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Dyeing of Textiles with Natural Dyes

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1. Introduction

Textile materials (natural and synthetic) used to be coloured for value addition, look and desire of the customers. Anciently, this purpose of colouring textile was initiated using colours of natural source, until synthetic colours/dyes were invented and commercialized. For ready availability of pure synthetic dyes of different types/classes and its cost advantages, most of textile dyers/ manufacturers shifted towards use of synthetic colourant. Almost all the synthetic colourants being synthesized from petrochemical sources through hazardous chemical processes poses threat towards its eco-friendliness.

Hence, worldwide, growing consciousness about organic value of eco-friendly products has generated renewed interest of consumers towards use of textiles (preferably natural fibre product) dyed with eco-friendly natural dyes. Natural dyes are known for their use in colouring of food substrate, leather as well as natural fibres like wool, silk and cotton as major areas of application since pre-historic times. Although this ancient art of dyeing textiles with natural dyes withstood the ravages of time, but due to the wide availability of synthetic dyes at an economical price, a rapid decline in natural dyeing continued. However, even after a century, the uses of natural dyes never erode completely and they are being still used in different places of the world. Thus, natural dyeing of different textiles and leathers has been continued mainly in the decentralized sector for specialty products besides the use of synthetic dyes in the large scale sector for general textiles/apparels.

Recently, most of the commercial dyers and textile export houses have started re-looking to the maximum possibilities of using natural dyes for dyeing and printing of different textiles for targeting niche market. Natural dyes produce very uncommon, soothing and soft shades as compared to synthetic dyes. On the other hand, synthetic dyes, which are widely available at an economical price and produce a wide variety of colours, sometimes causes skin allergy and other harmfulness to human body, produces toxicity/chemical hazards during its synthesis, releases undesirable/hazardous/toxic chemicals etc.

For successful commercial use of natural dyes for any particular fibres, the appropriate and standardized techniques for dyeing for that particular fibre-natural dye system need to be adopted. Therefore to obtain newer shade with acceptable colour fastness behaviour and reproducible colour yield, appropriate scientific dyeing techniques/procedures are to be derived. Thus, relevant scientific studies and its output on standardization of dyeing

methods, dyeing process variables, dyeing kinetics and test of compatibility of selective natural dyes have become very important, however the information on which is insufficient. That is why, this chapter is very much relevant to the current need of the textile dyers. An attempt has been made here to give scientific overview on dyeing of textiles with natural dyes and related issues.

2. Definition of natural dyes/colourants

The word 'natural dye' covers all the dyes derived from the natural sources like plants, animal and minerals. Natural dyes are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt, having an affinity for both the colouring matter and the fibre. Transition metal ions usually have strong co-ordinating power and/or capable of forming weak to medium attraction/interaction forces and thus can act as bridging material to create substantivity of natural dyes/colourants when a textile material being impregnated with such metallic salt (i.e. mordanted) is subjected to dyeing with different natural dyes, usually having some mordantable groups facilitating fixation of such dye/colourant. These metallic mordants after combining with dye in the fibre, it forms an insoluble precipitate or lake and thus both the dye and mordant get fixed to become wash fast to a reasonable level.

3. Advantages and disadvantages of natural dyes/ colourants

In the recent years, there has been a trend to revive the art of natural dyeing. This is mainly because in some aspects natural colourants are advantageous against synthetic dyes. Some of these advantages along with some limitations (disadvantages) are listed below:

3.1 Advantages of natural dyes/ colourants

- i. The shades produced by natural dyes/colourants are usually soft, lustrous and soothing to the human eye.
- ii. Natural dyestuff can produce a wide range of colours by mix and match system. A small variation in the dyeing technique or the use of different mordants with the same dye (polygenetic type natural dye) can shift the colours to a wide range or create totally new colours, which are not easily possible with synthetic dyestuffs.
- iii. Natural dyestuffs produce rare colour ideas and are automatically harmonizing.
- iv. Unlike non-renewable basic raw materials for synthetic dyes, the natural dyes are usually renewable, being agro-renewable/vegetable based and at the same time biodegradable.
- v. In some cases like harda, indigo *etc.*, the waste in the process becomes an ideal fertilizer for use in agricultural fields. Therefore, no disposal problem of this natural waste.
- vi. Many plants thrive on wastelands. Thus, wasteland utilization is an added merit of the natural dyes. Dyes like madder grow as host in tea gardens. So there is no additional cost or effort required to grow it.
- vii. This is a labour intensive industry, thereby providing job opportunities for all those engaged in cultivation, extraction and application of these dyes on textile/food/leather etc.
- viii. Application of natural dyes has potential to earn carbon credit by reducing consumption of fossil fuel (petroleum) based synthetic dyes.

- ix. Some of its constituents are anti-allergens, hence prove safe for skin contact and are mostly non-hazardous to human health.
- x. Some of the natural dyes are enhanced with age, while synthetic dyes fade with time.
- xi. Natural dyes bleed but do not stain other fabrics, turmeric being an exception.
- xii. Natural dyes are usually moth proof and can replace synthetic dyes in kids garments and food-stuffs for safety.

Despite these advantages, natural dyes do carry some inherent disadvantages, which are responsible for the decline of this ancient art of dyeing textiles.

3.2 Limitation/ disadvantages of natural dyes/ colourants

- i. It is difficult to reproduce shades by using natural dyes/colourants, as these agro-products vary from one crop season to another crop season, place to place and species to species, maturity period etc.
- ii. It is difficult to standardize a recipe for the use of natural dyes, as the natural dyeing process and its colour development depends not only on colour component but also on materials.
- iii. Natural dyeing requires skilled workmanship and is therefore expensive. Low colour yield of source natural dyes thus necessitates the use of more dyestuffs, larger dyeing time and excess cost for mordants and mordanting.
- iv. Scientific backup of a large part of the science involved in natural dyeing is still need to be explored.
- v. Lack of availability of precise technical knowledge on extraction and dyeing techniques.
- vi. The dyed textile may change colour when exposed to the sun, sweat and air.
- vii. Nearly all-natural dyes with a few exceptions require the use of mordants to fix them on to the textile substrate. While dyeing, a substantial portion of the mordant remains unexhausted in the residual dye bath and may pose serious effluent disposal problem.
- viii. With a few exceptions, most of the natural dyes are fugitive even when applied in conjunction with a mordant. Therefore, sometimes their colour fastness performance ratings are inadequate for modern textile usage.

4. Classification of natural dyes/ colourants

Natural dyes can be classified (Gulrajani & Gupta, 1992) in a number of ways. The earliest classification was according to alphabetical order or according to the botanical names. Later, it was classified in various ways, e.g. on the basis of hue, chemical constitution, application class etc.

- a. In "treatise on permanent colours" by Bancroft, natural dyes are classified into two groups: 'Substantive Dyes' such as indigo, turmeric etc. which dye the fibers directly and 'Adjective Dyes' such as logwood, madder etc. which are mordanted with a metallic salt.
- b. Humme classify the colouring matter as 'Monogenetic Dyes', those produce only one colour irrespective of the mordant present on the fibre or applied along with the dye and 'Polygenetic Dyes', those produce different colour with different mordant applied, e.g., alizarin (Dedhia, 1998)
- c. In the colour index the natural dyes are classified according to the hue (Predominating colour). The number of dyes in each hue are as follows in table-1:

CI Natural	No. of Dyes	Percent
Yellow	28	30.4
Orange	6	6.5
Red	32	34.8
Blue	3	3.3
Green	5	5.5
Brown	12	13
Black	6	6.5

Table 1. Showing the number of natural dyes in each hue as per the colour index.

On the basis of hues, natural dyes can be classified as follows:

- i. Red colour dyes: most red dyes are hidden in roots or barks of plants or camouflaged in the bodies of dull grey insects. They are almost invariably based on anthraquinone and its derivatives. These dyes are stable to light and washing.
 - ii. Yellow colour dyes: Yellow is the liveliest and perhaps the most abundant of all hues in nature. About 90% of the yellow dyes are flavonoids. Generally, they produce pale shade with quicker fading except turmeric, which produce dull deep shade but considered to be susceptible to light as they emit fluorescence. Wash fastness rating of natural yellow dyes ranges from fair to excellent, e.g., tesu, turmeric, kapila.
 - iii. Blue colour dyes are indigo and woad, give excellent fastness to light and washing.
 - iv. Black colour dyes: Black shades, generally obtained from tannin rich plant natural dyes and appreciably substantive towards cellulosic and protein fibre, imparts good overall fastness properties. Examples - logwood, harda, custard apple etc.
- d. On the basis of origin, natural dyes are broadly classified into three categories: vegetable, mineral and animal origin. About 500 vegetable origin dyes, colouring matter derived from root, leaf, bark, trunk or fruit of plants, are as follows in table-2

Part of the Plants	Dyestuffs
Root	Turmeric, Madder (Manjistha), Onions, Beet-root
Bark/ Branches	Purple bark, Sappan wood, Shillicorai, Khair, Red, Sandalwood
Leaf	Indigo, Henna, Eucalyptus, Tea, Cardamon, Coral Jasmine, Lemon Grass
Flowers (Petals)	Marigold, Dahlia, Tesu, Kusum
Fruits/Seeds	Latkan, Pomegranate rind, Beetle nut, Myrobolan (Harda)

Table 2. Showing some common natural dyestuffs obtained from different vegetable origin.

Mineral origin colourants are derived from specific mineral natural source or so-called mineral colours are produced from purified inorganic compounds. Some of the important mineral colourants are chrome-yellow, iron-buff, narkin-yellow, Prussian-blue and manganese brown. Animal origin lac, cochineal and kermes have been the principal natural dyes yielding from the insects.

- e. Natural dyes can also be classified on the basis of their chemical constitution (Dedhia, 1998).
- i. Indigoid dyes: Indigo and tyrian purple are the most common examples of this class. Another blue dye, woad also possesses indigo as the main dyeing component.
 - ii. Anthraquinone dyes: Almost all the red natural dyes are based on the anthraquinoid structure having both plant and mineral origin. Madder, lacs, kermes, cochineal are some of the dyes possess this type of structure. These are generally mordant dyes.
 - iii. Alphanaphthoquinones: Typical example of this class is lawsone (henna), cultivated mainly in India and Egypt. Another similar dye is juglone, obtained from the shells of unripe walnuts. These dyes are generally disperse dyes and give shades of orange.
 - iv. Flavonoids, which yield yellow dyes can be classified under flavones, isoflavones, aurones and chalcones. Flavones are colourless organic compounds. Most of the natural yellows are derivatives of hydroxyl and methoxy substituted flavones and isoflavones. Common example is weld (containing luteolin pigment) giving brilliant and fast colours on both wool and silk.
 - v. Di-hydropyrans: Closely related in chemical structure to the flavones are substituted di- hydropyrans, *viz.* haematin and its leuco form, haematoxilin. These are important natural dyes for dark shades on silk, wool and cotton. Logwood, brazil wood and sappan-wood are the common example.
 - vi. Anthocyanidins: The naturally occurring member of this class includes carajurin, a direct orange dye for wool and cotton. It is obtained from the leaves of bignonia chica.
 - vii. Carotenoids: The class name carotene is derived from the orange pigment found in carrots. In these, the colour is due to the presence of long conjugated double bonds.
- f. Another method of classifying natural dye is on the basis of the method of application (Gulrajani & Gupta, 1992).
- i. **Mordant dyes** are dyestuffs which require a mordant in their application as they have no affinity for the fiber being dyed. A mordant dye should have electron donating groups capable of forming a complex with the transition metal salt, e.g., madder, fustic, persian, berries, kermes, cochineal etc.
 - ii. **Vat dyes** are water insoluble dyes which are first converted to their water soluble form (reducing with Na- hydrosulphite and then solubilising it with alkali) and then applied to the fibres. The true colour is produced only on oxidation followed by treatment with a hot soap solution, e.g., indigo.
 - iii. **Direct dyes** are those dyes that have tremendous affinity for the cellulosic fibres. They are dyed from a boiling dye bath. Turmeric, harda, pomegranate rind etc. are the few of the direct natural dyes.
 - iv. **Acid dyes** are applied from an acidic medium. The dye molecules have either sulphonic or carboxylic group (s) which can form an electrovalent bond with amino groups of wool and silk. An after treatment with tannic acid known as back tanning improves the fastness of these type of dyes, e.g., saffron.
 - v. **Disperse dye** has a relatively low molecular mass, low solubility and no strong solubilizing groups. Disperse dyes can be applied on to hydrophobic synthetic fibre from neutral to mildly acidic pH. They can also be applied to silk and wool. These

dyes can be post-mordanted with chromium, copper and tin salts, *e.g.*, lawsone and many other flavone and anthroquinone dyes.

- vi. **Basic or cationic dyes** on ionization give coloured cations and form an electrovalent bond with the $-\text{COOH}$ group of wool and silk. These dyes are applied from neutral to mildly acidic pH. These dyes have poor light fastness, *e.g.*, berberine.

5. Extraction process of colour component from natural dyes

Extraction of colour component from source natural dye material is important step for dyeing any textile substrate to maximize the colour yield. Moreover, standardization of extraction process and optimizing the extraction variables both, for a particular source natural dye material have technical and commercial importance on colour yield and cost of extraction process as well as dyeing cost. The natural dyes can be taken from various vegetable sources like flowers, stem or wood, roots, bark, etc. as well as animal sources and mineral sources. The colour component present in these sources needs to be extracted so that it can be applied suitably on textiles. Natural dyes of different origin can be extracted using aqueous method *i.e.* by using water for the extraction with or without addition of salt/acid/alkali/alcohol in the extraction bath, supercritical fluid extraction, enzyme assisted extraction, alcoholic/organic solvent extraction by using relevant extracting equipment or soxhlet extraction method with use of alcohol and benzene mixture and finally to filterate, evaporate and to dry using ultra filtration equipment or centrifuge rotatory vacuum pump/or by extraction under reduced pressure. Now a days, there has been industrial methods available for extracting colour components/purified colour substances from natural dyes for their easy applications.

The collected source material is generally shadow dried in air or sun dried within a temperature range of 37-40°C for the moisture content of the source natural dye material is reduced to 10-15% with proper drying since most of the material have moisture content of 40-80% and can not be stored without drying. After drying, grinding is carried out to break down the material into very small units or preferably powder form. Extraction refers to separating the desired colour component by physical or chemical means with the aid of a solvent. Optimum conditions of extraction variables are determined through extracting the natural colour component from source material by varying extraction parameters of liquor and measuring the optical density of corresponding coloured liquor by using spectrophotometer. Also, the gravimetric yield of colour can be measured by filtering the extraction liquor through standard filtration process followed by evaporation of solvent, washing and finally drying to get the purified natural colour.

5.1 Aqueous extraction system

For optimizing the extraction method of colour component in aqueous medium, dried and finely cut source material of natural dye is grinded in powdered form and then the colour component is extracted in water employing a standard process. The aqueous extraction of dye liquor is carried out under varying condition, such as time of extraction, temperature of extraction bath, pH of extraction liquor, concentration of colour-source material (powdered form of source natural dye material) and Material-to-liquor ratio (MLR). In each case, the optical density or absorbance value at a particular (maximum) absorbance wavelength for the aqueous extract of the natural dye material can be estimated using UV-Vis absorbance spectrophotometer.

Many scientists have reported the optimized process of extraction of natural dyes from source. Colour from leaves of eucalyptus hybrid, seeds of cassia tora and *grewia optiva* are extracted by using aqueous medium under varying conditions (Dayal & Dobhal, 2001). Natural dyes are extracted from biomass products namely cutch, ratanjot, madder (Khan et al, 2006) and from hinjal, jujube bark (Maulik & Pradhan, 2005) in aqueous medium. An attempt has been made to extract natural dye from the coffee-seed for its application in dyeing textiles like cotton and silk (Teli & Paul, 2006). Grey jute fabric is dyed with extracts from deodar leaf (Pan et al, 2003) jackfruit wood and eucalyptus leaf by soaking it soft water and boiling it for 4 hours separately. Extraction (Verma & Gupta, 1995) of natural dyes is also reported from overnight soaked wattle bark in distilled water followed by boiled it in pressure vessel and filtered it to obtain a residual dye powder of about 15 to 20 % (w/w) of the bark. Colours are extracted from marie gold and chrysanthemum flowers by boiling the dry petals with acidified or salt water and reported it to be the best (Deo & Paul, 2000; Sarkar et al 2005 & 2006; Saxena et al, 2001). Natural colour extraction process has also been optimized in aqueous media for various source natural dye materials as follows (Konar, 2011):

- Pomegranate Rind: Pre-cut and dried rind is initially crushed to powder form and then it is extracted in water using an optimized condition of extractions using MLR- 1:20, temperature -90°C and time - 45 min and then it is filtered to obtain approximately 40% (w/w) clear extract of coloured aqueous solution of pomegranate rind having pH 11.
- Mariegold (Genda): Dried petal of mariegold is initially crushed to powder form and then extracted in water using an optimized condition of extraction using MLR 1:20 at 80°C for 45 min at pH 11 and then it is filtered to obtain approximately 40% (w/w) coloured aqueous extract of mariegold.
- Babool (Babla): Sun- dried chips (pre-cut) of babool bark is initially crushed to powder form and then it is extracted in water using an optimized condition of extractions, by boiling in water at 100°C for 120min. and using MLR 1:20 and then it is filtered to obtain 40% (w/w) clear extract of coloured aqueous solution of babool having pH 11.
- Catechu (Khayer): Pre-dried powder of catechu is initially crushed to powder form and then extracted in aqueous medium using an optimized condition of extractions by heating in water bath at 90°C having MLR 1:20 and then it is filtered to obtain 40% (w/w) extract of coloured aqueous solution of catechu having pH 12.
- Jack fruit wood: Pre-cut and dried chips of jack fruit wood is initially crushed to powder form and then colour is extracted in water using an optimized conditions of extractions by boiling in water at 100°C for 30 minutes and using ML ratio (MLR) 1:10 and then it is filtered to obtain 40% (w/w) clear extract of coloured aqueous solution of jack fruit wood having pH 11.
- Red sandal wood: Dried pre-cut chips are crushed to powder form and colour is extracted under optimized conditions by heating it in water at 80°C for 90 minutes at pH 4.5 and MLR 1:20.

5.2 Extraction by non-aqueous and other solvent assisted system

Due to increasingly stringent environmental regulations, supercritical fluid extraction (SFE) has gained wide acceptance in recent years as an alternative to conventional solvent extraction for separation of organic compound in many analytical and industrial process. In recent past decade, SFE has been applied successfully to the extraction of a variety of organic compounds from herbs, other plant material as well as natural colourant from

source natural dye material. With increasing public interest in natural products, SFE may become a standard extraction technique for source natural dye material and other herbs and food items. Supercritical fluid extraction using carbon dioxide as a solvent has provided an excellent alternative to the use of chemical solvents. Over the past three decades, supercritical CO₂ has been used for the extraction and isolation of valuable compounds from natural products.

Supercritical fluids are utilized to extract and purify natural colourant from eucalyptus bark (Vankar et al, 2001). Extraction of dye from food is best achieved with ethanol/oxalic acid. The comparative behaviour of other red food dyes is also studied and a process is developed for the extraction of natural dye from the leaves of teak plant is carried out using aqueous methanol (Nanda et al, 2001). A brick red shade from dyeing for silk/wool using the isolated dye in presence of different mordants is achieved. Attempts (Bhattacharya, 2002; Patel & Agarwal, 2001) has been made to standardize colourant derived from arjun bark, babool bark and pomegranate rind. Extraction (Agarwal et al 1992; Singh & Kaur, 2006) of well grounded henna leaves, directly in a solvent assisted dyeing process, employing organic solvent:water (1:9) as the dyeing medium is studied and superior dyeing properties are obtained, when applied to polyester. Natural dye (Raja & Kala, 2005) is obtained from the grape skin waste by using soxhlet extractor, and latter on distilled it under vacuum to obtain the concentrated dye solution. Colourant/dye is extracted by using a reflux condenser; source dye material is refluxed for 1 hour and filtered it to yield natural colourant (Eom et al, 2001).

5.3 Extraction by acid and alkali assisted system

Colour from euphorbia leaves (Dixit & Jahan, 2005) under acidic pH by adding hydrochloric acid and under alkaline pH by adding sodium carbonate both, in aqueous media are extracted for dyeing silk fabric. Extraction of colour in alkali media from nuts of acacia catechu (Sudhakar, 2006) is carried out for colouration of protein fibre based fabric. Dye extracted from jatropha seed gives a range of bright, even and soft colours on textiles when extracted under acid/alkali condition (Radhika & Jacob, 1999). Extraction of colour component from jackfruit wood under various pH conditions is carried out and reported that the optimum conditions for extraction is at pH-11.0 (Samanta et al, 2007). Red colour is extracted from red sandal wood (Samanta et al, 2006) under various pH conditions and it is reported that the optimum conditions for extraction of colour component is acidic pH like 4.0. Orangish yellow colour is extracted from tesu (palash flower) and maroon red colour can be obtained from Indian madder when extracted at alkaline conditions under aqueous medium (Samanta et al, 2010 & 2011).

5.4 Natural colour extraction by other methods

For ultrasound assisted extraction process (Sumate et al, 2008; Tiwari et al 2010) of natural colour, a standard extraction protocol may be used as 250 ml of solvent and 25 gm of powdered source natural dye material are taken in 500 ml beaker being immersed into the ultrasonic bath with working frequency of 27-30 MHz at 160 V under a controlled water level at about 2-3 cm from the bottom of the bath. To estimate the extraction yield at different time, temperature, pH and MLR for optimizing the extraction variables, 1.0 ml liquid is pipette out and then diluted to make 10.0 ml volume in each case. This solution is centrifuged at about 2000 rpm to remove the suspension. Finally, the concentration (% w/w) of the diluted solution is measured spectrophotometrically at a definite wavelength (λ_{max}).

For enzyme assisted extraction process (Tiwari et al 2010) single or mixed enzyme (e.g. pectinase : cellulase, 2:1) is sprayed on source material and left for overnight for better soaking. This material is then taken into 500 ml conical flask with 250 ml water of pH 10 and shaken in orbital shaker at 150 rpm for 40-80 minutes at optimum temperature. The extraction solution is ready for dyeing textile material or can be filtered and drying as ready purified dye material for further use.

6. Purification and characterization of natural dyes

The aqueous extraction of the corresponding dye solution is double filtered in fine mesh nylon cloth and sintered glass crucible and the filtrate is evaporated using a vacuum oven at lower temperature (70°C) to a semi-dried solid mass and the same is then put in a cage of the wrapped filter paper and further subjected to extraction in soxhlet apparatus using 1:1 alcohol:toluene mixture for 10 cycles for 2h at 70°C. The alcohol- toluene extract of the colour components is finally subjected to evaporation in a water bath at 50°C to get a semi-dry mass of the pure colour components. Finally, this dry mass of the colour components is washed with 100% acetone followed by washing with methyl alcohol and final drying in air to obtain the dry powder of the pure colour components of the corresponding natural dyes.

For characterization, purified dye powder is to be taken for preparation of 1% aqueous dye solution separately and is subjected to wavelength scan in a micro processor or computer attached UV-Vis absorbance spectrophotometer for 190-1100 nm range. Further, individual purified natural dye powder is washed once again in distilled water and in 100% acetone in sequence before final drying and may be subjected to FTIR Spectroscopy study in double beam FTIR spectrophotometer using KBr disc technique for characterization of its chemical nature and functional group present in the natural dyes, which are responsible for solubilisation and mordanting power of natural dyes as well as its hypsochromic/bathochromic shift of the main hue.

For study of thermal behaviour by DSC (differential scanning calorimetry) study, individual purified natural dye powder is to be washed in distilled water followed by further washing in 100% acetone before final drying and then may be subjected to DSC or TGA (thermogravimetric analyser) study by standard method, for determining the different transition temperature of the purified dyes including temperature of degradation/dissociation. Thermal characterization by DSC/TGA is necessary for understanding the nature of thermal dissociation of natural dye component at different dyeing temperatures as well as application temperature.

6.1 UV-Visible spectroscopic study

UV-Vis spectral scan of aqueous/non-aqueous extract/solution of purified natural dyes having both UV-zone and visible zone (190-700 nm or higher) indicating peaks and troughs in different wave length shows its main hue, absorption etc. Peaks and troughs in visible zone thus indicate main colour and absorption. UV-Zone with/without peaks shows the property of the dye under UV-light, this may be correlated with fastness behaviour.

UV-Visible spectroscopic studies are carried out by different scientists (Erica et al, 1995) to identify the UV-Vis spectral scan of a number of natural dyes viz, madder, cochineal, indigo, etc., using different solvents for extraction. Neem bark (Mathur et al, 2003) colourant shows two absorption maxima at 275 and 374 nm while beet sugar shows three absorption bands at

220, 280 and 530 nm as per recent study (Mathur et al, 2001). The visible spectra of ratanjot (Gulrajani et al, 1999) at acidic pH showed maximum absorption around 520-525 nm, but under alkaline pH there is a shift to 570 nm and another peak at 610-615 nm and red sandal wood shows a strong absorption peak at 288 nm, the maximum absorption at 504 and 474 nm at pH 10 in methanol solution (Gulrajani et al, 2003). *Gomphrena globosa* (Sankar & Vankar, 2005) flower colourant shows one major peak at 533 nm. The dye does not show much difference in the visible spectrum at pH 4 and 7. Absorption for dyes extracted from *mimusops elengi* and *terminalia arjun* are reported that depending on the concentrations of dyes in the dye-bath, the dye absorption on the fibre varies from 21.94 % to 27.46 % and 5.18 % to 10.78% respectively (Bhuyan et al, 2004). The colour components isolated from most of the barks contain flavonoid moiety. Extraction, spectroscopic and colouring potential studies of the dye in ginger rhizome (*zingiber officinale*) is studied and reported (Popoola et al, 1995) that the dye is soluble in hydroxyl organic solvents and gives one homogenous component of R_f value of 0.86 on chromatographic separation having wavelength of maximum absorption at 420 nm. Aqueous extract of different source natural dyes including red sandal wood, manjistha, tesu, catch etc. have been characterized by UV-vis spectra to optimize the extraction conditions.

6.2 Chromatographic analysis

Thin layer chromatography (TLC) is used by many workers to identify natural dyes in textiles (Kharbade et al, 1985). Dyes detected are insect dyes and vegetable dyes viz., yellow, red and blue colours. The natural scale insect, madder and indigoid dyes are also analysed by HPLC (Koren, 1994). TLC chromatography analysis (Guinot et al, 2006) is used to carry out a preliminary evaluation of plants containing flavonoids (flavonols, flavones, flavanones, chalcones/ aurones, anthocyanins), hydroxycinnamic acids, tannins and anthraquinones, which are the phylo-compounds (colour compounds) found in the plants. Identification of dyes in historic textiles through chromatographic and spectrophotometric methods as well as by sensitive colour reactions is highlighted (Blanc et al, 2006) and further the retention of carminic acid, indigotin, corcetin, gambogic acid, alizarin flavanoid, anthraquinone and purpurin are also studied (Szostek et al, 2003). A non-destructive method is reported for identifying faded dyes on textiles fabrics through examination of their emission and excitation spectra. The quantitative and qualitative analysis of red dyes such as alizarin, purpurin, carminic acid etc. by HPLC are also investigated/analysed (Balankina et al, 2006). High Performance Liquid Chromatography (HPLC) has been also used by several workers to identify natural dyes.

The separation and identification of natural dyes is carried out from wool fibres using reverse phase HPLC with a C-18 column (Mc Govern et al, 1990). Two quaternary solvent systems and one binary solvent system are used to obtain chromatograms of dyes, isomers and minor products present in the sample. A linear gradient elution method has been applied to the HPLC analysis of plant and scale insect, red anthraquinonoid, mordant dyes, and molluscan blue, red purple and indigoid vat dyes (Koren, 1994). The method enables the use of the same elution programme for the determination of different chemical classes of dyes. In addition, it significantly shortens the retention time of natural anthraquinonoid dyes. Quantitative analysis of weld by HPLC shows that after a 15 min extraction in a methanol-water mixture, 0.45% luteolin, 0.36 % luteolin 7-glucoside and 0.23% luteolin-3'-7-diglucoside are obtained (Cristea et al, 2003). HPLC analysis of indigo is reported (Son et al, 2007) and it is found that as the dyeing time is increased, structural changes of indigo component are attributed to decrease in colour strength of dyeing.

Detection of annatto dyestuff, norbixin and bixin is reported by means of derivative spectroscopy and high performance liquid chromatography (HPLC) (Bhattacharya, 1999). The sample preparation involved extraction with acetone in the presence of HCl and removal of water by evaporation with ethanol. This residue is dissolved in chloroform-acetic acid for derivative spectroscopy or with acetone for HPLC. Derivative spectra are recorded from 550-400nm. Analysis of cochineal colour in foods utilizing methylation with diazomethane is carried out employing TLC and HPLC using a mobile phase of butanol/ethanol and 10% acetic acid.

6.3 Test of toxicity, biotechnological processing and environmental impact of natural dyes

Toxicity is the ability of a substance to cause damage to living tissue, impairment of nervous system or severe illness when ingested, inhaled or being absorbed by skin. The toxicity (Zippel, 2004; Joshi & Purwar, 2004) data provide evidence about the adverse effect of natural dyes to human body. The LD₅₀ is the best-known figure for toxicity rating of any substance. It describes the 'lethal dose for 50% of the test animals' which is the amount of substance in kg/kg of body weight which kills half of the animals.

Most of the natural dyes are found to be non-carcinogenic in nature. Moreover, natural dyes have positive effect on antifungal and anti bacterial growth. The crude methanolic extracts of stem and roots stem, leaves, fruit, seeds of artocarpus hetrophyllus (Khan et al, 2003) and their subsequent partitioning with petrol, dichloromethane, ethyl acetate and butanol fractions exhibit a broad spectrum of antibacterial activity. The butanol fractions of the root, bark and fruit are found to be the most active. None of the fraction is found to be active against the fungi tested. Mariegold (<http://www.mdidea.com>, 2005) shows negative test against microbiology control E-coli and salimonella. Chemo-preventative effects (Dwivedi & Ghazaleh, 1997; Dwivedi & Zhang, 1999; Benencia & Courreges, 1999) of red sandal wood oil are observed on skin papillomas in mice. Further, it is studied for red sandal wood's prevention of skin tumor development in CD1 mice and antiviral activity against herpes simplex virus-1 and 2. The hepatoprotective (Gilani & Janbaz, 1995) activity of an aqueous-methanol extract of rubia cardifolia (madder) is investigated against acetaminophen and CCL₄-induced damage. Acetaminophen produced 100% mortality at a dose of 1 g/K in mice while pretreatment of animals with plant extract (natural dye source material) reduced the death rate to 30%. Test of acacia catechu (cutch), kerria lacca (lac), quercus infectoria (gallnut), rubia cordifolia (madder) and rumex maritimus (golden dock) against pathogens like escherichia coli, bacillus subtilis, klebsiella pneumoniae, proteus vulgaris and pseudomonas aeruginosa are also reported (Singh et al, 2005). Minimum inhibitory concentration is found to be varying from 5 to 40 µg. Using a bioassay-directed purification scheme, the active antibacterial principle from caesalpina sappan (sappan wood or red wood) is isolated and identified (Hong & Lee, 2004). The trypan blue dye exclusion test shows that brazilian lacks cytotoxicity against vero cells; it has potential to be developed into an antibiotic. It is reported (Bhattacharya et al, 2004) that arjun bark, babool bark and pomegranate rind are eco-safe, however sometime contains traces amount of red listed heavy chemicals in permissible limit. A critical and realistic evaluation of dyeing with vegetable dyes highlighting its metal toxicity of substances used in processing has been reported (Shenai, 2002) and it is mentionworthy that mordanting with metal salt as pre-requisite for application of most of the natural dyes may contaminate the dyed textiles with objectionable heavy metals resulting carcinogenic

effect. Therefore, selection of mordanting metal salt and its purity are important criteria to produce eco-friendly natural dyed textiles. Attempts (Mondhe & Rao, 1993a & 1993b) has been made to prepare azo-alkyd dyes by the reduction of nitro alkyds, followed by diazotization of aminoalkyds and coupling with different phenolic compounds present in *Jatropha curcas* seed oil confirmed by using IR spectra.

7. Types of mordants

Limitation on colour yield and poor fastness properties prompted a search for ideal mordants, the chemicals which increase natural dye uptake by textile fibres. Different types of mordants yield different colours even for the same natural dye. Therefore, final colour, their brilliance and colour fastness properties are not only dependant on the dye itself but are also determined by varying concentration and skillful manipulation of the mordants. Thus, a mordant is more important than the dye itself. Moreover, the ideal mordant for bulk use should produce appreciable colour yield in practicable dyeing conditions at low cost, without seriously affecting physical properties of fibre or fastness properties of the dyes. Also, It should not cause any noxious effect during processing and the dyed textile material should not have any carcinogenic effect during use. Mordants can be classified into the following categories:

7.1 Metallic mordants

They are generally metal salts of aluminium, chromium, iron, copper and tin. The metallic mordants are of two types.

7.1.1 Brightening mordants

- i. **Alum:** Among all types of alum, potash alum is cheap, easily available and safe to use mordant. It usually produces pale versions of the prevailing dye colour in the plant.
- ii. **Chrome (potassium dichromate):** It is also referred to as red chromate. It is relatively more expensive. However, Cr^{3+} or Cr^{6+} is considered to be harmful for human skin as objectionable heavy metal beyond a certain limit of its presence. Its use has been limited as per the norms of the eco-standards. The dichromate solution is light sensitive and therefore it changes colour under light exposure.
- iii. **Tin (stannous chloride):** It gives brighter colours than any other mordant. However, they are oxidized on exposure to air and may impart a stiff hand to the fabric. Stannous chloride also causes higher loss of fabric tenacity (tensile strength) if applied beyond a certain concentrations.

7.1.2 Dulling mordants

- i. **Copper (cupric sulphate):** Known as blue vitriol, it is readily soluble in water and easy to apply. It gives some special effects in shades, which otherwise cannot be obtained. However, copper beyond a certain limit is also under the eco-standard norms as objectionable heavy metals.
- ii. **Iron (ferrous sulphate):** It is also known as green vitriol and is readily soluble in water. It is used for darkening /browning and blackening of the colours/ shades. It is easily available and one of the oldest mordants known. It is extensively used to get grey to black shades.

7.2 Tannins

The term 'tanning agent' is given initially to those water-soluble cellulosic materials that predicated gelatin from solution. But all gelatin precipitation did not identified as tanning agent. Tannins are polyphenolic compounds having capacity of gelling under certain conditions. (a) It may be hydrolysable pyrogallol tannins exemplified by 'tannic acid', by Chinese or Turkish gallotannins (galls) and by Sicilain and Stagshorn sumac, (b) hydrolysable ellagitannins that give ellagic acid or similar acids on hydrolysis, exemplified by valonea, chestnut, and (c) condensed or catechol tannins that contain little or no carbohydrates and are converted to acids to insoluble amorphous polymers. Among the tannins, myrobalan (harda) and galls/sumach are most important.

7.3 Oils type mordants

Vegetable oils or Turkey red oil (TRO) are such type of mordants. TRO as mordant is mainly used in the dyeing of deep red colour from madder. The main function of the TRO as oil mordant is to form a complex with alum when used as a main mordant. Sulphonated oil posses better binding-capacity than the natural oils. Oil mordanted samples exhibit superior fastness and hue.

8. Different mordanting methods and application of natural dyes

Mordanting can be achieved by pre-mordanting (before dyeing), simultaneously mordanting and dyeing or it may be a post mordanting system (after dyeing). Different types of mordants can be applied on the textile to increase the dye uptake of natural dyes. Extensive work has been reported (Paliwal, 2001; Jahan P & S, 2000; Sengupta, 2001; Prabu & Premraj, 2001; Sunita & Mahale, 2002; Moses, 2002; Rani & Singh, 2002; Bain et al, 2002; Paul et al, 2002) for dyeing of textiles with natural dyes adopting specific mordanting system for a particular textile material.

In pre-mordanting method, the textile substrate is first treated in aqueous solution of mordant for optimized time (e.g. 30 - 60 minutes) and temperature (e.g. 70 - 100 °C) with a ML ratio of 1:5 to 1:20 and then dried with or without washing. The mordanted textile material is then dyed following optimized dyeing conditions may be required as salt, soda ash or acid depending on type of textile material and type of natural dye. After dyeing, the textile material is washed properly and soaping is carried out by 2 g/L industrial soap solution as described in standard method of AATCC or ISO method.

For simultaneous mordanting and dyeing system, the textile substrate is immersed in a dye bath solution containing both mordant and dye in a definite quantity and dyeing may be started at the pre-determined optimum condition. Dyeing auxiliaries may be added as required for the standard dyeing process. However, for optimization of dyeing condition, dyeing process variables can be studied for specific fibre-mordant-natural dye system in order to maximize colour yield on textiles. After dyeing, the textile material is washed properly and soaping is carried out by 2 g/L industrial soap solution.

In case of post-mordanting method of natural dyeing, the dyeing process is carried out for bleached textiles in the absence of mordant at pre-determined dyeing condition and the dyed fabric is treated in a separate bath called saturator containing suitable mordanting solution. Treatment condition may vary depending on type of fibre, dye and mordant system. After dyeing, the textile material is washed properly and soaping is carried out by 2g/L industrial soap solution.

There is study (Dayal et al, 2006) for effect of copper sulphate and potassium dichromate on silk, wool and cotton fibre and reported their effects on colour fastness properties. The wool treated with metal ions such as Al(III), Cr (VI), Cu (II), Fe (II), Sn (II) and rare earths such as La (III), Sm (III) are used for beet sugar colourant, it can withstand the requirement of BIS fastness standards. Optimization (Agarwal et al, 1993) of the various concentrations of mordant are reported for shades can be produced by 0.15% of alum, 0.08% copper sulphate and stannous chloride, 0.04% ferrous sulphate and 0.06% potassium dichromate on mulberry silk fabric. Extraction of natural dye from the leaves of teak plant by using aqueous methonal produced brick red shade on dyeing of silk/ wool using the isolated dye in presence of different mordants as it is reported (Nanda et al, 2001). Irrespective of mordanting methods, silk (Mahale et al, 2003) treated with potash alum shows increase in colour when subject to sunlight test and those treated with potassium dichromate, copper sulphate and ferrous sulphate shows excellent to good fastness properties. Wool yarns dyed with turmeric (Mathur & Gupta, 2003) when subject to different concentration of natural mordant and chromium under identical mordanting conditions, shows similar colour fastness. Application of tulsi leave extract on textiles with or without using metallic salts produces pale to dark green and cream to brown shades with adequate fastness (Patel et al, 2002). Silk (Maulik & Pal, 2005) fabric being mordanted with magnesium sulphate produces lower depth of shade, whereas copper sulphate produces highest depth. It is reported (Bhattacharya & Shah, 2000) that the colour depth of dyeing textiles can be improved by using different metal salt as mordants. Pre-mordanting and post-mordanting (Das et al, 2005 & 2006) employing ferrous sulphate and aluminium sulphate improve the colour uptake, light fastness and colour retention on repeated washing for application of many natural dyes on textiles. The use of such mordants, however, does not improve wash fastness property of textile substrate dyed with pomegranate. Dyeing of wool (Chan et al, 2000) with four varieties of tea employing different mordant shows that coloured protein fibres became blackish, when ferrous sulphate is employed as mordanting agent. The effect of mordants on yellow dyes such as kapila, onion, tesu, and dolu are also reported.

Tin, as mordant imparts good wash fastness to cotton dyed with golden rods; chrome for mariegold dyeing and alum and tin for dyeing with onion skins (Vastard et al, 1999). Turmeric dye (Devi et al, 1999) can be applied for dyeing cotton fabric by using different mordants like tannic acid, alum, ferrous sulphate, stannous chloride and potassium dichromate to obtain various shades of colour. The use of gluconic acid as a ligand for complexing iron (II) salts and for vat dyeing of cotton has been studied. It is reported (Chavan & Chakraborty, 2001) for use of iron (II) salts complexed with ligands as tartaric acid and citric acid for the reduction of indigo at room temperature and subsequent cotton dyeing. Wash fastness (Kumar & Bharti, 1998) and light fastness (Sudhakar et al, 2006) can be increased by the use of metal salts or tannic acid on cotton fabrics. Cotton yarns treated with acalypha (Mahale, 2002) dye after pre-mordanted with potash alum, potassium dichromate, copper sulphate and ferrous sulphate shows excellent fastness rating.

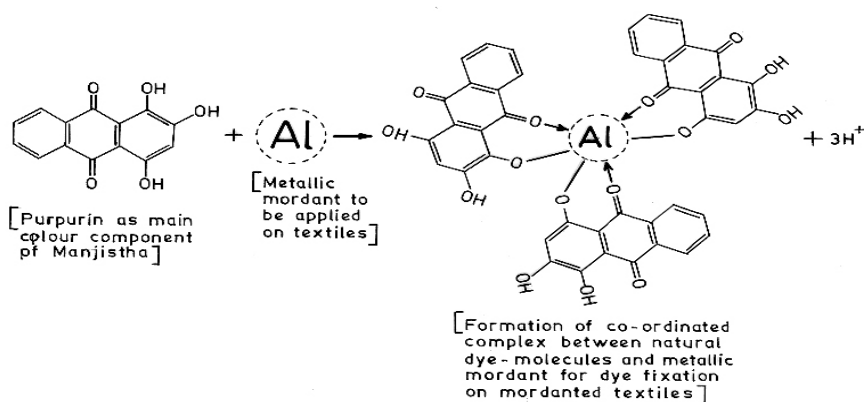
Pre-mordanting route favours dyeing of jute (Samanta et al, 2003) fabric with direct type of natural dyes, when aluminium sulphate is used as a mordant, while simultaneous mordanting route gives better results for madder on cotton with the same mordant. It has also been proposed that alum (Potsch 1999) and aluminium sulphate should be used as mordants in dyeing with natural dyes, as their environmental toxicity is almost nil. The effects of different natural and chemical mordants like aluminium sulphate, tartaric acid and

cetrimide on colour yield for bleached jute fabric are studied and reported (Samanta et al, 2006 & 2007). As the mordant concentration and dye concentration is increased, there is improvement in the light fastness by $\frac{1}{2}$ to 1 grades. Different type of mordant and method of mordanting significantly affected the rate and extent of photofading. The use of copper or ferrous sulphate give high resistance to fading, whereas stannous chloride or alum did not. On the other hand, light fastness is improved when post-mordanting is conducted with copper or ferrous ion, but pre-mordanting is superior in the case of stannous chloride or alum as investigated and reported (Gupta et al, 2004). Harda-tartaric acid combination is found to be the best followed by tannic acid-harda and tartaric acid-tannic acid combinations. Synergistic effect of mordant is observed while using the binary combinations of mordants. Meta-mordanting gives the best results for harda-tartaric acid and tartaric acid-tannic acid combinations, while pre-mordanting gives the best results for tartaric acid-harda combination as studied (Deo & Paul, 2000a & 2000b). The colour fastness properties of goldendrop root dyed on wool (Bains et al, 2005) are studied using combinations of mordants such as alum: chrome, alum: copper sulphate, alum: ferrous sulphate, chrome: copper sulphate, chrome: ferrous sulphate and copper sulphate : ferrous sulphate in ratio of 1:3, 1:1 and 3:1. Studies are available for the effects of combination of mordant on colour fastness properties of cotton dyed with peach (Bains et al, 2003). There are lots of literatures available for mordanting prior to normal dyeing and the effects of mordants on colour fastness properties, shade development and other physical properties when applied singly (Fatima & Paul, 2005; Deo & Paul, 2003) or in combination (Yu et al, 2005) on cellulosic, proteinic and synthetic fibres. An effective double pre-mordanting system is recommended (Samanta et al, 2006, 2007, 2010, 2011) for dyeing jute and cotton fabric using harda (as mordant assistant cum catcher) and aluminium sulphate (metallic mordant) without intermediate drying after mordanting, facilitating wet on wet dyeing in jigger. The myrobolan (harda) powder is soaked in water (1:10 volume) for overnight (12h) at room temperature to obtain the swelled myrobolan gel. This gel is then mixed with a known volume of water and heated at 80°C for 30 min. The solution is then cooled and filtered in a 60 mesh nylon cloth and the filtrate is used as final harda solution (10-40%) for 1st mordanting, using MLR of 1:20 (for dyed in bath) or 1:5 (for jigger). Pre-wetted conventional H₂O₂ bleached jute and cotton fabrics are separately treated with the harda solution in separate bath initially at 40-50°C and then the temperature is raised to 80°C. The mordanting is continued for 30 min. After the harda mordanting, fabric samples may be subjected to immediate wet on wet dyeing or may be dried in air without washing for storing purpose. Second mordanting is carried out using 10-40% of any one of the chemical mordants, (e.g., aluminium sulphate, potash alum, ferrous sulphate, stannous chloride and EDTA) at 80°C for 30 min using ML ratio of 1:20 (for dyed in bath) or 1:5 (for jigger). After the mordanting, the fabric samples may be finally dried in air without washing for storing purpose to make them ready for subsequent natural dyeing or may be subjected to immediate wet on wet dyeing without drying.

9. Principle of natural dyeing

Most of the natural dyes have no substantivity on cellulose or other textile fibres without the use of a mordant. The majority of natural dyes need a mordanting chemical (preferably metal salt or suitably coordinating complex forming agents) to create an affinity between the fibre and dye or the pigment molecules of natural colourant. These metallic salts as mordant

form metal complexes with the fibres and the dyes. After mordanting, the metal salts anchoring to the fibres, attracts the dye/organic pigment molecules to be anchored to the fibres and finally creates the bridging link between the dye molecules and the fibre by forming coordinating complexes. Aluminium sulphate or other metallic mordants anchored to any fibre, chemically combine with certain mordantable functional groups present in the natural dyes and bound by coordinated/covalent bonds or hydrogen bonds and other interactional forces as shown below:



Mechanism of fixation of natural dyes through mordants

Thus, for proper fixation of natural dyes on any textile fibre, mordanting is essential in most of the cases. The said mordanting can be accomplished either before dyeing (pre-mordanting), or during dyeing (simultaneous mordanting) or after dyeing (post-mordanting).

9.1 Conventional methods of natural dyeing

Dyeing can be carried out in an alkaline bath, acidic bath or in a neutral bath. There are various reports available on different methods of mordanting on different fibers such as cellulosic, protenic and synthetic for dyeing with different natural dyes. Dyeing of cotton and silk with babool, tesu, manjistha, heena, indigo, mariegold etc is reported (Gulrajani et al, 1992; Saxena et al, 2001; Vankar et al, 2001; Nanda et al 2001; Patel & Agarwal, 2001). Various kinds of shades like black to brown, green to yellow to orange, etc can be obtained by application of different mordants.

9.1.1 Preparation of cotton fabric and dyeing with natural dyes

Cotton is purely cellulosic fibre and found throughout the world with many varieties and qualities. In general, cotton fibre based textiles is desized (for woven fabric only), scoured and bleached as preparatory process before dyeing with synthetic dyes. In many places of world, the age-old process followed in preparing a cotton cloth and its dyeing with natural dyes followed by artisan/cottage level dyers is given below (Mohanty et al, 1987):-

- a. Dugging - The cloth is soaked for one night in a solution of water and fresh dung.
- b. Washing - Next morning, cloth is thoroughly washed, rinsed and water sprinkling is continued over the cloth at short interval until evening, then it is finally washed and dried

- c. Steaming- Then the cloth is steamed for one night in an ordinary Khumb or washerman's steaming pot
- d. Steeping in alkaline lye- The cloth is soaked in a mixture of water, oil [castor oil or gingili oil], and alkali (sodium carbonate or soda known as sajkar or papadkhar).
- e. Rinsing- Cloth is then again rinsed thoroughly and spread out to dry.
- f. The last two processes are repeated for several days, the details varied in different localities, but generally from 3 to 7 days. In specific case, the cloth is kept in the solution for sometimes, and then taken out, rinsed and dried twice daily.
- g. Washing- The cloth is then finally washed in clean water, but not so thoroughly as to remove the whole of the oil, and finally dried in air under the sun.
- h. Galling-The cloth is then soaked in a solution of harda (haritaki) or myrobolan (Terminala chebula) extracts. Behda or bahedas (terminala belerica) is also used instead of harda. The period during which the cloth is kept in the harda extract varied in different places but it is continued until the fabric assume a yellowish tint.
- i. Drying- The cloth is spread or wrung out for drying.
- j. Mordanting- The cloth is then pre-mordanted by dipping it in a solution of potash alum and water. In some places, gum or a paste of tamarind seed (tamarind kernel powder) is added to make it sticky. In some parts of kutch, fuller's earth is also used by some dyers. The cloth is thus ready for subsequent dyeing.
- k. Dyeing- For dyeing the cloth is generally boiled with an aqueous extracted solution of the natural dye until all the colouring matter is absorbed by the cloth.
- l. Further dunging- In some places, the cloth is further soaked in dung for one night and batched before final wash and dry.
- m. Drying- The dyed fabric is next washed and spread out to dry gradually in air under the sun. Water is sprinkled at certain interval over the cloth, so as to brighten the colour, this process is continued for 2-4 days.
- n. Finishing- If required, the cloth is finally starched by dipping it in a paste of rice or wheat flour, or in a solution of babool gum and then dried.

However, now a days, many small scale dyers/export oriented units follow much shorter economical and standard recipe based optimized processes for natural dyeing of cotton yarns/fabrics. Before natural dyeing usual method of desizing (acid bath), scouring (soap & soda) and H₂O₂ bleaching are followed. Well prepared cotton textiles are then mordanted (single or double mordanting using harda and aluminium sulphate individually or in combination) before subjecting to dyeing with aqueous extract of selective natural dyes at standardized condition of process variables of dyeing. For e.g., the dyeing conditions may be as follows : dyeing time, 30 -120 minutes (depending on shades); dyeing temperature, 70-100°C; material to liquor ratio, 1:20 -1:30; concentration of natural dye, 10-50% (owm) or more; common salt concentration, 5-20g/L and pH, 10-12. In each case after the dyeing is over, the dyed samples are repeatedly washed with hot and cold water and then finally, the dyed samples are subjected to soaping with 2g/L soap solution at 60 °C for 15 min, followed by repeated water wash and line dried. For improving its wash fastness, treatment with eco-friendly cationic dye fixing agent is advisable.

9.1.2 Dyeing process for natural colouration of wool and silk fibre

Wool and silk are natural protein fibres and are available in wide variety having varied qualities. Both the fibres has complex chemical structure and very much susceptible to alkali attack (at pH >9). Hence, dyeing of these fibres with natural colours needs special care to

avoid fibre damage by alkaline pH. Moreover, both wool and silk contain both amino and carboxylic functional groups. While, unlike silk, wool contains equal number of amino and carboxylic groups held together as salt linkages which bridge the main peptide chains. Therefore, in aqueous solution, wool carries no net charge. However, silk fibre has a slightly cationic character with the isoelectric point at about pH 5.0. Also, unlike wool fibre, silk is less sensitive to temperature. Therefore, selection of mordants, conditions of mordanting, pH and other conditions for dyeing, necessary cares are to be taken for colouration of these textile fibres for mordanting and application of natural dyes.

Wool and silk fibre based textiles can be dyed with different natural colours mostly through pre-mordanting or post mordanting system. Mordanting is done with tannin rich natural source chemicals like harda, gall nut etc and/or metal salts like, alum, aluminium sulphate, ferrous sulphate etc. Depending on shade depth requirement, mordant and dye concentration are to be determined. Dyeing conditions for a particular fibre-mordant-dye system need to be optimized by study of dyeing process variables before bulk dyeing.

In pre-mordanting system, these animal fibre based textiles are selectively mordanted (single or sequential double mordanted) with 5-20% (owm) mordant at 80-90°C for about 30-40 minutes having ML ratio 1:5-1:20 and can be taken for subsequent dyeing generally without washing. The pre-mordanted samples are entered in the dye bath (generally acidic dye bath) at 50-60°C and ML ratio 1:20, raise temperature upto the optimum dyeing temperature (may be 90°C) and dyeing is then continued for further 30 to 40 minutes followed by thorough rinsing, soaping and washing. However, in post mordanting system of applying natural colour on wool and silk textiles, dyeing is done at optimum dyeing condition and the dyed samples are dip into a mordant bath containing mainly 1-2% metal salt (owm) for true colour development followed by rinsing, soaping and thorough washing.

9.1.3 Dyeing process for natural colouration of jute and other lignocellulosic fibres

Application of natural colours on ligno-cellulosic fibres through double pre-mordanting system is found to be the best method, e.g., 10-20% harda treatment followed by 10-20% alum treatment or aluminium sulphate treatment is best suited mordanting system for subsequent dyeing of lingo-cellulosic fibre based textiles with different natural colours/dyes. Conventionally bleached and double pre-mordanted jute and linen textiles without wash, is dyed with tesu, madder, catechu, pomegranate rind, babool, jackfruit wood, haldi, marie gold, red sandal wood etc individually and in mixtures. Most of the above said natural dyes are applied in alkaline pH like 11-12 at higher temperature like 80-90°C having ML ratio 1:20 for 60 to 90 minutes. After dyeing, the dyed samples are washed and soaping is carried out at 60°C for 15 minutes. For getting higher fastness to wash and light, the samples can be further treated with 2% cationic dye fixing agents and/or 1% benzotriazole.

9.1.4 Dyeing process for natural colouration of synthetic fibres

Different synthetic fibres like nylon, polyester etc are dyed with various source natural dyes/colourants like onion skin extract, babool bark extract, henna etc. through exhaust, HT-HP and padding methods (cold-pad-batch) with or without mordanting. Mordanting facilitates to get wide range of shades from the same source of natural dye as per requirement by variation of mordant chemicals as well as mordanting techniques. In case of dyeing synthetic fibres, dyeing is carried out at acidic pH and HT-HP dyeing technique

results an overall best dyeing performance in terms of colour strength and fastness properties provided the natural colourants are stable at that high temperature employed for dyeing. Also energy consumption is higher in case of HT-HP dyeing method than exhaust method as well as cold-pad-batch method of dyeing.

Reports are available (Lokhande et al, 1998; Lokhande and Dorugade, 1999) for nylon is dyed with three different natural dyes using various mordants by two different techniques (open bath and high temperature high pressure dyeing methods), of which HT-HP dyeing is found better as compared to open bath. Application of babool bark extract on nylon substrate by cold-pad-batch and pad-dry-steam technique of dyeing can be considered as an effective eco-option and can be commercialized. HT-HP method is used for dyeing polyester fibre with pomegranate rind, catechu, nova red and turmeric (Bhattacharya and Lohiya, 2002).

9.2 Non-conventional dyeing methods

Nanotechnology is increasingly attracting worldwide attention because it is widely perceived as offering huge potential in a wide range of end uses. The unique and new properties of nanomaterials have attracted not only scientists and researchers but also businesses, due to their huge economical potential. One possible application is to directly employ pigment nanoparticles in textile coloration. Such an approach could be achieved if the nanoparticles can be reduced to a small enough size and the particles can be dispersed well to avoid aggregation of the nanoparticles in dye baths. Exhaust dyeing of cationized cotton with nanoscale pigment dispersion has recently been achieved and the results indicated that the dyeings obtained have better soft handle and more brilliant shade with reduced pigment requirement than those obtained with a conventional pigment dispersion (Fang et al, 2005).

Ultrasonic energized dyeing conditions for neem leaves gives better dye uptake, uniform dyeing, better light and wash fastness on cotton fabric (Senthikumar et al, 2002). Unconventional natural dyeing of cotton with sappan wood by ultrasound energy as well as new methods using microwave and sonicator for application of natural dye from alkanet root bark on cotton and dyeing of cotton fabrics with tulsi leaves extract by use of ultrasonic energy dyeing are also reported (Ghorpade et al, 200; Tiwari et al, 2000a & 2000b).

The application of supercritical carbon dioxide ($scCO_2$) in the textile industry has recently become an alternative technology for developing a more environmentally friendly coloration process. $scCO_2$ coloration technology has the potential to overcome several environmental and technical issues in many commercial textile applications such as yarn preparation, coloration and finishing. $scCO_2$ represent a potentially unique media for either transporting chemical into or out of a polymeric substrate, because of their thermo-physical and transport properties. Supercritical fluids exhibit gas-like viscosities and diffusivities and liquid-like densities. Additionally, carbon dioxide is nontoxic, non-flammable, environmentally friendly, and chemically inert under many conditions; however, its production is remained to be cost-effective. The dissolving power of $scCO_2$ for disperse dyes and its use as the transport media for coloration polyester is studied from all theoretical aspects at DTNW in Krefeld, Germany. Studies have revealed that the presence of intramolecular hydrogen bonds and/or the hydrophobicity of dye molecule are positive factors for better solubility in supercritical carbon dioxide, as indicated from its improved dye-uptake (Shakra et al, 1999 & 2000)

The use of $scCO_2$ as a fluid medium for coloration of textile fibers, especially polyester, has been examined. This technology has become so promising that it has provided new

opportunities to develop suitable dyes for this medium. The coloration is conducted in a stainless steel high pressure apparatus. Process and equipment are developed for textile dyeing in supercritical carbon dioxide (Kraan, 2007). A technical-scale, 100-L dyeing machine is designed and built for polyester beam dyeing in scCO_2 at 300 bar.

10. Physico-chemical studies on dyeing process variables and dyeing kinetics

The natural dyes have a variable chemical composition, which is influenced by a number of factors, out of which the most important are: the vegetal part of the plant where the extract is obtained from, its place and growing conditions, harvesting period, extraction operation and application or technological process followed. Many workers (Gupta, 1999) have reported some of the most significant experimental results, laboratory trials regarding techniques and best parameters for extraction and application of natural dyes, i.e. observations on varying extraction parameters, such as: extraction temperature, extraction time, extraction solvent-vegetal material ratio, type of solvent and observations on varying mordanting and dyeing parameters. However, most of such studies are concentrated on wool and silk.

The effects of dye-extraction medium, optimum concentrations of dye source material, extraction time, dyeing time, mordant concentration and methods of mordanting on silk dyed with natural dyes has been reported (Grover et al, 2005; Dixit & Jahan, 2005; Dumitrescu et al, 2005; Srivastava et al, 2006; Das et al, 2005; Agarwal et al, 1992; Bansal & Sood, 2001; Sati et al, 2003; Rose et al, 2005; Maulik & Bhowmik, 2006; Siddiqui et al, 2006). The acidic media exhibited maximum percent absorption for jatropa, lantana, hamelia and euphorbia dye, while kilmora and walnut showed good results in alkaline medium. The result obtained from different experiments lead to the optimization of a standard recipe for particular dye-mordant-fibre combination. The optimum concentration of beet sugar (Mathur et al, 2003) colourant for dyeing wool is found to be 0.03g per g of wool at pH 4.5 and temperature 97.5°C. Dyeing of wool under the optimum (Mathur et al, 2001) condition pH 4.5, colourant concentration-0.05g per gram of wool; time-60 min and treatment temperature- 97.5°C shows very good light and wash fastness properties without deteriorating the quality of wool. Optimum dyeing technique for colouration of wool by determining the optimum wavelength, dye material concentration, extraction time, dyeing time, pH, concentration of mordant etc. helps to standardize the dyeing process (Srivastava et al, 2006). Colouring component of tea shows highest affinity for both wool and silk at pH 2 to 4 in presence and absence of ferrous sulphate and aluminium sulphate as mordants (Das et al, 2005). Optimisation of dyeing process variables for wool with natural dyes obtained from turmeric has been studied and reported (Agarwal et al, 1992). The optimum conditions for development of vegetable dye on cotton from eupatorium leaves are studied and reported (Bansal & Sood, 2001). The optimization of wool by using rhododendron arboretum as a natural dye source is reported (Sati et al, 2003). The effect of process variables on colour yield and colour fastness properties for application of selective natural dyes for different textiles are also studied and reported (Rose et al, 2005; Maulik & Bhowmik, 2006; Siddiqui et al, 2006).

The dyeing absorption isotherm for wool, human hair, silk, nylon and polyester is found to be linear indicating a partition mechanism of dyeing for application of juglone as natural dye (Gupta & Gulrajani, 1993). The slope of isotherms increases with the increasing

temperature in all cases. ΔH and ΔS values are positive for all the dyeings. The apparent diffusion coefficient is highest for wool and lowest for silk. For investigation of the conditions of extraction and application of african mariegold on silk yarn, optimum conditions are found to be 60 minutes dye extraction time, 30 minutes mordanting, 30 minutes dyeing using mixtures of 5% potash alum, 1% potassium dichromate and 1% copper sulphate as mordants (Mahale et al, 1999). Studies of dyeing absorption isotherm, heat of dyeing, free energy and entropy of dyeing for red sandal wood (Samanta et al, 2006) and jackfruit wood (Samanta & Agarwal, 2008) reveals that both the dyeing process follows a linear Nernst absorption isotherm. An adsorption and thermodynamic study of lac dyeing on cotton pre-treated with chitosan showed Langmuir isotherm (Rattanaphani et al, 2007). The colour can vary significantly for indigo dyeing on denim yarns as the result of the variation of parameters (Kin et al, 2007).

11. Compatibility of mixture of selective natural dyes

Newer shades can be achieved by applying mixture of natural dyes. For the use of mixture of natural dyes, the dyers must know whether the natural dyes are compatible with each other or not. For test of compatibility of a pair of natural dyes, bleached and pre-mordanted samples are dyed in two different sets of progressive depth of shade of binary mixture of natural dyes as follows:-

Bleached and pre-mordanted textiles are dyed with the specific binary mixtures of natural dye pair. The dyeing is started at 40°C and the temperature is gradually raised to 100°C taking total time of 60 min (approximately) to raise this temperature at a heating rate of around 1°C/min, using precision temperature controller open bath Laboratory beaker-dyeing machine.

In set I, (progressive depth of shade developed by varying dyeing time and temperature profile during dyeing), for 1% shade with binary mixture (50:50) of a pair of dyes, pre-mordanted samples are separately dyed for different dyeing period (10, 20, 30, 40, 50 and 60 min), by withdrawing separately dyed samples from the dye bath at the intervals of 10 min from 50°C onwards maintaining the heating rate of around 1°C/min. The penultimate sample is taken out after 50-60 min at 90°C and the last one at the end of the dyeing carried out for 60 min at 100°C.

In set II (progressive depth of shade developed by varying total concentrations of dye mixture using 20-100 parts of 1% shade depth using purified natural dye-stuff colourants) for a pair of binary mixture dyes, pre-mordanted samples are separately dyed at increment of twenty percentage points by applying 20 -100 parts of 1% dye (on weight of fabric) for each pair of natural dye-mixture taken in equal proportion (50:50) at 100°C for 60 min. For both Set I and Set II, after dyeing, all the dyed samples are subjected to normal washing, soaping, and rinsing before final air-drying. The corresponding surface colour strength (K/S value) and the differences in the CIELAB coordinates namely, ΔL , Δa , Δb and ΔC for all dyed fabric samples for Set I and II obtained indicate for the samples dyed with using purified natural dyes, the colour yield (K/S), lightness/darkness (ΔL), redness/greenness (Δa), yellowness/blueness (Δb) and differences in saturation/chroma (ΔC) values with respect to the standard un-dyed sample, which are measured and obtained from separate measurement of the same using the reflectance spectrophotometer and associated software and computer. Plots of K/S vs ΔL and/or ΔC vs ΔL , i.e., two sets of curves obtained for the said two sets (Set-I & Set-II) of dyed samples indicate the nature of compatibility by

closeness of the pattern of the two sets of curves (Konar, 2011). However, another easy method of Relative Compatibility Rating (RCR) method (Samanta et al, 2009) has been established based on differences between lowest and highest colour difference index (CDI) values [$CDI = (\Delta E \times \Delta H) / (\Delta C \times MI)$] for a binary mixture of natural dyes dyed in different proportions with fixed shade % at standardized dyeing conditions.

12. Colour fastness properties of natural dyes

Colour fastness is the resistance of a material to change in any of its colour characteristics or extent of transfer of its colourants to adjacent white materials in touch or both for different environmental and use conditions or treatments like washing, dry cleaning etc or exposure to different agency heat, light etc. Fading means changes in the colour with or without loss of depth of shade for exposure to particular environment/agency/treatments either by lightening or darkening of the shades. Bleeding is the transfer of colour to a secondary material in contact accompanying white fibre material of similar/dissimilar nature. The colour fastness is usually rated either by loss of depth of colour/ colour change in original sample or it is often expressed by staining scale meaning that the accompanying material gets tinted/stained by the colour of the original fabric, when the accompanying white fabrics of similar/dissimilar nature are either in touch/ made to touch by some means of test procedure/protocol.

12.1 Light fastness

An extensive work has been carried out to improve the light fastness properties of natural dyed textiles. A comprehensive review on different attempts taken for improving colour fastness properties of dyes on different textile fibres by different means is reported (Cook, 1982). The said review includes tannin-related after-treatments for improving the wash fastness and light fastness of mordantable dyes on cotton; some of these treatments might be applicable to selective/specific natural dyes.

Most of the natural dyes have poor light stability (as compared to that of the best synthetic dyes), and hence the colours in museum textile are often different from their original colours. The relative light stability of a range of dyes has been reviewed (Padfield & Landi, 1966) along with studies involving change in qualitative fashion. These changes in colour are studied quantitatively (Duff et al, 1977) where it is expressed the changes in terms of the Munsell scale and also in CIE colour parameters. Wool dyed with nine natural dyes is exposed in Microscal MBTF fading lamp. The fastness ratings are similar to those found earlier in day light fading. After rating by the blue wool standards for light fastness rating, yellow dyes (old fustic, persian berries) shows poor light fastness between 1-2; red colours like cochineal (tin mordant), alizarin (alum and tin mordant), lac (tin mordant) shows better light fastness between 3-4; indigo shows light fastness 3-4 or 5-6 (depending on the mordant); and logwood black (chrome mordant) shows light fastness 4-5 or 6-7 (other mordants). It is also reported the effects of chemical structure of natural dyes on light fastness and other colour fastness properties (Gupta, 1999a & 1999b).

A large proportion of natural dyes are, of course, mordant dyes. There is strong influence on nature, type and concentrations of mordants on wash and light fastness grades. The influences of different mordants are found to play important role in fading of 18 yellow natural dyes (Crews, 1982). Where wool dyed with different natural dyes specimens are exposed to a xenon arc lamp for assessing their light fastness upto 8 AATCC Fading Units

equivalent to BS-8B Blue wool standards. The corresponding colors changes after exposure to xenon arc lamp are also assessed in each case.

Turmeric, fustic and marigold dyes faded significantly more than any of the other yellow dyes. However, use of tin and alum mordants resulted in significantly more fading than the same for use of chrome, iron, or copper mordant. Thus the type of mordant is found to be more important than the dye itself in determining the light fastness of natural colored textiles.

Natural dyes that may have been used in the traditional Scottish textile industry have been described (Grierson, 1984) that the light fastness of such dyes on wool has been compared with those of dyeing with 'imported' dyes to similar shades (Duff et al, 1985; Grierson et al, 1985), again using Microscal fading MBTF lamp.

Numerous attempts (Samanta et al, 2006, 2010 & 2011; Hofenk, 1983; Oda, 2001; Cristea & Vilarem, 2006; Lee, 2001; Micheal & Zaher, 2005; Gupta, 2001) has been made to improve the light fastness of different textiles fabric dyed with natural dyes which include the effects of various additives on the photofading of carthamin in cellulose acetate film, critical examination of fading process of natural dyes with a view to determining the original colours of faded textile etc. The rate of photofading is remarkably suppressed in the presence of nickel hydroxy-arylsulphonates, while the addition of UV absorbers afforded little retardation in the rate of fading.

12.2 Wash fastness

With a view to examine and improving wash fastness (Duff et al, 1977), tests are carried out under standard condition (50°C) and also at 20°C with a washing formulation used in conservation work for restoration of old textiles. Some dyes undergo marked changes in hue on washing, shown to be attributed to even small amounts of alkali in washing mixtures, high-lighting the necessity of knowing the pH of alkaline solutions used for cleaning of textiles dyed with natural dyes. As a general rule, natural dyes (on wool) have only moderate wash fastness as assessed by the ISO 2 test. However, logwood and indigo dyes exhibit better fastness when applied to different textiles. The nature of detergent solution suitable for conservation of natural coloured art work has been examined (Hofenk, 1983). A liquor containing 1g/l of sodium polyphosphate is found to be best resulting marginal changes in hue with natural dyes applied on wool or silk (Duff et al, 1977). The small increase in cleaning efficiency attributable to the alkali must be balanced against possible colour change in the natural dyes, apart from possible damage to the protein fibre under alkaline conditions.

In the ISO 2 test, the fastness of the indigo and logwood is superior to that of the native natural dyeing such as privet berries and water lily root respectively, but in the comparison of native and imported yellow, reds, red/purples, greens and browns, there is little difference between the two groups (Duff et al, 1977). It is found from a recent report that treatment with 2% CTAB or sandofix-HCF improve the wash fastness to nearly 1 unit and treatment with 1% benzotriazole improved the lightfastness of dyed jute textiles nearly half to one unit (Samanta et al, 2006; 2007; 2010 & 2011; Samanta & Agarwal, 2008)

12.3 Rubfastness

Rub fastness of most of the natural dyes have been found to be moderate to good and dose not require any after treatment. Jackfruit wood, manjistha, red sandal wood, babool,

mariegold etc have good rubfastness (Samanta et al, 2006; 2007; 2010 & 2011). Good rub fastness is seen for mariegold on cotton, silk and wool (Sarkar et al, 2005; Sarkar, 2006). Good rub fastness (dry and wet rubfastness) is reported for silk dyed with acalyphya and other natural dyes (Mahale et al, 1999; 2002 & 2003). Cutch and ratanjot shows moderate to good dry rub fastness but the wet rub fastness is found to be average (Khan et al, 2003 & 2006).

13. Concluding remark

Most of the natural dyes/ colour are eco-safe, except a few. Some of the natural colours are not only eco-safe, but also has added value for its medicinal effects on skin and are more than skin friendly. Textile dyers must know the chemistry of these natural colours and its added advantages of medicinal; values. Use of suitable binary or ternary mixtures of similar or compatible natural dyes for colouring natural eco-friendly textiles in variety of soothing / uncommon shades with eco-friendly mordants and finishing agents are the most desirable product of the customers for future. The non-reproducibility and poor colour fastness etc, have been partly solved by many researchers' continuous efforts in this endeavour. So, a textile dyer must know the effects of variability for extraction, mordanting and dyeing and should follow only the standardized recipe for selection fibre-mordant-natural dye system to get reproducible colour yield and colour matching besides to follow different eco-friendly ways to improve colour fastness to a possible extent. This chapter is a highlight of all these efforts towards popularizing natural dyeing not only in small/cottage dyers but also textile yarn/fabrics industrially using common dyeing machine. Some of the study mentioned above explained this clearly. So, natural dyeing/colouration of textiles by industrial processes in large scale dyeing unit is now a reality in the textile market of eco-friendly textiles.

14. References

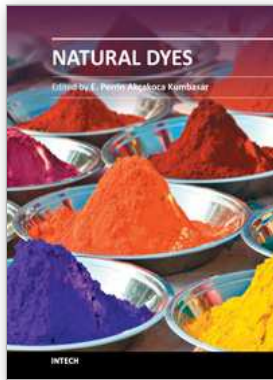
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Textile materials without colorants cannot be imagined and according to archaeological evidence dyeing has been widely used for over 5000 years. With the development of chemical industry all finishing processes of textile materials are developing continuously and, ecological and sustainable production methods are very important nowadays. In this book you can find the results about the latest researches on natural dyeing.

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