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Plant based natural dyes and mordnats: A Review

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ABSTRACT

Natural dyes, which were pushed during the last sixty years into the background by synthetic dyes, are recently again becoming object of consumer interests. This is due to the awareness of possible risks during production of synthetic dyes which involve use of petrochemical based raw materials and the violent chemical reactions for their synthesis. The manufacture of such dyes is energy intensive with adverse impact on environment adding to its pollution. Many of these dyes, especially the azo- based ones, are found to be carcinogenic. In this background, a brief review of natural colourant from plant sources, their classification, chemical constituents responsible for producing different colours, its activities and effect of different mordants on the hue is discussed. Different classes of mordants employed for fixation of natural colouration on textiles substrated, its mechanism and plant sources are also discussed.

Key words: Natural dyes, Natural mordants, Textiles, Sources

INTRODUCTION

Natural colourants covers all the dyes and pigments derived from plants, insects and minerals, i.e. derived from natural resources. The dyeing with natural colourants was one of the oldest techniques practiced by the ancient civilization people. This is evident from the Ajanta, Ellora, Sithannavasal, Mithila wall paintings (mural art)[1] and Egyptian pyramids which had been exclusively done with natural colourants. Moreover, at the Spanish caves of Altamira and Elcatillo and French Pyrene caves of Niaux [2], mineral earths and other inorganic pigments like ferric oxide for red, ferrous oxide for yellow and copper carbonate for blue have been used extensively in their mural paintings. Vedas [3] also mentioned red, yellow, blue, black and white as main dyeing colours and expressed that, the ancient craftsmen dyed blue form indigo, yellow from turmeric and saffron, brown from cutch and red from lac, safflower and madder. Thus, natural dyes have been an integral part of human life since time immemorial.

The invention of the first synthetic dyes by William Henry Perkin in 1856 changed the situation and later, the synthetic dyes received faster acceptability due to a wide range of applications in various fields like food [4], cosmetic [5], photodynamic therapy [6], non-linear optical activity [7, 8, 9] and more importantly in textile industries [10, 11] due to ease in dyeing, and overall cost factor. But, during the last few decades, the use of synthetic dyes is gradually decreasing due to an increased environmental awareness and harmful effects because of either toxicity or their non-biodegradable nature. In addition to above, some serious health hazards like allergic and, carcinogenicity are associated with the synthetic dyes. As a result, recently a ban has been imposed all over the world including European Economic Community (EEC), Germany, USA and India on the use of some synthetic dyes. The advantages of using natural colourants are manifolds as they are eco-friendly, safe for body contact, unsophisticated and harmonised with nature [12], obtained from renewable sources and also their preparation involves a minimum possibility of chemical reactions. The shades produced by natural dyes/colourants are usually soft, lustrous and soothing to the human eye. Generally natural dyes do not cause health hazards; on the contrary, they sometimes act as a health-care substance. Furthermore, the use of natural dyes offers no disposal problems. However, the natural dyes have their own limitations like availability, colour yield, stability, and complexity of dyeing process and reproduction of shades. Furthermore, natural dyes cannot entirely replace synthetic dyes, but they have their own place in the market.

India is richly endowed with vast variety of natural flora. It is estimated that, in India there are some 500 varieties of plants that can yield natural colours [13, 14]. The art and craft of producing natural dyed textile is being practiced in many villages by expert's craftsmen in the country. Natural dyes, when used by them have many limitations of fastness and brilliancy of shade. However, when used along with metallic mordants they produce bright and fast colours. The use of metallic mordants is not always eco-friendly. Therefore, instead of using violent technology for producing colours one can use natural mordants a eco-friendly way to achieve almost similar results. Keeping this mind, an attempt has been made in this paper here to give scientific overview on natural colourants and mordants from plants, their classification, list of sources and its application for textile colouration.

Classifications of Natural Dyes

Natural Colourants are classified in various ways broadly depending on chemical functional groups (Structure) and their Hue which are discussed below.

Based on Structure

Most commonly available natural colourants falling under this system of classification includes indigoids, anthraquinones, alpha napthoqinones, flavones, dihydropyrans, anthocyanidin and carotenoids [15].

Indigoid dyes

This class is the oldest dye known to the world since about 400 years. The Egyptian mummies burried in tombs were wrapped in cloths dyed with Indigo. Earlier, Indigo was used as a black dye till its property to dye blue was discovered. The main colouring principle is a glucoside of **Indican (Fig.1)**, occurs in the leaves of *Indigofera tinctoria* (native to Asia) and several other species like, dyer's woad *Isatis tinctoria* [16] (indigenous to Europe), *Polygonum tinctorium* [17], Eupatorium leave[18], *Wrightia tinctoria* and *Mercurialis leiocarpa* [19]. In India, there are about 54 species of Indigofera available of which 10–12 species yield dye and only 4 of them have been commercialised. The Indigo and Indigoids are vat dyes applicable to both cellulose and protein fibres. Besides this, Indigo is used in medicine [20] as anticancer agent, astringent, anti-inflammatory and antiulcerous.

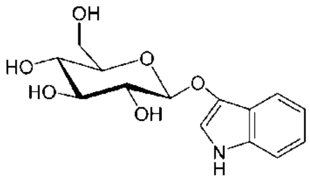


Fig. 1: Indican

Anthraquinone dyes

Quinonoids are fused benzenoid ring systems (three rings in case of anthraquinone and two rings in case of naphthaquinones) posses enough conjugation to achieve colour. Almost all the red natural dyes are based on the anthraquinoid structure having both plant and mineral origin. *Rubia tinctorium* and *R. cordifolia*, used for dyeing textiles since 2000 B.C.), Alizarin **(Fig. 2)** (is the first natural dye produced synthetically in 1869)[21] Mungistin **(Fig. 3)** and Purpurin **(Fig. 4)** (dyes cotton Turkey red with alum), Emodin **(Fig. 5)** from Persian berries and the insect dye cochineal or carminic acid **(Fig. 7)** from *Coccus cacti* (produce brilliant scarlet on tin and alum mordanted wool and silk. Kermes or kermisic acid **(Fig. 7)** from female insect *Coccus ilicis* is used to dye silk, tassar and wool with reddish tones [22]. These are generally mordant dyes.

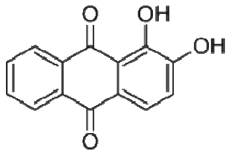


Fig. 2: Alizarin

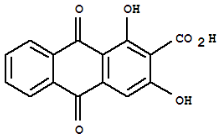


Fig. 3: Munjistin

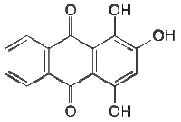


Fig. 4: Purpurin

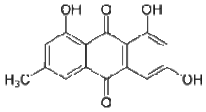


Fig. 5: Emodin

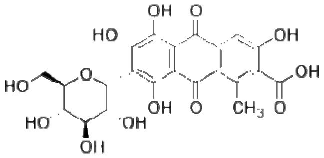


Fig. 6: Carminic acid

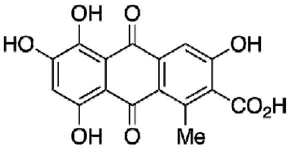


Fig. 7: Kermisic acid

Alphanaphthoquinones

Typical example of this class is lawsone (henna) **(Fig.8)**, cultivated mainly in India and Egypt. Another similar dye is juglone **(Fig. 9)**, obtained from the shells of unripe walnuts. These dyes are generally disperse dyes and give shades of orange.

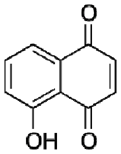


Fig. 8: Juglone

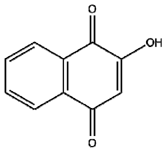


Fig. 9: Lawsone

Flavonoids

Flavonoids are aromatic oxygen containing heterocyclic pigments (in latin '*flavus*'means yellow) specially located in the epidermal cells of plant parts and are chemically known as 2-phenyl-1,4-benzopyrone systems. These are one of the most widespread groups of natural constituents which are important to man not only because they contribute to plant colour but also because of their physiological activities. They yield yellow dyes which can be classified under flavones, isoflavones, aurones and chalcones. Most of the natural yellows are derivatives of hydroxyl and methoxy substituted flavones and isoflavones. Common example is weld (containing luteolin pigment **(Fig. 10)**) giving brilliant and fast colours on both wool and silk. Some of the other pigments are Fisetin, Isohamnetin, Quercetin **(Figs.11-13)** as shown below.

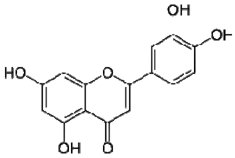


Fig. 10: Luteolin

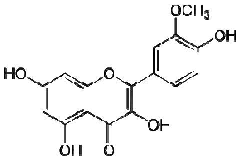


Fig. 12: Isohamnetin

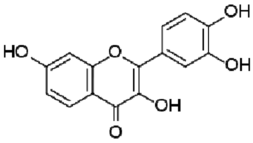


Fig. 11: Fisetin

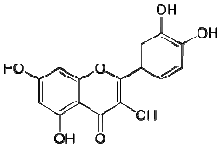


Fig. 13: Quercetin

Di-hydropyrans

Closely related in chemical structure to the flavones are substituted di- hydropyrans, viz. haematin and its leuco form, haematoxylin. These are important natural dyes for dark shades on silk, wool and cotton. Logwood, brazil wood and sappan-wood are the common example.

Anthocyanidins

Anthocyanins (in Greek, antho means flower, kyanos means blue) are glycosides of 2-phenyl benzopyrillium salts (flavilium ionic form is stable out of all other possible forms), intensely coloured sap-soluble plant pigments responsible for different colours in higher plants. These are probably the best-known natural food colourants since they are widely distributed in plant kingdom and their colour range from red of apples, to blue of grapes, to purple of brinjals. The large variation in the colours is attributed to the corresponding number of hydroxyl groups, the degree of methoxylation, the nature and number of monosaccharides attached to the cation and their position of attachment, the nature and number of carboxylic acids attached to the monosaccharides[23], the acylated derivatives of monosaccharides and the pH of biological environment (e.g. cyanin is red under acidic conditions, violet at neutral and blue under basic conditions). The naturally occurring member of this class includes carajurin as shown in **Fig. 14**, a direct orange dye for wool and cotton. It is obtained from the leaves of *Bignonia chica*.

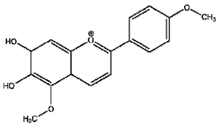


Fig. 14: Carajurin

Carotenoids: Linearly conjugated polyene tetraterpenes are represented by carotenoids which are widely distributed in plants and animals. The carotenoids are brightly coloured pigments in which the highly conjugated -electron system confers different colours like yellow, orange and red to the molecule. The name carotene is derived from the orange pigment found in carrots separated by Wackenroder (1831)[24]. There are two types of carotenoids present in nature, carotene (e.g. β-carotene **(Fig. 15)** from *Daucus carota*) and xanthophylls (e.g. lutein **(Fig. 16)** from *Tagetes erecta*)[25].

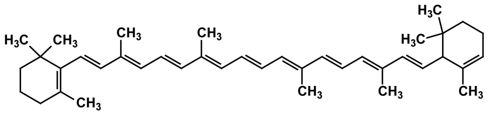


Fig.15: β-carotene

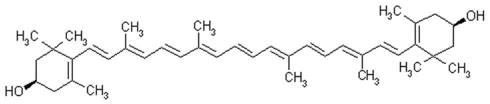


Fig.16: Lutein

Based on Hue

In the Colour Index, the dyes are classified according to chemical constitution as well as major application classes. Within application class, the dyes are arranged according to hues. Natural dyes form a separate section. The no. of dyes in each hue are given below. Some dyes produce more than one hue.

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

C.I. 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	13.0
Black	6	6.5

Of the 92 natural dyes listed in Colour Index, chemical structure of 67 dyes is disclosed. Many dyes have more than one compound and some dyes have identical structures[26]. About more than 100 vegetable origin dyes, colouring matter derived from root, leaf, bark, trunk or fruit of plants, list of the important sources are given in **Table-2.**

Extraction of plant natural colourants

Natural Dyes cannot be used directly from their renewable sources. Using raw materials for dyeing has many limitations. Safe and cheap extraction of main colouring component is most important without affecting the extraction conditions and avoiding any contamination in various extraction techniques. Several extraction methodologies for natural dye that comply with both consumer preference and regulatory control and that are cost effective are becoming more popular. Some of the techniques of extractions of natural dyes [76] are

- Simple Aqueous Methods
- Complicated Solvent Systems
- Supercritical Fluid Extraction
- Ultrasonic Extraction

Table 2: List of natural dyes source and their applications [27-75]

Species (Family Name)	Common name	Part used	Colour obtained	Colour Application
Acacia catechu (Mimosaceae)	Cutch tree, Khair	Heart wood	Red	Textile (shipsails, mailbags), Calico printing
Aegle marmelos (Rutaceae)	Bael, Brel tree	Fruit	Yellow	Food colourant
Alcea rosea (Malvaceae)	Hollyhock	Flower	Red	Food colourant
Alkanna tinctoria (Boraginaceae)	Dyer's alkanet	Root	Purple	Pharmaceutical, Colourant
Allium cepa (Liliaceae)	Onion, Piyaz	Skin	Orange	Textile dyeing
Alnus sieboldiana (Betulaceae)	Alnus	Fruit	Red	Textile dyeing
Annona reticulate (Annonaceae)	Ramaphal, Bullock heart	Unripe fruit	Black	Textile dye
Anthemis tinctoria (Asteraceae)	Dyer's chamomile	Flower	Yellowish	Textile dyeing, hair dye and stimulant
Ardisia humilis (Myrsinaceae)	Aringudi	Fruit	Yellowish	Textile dye
Artocarpus heterophyllus (Moraeceae)	Kathal	Stem, Root	Yellow	Textile dyeing (silk)
Baptisia australis (Fabaceae)	Baptisia	Flower	Yellowish	Textile dye
Berberis vulgaris (Berberidaceae)	Kashmal	Root, Bark	Yellowish	Food and textile colourant
Beta vulgaris (Chenopodiaceae)	Red beet	Root	Red, Yellow	Industrial food colourant
Bidens pilosa (Asteraceae)	Lumb	Leaf	Yellow	Textile dye
Caesalpinia sappan (Fabaceae)	Sappan	Wood	Red	Textile dyeing
Caesulia axillaris (Asteraceae)	Balonda	Plant	Yellow	Textile dye
Cassia auriculata (Fabaceae)	Tarwar	Flower	Yellow	Textile dye
Casuarina equisetifolia (Casuarinaceae)	Janglisaru, Beef wood	Bark	Brown	Textile dye
Cheiranthus cheiri (Brassicaceae)	Wallflower	Leaf, petal	Yellow	Textile dye
Chlorophora tinctoria (Moraceae)	Fustic	Wood	Yellow	Textile dye
Chloroxylon swietenia (Rutaceae)	Satin wood, Bhirra	Bark	Yellow	Textile dye
Coccus cacti (Coccidae)	Carmine	Dried insect body	Red	Textile dye
Coccus ilicis (Coccidae)	Kermes	Insect body	Red	Textile dye
Coreopsis tinctoria (Asteraceae)	Coreopsis	Flower	Yellowish	Textile dye
Coriaria nepalensis (Coriariaceae)	Makola	Wood	Red	Textile dye
Cotinus coggygria (Anacardiaceae)	Young fustic	Wood, leaf	Yellowish orange	Textile dye
Curcuma longa (Zingiberaceae)	Haldi, Turmeric	Rhizome	Yellow	Food, cosmetic, textile colourant
Dahlia indica (Asteraceae)	Dahlia	Petals	Peech gold	Textile dye
Datisca cannabina (Datiscaceae)	Akalbir, Hemp	Root	Yellow	Textile dyeing (wool, silk), in calicoprinting
Delonix regia (Fabaceae)	Gul Mohar	Flower	Deep crimson	Textile dyeing
Delphinium zalil (Ranunculaceae)	Guljali, Larkspur	Flower	Yellow	Textile dyeing and in Calicoprinting
Diospyros malabarica (Ebenaceae)	Galab	Unripe fruit	Brown	Textile dyeing and tanning
Embellia ribes (Myrsinaceae)	False pepper, Barberang	Fruit	Red	Textile dyeing
Fagopyrum esculentum (Polygonaceae)	Buckwheet, Kota	Grain	Yellow	Textile dye
Galium verum	Lady's Bedstraw	Root	Red	Food and Textile dye

(Rubiaceae)				
Gardenia jasminoides (Rubiaceae)	Gandhraj, Cape jasmine	Fruit	Yellow	Textile and Food colorant
Garuga pinnata (Burseraceae)	Chogar	Leaf	Red	Textile dye
Genista tinctoria (Fabaceae)	Dyer's greenweed	Flower	Yellow	Textile dye
Girardinia diversifolia (Urticaceae)	Girardinia	Fiber	Blue	Textile dye
Gossypium herbaceum (Malvaceae)	Cotton	Flower	Yellow	Textile dye
Haematoxylum campechianum (Fabaceae)	Logwood/Blood wood	Heart wood	Violet-purple	Textile dyeing (silk,wool) and in inks
Hedera nepalensis (Araliaceae)	Ivy	Bark	Yellow	Textile dye
Hyptyis suaveolens (Labiatae)	Mint weed	Plant	Yellow	Textile dye
Indigofera tinctoria (Fabaceae)	Neel	Leaf	Blue	Textile dye
Isatis tinctoria (Fabaceae)	Woad	Leaf	Blue	Textile dyeing
Jatropha curcas (Euphorbiaceae)	Safed arand, Barbados nut	Bark	Blue	Textile dyeing
Juglans regia (Juglandacea)	Walnut	Walnut shell, bark leaf	Red	Textile dyeing and supporter for hair dye
Kigelia pinnata (Bignoniaceae)	Sausage tree, Kajela	Wood, roots	Grayish brown	Textile dye
Laccifer lacca (Coccidae)	Lac dye, Lach	Insect deposit	Red	Textile dyeing (silk, wool and leather)
Lawsonia inermis (Lythraceae)	Henna, Mehandi	Leaf	Red	Textile dye and Hair dye
Lotus corniculatus (Fabaceae)	Birds foot trefoil	Flower/Leaf	Orange, Yellow	Textile dye
Maclura pomifera (Moraceae)	Osage-orange	Wood, Bark, Root	Yellow	Textile dyeing and tanning
Mangifera indica (Anacardiaceae)	Aam, Mango	Bark, Root, Fruit	Yellow	Textile dye (cotton, silk)
Memecylon umbellatum (Melastomataceae)	Iron wood tree	Flower, Leaf	Yellow	Colouring mats
Mimusops elengi (Sapotaceae)	Bakul, Spanish Cherry	Bark	Brown	Textile dye
Morinda citrifolia (Rubiaceae)	Awl, India, Mulberry	Root, Bark	Red, Yellow	Textile dye
Nyctanthes arbor-tristis (Oleaceae)	Harshinghar, Night Jasmine	Flower (corolla)	Bright orange	Textile dye
Pfaffia iresinoides (Amaranthaceae)	Brazilian ginseng	Roots	Yellow	Textile dye
Phyllanthus emblica (Euphorbiacea)	Amla	Bark	Brown red	Textile dye
Plecospermum spinosum (Moraceae)	Gumbenfong	Bark, Wood	Yellow	Textile dyeing (silk)
Polygonum tinctorium (Polygonaceae)	Niala	Flower	Yellow	Textile dye
Pterocarpus santalinus (Fabaceae)	Red sandal wood	Wood	Red	Textile and cosmetic colourant
Punica granatum (Lythraceae)	Anar, Pomegranate	Rind	Yellowish Brown	Textile dye
Quercus infectoria (Fagaceae)	Gallnut, Majuphal	Oak gal	Khaki, Yellowish	Textile dyeing and in making inks
Reseda luteola (Resedaceae)	Weld, Dyer's rocket	Whole plant	Deep yellow	Textile dye
Rheum emodi (Polygonaceae)	Dolu, Himalayan Rhubarb	Rhizome	Reddish yellow	Textile dye
Rhizophora mucronata (Rhizophoraceae)	Kandal, True Mangrove	Bark	Chacolate	Textile dye
Rubia cordifolia (Rubiaceae)	Indian madder-E,Manjit	Root	Brick red	Textile dyeing (blankets, carpets)
Rubia tinctorium (Rubiaceae)	European madder, Bacho	Root	Red	Textile dye
Salix caprea (Salicaceae)	Goat willow	Bark	Pink	Textile dye
Sarothamnus scoparius (Fabaceae)	Broom	Flower	Yellow	Textile dye

Scutellaria comosa (Labiatae)	Comosa	Roots	Yellow	Textile dye
Semecarpus anacardium (Anacardiaceae)	Marking nut tree	Bark, Nut	Black	Textile dye
Serratula tinctoria (Asteraceae)	Sawwort	Whole plant except root	Yellow	Textile dye
Shorea robusta (Dipterocarpaceae)	Sal	Bark	Red, Black	Textile dye
Solidago Canadensis (Asteraceae)	Goldenrod	Plant	Golden yellow	Textile dye
Symplocos racemosa (Symplocaceae)	Lodh	Leaf, bark,	Yellow	(silk)
Tagetes erecta (Asteraceae)	Marigold	Petal	Yellow	Textile dye
Tectona grandis (Verbenaceae)	Teak, Sag	Leaf	Yellow	Textile dye
Terminalia catappa (Combretaceae)	Indian almond	Bark	Pinkish Red	Textile dye
Terminalia chebula (Combretaceae)	Chebulic Myrobolan, Harda	Bark, ripe and unripe fruit	Pink, Yellow, brown	Textile dye
Toona ciliate (Meliaceae)	Tun, Red cedar	Flower, sawdust	Red, pink	Textile dye (cotton)
Ventilago denticulate (Rhamnaceae)	Pitti	Bark, Root	Red	Textile dye
Ventilago madraspatna (Rhamnaceae)	Red creeper	Bark, Root	Red	Textile dye
Zingiber officinale (Zingiberaceae)	Adrak, Ginger	Rhizome	Brown	Textile dye (cotton)

Simple aqueous methods

This is the one of the simplest and oldest method employed for the extraction natural colouring components globally. Here in this technique, the raw materials are first dried, and finely cut, most of the times grinded in the powder form and then the colouring components were extracted in water at boil. After the boiling for specific time, the content is cooled to room temperature and filtered. The filtrate is used as a dye for dyeing. The aqueous extraction of colorants liquid are carried out under various conditions such as temperature, time of extraction, pH, raw material concentration and Material to Liquor ration (MLR). Thus, the optimum extraction condition is determined for a particular dye by studying the maximum absorbance or optical density value at a particular (maximum) absorbance wavelength for the aqueous extracted solution using UV-Visible absorbance spectrophotometer.

There are different researchers who have explored the extraction by aqueous method and optimized the process. Khan et.al (2006) [77] have explored the extraction of biomass products namely cutch, ratanjot, madder. Maulik and Pradhan (2005) [78] studied hinjal, jujube bark in aqueous medium. Natural colour extraction process has also been optimized in aqueous media for various source natural dye materials [79] are carried out and given in **Table 3**.

Table 3: Different natural dye extraction with optimum conditions

Sr. No	Natural Source	Material Form	Temp.. ^{0}C	Time, min	MLR	pH	Yield (w/w) %
1	Pomegranate Rind	Pre-cut dried rind crushed to powder form	90°C	45 min	1:20	11	40%
2	Mariegold (Genda)	Dried petal crushed to powder form	80°C	45 min	1:20	11	40%
3	Babool (Babla)	Sun- dried bark rushed to powder form	100°C	120 min	1:20	11	40%
4	Catechu (Khayer)	powder form	90°C	60 min	1:20	12	40%
5	Jack fruit wood	Pre-cut and dried chips crushed to powder form	100°C	30 min	1:20	11	40%
6	Red sandal wood	powder form	80°C	90 min	1:40	4.5	40%

Complicated solvent systems

The dried material (leaves, roots, barks, wood, resinous secretion of insects etc) are ground to very fine particles. The crude dried powder is weighed and solvent extracted using Soxhlet Apparatus, Steam Heated Extractor. Different solvents (such as Acetone, chloroform, ether, n-hexane, alcohol, soda ash, etc.) are used for Extraction. The process is carried out for 4 hours. The dye extract is evaporated in an evaporating dish over a water bath. After evaporating to dryness, the solute is weighed and the percentage yield is calculated.

Supercritical fluid extraction

Today, safety of both producers and consumers is now a major requirement of any new product or process. Accordingly, compelling regulations on the usage of hazardous, carcinogenic, or toxic solvents as well as high energy costs for solvent regeneration have curtailed the growth of the natural extract industries. One of such major technologies that have emerged over the last two decades as the alternative to the traditional solvent extraction of natural products is the Supercritical Fluid Extraction Techniques. It uses a clean, safe, inexpensive, non-flammable, non-toxic, environment-friendly, non-polluting solvent, such as CO_2. Supercritical Fluid Extraction Technology is thus increasingly gaining importance over the conventional techniques for extraction of natural products. Supercritical fluid extraction is an advanced separation technique based on the enhanced solvating power of gases above their critical point. CO_2 is an ideal solvent in the food, dye, pharmaceutical and cosmetic industries, where it is essential to obtain final products of a high degree of purity. Main pigments of ripe tomatoes are the carotenes, compounds of colours ranging between yellow and red, i.e. α, β and γ-carotene, lycopene and Xanthophylls at very low concentrations. Vankar et.al (2001) [80] studied the extraction and purification of natural colourant from eucalyptus bark using SCF process.. Attempts (Bhattacharya et.al (2002) [81], Patel & Agarwal (2001) [82]) has been made to standardize colourant derived from arjun bark, babool bark and pomegranate rind. Natural dye is obtained from the grape skin waste by using soxhlet extractor, and latter on distilled it under vacuum to obtain the concentrated dye solution.

Ultrasonic extraction

The combined effect associated with Ultra-Sound Energy is of cavitations, compressions, rarefactions, and micro-streaming results in intermolecular tearing and surface scrubbing. In particular, it has been noted that, some reactions when exposed to ultrasonic energy become faster with lower temperature that is the most beneficial effect as it reduces processing time and energy consumption and improves product quality in the colouration of textiles [83, 84, 85].

MORDANTS

The natural dyes having limited substantively for the fibre, require use of the mordant which enhances the fixation of the natural colorant on the fibre by the formation of the complex with the dye. Some of the important mordants used are alum, potassium dichromate, ferrous sulphate, copper sulphate, zinc sulphate, tannin, and tannic acid [86, 87]. Although these metal mordants contribute to developing wide gamut of hues after complexing with the natural colouring compounds, most of these metals are toxic in nature and only in trace quantity their presence is found to be safe for the wearer.

The word mordant comes from the Latin word *"mordere"*, meaning *"to bite"*. A mordant is a chemical which can itself be fixed on the fibre and also forms a chemical bond with the natural colourants. It helps in absorption and fixation of natural dyes and also prevents bleeding and fading of colours i.e., improves the fastness properties of the dyed fabrics. This complex may be formed by first applying the mordant and then dyeing (pre-mordanting process) or by simultaneous application of the dye and the mordant (meta- mordanting process) or by after treatment of the dyed material with the mordant (post-mordanting process). There are three types of mordants namely Metal salts or Metallic mordants, tannic acid (Tannins) and Oil mordants[15].

Metal Salts or Metallic Mordants

Metal salts of Aluminium, chromium, iron, copper and tin are used. Some of the common mordants used are Alum, Copper sulphate, Ferrous sulphate, Potassium dichromate, Stannous Chloride and Stannic Chloride. Based on the final colour produced with the natural dyes, these metallic mordants are further divided in to two types i.e., Brightening Mordants and Dulling Mordants. Alum, Potassium dichromate and Tin (Stannous chloride) falls under the category of brightening mordants and Copper sulphate and Ferrous sulphates are dulling mordants.

Tannin

The name 'tannin' is derived from the French 'tanin' (tanning substance) and is used for a range of natural polyphenols[88]**.** The term 'tannin' was first used by Seguin in 1796 and used to describe the process of transforming animal hides into leather by using plant extract from different parts of different plant species. Tannin is an astringent vegetable product found in a wide variety of plants. Plant parts include bark, wood, fruit, fruit pods, leaves, roots and plant galls. Tannin is defined as naturally occurring water soluble polyphenolic compounds of high molecular weight (about 500-3000) containing phenolic hydroxyl groups to enable them to form effective crosslink between proteins and other macromolecules. The molecular formula of tannin is $C_{76}H_{52}O_{46}$, molecular weight of 1701.22 and it melts at 220^oC [89].Tannins do not denote a single compound. They include a large class of organic substances which often differ widely in their chemical composition and reactions.

The tannins are divided structurally into two distinct classes depending on the type of phenolic nuclei involved and the way they are joined. The first class is referred to as hydrolysable tannins while the other class is termed as condensed tannins.

Hydrolysable tannins

These tannins are hydrolysable by mineral acids or enzymes such as tannase. Their structures involve several molecules of polyphenolic acids such as gallic, hexahydrodiphenic or ellagic acids (Fig. 17-20), bounded through ester linkages to a central glucose molecule. On the basis of the phenolic acids produced after the hydrolysis, they are further categorized under gallotannins composed of gallic acid or ellagitannins which contains hexahydrodiphenic acid which after intraesterification produces ellagic acid. Hydrolysable tannins are sometimes referred to as pyrogallol tannins as the components of phenolic acids on dry distillation are converted to pyrogallol derivatives. The hydrolysable tannins are soluble in water and their solution produces blue colour with ferric chloride [90].

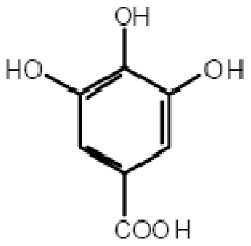


Fig.17: Gallic acid

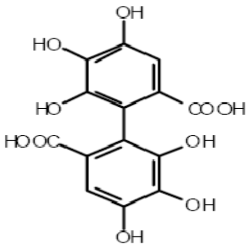


Fig.18: Hexahydroxydiphenic acid

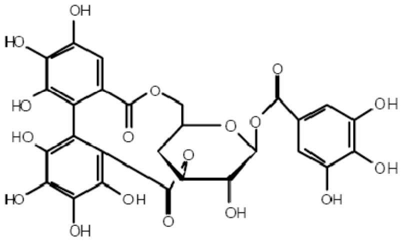


Fig. 19: Corilagrin (Gallotamine)

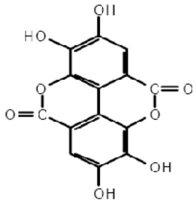


Fig. 20: Ellagic acid

Condensed tannins

Condensed tannins are not readily hydrolysable to simpler molecules with mineral acids and enzymes thus they are also referred to as nonhydrolysable tannins. The term proanthocyanidins is sometimes alternatively used for these tannins. The compounds containing condensed tannins contain only phenolic nuclei which are biosynthetically related to flavonoids. Catechin which is found in tannins is flavan-3-o1 while leucoanthocyanidins are flavan-3,4-diol structures. These phenolics are frequently linked to carbohydrates or protein molecules to produce more complex tannin compounds. When treated with acids or enzymes, they tend to polymerise yielding insoluble red coloured products known as phlobaphens. The phlobaphens give characteristic red colour to many drugs such as cinchona and wild cherry bark. On dry distillation, they yield catechol derivatives. Condensed tannins are also soluble in water and produces green colour with ferric chloride [91].

Natural Tannin Sources

The families of the plants rich in both of the above groups of tannins include Rosaceae, Geraniaceae, Leguminosae, Combretaceae, Rubiaceae, Polygonaceae, Theaceae, etc. The members of families Cruciferae and Papaveraceae on the other hand are totally devoid of tannins. In the plants in which tannins are present, they exert an inhibitory effect on many enzymes due to their nature of protein precipitation and therefore contribute a protective function in barks and heartwood. Some of the plant species containing tannins are Gall Nuts (50-70%), Treripod (65%), Myrobalan (30-35%), Tara (43-51%) and Chest Nut (30%) [90, 87]. A list of principle tannin producing plants and their tannin content are given in **Table 4**.

Tannin bonding with textile substrates

Tannins form following three type of bonds with proteins (eg., wool and silk) and cellulose fibres.

1. Hydrogen bonds between the phenolic hydroxyl groups of tannins and both the free amino and amido groups of proteins.
2. Ionic bonds between the suitably charged anionic groups on tannin and cationic groups on protein.
3. Covalent bonds formed by the interaction of any quinine or semi quinone groups in the tannins and any other suitable reactive groups in the protein or other polymer.

Table 4: Principle tannin producing plants and their tannin content

Sr. No	Botanical Name (Common Name)	Parts	Tannin Content, (%)
1	Acacia catechu (Khair)	Wood	57-60
2	Acacia. Mollissima (Mimosa)	Bark	35-65
3	A. Mearnsil (Black Wattle)	Bark	35
4	A. Nilotica (Babool)	Bark	12-18
5	Anogeissus Latifolia (Dhawada)	Leaves	16-18
6	Anacardium Occidentale (cashew)	Leaves	20-25
7	Astronium balansal (urun day)	Wood	10
8	Casealpinia brevifolia (Algarbilla)	Pods	50
9	C.coriaria (Dividiv)	Pods	35-50
10	Cassia auriculata (Avaram)	Bark	15-20
11	C.fistula (Amaltas)	Bark	9-12
12	Castanea Spp. (chestnut)	Wood	30
13	Casuarina Equisetifolia (Casuarina)	Bark	7-8
14	Ceriops roxburghiana (Goran)	Bark	20-40
15	C. Tagal (Goran)	Bark	20-40
16	Cleistanthus Collinus (Karad)	Bark	23-27
17	Emblica Officinails (Amla)	Stem Bark, Twig Bark, Fruit, Leaves	8-9, 21-24, 28, 22
18	Ecualyptus Occidentalis (Mallet)	Bark	40
19	Eucalyptus Spp. (Eucalyptus)	Bark & Wood	55
20	Eugenia Jambolana (Jamun)	Bark	13-19
21	Hopea Parviflora (Hopea)	Bark	21
22	Larix Spp. (Larch)	Bark	10
23	Mangifera Indica (Mango)	Bark	17
24	Peltophorum Ferrugineum (Peltophorum)	Bark	20-22
25	Pithecelobium Dulce (Jungli Jalebi)	Bark	30-35
26	Punica Granatum (Pomegranate)	Fruit rind	26
27	Quebracho Colorado	Heart wood	20-27
28	Quercus aegilops (Oak)	Bark	30
29	Q. Marolepis (valonia)	Cup & Bread	25-35
30	Q. Montana (chestnut Oak)	Bark	6-15
31	Rhizophora mucronata (Mangrove)	Bark	30
32	Rhus. Spp. (Sumach)	Leaves	20-35
33	Rhus Pentaphylla (Tizrah)	Roots &Wood	30
34	Shorea Robusta (sal)	Bark	7-9
35	Terminalia Alata (saja, Laurd)	Bark	15
36	T.arjuna (Arjun)	Bark	23
37	T. bellirica (Beheda)	Nut	12
38	T.chebula (Myrobalan)	Nut	30-55
39	T.tormentosa	Fruit	10-23
40	T.Suga (anadenosis Hemlock)	Bark	25
41	T. heteropkylla (western Hemlock)	Bark	25
42	Tamarindus indica (Tamarind)	Fruit	20
43	Uncaria Gambir (Gambier)	Leaves	35-40

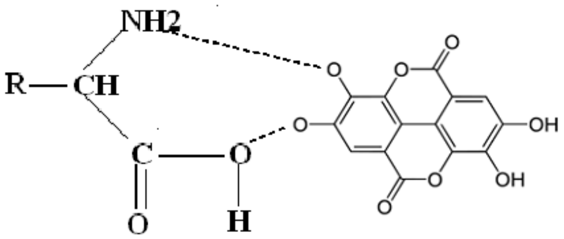


Fig. 21: Reaction of protein (wool/silk) petide chain with natural tannins

Properties of tannins

Tannins are non-crystallisable, amorphous compounds. They are soluble in water, ethyl alcohol, glycerol, acetone and in dilute alkalis. Their aqueous solution shows an acidic reaction and a sharp astringent taste. Most of the tannin compounds cause precipitation of solutions of alkaloids, glycosides, gelatine and heavy metal salts of copper, lead and tin. Tannins produce a deep red colour with potassium ferricyanide and ammonia. With freshly prepared ferric chloride solution hydrolysable tannins produce blue-black precipitate while condensed tannins show brownish green precipitate.

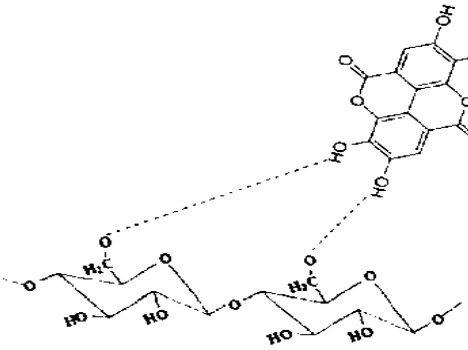


Fig. 22: Reaction of cellulosewith natural tannins

Application of tannins

Tannin in leather processing [89]

Leather making is an age old antique craft, which has been in existence since 1500 B.C. Tannins are used to convert animal hide into leather using “tan liquor”, which in term gives greater stability and resistance to water, heat, bacteria and abrasion. During this tanning process, the collagen chains in hide are cross linked by tannin to give leather. This is due to various tannin protein polymer combinations taking place.

Tannin in medicine [92]

Most of the Indian systems such Ayurveda, Siddha and Unani formulation have churana, rasa, bhasma, sindura and khurs, etc. contains many types of tannins as ingredients. Tannins are astringent in nature and used in Ayurveda and Siddha tooth powder in order to strengthen the gums. They also promote rapid healing and the formation of new tissues on wounds and inflammed mucosa. Tannins are used in the treatment of varicose ulcers, haemorrhoids, minor burns, frostbite as well as inflammation of gums. Internally tannins are administered in cases of diarrhoea, intestinal catarrh and in cases of heavy metal poisoning as an antidote. In recent years, these compounds have demonstrated their antiviral activities for treatment of viral diseases including AIDS.

Tannin in textiles

Tannins are used as mordant in dyeing, manufacture of ink, sizing paper and silk, and for printing fabrics. Tannins are significant in textile dyeing for several reasons. Firstly, they produce indispensable mordants for the dyeing of vegetable fibres like cotton and linen. Secondly, they are very often associated in the plants with the yellow orange, red and violet colourants, whose colour is reinforced by them in the dye bath by their own pigment. Materials dyed with tannins have good fastness for washing and light. Harda powder is used as mordant throughout India by the vegetable dyers and printers since ancient times and so far there is no substitute for harda known to the users which is commercially viable and can replace harda by achieving the same. The study reported by Rafai et.al (1992) [93] states that the fabric to be printed in the Multani style was mordanted with myrobalan after removal of starch and treatment with oil. Divi-divi (Caesalphinia coriaria) fruits are used as a mordanting agent in the textile dyeing process [94]. Gulrajani et.al (1992) [95] studied dyeing of wool with turmeric using several mordants such as alum (10%), copper sulphate (5%), iron (3%), potassium dichromate (5%), tin (1%), tannic acid (5%) and harda (10%) as a natural mordant. The mordant application resulted in increased a* and b* values of the dyed samples. These values were higher for harda mordanted samples than many synthetic mordants. Also, harda mordanted samples showed better wash fastness than alum, tin mordanted samples and it was equal to iron and copper mordanted samples. Jain [96] reported that the Weavers Service Centre, Delhi had developed a style of printing wool with vegetable dyes which involved the treatment to the scoured woollen cloth with a solution containing tannin followed by printing with a synthetic mordant mixed with thickener. Therefore, the fabric is steamed and developed in a bath containing vegetable dye, resulting in the development of different colour on printed portions. Teli et.al (2001) [97] reported the use of eco-friendly mordants namely alum and harda on denim with onion extract. The uses of alum or harda alone or in combination as a substitute were employed. The results produced brilliant shades.

Oil-mordants

Oil mordants are used mainly in dyeing of Turkey Red colour from madder. The main function of the oil mordants is to form a complex with alum used as the main mordant. Since alum is soluble in water and not it has affinity for cotton, it is easily washed out from the treated fabric. The natural occurring oil contains fatty acid such as palmetic, Stearic, oleic etc., and their glycerides. The –COOH group of fatty acid react with metal salts and gets converted in to –COOM, where M denotes the metal. Subsequently, it was found that the treatment of oils with concentrated sulphuric acid produces sulphonated oils which possess better metal binding capacity than the natural oil due to the introduction of sulphonic acid group, -SO_3H. The sulphonic acid can react with metal to produce –SO_3M. This bound metal can form complex with mordant dye such as madder to give Turkey Red colour of superior fastness and hue. Therefore, the sulphonated oils were called Turkey Red Oils (TRO). The term TRO is now used only for the sulphonated castor oil. TRO is also forerunner of the modern synthetic surfactants.

Dyeing using plant dyes and mordants

Dyeing of cotton

Cotton is a cellulosic fibre. The most commonly used dyes for cotton are reactive dyes, direct dyes, vat dyes and sulphur dyes. The reactive dyes form covalent bond with hydroxyl groups of cotton fibre. Acid dyes and cationic dyes lack affinity for the cotton fabric and only surface deposition occurs due to the ionic attraction. Natural dyes can be fixed on cotton with the help of natural or metallic mordant. The natural mordant also acts as primary mordant for metallic salts. For instance, cotton on treatment with tannic acid can absorb all types of metallic mordants. The metallic mordants form complex with the carboxylic groups of tannic acid. Generally, cotton lacks affinity for the natural dyes. Hence, the use of mordant is necessary for the application of natural dyes, acid and basic dyes on cotton.

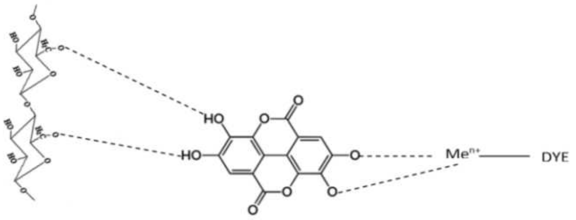


Fig. 23: Mechanism of cotton with tannin, metallic mordants & dye

Dyeing of wool and silk

Wool is more receptive towards mordants. This is due to its amphoteric nature wool can absorb acids and bases equally and effectively. When wool is treated with a metallic salts it hydrolyses the salt into an acidic and a basic component. The basic component is absorbed at the –COOH groups and the acidic component is removed during washing. Like wool, silk is also amphoteric and can absorb both acids as well as bases.

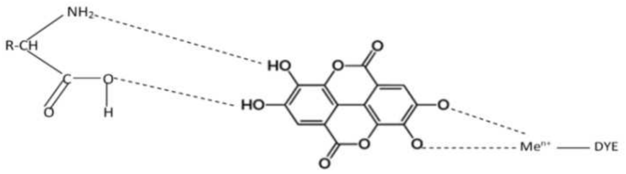


Fig. 24: Mechanism protein petide chain with tannin, metllic mordants & dye

Fastness properties of natural dyes

Fastness is the fundamental requirement that coloured textiles should exhibit, to the conditions encountered during the processes following colouration and during their subsequent usage. The fastness requirements, however, are largely determined by the end-use of dyed fabrics. Some of the basic fastness properties required are as follows:

Light fastness

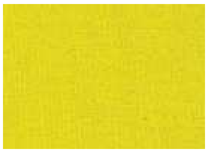
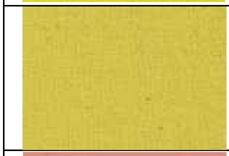
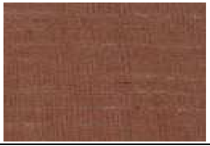
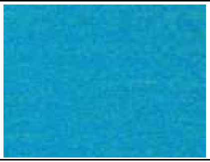
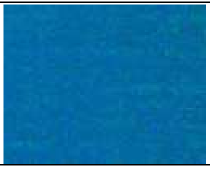
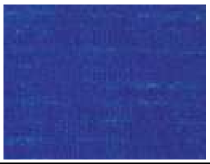
Most of the natural dyes have poor light stability as compared to that of the best synthetic dyes, and hence the colours in historical old textile are often different from their original colours. Fading of colour on the textile occurs on exposure to light. This degradation occurs when light breaks chemical bonds in dyes. Sunlight is made up of ultra violet light, visible light and infrared radiation. While short wave UV causes most of the physical property damage to fibres, it is generally the longer wave UV and visible light that causes dyed textile fade. Poor light fastness of some of the natural dyes can be attributed to propensity of the dye chromophore to the photochemical oxidation. The chromophore in some classes can be protected from photochemical oxidation by forming complex with transition metals, where by a six member ring is formed. The photons sorbed by the chromophoric group dissipate their energy by resonating within the ring and hence dye is protected. The post mordanting process with metal increases the light fastness of natural dyed samples. However, the post mordanting with metal salts also results in change in hue of the dyed fabric, hence the post treatment should be selected rightly. Attempt by Prabhu et.al (2011a,b) [98, 99] has been made to improve the light fastness properties of popular natural colourants namely turmeric, henna, madder and pomegranate rind using natural mordants namely tamarind seed coat and emblica officinal’s tannins and also metallic mordant (safer limit) combinations. The rate of fading has been greatly reduced due to the combined effect of natural tannins and metal mordant bonding. Additional, the dyed fabric resulted in good antimicrobial protective fabric using this eco-friendly process.

Washing fastness

Some of the natural dyes undergo a little change in their hue on washing, this may be due the alkaline nature of the washing mixture mainly the pH. In general, 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 [100]. 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 [101]. 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 general, the fastness of a colour can vary with the type of dye, the particular shade used, the depth of shade and the dyeing process and mainly the nature of the washing mixture.

Some of the shades obtained using natural colourants and modrants are shown in Table 5.

Table 5: Natural dye Shades

Shade	Natural dye & mordent	Shade	Natural dye and mordent
	**Barberry & Myrobalan**		**Eclipta**
	**Myrobalan**		**Madder A.Catechu**
	**Achaia Catechu**		**Myrobalan & Banana soup**
	**Vemadam bark**		**Madder A. Catechu**
	**Iron & Myrobalan**		**Indigo era (Light)**
	**Iron & Myrobalan**		**Indigo era (Medium)**
	**Iron Water & Sugar**		**Indigo era (Dark)**

CONCLUSION

More interest in natural dyes has been mainly manifested as conservation and restoration of textiles with replacement of synthetic dyes by natural dyes for textiles, food, and safety using mild chemistry. The research and development work in standardization of natural dyes are very less. Very few serious attempts have been made to generate new information on the use of natural dyes. As there is much catching up to do after 150 years of neglect, there is rapid scope for developments. The contributions for standardization of natural dyes are made by some companies like Alps Industries Ltd. that uses Supercritical CO_2 plant for extraction of dyes for a step towards standardization. The standardized natural extracts are very much useful for Textiles, food, pharmaceuticals and cosmetics. On the other hand, the uses of natural dyes are often linked to term of fastness properties mainly wash and light fastness. This can be improved by proper selection of natural mordants and extraction along with best application of technology and ecological process. In this way, commercialization of such plant dyes for colouration of textiles material is needed which is highly useful for the local rural dyers and plant cultivators. Thus, natural dyeing of textiles by industrial processes in large scale dyeing unit is now a reality in the textile market of eco-friendly textiles.

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