treatment with natural binders or different natural reactive thickeners and ecofriendly synthetic binding agents are required, besides approaches to improve antimicrobial and UV protection activity of such natural dyed textiles. It is also important to know and understand well the exact fiber-mordant dye interaction and role of different pre and post treatments on promoting color yield (in terms of K/S values), uniformity of color yield (measurable by CV % of K/S values) as well as rating for antimicrobial and UV protection factor for different fiber-mordant-natural dye combination as applicable particularly to cotton, silk, wool and jute fibers when dyed with aqueous extract of any selected natural dye.

Hence application of natural dyes on high value apparel and functional textiles are gaining worldwide interest for its less toxic nature, better biocompatibility, biodegradability, producing elegant hues and highly functional value-added textiles as environment friendly oeko-tech/ecofriendly textiles for gaining popularity for natural dyed and finished as high valued textiles of tomorrow, if its revival strategies are well created and executed with utmost care with back up of sufficient scientific study with time bound growth plan and correct revival strategy.

Some of the revival strategies include (i) availability of commercially standardized process and standard commercial shade cards for developing desired shades

with acceptable repeatability and appreciable color fastness results; (ii) availability of standardized test methods for identifying and assuring customers for proving a dyed textiles is really 100% dyed with natural dye(s) without any synthetic dyes used as adulterant/topping to match shade; (iii) commercial process variables need to be standardized for different dyes for desired shades at economical minimum cost; (iv) to train and educate concern dyers and weavers and any big or large textile industry sector for successful extraction and dyeing with natural dyes and finally (v) future creation of a natural dye mark certification method by suitable national and international bodies for consumer assurance service like khadi mark, silk mark, etc.

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