Natural Dyes: Sources, Chemistry, Application and Sustainability Issues

Sujata Saxena and A. S. M. Raja

Abstract Dyes derived from natural materials such as plant leaves, roots, bark, insect secretions, and minerals were the only dyes available to mankind for the coloring of textiles until the discovery of the first synthetic dye in 1856. Rapid research strides in synthetic chemistry supported by the industrialization of textile production not only led to the development of synthetic alternatives to popular natural dyes but also to a number of synthetic dyes in various hues and colors that gradually pushed the natural dyes into oblivion However, environmental issues in the production and application of synthetic dyes once again revived consumer interest in natural dyes during the last decades of the twentieth century. Textiles colored with natural dyes are preferred by environmentally conscious consumers and today there is a niche market for such textiles. But the total share of natural dyes in the textile sector is approximately only 1 % due to certain technical and sustainability issues involved in the production and application of these dyes such as nonavailability in ready-to-use standard form, unsuitability for machine use, and limited and nonreproducible shades. Natural dyes per se are sustainable as they are renewable and biodegradable but they cannot fulfill the huge demand from the textile sector in view of the preferential use of land for food and feed purposes. Also, overexploitation of natural resources to obtain dyes may result in deforestation and threaten endangered species. For these reasons, the Global Organic Textiles Standard (GOTS) permits the use of safe synthetic dyes and prohibits the use of natural dyes from endangered species. Various research efforts have been undertaken all over the world to address the shortcomings of natural dyes in view of the tremendous environmental advantage they offer. This book attempts to review the current status of natural dyes and various sustainability issues involved in their production and application and examines their future prospects.

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1 Introduction

The art of dyeing is as old as our civilization. Dyed textile remnants found during archaeological excavations at different places all over the world provide evidence to the practice of dyeing in ancient civilizations. Natural dyes were used only for coloring of textiles from ancient times till the nineteenth century. As the name suggests, natural dyes are derived from natural resources. Coloring materials obtained from natural resources of plant, animal, mineral, and microbial origins were used for coloration of various textile materials. Different regions of the world had their own natural dyeing traditions utilizing the natural resources available in that region. Use of natural dyes started to decline after the invention of synthetic dyes in the second half of the nineteenth century. Concerted research efforts in the field of synthetic dyes and rapid industrialization of textile production resulted in almost complete replacement of natural dyes by synthetic dyes on account of their easy availability in ready-to-apply form, simple application process, consistency of shades, and better fastness properties. The tradition of using natural dyes could survive only in certain isolated pockets. Recent environmental awareness has again revived interest in natural dyes mainly among environmentally conscious people. Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer. Natural dyes can be used for dyeing almost all types of natural fibers. Recent research shows that they can also be used to dye some synthetic fibers. Apart from their application in textiles, natural dyes are also used in the coloration of food, medicines, handicraft items and toys, and in leather processing, and many of the dye-yielding plants are used as medicines in various traditional medicinal systems. There are several challenges and limitations associated with the use of natural dyes. The current dyestuff requirement from the industry is about 3 million tonnes. Considering this fact, the use of natural dyes in mainstream textile processing is a big challenge. As agricultural land is primarily required to feed an ever-increasing world population and support livestock. and biodiversity should not be compromised for the extraction of dyes, sustainability of natural dyes is a major issue. This chapter discusses various issues related to the use of natural dyes in textiles such as potential sources, chemistry, extraction methods, application methods, and sustainability issues.

2 Potential Sources of Natural Dyes

Natural dyes are derived from natural resources and based upon their source of origin, these are broadly classified as plant, animal, mineral, and microbial dyes although plants are the major sources of natural dyes. As interest in natural dyes grew, information from the old literature was collected and traditional dyeing practices in different regions were documented and compiled by various researchers. Adrosko [1] published a book on natural dye sources and processes for their application to textiles at the household level. DOBAG, the Turkish acronym for Natural Dye Research and Development Project, launched in Turkey with German assistance in cooperation with Marmara University, Istanbul in 1981 was a big success in reviving the lost art of producing naturally dyed carpets. Natural dyeing processes of India were documented in a book by Mohanty et al. [32]. Chandramouli [9] also published a book on natural dyeing processes of India. Dyes traditionally used in the Scottish Highlands were reviewed by Grierson et al. [15]. Buchanan [8] presented a detailed account of dye plants used for natural dyeing of textiles such as alkanet, annatto, chamomile, coreopsis, madder, safflower, indigo, and so on, and methods for dyeing of textiles with these. Later information on various dye-yielding plants, methods to grow them, harvesting dye parts, methods to dye wool and silk with them, and color shades obtained were also detailed by her [7]. Research efforts by individuals and organizations and exchange of available information through various seminars, symposiums, workshops, and research articles have now revealed various natural dye sources. Plenty of information about different sources of natural dyes is now available in the literature [54, 55]. A brief account of the potential dye resources according to their source of origin is listed below.

2.1 *Plant Origin*

Historically, plants have been used for the extraction of a majority of natural dyes. Various plant parts including roots, leaves, twigs, stems, heartwood, bark, wood shavings, flowers, fruits, rinds, hulls, husks, and the like serve as natural dye sources. The famous natural blue dye, indigo is obtained from the leaves of the plant *indigofera tinctoria.* Some plant-derived dyes have other applications also, for example, as food ingredients and medicines in traditional medicine systems and hence a commercial supply chain of these dyes is in place. Some of the natural dyes were well known in the past for their dyeing properties and have remained in use even now, albeit on a small scale. A renewed interest in natural dyes has increased their commercial availability. Some such important dyes reported in many publications [6, 19, 26] are listed below.

2.2 *Blue Dyes*

Indigo is the only important natural blue dye. Leaves of the plant *indigofera tinctoria* are the best source of this dye. This very important dye popularly known as the “king of natural dyes” has been used from ancient times till now for producing blue color and is today most popular for denim fabrics. The coloring matter is present in indigo plant leaves as a light yellow substance called indican

(1H-indol-3yl β-D-glucoside). The leaf production from one acre of cultivated indigo plants is approximately 5,000 kg which can yield about 50 kg of pure natural indigo powder after processing. It is produced by fermenting the fresh plant leaves, and cakes thus prepared are used for dyeing purposes. Apart from *indigofera* species, there are several plants that can be used to produce indigo dye. Woad is a natural indigo-producing plant in Europe. Apart from this, dyers knotweed (*Polygonum tinctorium*) and Pala Indigo (*Wrightia tinctoria*) are some of the plants used to produce indigo traditionally. The use of natural indigo started declining after the manufacture of synthetic indigo by BASF in 1987.

2.3 Red Dyes

There are several plant sources of red natural dyes. A few popular sources are listed below.

2.4 Madder

Madder is the red color producing natural dyes from the plants of various *Rubia* species. The dye is obtained from the roots of the plant. It is also popularly known as the "queen of natural dyes." The main coloring constituent of European madder *Rubia tinctorum* is alizarin. The yield of roots from the 3-year-old plant is between 3–5 tonnes per hectare and about 150–200 kg of dye. As with indigo, the use of natural madder powder started declining after the manufacture of synthetic alizarin by the BASF. *Rubia cordifolia* is known as Indian madder, manjishth, or manjeet, and its coloring matter is a mixture of munjistin and purpurin. In addition to roots, dye is also present in the stems and other parts of the plant.

Dye is usually extracted by boiling dried root chips or stem pieces with water but sometimes, these are merely steeped in cold water for few hours. As it is a mordant dye, it produces brightly colored insoluble complexes or lakes with metal ions present on the mordanted fabric. Alum is widely used to get pink and red shades. A mixture of alum and iron produces purple shades. Alum can be used as a primary metallic salt in combination with other mordants to develop a range of red shades. Dyed materials possess good fastness properties.

2.5 Brazil Wood/Sappan Wood

A red dye is obtained from the wood of *Caesalpina sappan*, a small tree found in India, Malaysia, and the Philippines which is known as sappan wood or "Patang." The same dye is also present in Brazil wood (*Caesalpinia echinata)*, the name being derived from the word braza meaning glowing like fire due to the bright red color of its wood. Aqueous extraction can be used to extract the dye. Alkali extraction deepens the red color. Textile materials can be dyed to get the red color with or without the use of alum mordant. A combination of this dye with turmeric produces orange shades and a deep maroon color is produced with catechu.

2.6 Morinda

The root and bark of the tree *Morinda citrifolia* growing in India and Sri Lanka is used for getting red shades. Maximum coloring matter can be obtained from the 3 to 4-year-old tree. Mature trees have very little dye. Dye is extracted from the chipped material with water after a preliminary wash to remove free acids. Various shades including purple and chocolate can be produced with the use of mordants.

2.7 Safflower

Safflower is an annual herb known to have originated in Afghanistan. It is mainly cultivated for oil from its seeds which are rich in polyunsaturated fatty acids. The safflower florets were traditionally used for extracting dye which was valued for its bright cherry-red color. It contains two coloring matters, a water-soluble yellow present in abundance (26–36 %) which was not used as a dye and the scarlet red water-insoluble carthamin present only to the extent of 0.3–0.6 %. The yellow amorphous coloring matter has to be completely removed from carthamin before the latter is used for dyeing as its presence even in small quantities affects the pure pinkish shade imparted by the red dye. Safflower has been employed to give cherry-red direct dyeings on silk and cotton. The dye is extracted from dried safflower florets by continuously washing it with acidulated water to remove all the water-soluble yellow coloring matter. The residue containing insoluble red dye is either dried partially and molded into cakes for use in dyeing or it is extracted with a sodium carbonate solution and precipitated by dilute acids. The washing and light fastness of the dye is poor. Yellow dye has now also been used to dye mordanted cotton.

2.8 Yellow Dyes

Yellow dyes are available from several plant resources. Some of the prominent sources are listed below.

2.9 Turmeric

Turmeric is a well-known natural dye. The dye is extracted from the fresh or dried rhizomes of turmeric. The dye present is chemically curcumin belonging to the Diaroylmethane class. It is a substantive dye capable of directly dyeing silk, wool, and cotton. The shade produced is fast to washing but its fastness to light is poor. The natural mordants such as tannin obtained from myrobolan can be used to improve the fastness properties. Turmeric dyeings can be overdyed with indigo for production of fast greens.

2.10 Saffron

Saffron is an ancient yellow dye belonging to the family Iridaceae and is obtained from the dried stigmas of the plant *Crocus sativus*. It is grown in the Mediterranean, Iran, and India, and used for cooking as well as medicinal purposes. The dye is extracted from the stigmas of flowers by boiling them in water. It imparts a bright yellow color to the materials. It can directly dye wool, silk, and cotton. Alum mordant produces an orange yellow known as saffron yellow.

2.11 Annatto

Annatto *Bixa orellana* is a small tree belonging to the family Bixaceae. The tree is known for the yellow orange dye obtained from its seeds. It is extensively used for the dyeing of cotton, wool, and silk and also used for coloring butter, cheese, and the like. The pulp is rich in tannin. The alkali extraction method is used for extracting dye at boiling conditions. It produces reddish orange shades on cotton, wool, and silk.

2.12 Barberry

The barberry *(Berberis aristata)* plant roots, bark, and stems are used to extract the dye. The main constituent of the dye is berberine which is an alkaloid. It is a basic dye and can be used to dye silk and wool directly. The dye produces a bright yellow color with good washing fastness and average light fastness. Cotton can be dyed after mordanting.

2.13 Pomegranate

Rinds of pomegranate (*Punica granatum*) fruits are rich in tannins and are used for mordanting purposes. A yellow dye is also present which can be used to dye wool, silk, and cotton with good fastness properties. It is also used along with turmeric for improving the light fastness of the dyed materials.

2.14 Myrobolan

Dried myrobolan (*Terminalia chebula*) fruits have high tannin content and also contain a natural dye that is used for producing bright yellow shades for all textile materials. Myrobolan is also used as a natural mordant to fix different natural dyes on textile materials. Myrobolan is a part of the famous Ayurvedic preparation "triphala" and dyed materials are also imparted with medicinal properties such as antimicrobial, antifungal, and so on.

2.15 Marigold

Marigold (*Tagetus spp.*) is a bright yellow flower-yielding plant. It is commonly used for making garlands and floral decorations. It is available in different colors including yellow, golden yellow, orange, and the like. The main coloring component is quercetagetol, a flavonol along with two of its glycosides and lutein. It dyes wool and silk in deep yellow colors with good fastness properties. Cotton can be dyed with this dye in combination with mordants to get fast colors. Cotton fabrics are pretreated with tannic acid/tannin-containing mordants followed by metallic mordants before dyeing to get various shades.

2.16 Flame of the Forest

The flame of the forest (*Butea monosperma*) tree, locally known as tesu in India, produces bright orange color flowers. The dye extracted from the flowers can be used for dyeing all natural fibers. Bright yellow to brown and orange colors can be produced with suitable mordant.

2.17 Kamala

The dried fruit capsules of kamala (*Mallotus phillipensis*) yield a red-orange powder that can be used for dyeing wool and silk to bright orange-yellow and golden-yellow colors. Colors produced on cotton are not so good with moderate fastness properties.

2.18 Onion

The outer skin of onion (*Allium cepa*) which is generally thrown away as waste can be used to extract yellow color natural dye. The dye is flavonoid in chemical constitution, and produces bright colors on wool and silk. Cotton can be dyed with suitable mordant. The washing and light fastness of the shade produced are moderate.

2.19 Weld

Weld (*Reseda luteola*) was a very important yellow dye plant in Europe. The coloring matter is a flavonoid and it produces a good yellow color on natural fiber textiles that have very good fastness properties.

2.20 Dolu

Roots and rhizomes of Himalayan rhubarb *(Rheum emodi*) yield a yellow dye that can be used to dye wool, silk, and cotton after mordanting with exceptional fastness properties.

2.21 Brown and Black Dyes

Oak galls are rich in tannin and are used for mordanting. They can also be used to get a brown color. Catechu or cutch obtained from the heartwood of *Acacia catechu* is used to dye cotton, wool, and silk to brown color directly. It is also rich in tannins and can be used to get black color with iron mordant. Black color can also be obtained from many yellow and red dyes by iron mordanting. Famous logwood black color having very good fastness properties was obtained by using iron mordant and the extract of logwood obtained from the heartwood of the tree *Haematoxylon campechianum* found in Mexico and the West Indies.

Apart from the above-mentioned sources, there have been efforts by various researchers to explore local flora for their potential to dye textiles. Leaves, flowers, wood, bark, and so on of several plant materials have been utilized for the dyeing of various textile substrates with varying results in terms of deepness of color produced on the substrates and their colorfastness properties. Every year new additions are being made to the list of plant species that can be used as dye sources. Some of the promising natural dyes reported in the literature [20, 21, 33, 35, 45, 57] are given in Table 1.

In an UNDP-sponsored project executed in India, the potential of about 120 plant materials from the Western Ghats of India, a biodiversity-rich region was

Table 1 Some promising natural dye sources

S.No	Common name of the plant	Botanical name	Part used	Color obtained
1	Siam weeds	*Eupatorium odoratum*	Whole plant	Yellow
2	Goat weed	*Ageratum conyzoides*	Whole plant	Yellow
3	Jack fruit tree	*Atrocarpus heterophyllus*	Bark	Yellow
4	Gulmohar	*Delonix regia*	Flower	Olive green
5	Teak	*Tectona grandis*	Leaves	Yellow
6	Babool	*Acacia nilotica*	Leaves, bark	Yellow/brown
7	Water lilly	*Nymphaea alba*	Rhizomes	Blue
8	Dahlia	*Dahlia variabilis*	Flowers	Orange
9	Amla	*Emblica officinalis*	Bark, fruit	Grey
10	Indian Jujube Ber	*Ziziphus mauritiana*	Leaf	Pink
11	Drumstick	*Moringa pterygosperma*	Leaf	Yellow
12	Sausage tree	*Kigelia pinnata*	Petals, heartwood, bark	Yellow, pink
13	African tulip tree	*Spathodeacompanulata*	Flower	Yellow/orange
14	Tamarind	*Tamarindus indica*	Leaves, seeds	Yellow, brown
15	Golden dock	*Rumex maritmus*	Seeds	Brown
16	Eucalyptus	*Eucalyptus camaldulensis*	Bark	Yellow and brown
17	Red sandalwood	*Pterocarpus santalinus*	Wood	Red

explored for the dyeing of cotton. Based on the color produced and colorfastness of dyed material to light and washing, more than a hundred of these were found to be promising [3].

2.22 *Animal Origin*

Insects were the main source of natural dyes of animal origin and most of these provided red colors. The oldest animal origin dye, Tyrian purple, produced from the secretions of the sea mollusc *Murex* is an exception. This dye produced a very fast deep violet color on fabrics. It was very expensive as thousands of molluscs were needed to get a gram of the dye. Hence it was considered a symbol of royalty and was used to color the clothes of the royal family. Cochineal was an important animal origin dye obtained from the insects of the species called *Dactylopius coccus* which is still being used to dye textiles. The dye is obtained from the bodies of female insects that live on cactus (*Opuntia* species). The principal coloring matter is carminic acid. The cochineal dye produces crimson red color on animal fibers and has good washing and light fastness properties. Its bright red aluminum calcium chelate known as carmine is used as food color. Kermes is another animal origin crimson red dye derived from the insect *Kermes licis.* This dye has been known since ancient times to color animal fibers but was inferior to cochineal in fastness properties. Lac was also well known in ancient times for coloration of animal fibers. It is obtained from the hardened secretions (stick lac) of the insect *Kerria lacca* found on the twigs of certain tree varieties in India and the SouthEast Asia region. It is obtained as a by-product during the processing of stick lac for obtaining shellac. Traditionally, it was used for coloration of animal fibers only as it had good affinity for those but it has now also been used by many researchers [44, 48] to color cellulosic fibers such as cotton as it is available in fairly large quantities as a by-product. Recently the kinetics for the dyeing of cotton with this dye has been studied by Chairat et al. [10].

2.23 Mineral Origin

Some mineral pigments found in nature such as cinnabar, red ocher, yellow ocher, raw sienna, malachite, ultramarine blue, azurite, gypsum, talc, charcoal black, and so on, have been used for coloration purposes. Apart from the red ocher that was used by the monks for coloration of their robes, these were mainly used in paintings and murals along with gum as binder. Extensive details of the natural mineral pigments used in India have been provided by Agarwal and Tiwari [2]

2.24 Microbial and Fungal Origin

Some bacteria produce colored substances as secondary metabolites. *Bacillus, Brevibacterium, Flavobacterium, Achromobacter*, *Pseudomonas, Rhodococcus spp.* are some of the pigment-producing bacteria [27]. Some bacteria have also been reported to produce indigo upon exposure to petroleum products. A list of pigment-producing microorganisms and chemical classes of pigments produced by them has been provided in a review by Malik et al. [30].

Microbes as a dye source offer an advantage as these can be easily grown on cheap substrates under controlled conditions. The dyeing of nylon with prodigiosin pigment extracted from *Serratia marcescens* was attempted by Vigneswaran et al. [56]. They investigated the growing conditions of the *Serratia* strain for pigment production and its extraction. Extracted pigment was characterized and its heat stability and dyeing characteristics for various textile substrates were studied. Pink coloration obtained on wool was fast to washing but its very poor fastness to light did not encourage future work for use as textile dye.

Pigments from the fungus *Monascus purpureus* are used for coloration of some traditional oriental food items. It has been used for fabric coloration also. *Trichoderma* sp. has been used for coloration of silk and wool with excellent washing fastness [17].

Lichens and mushrooms have been used as sources of colorants in Europe and in some other parts of the world. Orchil dye from lichens was used to create violet and purple shades as a cheap alternative to costly purple dye from molluscs. They have also been used to dye wool to shades of yellow, brown, and reddish brown. Orchil and litmus colorants obtained from lichens are not found in higher plants.

Dyes derived from mushrooms have become popular since the 1970s. Some *Cortinarius* species have intensely colored fruiting bodies and are the best mushroom dyes. *Cortinarius sanguineus* (blood-red webcap) contains anthraquinone pigments emodin and dermocybin in glucoside form. The dye content is about 6 % and a preparative scale extraction process has been described by Hynninen et al. [24]. These pigments were used by Raisanen et al. [40, 41] to dye both natural and synthetic fibers with low to excellent fastness properties. A list of pigments present in various lichens and fungi along with their chemical structures has been compiled by Raisanen [42] and a very elaborate account of different lichens and mushroom types consisting of their description, habitat, distribution, harvesting procedures, dye composition, dyeing methods, color obtained, historical importance, other uses, and possible future developments has been presented by Cardon (2007).

3 Chemistry and CI Numbers

As dyes have complex chemical structures, their chemical names are difficult to understand and remember and common names are in the local languages and are area specific, a color index has been developed for identifying the dyes. It serves as reference for both the chemical and technical properties of dyes. Earlier published by the Society of Dyers and Colorists (SDC), United Kingdom, it is now jointly published by SDC and the American Association of Textile Chemists and Colorists (AATCC), United States. In the color index, dyes are classified according to major application classes. Within the application class, the dyes are arranged according to the hue. Dyes whose chemical structures are known are also given a constitution number that denotes their chemical constitution. Thus a dye has a CI constitution number assigned to its chemical constitution and also a name in the color index which denotes the type of dye. For example, the CI number of natural indigo dye is 75780 with the name CI Natural Blue 1 in which CI denotes Color Index, Natural indicates type of dye, Blue indicates the hue, and 1 is the identifying number. Natural dyes have been grouped together as a class in the color index. In Volume 3 of the color index, 32 natural reds, 6 natural oranges, 3 natural blues, 5 natural greens, 29 natural yellows, 12 natural browns, 6 natural blacks, and 1 natural white have been listed.

Natural dyes have a complex chemical constitution. Unlike synthetic dyes, they are usually not a single entity but a mixture of closely related chemical compounds. On the basis of major chemical constituents present, they are divided into:

1. Indigoid dyes
2. Anthraquinone dyes
3. Naphthoquinone, Benzoquinone dyes
4. Flavonoid dyes
5. Carotenoid dyes
6. Tannin-based dyes.

3.1 Indigoid Dyes

Indigo is the major and most important dye in this class as among natural dyes, it is almost always the source of the primary color blue. Chemically it is indigotin (C.I. Natural Blue1, C.I. 75780) and is found in largest concentration in the leaves of some Indigofera species such as *I. tinctoria, I. errecta*, and *I. sumatrana*, among others. It is also the coloring matter of pala indigo (*Wrightia tinctoria*), Assam indigo (*Strobilanthes flaccidifolius*), and woad (*Isatis tinctoria*); the last one was used in Europe for blue color before being replaced by superior indigo from India. Indigo is not soluble in water and has to be reduced to its water-soluble leuco form through a reduction process. This water-soluble form of indigo is used for dyeing textiles. After dyeing, the leuco form is oxidized by atmospheric air to its original blue indigotin structure. It has excellent colorfastness properties. It is similar in structure to synthetic indigo (C. I. Vat Blue1, C.I. 73000) but it also contains some amount of red dye indirubin which imparts a rich reddish tone to the textiles dyed with natural indigo.

Tyrian purple obtained from Mediterranean molluscs of the *Purpura* and *Murex* genus is another indigoid dye that also has excellent fastness properties. Chemically, it is the 6, 6’ dibromo derivative of indigo (Fig. 1).

3.2 Anthraquinone Dyes

The basic chemical structure of anthraquinone is depicted in Fig. 2. A large number of natural dyes especially red color-producing dyes fall into this category. The most famous natural dye in this category is alizarin obtained from European madder (Rubia tinctorum). Other dyes include lac, cochineal, morinda, and Indian madder (manjishth/manjeet) among others. The chemical names, CI numbers, and names of some anthraquinone dyes and their sources are given in Table 2.

Carthamin from safflower (*Carthamus tinctorius*) florets is an old traditional red dye having a benzoquinone structure. It gives cherry red and pink shades on silk and cotton but fastness properties are not good.

3.3 Naphthoquinone Dyes

The basic structure of the Naphthoquinone is depicted in Fig. 3. Some of the natural dyes belonging to this category are henna, walnut shells, and so on. The coloring matter of henna is lawsone which is 2-hydroxy naphthoquinone and walnut shells contain juglone which is 5-hydroxy naphthoquinone. These dyes also produce orange, red, or reddish brown shades like anthraquinone dyes (Fig. 4 and Table 3).

Fig. 1 Indigotin

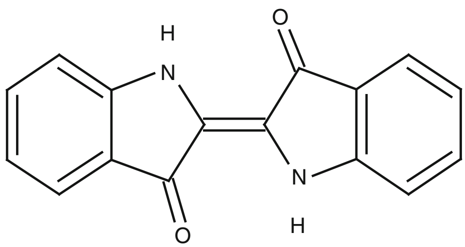


Fig. 2 Alizarin (1, 2-dihydroxy anthraquinone)

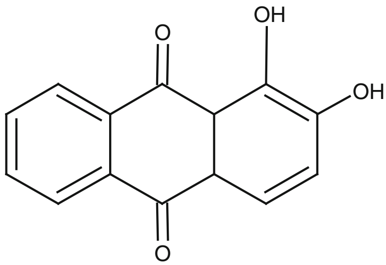


Table 2 Some anthraquinone dyes [14]

Dye name	CI number	CI name	Natural sources
Alizarin	75330	Natural red 6, 8, 9, 10, 11, 12	Madder, chayroot
Purpuroxanthin or xanthopurpurin	75340	Natural red 8, 16	Madder, munjeet
Morindadiol	75380	Natural red 18	Morinda root
Soranjidiol	75390	Natural red 18	Morinda root
Purpurin	75410	Natural red 16, 8	Munjeet, madder
Pseudopurpurin	75420	Natural red 14, 9, 8	Gallium, madder
Laccaic acid	75450	Natural red 25	*Coccus laccae* (Lac dye)
Kermesic acid	75460	Natural red 3	*K. licis*
Carminic acid or cochineal	75470	Natural red 4	*C. cacti*

Fig. 3 Naphthoquinone

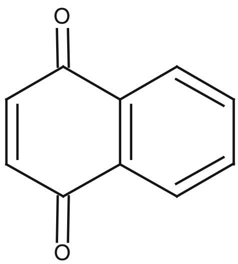


Fig. 4 Lawsone

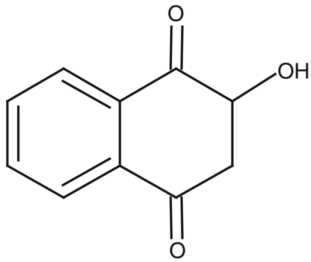


Table 3 Some naphthoquinone dyes [14]

Dye name	CI number	CI name	Natural sources
Lawsone	75480	Natural orange 6	Henna
Lapachol	75490	Natural yellow 16	Taigu or lapachol wood
Juglone	75500	Natural brown 7	Walnut shells
Alkanan	75520	Natural red 20	Ratanjot, *Anchusa tinctoria*

3.4 Flavonoid Dyes

Most of the yellow natural dyes have an hydroxyl or methoxy substituted flavone structure. Dyes with this chemical constitution are found in a wide variety of natural resources. Weld (*Reseda luteola*) or dyer's rocket was widely used in Europe to produce fast and brilliant colors on wool and silk. The coloring matter present is flavone luteolin (CI Natural yellow 2) and its structure is given in Fig. 5. Marigold (*Tagetus* spp.) flowers contain a flavonol dye quercetagetol. Some other flavonoid dyes are listed in Table 4.

Dihydropyrans are closely related to flavones in structure. Haematin and its leuco form haematoxylin, which are the main coloring substances present in Logwood (heartwood of *Haematoxylon campechianum*, CI natural black 1), belong to this category. Dye from the wood of *Caesalpinia echinata* (Brazil wood) and *Caesalpinia sappan* (Sappan wood) also belongs to this group. The coloring matter present in both is brazilin which gets oxidized to the red-colored compound brazeilein.

Butein, a yellow-orange dye from *Butea monosperma* (tesu) flowers, and rottlerin, the main coloring matter of orange red powder from ripe fruit capsules of *Mallotus phillipensis* (Kamala) (CI Natural orange 2) which produces a yellow color, have chalcone structures which can be considered as open chain analogues of flavonoids (Fig. 6).

Fig. 5 Luteolin

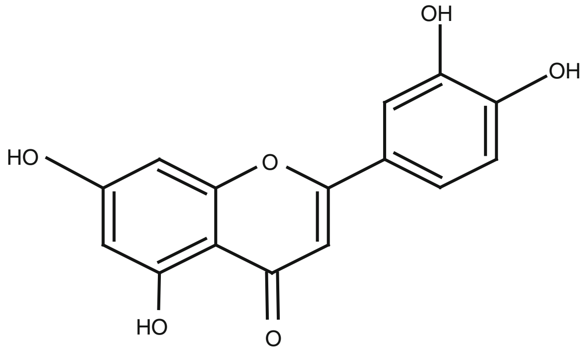
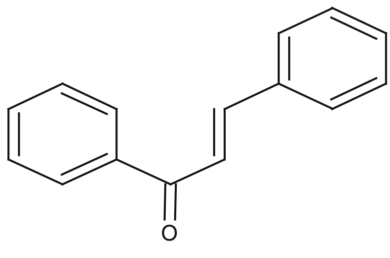


Table 4 Some flavonoid dyes [14]

Dye name	CI number	CI name	Natural sources
Luteolin	75590	Natural yellow 2	Dyers rocket, dyers wood,
Kaempferol, trifolitin or indigo yellow	75640	Natural yellow 13,10	Natal indigo, saffron
Kaempferol 7-methyl ether	75650	Natural green 2, natural yellow 13	Sap green, Hungarian berries
Quercetin, meletin or sophoretin	75670	Natural yellow 10, Natural red I	Persian berries, toon or Indian mahogany tree
Quercitrin	75730	Natural yellow 10	Quercitron bark
Rutin	75740	Natural yellow 10	Chinese or Avignon berries

Fig. 6 Chalcone



3.5 Carotenoid Dyes

The major dyes in this class are bixin and nor bixin found in annatto seeds and crocin found in saffron stigma (CI Natural orange 4). Orange dye from the corolla tubes of *Nyctanthes arbor-tristis* flowers or nictanthin also has a similar carotenoid structure (Fig. 7).

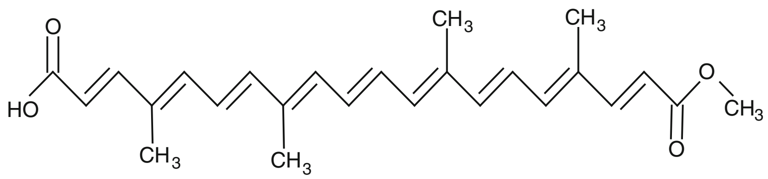


Fig. 7 Bixin

3.6 Tannin-Based Dyes

Tannins are polyphenolic compounds that are present in many natural resources used for dyeing purposes. The dyes with tannin generally require mordants for fixing onto the fabric. This class of dyes also tends to change color with the change in mordant depending upon the dye-mordant complex. Dye obtained from the bark of *Acacia nilotica* (Babool; CI Natural Brown 3) and wood of *Acacia catechu* (Cutch) have a polyphenolic structure.

3.7 Others

Curcumin, the yellow coloring matter of turmeric, a well-known spice and food color, belongs to the diaroyl methane class. Berberine present in *Berberis aristata* and *B. vulgaris* root and stems and bark of the Amur cork tree (*Phellodendron amurens)* belongs to the alkaloid category and is the only known basic natural dye.

4 Production Techniques for Natural Dyes

Unlike synthetic dyes, which are synthesized from chemical precursors, natural dyes are mostly obtained from various plant parts. These dye-bearing materials contain only a small percentage of dye usually 0.5–5 %. These plant materials cannot be directly used for dyeing textiles. Also, many plant materials such as flowers and fruits are seasonal and contain a large amount of water and hence cannot be stored as such. Therefore, in order to make them suitable for textile dyeing purposes and to make them available throughout the year, these are subjected to some processing operations. Collected plant materials are first dried: either in shade or in a hot air drier at a low temperature of about 40–50 °C to reduce their water content to about 10–15 % or less. Many materials can also be sun dried. Dried material is then powdered in a pulverizer to reduce particle size and to facilitate better dye extraction. These powdered and dried materials in most cases can be stored in airtight bags and containers for at least a year and can be used for dyeing whenever required. Storage under nitrogen can further prolong their shelf-life. Many natural dye manufacturers sell such finely powdered materials and these are used by many cottage-level dyers practicing hand-dyeing as it works out cheaper. However, these powders are unsuitable for use in various dyeing machines such as a package dyeing machine as the textile material acts as a filter and the dye particles get trapped within it, resulting in patchy and uneven dyeing. Therefore purified dye powders are required for use in dyeing machines. For producing purified dye powders, dye has to be first extracted from dye-bearing materials and the extract thus obtained is then concentrated or dried to get liquid concentrates or purified ready-to-use powders. These purified forms are costly due to the involvement of various machines and increased consumption of energy in various processing operations. Also, the efficiency of dye extraction is less in comparison to the use of powdered crude dye-bearing material for dyeing as the dye extraction process also continues during the dyeing process. Various extraction and drying processes for production of purified natural dyes are described in the following text.

4.1 Extraction Methods

As natural dye-bearing materials contain only a small percentage of coloring matter or dye along with a number of other plant and animal constituents such as water-insoluble fibers, carbohydrates, protein, chlorophyll, and tannins, among others, extraction is an essential step not only for preparing purified natural dyes but is also required to be carried out by users of crude dye-bearing materials. As natural coloring materials are not a single chemical entity and the plant matrix also contains a variety of nondye plant constituents, extraction of natural dyes is a complex process. The nature and solubility characteristics of the coloring materials need to be ascertained before employing an extraction process. The different methods for extraction of coloring materials are:

- Aqueous extraction
- Alkali or acid extraction
- Microwave and ultrasonic assisted extraction
- Fermentation
- Enzymatic extraction
- Solvent extraction
- Super critical fluid extraction.

4.2 Aqueous Extraction

Aqueous extraction was traditionally used to extract dyes from plants and other materials. In this method, the dye-containing material is first broken into small pieces or powdered and sieved to improve extraction efficiency. It is then soaked with water in earthen, wooden, or metal vessels (preferably copper or stainless steel) for a long time usually overnight to loosen the cell structure and then boiled to get the dye solution which is filtered to remove nondye plant remnants. The process of boiling and filtering is repeated to remove as much dye as possible. When the extraction is to be carried out on a larger scale for preparation of purified dye powders, stainless steel vessels are used and the time of soaking the materials in water may be reduced by boiling the solution for an extended time period. Generally, centrifuges are used to separate residual matter. Use of trickling filters can ensure removal of fine plant material particles and ensure better solubility of the purified natural dye.

As most of the dyeing operations are carried out in aqueous media, the extract obtained by this method can be easily applied to the textile materials. Disadvantages of this extraction method are long extraction time, large water requirement, use of high temperature, and low dye yield as only water-soluble dye components get extracted whereas many dyes have low water solubility. Also, along with dye, other water-soluble substances such as sugars and the like get extracted that may have to be removed if the extract is to be concentrated and converted to a powder form. Yield of heat-sensitive dye substances gets reduced at boiling temperature, therefore a lower temperature should be used for extraction in such instances.

4.3 Acid and Alkali Extraction Process

As many dyes are in the form of glycosides, these can be extracted under dilute acidic or alkaline conditions. The addition of the acid or alkali facilitates the hydrolysis of glycosides resulting in better extraction and higher yield of coloring materials. An acid hydrolysis process is used for the extraction of dye from tesu (*Butea monosperma*) flowers. Acidified water is also used for extracting some flavone dyes to prevent oxidative degradation.

Alkaline extraction is suitable for dyes having phenolic groups as they are soluble in alkali, which improves the dye yield. Dyes can be later precipitated by the use of acids. Dye from annatto seeds can be extracted by this technique. This process is also used to extract lac dye from lac insect secretions and red dye from safflower petals [32]. The disadvantage of this process is that some coloring materials may be destroyed under alkaline conditions considering the fact that some of the natural dyes are pH sensitive.

Inasmuch as natural dyes are usually a mixture of different chemical constituents, changing the pH of the extraction medium by adding acid or alkali can lead to the extraction of different dye constituents which can lead to different hues upon subsequent dyeing and differences in colorfastness properties. Many researchers have studied the extraction of natural dyes under various pH conditions and compared the color and fastness properties of dyed fabric to find out the optimum dye extraction conditions and further additions to this information continue to be made every year in the scientific literature.

4.4 Ultrasonic and Microwave Extraction

These are actually microwave- and ultrasound-assisted extraction processes where extraction efficiency is increased by the use of ultrasound or microwaves thus reducing the quantity of required solvent, time, and temperature of extraction. When the natural dye containing plant materials is treated with water or any other solvent in the presence of ultrasound, very small bubbles or cavitations are formed in the liquid. These increase in size but upon reaching a certain size, they cannot retain their shape. When this happens, the cavity collapses or the bubbles burst creating high temperature and pressure. Millions of these bubbles form and collapse every second. The creation of very high temperature and pressure during extraction increases the extraction efficiency within a short time. Also the process can be performed at lower temperature and therefore extraction of heat-sensitive dye molecules is better. As exploration of new dye sources and attempts to optimize the dye extraction process is continuing, use of this extraction technique has been recently reported by many researchers [29, 31, 37, 38].

In microwave extraction, the natural sources are treated with a minimum amount of solvent in the presence of microwave energy sources. Microwave increases the rate of the processes so the extraction can be completed in a shorter time with better yield. Sinha et al. [53] have reported extraction of annatto colorant with microwave energy. Earlier their group had reported microwave-assisted extraction of blue pigment from the butterfly pea [52]. Microwave and ultrasound extractions can be considered as green processes due to reduction of extraction temperature, solvent usage, and time which results in lower consumption of energy.

4.5 Fermentation

This method of extraction uses the enzymes produced by the microorganisms present in the atmosphere or those present in the natural resources for assisting the extraction process. Indigo extraction is the most common example for this type of extraction. Freshly harvested indigo leaves and twigs are soaked in warm water (about 32 °C). Fermentation sets in and the colorless indigo containing glucoside indican present in the leaves is broken down into glucose and indoxyl by the indimulsin enzyme also present in the leaves. Fermentation is complete in about 10–15 h and the yellow liquor containing indoxyl is then taken to beating vats where indoxyl gets oxidized by air to the blue-colored insoluble indigotin which settles down at the bottom. It is collected, washed, and after removing excess water is pressed into cakes. Extraction of indigo from other indigo-containing plants such as woad is also carried out by fermentation. This process can also be used for extraction of certain other colorants such as annatto. The fermentation method is similar to aqueous extraction with the exception that this method does not require high temperatures. The microorganisms disintegrate the coloring matter binding substances in natural way. Long extraction time, need for immediate extraction of pigments after harvesting, foul smell due to microbial action, and so on, are some of the disadvantages of this method.

4.6 Enzymatic Extraction

As plant tissues contain cellulose, starches, and pectins as binding materials, commercially available enzymes including cellulase, amylase, and pectinase have been used by some researchers to loosen the surrounding material leading to the extraction of dye molecules under milder conditions. This process may be beneficial in the extraction of dye from hard plant materials such as bark, roots, and the like.

4.7 Solvent Extraction

Natural coloring matters depending upon their nature can also be extracted by using organic solvents such as acetone, petroleum ether, chloroform, ethanol, methanol, or a mixture of solvents such as mixture of ethanol and methanol, mixture of water with alcohol, and so on. The water/alcohol extraction method is able to extract both water-soluble and water-insoluble substances from the plant resources. The extraction yield is thus higher as compared to the aqueous method as a larger number of chemicals and coloring materials can be extracted. Acid or alkali can also be added to alcoholic solvents to facilitate hydrolysis of glycosides and release of coloring matter. Purification of extracted color is easier as solvents can be easily removed by distillation and reused. Extraction is performed at a lower temperature thus chances of degradation are fewer. The disadvantages of the method are the presence of toxic residual solvents and their greenhouse effect. Another disadvantage of this method is that the extracted material is not readily soluble in water and the subsequent dyeing process has to be carried out in an aqueous medium. Coextraction of substances such as chlorophylls and waxy materials also creates problem.

4.8 Supercritical Fluid Extraction

Supercritical fluid extraction is an emerging area in natural product extraction and purification. A gas functions as a supercritical fluid above its critical values of temperature and pressure. Such a fluid has physical properties somewhere between those of a liquid and a gas. They are able to spread out along a surface more easily than a true liquid because they have much lower surface tension than liquids. As their viscosity is also low, they have very good diffusivity and thus better interaction with the substrate. At the same time, a supercritical fluid is able to dissolve many substances like a liquid as solubility of a substance in any solvent is higher at higher pressure and temperature and such conditions are needed to maintain a gas in the supercritical state. Supercritical fluid extraction using carbon dioxide (CO_2) is a good alternative to solvent extraction as it is nontoxic, cheap, easily available, and does not leave residues. Critical temperature and pressure values for carbon dioxide are 31.4 °C and 1,070 pounds per square inch (psi) or 73.8 bars, respectively. Supercritical extractions using CO_2 typically operate at temperatures between 32 and 49 °C and pressures between 1,070 and 3,500 psi. As the CO_2 is a nonpolar molecule it behaves as does a nonpolar organic solvent. A cosolvent or a modifier may be added to improve the solubility of slightly polar solutes. The advantage of the process is that the extract is free from residual solvent traces and heavy metals and is light colored due to the absence of polar polymerizing substances hence the process has gained popularity in extraction of purified natural products for food and pharmaceutical applications. The disadvantage of the method is the high cost of the equipment and poor extraction of polar substances.

4.9 Drying Techniques

Coloring matter extract obtained from natural sources is mostly in aqueous media. If it is to be immediately used for dyeing as in many small-scale or cottage-dyeing establishments, it can be used as such after adjustment of concentration according to the shade requirements. However, if it is to be used at a later date for dyeing or in dye extract producing units, it has to be converted into either powder form or concentrated solid rich form for long-term storage and ease of transport. This also ensures uniformity of shade for the entire batch of dye powder or concentrate produced and natural dyes thus converted into powder form or liquid concentrates can be used like synthetic dyes by the industries. The following techniques are generally used for converting natural dye extracts into powder form or concentrates.

- Spray drying
- Drying under vacuum
- Freeze drying.

Spray drying is the most commonly used technique for converting natural dye extracts into powder form as it is simple and cost effective. The plant extract is sprayed into the spray chamber as fine droplets through an atomizer or spray nozzle. These droplets come into contact with hot air flowing into the chamber which removes the solvent; the resulting dry particles aggregate and fall to the bottom of the chamber where this powder can be collected. Natural dyes in ready-to-use dry powder form are mostly produced by this method. Dye molecules should be sufficiently stable to heat to follow this method of drying as dry powder is exposed to dry heat from the hot air. Also many fine dye particles that are too small to settle at the chamber bottom are carried away by the hot air and are lost resulting in lower recovery. Also higher dye content is needed to get larger size particles and lower losses that may be achieved by preconcentration of the extract or addition of inert compounds such as lactose and so on.

Extracts can also be concentrated under vacuum by use of a rotary evaporator or tray dryers and the concentrated dye can be purified further by the use of various solvents.

Another drying technique, lyophilization or freeze-drying can also be used for preparation of natural dye powders. In this process, the natural dye extract is subjected to freezing and water is removed from the frozen extract through sublimation by reducing the pressure. The equipment is costly and operating cost is also higher but heat-sensitive dyes can also be converted into dry powders as the process takes place at low freezing temperatures. Any one of the above techniques can be used for producing natural dye powder depending upon the dye extract properties and costs. Very pure dye extracts are now available for use in many countries especially the United States, but these are very costly and are mainly used by hobby groups for their uniqueness.

5 Application of Natural Dyes on Textiles

Natural dyes are mostly employed for dyeing of natural fiber textiles to enhance their eco-friendly characteristics. They are usually applied to textiles by dyeing. Apart from indigo, other natural dyes are usually not used for printing directly. For producing printed fabrics, the printing is usually done with mordant and the whole material is dyed whereby only the area printed with mordants picks up the color.

Natural dyes, like synthetic dyes, can also be used to dye textiles at all stages such as fiber, yarn, or fabric. Fiber dyeing has the advantage that any shade variation can be easily adjusted by blending and therefore has been practiced at industrial scale also but is costly due to problems in spinning and loss of dyed fibers. Wool is generally dyed in yarn form and traditional dyers prefer yarn dyeing for all materials as it offers versatility in designing during weaving. Dyeing in hank form is preferred by traditional dyers operating at the cottage level due to its simplicity and low investment and also its compatibility with their usage of crude dye-bearing natural resources for reasons of authenticity as well as cost effectiveness. Dyeing is normally carried out by these artisans by hand in large vessels. Iron, stainless steel, copper, and aluminum vessels are used. Dyeing in copper vessels is considered to produce bright shades. Aluminum vessels are normally stained with a particular dye hence should be used if only one type of dye is used. Stainless steel vessels are most preferred for the natural dyeing process. On a larger scale, hank-dyeing machines have been successfully used. Fine purified powders or concentrates are needed for package dyeing as otherwise dyeing is uneven. Fabric dyeing is also carried out in metal vessels at the cottage level. Machines such as the jigger and winch have been employed for dyeing larger lots.

Suitable dyes or dye-bearing resources are selected based on the color requirement. Information about some dye sources has been provided earlier. In general, tannin-containing barks are used to produce brown and grey colors. Flowers and leaves containing flavonoids are used to produce yellow color shades. Anthraquinone dyes from both animal and plant resources can be used for red color. Indigo is normally used to produce blue color shades. Secondary colors such as orange can be obtained by proper selection of dye and mordant or mixing two compatible dyes. However to get a green color or wherever blue color is needed to make a secondary color, material is first dyed with indigo and then overdyed with the other dye. If raw plant materials are used (which is usually the case at the cottage level), dye has to be extracted prior to dyeing. Details of various dye extraction methods have already been discussed. Aqueous-based extraction methods are employed. If purified natural dyes are used, these can be directly used for dyeing. The process for the dyeing of textiles with natural dyes differs from the synthetic dye application process because only some natural dyes can be applied directly to textiles. In most of the cases the dye is not substantive to the fiber on which it is being dyed therefore an additional step of mordanting is involved, making it a two-step process.

5.1 Mordanting

Textile fibers, especially cellulosics, do not have much affinity for the majority of the natural dyes; hence these are subjected to an additional step known as mordanting. Mordants are the substances that have affinity for both textile fibers and dyes, thus they act as a link between the fiber and dyestuff. Those dyes that do not have affinity for a fiber can be applied by using mordants. In the case of dyes having affinity for the fiber, the use of mordants increases the fastness properties by forming an insoluble complex of the dye and the mordant within the fibers, which also improves the color. Unlike animal fibers, vegetable fibers such as linen and cotton do not readily hold the mordants resulting in duller color compared to the bright colors obtained on wool and silk. Mordanting is very important for cotton as it is more difficult to dye than wool or silk due to the absence of amino and carboxyl groups that provide attachment sites to dye molecules. There are three types of mordants, namely metal salts or metallic mordants, oil mordants, and tannins which are discussed below.

5.2 Metallic Mordants

Metal mordants are often used for the dyeing of textiles with natural dyes. Metal salts of aluminum, chromium, tin, copper, and iron were being used as mordants by traditional dyers. Now chromium has been red-listed under eco-regulations and therefore should not be used to maintain the eco-friendly nature of dyed textile material as well as the discharged effluent. Copper is also in the restricted category but its permissible levels are higher and can therefore be used in small amounts so as not to cross the permissible limit on dyed textile. Tin is not restricted by many eco-labels but its presence in effluent is not desirable from an environmental viewpoint. Alum and iron can be considered ecologically safe mordants as they are naturally present in the environment in large amounts.

Different colors from the same dyestuff can be obtained by use of different metallic mordants because color obtained with many natural dyes is due to the formation of colored insoluble dye complexes with metal salts or mordants. Dye complexes with different metals have different colors and may also differ in fastness properties. For example, alizarin forms a red lake or complex with aluminum and a violet lake with iron. Similarly, onion natural dye which is yellow in color will change to orange color with stannous chloride mordant and grey color with ferrous sulphate. Information about some metallic mordants is provided below.

5.3 Aluminum

Potash alum, which is the double sulphate of potassium and aluminum, is the most widely used aluminum mordant for natural dyeing. It can be used alone or with cream of tartar or as basic alum for mordanting. When used alone, the material before dyeing is merely boiled in a solution of alum. The amount of mordant required depends on the shade to be dyed. If deeper shades are being dyed, more mordant is needed. Generally 10–20 % of alum can be used on the weight of the material (owm). If used along with cream of tartar, alum powder (20 % owm) is mixed with cream of tartar (40 % owm) in a little warm water and diluted to the required volume.

Alum in the form of basic aluminum sulphate (neutral alum) is used as a mordant for cotton. It is prepared by adding sodium hydroxide or carbonate solution to the aqueous solution of alum till the precipitate formed redissolves upon stirring. The material to be treated is dipped in the alum solution and the latter is then fixed by other chemicals or ageing. It is preferable to fix the alumina on the fiber by precipitating it with salts such as sodium carbonate or sodium phosphate to obtain good dyeing results. Neutral soap solution can also be used.

In another method the material is dipped in vegetable tannins/tannic acid or oil mordant such as Turkey Red Oil (TRO) before treatment with basic alum which results in good fixation of aluminum. Other aluminum salts such as aluminum sulphate or acetate can also be used for mordanting.

5.4 Iron

Iron salts in the form of ferrous sulphate (also known as green vitriol or copperas) are extensively used in dyeing and printing. Application of iron salts imparts a black or grey color to the fabric and dulls the shade. Ferrous sulphate if applied alone leaves only a very small quantity of iron on the fabric. Tannin-pretreated cotton picks up a good amount of iron. Cream of tartar can be used along with iron to fix it on the animal fibers. Traditional dyers use a fermented iron solution for iron mordanting where iron is present as acetate.

5.5 Copper

Copper sulphate or blue vitriol is generally used for copper mordanting. It is known to improve the lightfastness of various natural dyed materials and is necessary to obtain brown color from catechu and black color from logwood according to traditional recipes. As eco-standards limit the content of extractable copper in textile materials to 3–100 ppm depending upon the standard and clothing type, it should be used judiciously in small amounts.

5.6 Tin

Tin mordant brightens the color. Stannous and stannic chloride are used as mordants. Stannic chloride is preferred for cotton. It is generally used on tannin-pretreated cotton. For wool, cream of tartar may also be added to the bath. Although not restricted by many eco-standards, its use is not recommended from an environmental pollution viewpoint. It is not permitted to be used under the recent Global Organic Textiles Standard (GOTS) where its amount has been restricted to below 0.2 ppm.

5.7 Chromium

Earlier used by many dyers in the form of potassium dichromate and referred to as Chrome, its presence on textiles is now restricted by most of the standards to a level of >0.2 ppm, therefore it is better to avoid this mordant.

5.8 Oil Mordants

These mainly find application for dyeing madder to obtain Turkey red color. Alum is the main mordant used here. It gets fixed onto the cotton material by forming a complex with the oil mordant and then combines with madder to produce the Turkey red color. In the past, castor and til (sesame) oils were used as mordants but they were later replaced by Turkey Red Oil (TRO) which is sulphonated castor oil.

5.9 Tannins and Tannic Acid

Tannic acid or tannins are used as a primary mordant for cotton and cellulosic fibers as they do not have much affinity for metallic mordants. A cotton fabric treated with tannic acid can absorb all types of metallic mordants. Tannins may be in the form of tannic acid or vegetabl-tannin–containing substances such as myrobolan (Harda, *Terminalia chebula*), oak galls, sumac, or pomegranate rind may be used for mordanting. Vegetable tannins are cheaper and occur as excretions in the bark and other parts such as leaves, fruits, and galls. The tannin in myrobolan is of the ellagitannin type and occurs mainly in the peel of the fruit. It also contains a yellowish-brown coloring matter that imparts a yellowish coloration to textile material. It is widely used as a mordant in the dyeing of cotton and for producing black shades. Leaves and twigs from various species of *Rhus* or sumac contain 15 to 20 % tannin which is of the gallotannin type. It has an olive-green color. The presence of some reddish coloring matter in sumac prohibits it from being employed for light and brilliant shades.

5.10 Mordanting Methods

There are three types of methods for application of mordants based on the time of their usage. They are:

1. Premordanting
2. Postmordanting
3. Metamordanting or simultaneous mordanting.

As suggested by the name, in premordanting, the mordants are applied to the fabric prior to dyeing. It is most common for cotton and cellulosics as in the unmordanted state they do not have affinity for many natural dyes. Even for animal fibers, some natural dyes such as cochineal require this type of mordanting process for producing good shades. Various famous traditional printing styles with natural dyes from India such as "Kalamkari" in Andhra Pradesh and "Sanganeri" in Rajasthan use this mordanting method. The advantage of this method is that standing baths can be used for mordanting; that is, the bath can be reused many times after replenishing with the mordants. This makes the process economical as well as reduces the pollution load hence is useful for large-scale applications.

In the postmordanting method, the fabric after dyeing is treated with mordant in a separate bath. The final color is developed during the last phase. Iron salts are very often applied in this manner for producing grey and black colors.

In the metamordanting or simultaneous mordanting method, both dyeing and mordanting processes are carried out in the same bath itself. Usually for cotton and cellulosics, mordant is also added to the dye bath at the start of dyeing so that both dyeing and mordanting processes take place simultaneously in the same bath. For animal fibers such as wool, mordant may sometimes be introduced into the dye bath towards the end of the dyeing process when much dye has already been exhausted onto the textile. The dyeing duration is reduced in this method due to a reduction in the number of steps. This method produces darker shades for some dyes whereas for others, color yield may reduce due to the loss of some dye and mordant to dye–mordant complex formation in the dye bath which may also cause uneven dyeing. As the mordant cannot be reused, this process is more useful for small lots.

5.11 Dyeing

As for synthetic dyes, the amount of dye to be taken is normally given as % shade. It denotes the amount of dye (in grams) to be taken for dyeing 100 g of textile material. The terminology remains the same for both crude dye material and purified extracts. As the dye content of raw materials is low, it is common to use 10–30 % shade whereas the amount can be reduced to 2–5 % for the purified dye extracts. The amount of mordants is also selected in relation to the shade dyed. A larger quantity of mordants is needed for higher shades.

As is the case with synthetic dyes, the amount of water to be taken in the dye bath is an important parameter. In technical terms, it is given in the recipe as the material-to-liquor ratio (MLR). The MLR denotes the amount of water in ml required per gram of the fabric to be dyed.

As natural dyes differ in their chemical constituents, their dyeing procedures also differ but their basic dyeing process is similar. There may be different optimum temperature, time, and pH of dyeing but the basic steps remain the same. Many natural dyes are dyed at near boiling temperature on cotton. Wool and silk are dyed at a lower temperature although some dyes may dye cotton also at lower temperature. Most dyes require neutral pH but some dyes require acidic pH and some may need alkaline pH. For dyeing animal fibers wool, pashmina, and silk, generally 1–2 % of acetic acid is added during dyeing. The material to be dyed premordanted or otherwise is introduced into the dyeing bath at room temperature and the temperature is then increased slowly to ensure uniformity of dyeing. The material is usually dyed for at least an hour to allow the dye to penetrate well inside the textile material. The movement of textile material in the dye bath is very essential. If the dyeing is carried out in dyeing machines, movement of the material is taken care of but in hand dyeing, the fabric needs to be continuously stirred in the dye bath, otherwise uneven dyeing may result. If delicate fabrics such as pashmina are to be dyed, the dye bath should not be stirred continuously as that will damage the fabric structure. In such cases, it is advisable to have a material-to-liquor ratio of at least 1:100 so that the fabric is completely immersed in the dye liquor during dyeing and dyeing is uniform. If simultaneous mordanting is to be carried out, the required quantity of mordant is also added to the dye bath. After the dyeing is over, the dyed materials are removed and allowed to cool down a little and then washed with water. Some traditional dyers leave the material in the dye bath itself to cool and then remove the material for washing. The washed dyed material is then soaped with a hot soap or nonionic detergent solution to remove loosely held dye and is again rinsed with water and air dried in shade. At industrial scale, hydroextractors are used to remove excess water during washing. If post-mordanting is to be carried out, the washed material is taken up for postmordanting without soaping and soaping is carried out on the postmordanted material after washing. When cotton materials are dyed with dyes such as madder which do not have affinity to it without mordants, the premordanted dyed material may be further postmordanted to get different shades and improvements in fastness properties. Treatment with small amounts of copper mordant improves the fastness to light for many dyes although it also results in slight hue changes. Such treatment with copper to improve lightfastness was also practiced earlier for certain synthetic dyes. A postdyeing treatment with tannins and alum can help in improving the fastness to washing.

5.12 Indigo Dyeing Process

The indigo dyeing process is different from the general natural dyeing process using mordants or direct dyeing as it is a vat dye. That is the reason why indigo dyeing cannot be combined with any other natural dyeing process. The process for indigo dyeing consists of reduction of indigo to its leuco form which is soluble in alkali. In olden days, a fermentation process was used to reduce the indigo and seashells, limestone, plant ashes, or alkaline earth provided the alkali for its dissolution. Continuous vats were maintained continuously for a number of years in which indigo-reducing microorganisms thrived. Indigo and other materials were added to these vats before dyeing as per the requirement. Nowadays, only some dyers maintain the traditional fermentation vats for small-scale applications. Mostly, reducing agents used for reducing synthetic indigo including hydrosulphite, thiourea, and the like are also being used for natural indigo and caustic soda is used as alkali. After reduction, the materials to be dyed are immersed in the bath and dyeing is continued for the stipulated time, which is usually a few minutes. Finally, the materials are removed from the bath and exposed to air to oxidize the leuco form of indigo to its original insoluble blue form. These are then soaped to remove unfixed dye thereby improving the rubbing fastness, rinsed with water, and air dried in shade.

6 Advantages of Natural Dyes

Natural dyes are considered to be eco-friendly as these are obtained from renewable resources as compared to synthetic dyes which are derived from non-renewable petroleum resources. These are biodegradable and the residual vegetal matter left after extraction of dyes can be easily composted and used as fertilizer. They produce soft colors soothing to the eye which are in harmony with nature.

In addition to these environmental benefits, natural dyes also offer functional benefits to the wearer and users of such textiles. Many of the natural dyes absorb in the ultraviolet region and therefore fabrics dyed with such dyes should offer good protection from ultraviolet light. Improvement in UV protection characteristics of natural cellulosic fibers after treatment with natural dyes has been reported by various researchers [11, 28, 47]. Griffony et al. [16] observed that treatment with tannins during mordanting itself improved the UV protection of fabrics. Saxena et al. [50] also observed that extracts of tannin-rich pomegranate rind showed strong absorption in UV region and cotton fabrics treated with these extracts showed excellent UV protection which was durable to washing. As cotton and other cellulosics are frequently treated with tannins in the mordanting step during dyeing with natural dyes, it is likely that such dyed fabrics would also show good UV protection. Many of the natural dye materials possess antimicrobial properties. Therefore, textiles dyed with such materials are also likely to show antimicrobial properties and the same has been reported by many researchers [12, 18, 36]. Ibrahim et al. [25] have reported improvements in both UV protection and anti-bacterial activity for polyamide 6 fabrics after treatment with natural dyes. Fabrics dyed with some natural dyes have been reported by the wearers to be free of odor perhaps due to the antibacterial or bacteriostatic properties of natural dye materials. Users of natural dyed fabrics have also found such fabrics to be mosquito repellent and/or moth repellent as perhaps the plant material from which these dyes were derived might also have contained natural repellent substances. In addition, recently, cellulosic textiles treated with natural plant extract have been found to exhibit flame-retardant properties [4].

Many natural dyes such as myrobolon fruits, turmeric, manjishth root, Arjuna (*Terminalia arjuna*) bark, and safflower florets, among others possess curative properties and have been used in various traditional medicinal systems. Textiles dyed with these materials may also possess healing properties by absorption of medicinal compounds through the skin. Textiles produced in Kerala, India by dyeing with herbs as per the traditional Ayurvedic system of medicine and known as “Ayurvastra” have become very popular as health and well-being textiles and also as medicinal or curative textiles and are being exported to various countries. Various companies are now marketing naturally dyed textiles as health and well-being textiles.

7 Drawbacks of Natural Dyes

Natural dyes are considered to be an eco-friendly alternative for dyeing of textile materials, especially natural fiber textiles. However, there are many limitations in the usage of natural dyes some of which are listed below.

7.1 Tedious Application Process

Natural dyes require a longer dyeing time in comparison with synthetic dyes as very often an additional mordanting step is required. Use of raw dye-bearing materials ensures authenticity but at the same time involves additional dye extraction steps that require time and separate set-up. Natural dyes in this form are also not suitable for use in many commercial textile dyeing machines which makes the process labor intensive. Also in an industrial set-up, disposal of solid residual biomass is problematic. Purified extracts, although suitable for machine application, are costly and not economical. Logistics for making agricultural by-products such as pomegranate rind, onion skins, or fruits and leaves of trees from the forests available for dyeing purposes are not in place which would have helped in reducing the costs. Exhaustion of most of the natural dyes on textile materials is poor in spite of using the mordants which leaves a large quantity in the dye bath after dyeing. That increases the cost of dyeing although it may not have other environmental implications as seen for synthetic dyes due to the biodegradable nature of these dyes. Traditional dyers reused the dye bath but the color obtained is different from the earlier lot which may not be acceptable by today's standards. All these increase the cost of naturally dyed textiles.

7.2 Limited Shade Range

Shade range of natural dyes is limited. Out of the three primary colors—red, yellow and blue—although there are several sources for red and yellow dyes, there is only one major source of the blue dye: indigo. As natural dyes differ in their application process, only few dyes can be applied in mixtures and differences in fastness properties further limit the choice. Even a common secondary color such as green needs to be produced by overdyeing as blue dye indigo being a vat dye has an entirely different application process that increases the dyeing time and cost.

7.3 Nonreproducible Shades

Difficulty in reproducing the shades is another major drawback of natural dyes which is caused by the inherent variations in the proportion of chemical constituents in the natural material and thus in its crude extract depending upon the maturity, variety, and agroclimatic variations such as soil type, region, and so on. Therefore it is not possible to produce the same shade with a particular natural dye in every dyeing operation [51]. Production of standardized dye powders is an expensive and complicated exercise as most of the natural dyes contain various chemical constituents. Some of the natural dyes are pH sensitive and tend to change color due to change in pH. As natural dyes tend to form colored complexes with metal ions, the mineral composition of water may also cause shade variations. Hence even the same standardized powder may give different shades at two different places due to the differences in mineral content and pH of the water which makes it very difficult to reproduce the shades.

7.4 Fastness Properties

Colorfastness to light and washing are most important parameters to evaluate the performance of a textile and deciding about its end use although colorfastness to rubbing and perspiration are also important especially if it is to be used as apparel. A material should have good fastness to light if it is to be used for making curtains although a little lower fastness to washing may be satisfactory for this application. Colorfastness properties of natural dyes are a cause of concern. Only a few natural dyes possess fastness properties conforming to modern textile requirements. Restrictions on the use of certain metal salts for mordanting such as chromium, copper, tin, and so on by eco standards has not only reduced the color gamut of natural dyes but has also made the task of producing shades with good fastness properties difficult. Improper application procedures used by certain practitioners of natural dyes are also sometimes responsible for poor fastness properties. Improvements and optimization of mordanting and dyeing procedures can help in solving this issue. Exploring the new sources for dyes can increase the number of dyes with better colorfastness properties.

7.5 Safety Issues

Exploration of new sources for dyes can certainly help in increasing the shade range of natural dyes with good fastness properties. However, extensive research on the safety of these materials to humans and the environment would be needed before propagating their usage as everything of natural origin may not be safe.

Nature is known to produce poisonous substances also; therefore thorough toxicological evaluations for the new sources are necessary. Use of metallic mordants also requires caution so as not to cause adverse health effects during handling. Precautions should also be taken to prevent pollution problems in the usage of these mordants and it should be ensured that the amount of restricted mordants in the dyed textile is within the limits set by eco regulations.

7.6 Characterization and Certification Issues

Although dyeing of textile fabrics with dyes obtained from various natural resources has been extensively investigated, little information is available on the identification and characterization of the natural dyes. Natural dyes, being plant metabolites, are present only in small amounts in dye-bearing materials along with large quantities of other nondye materials. The dye content may vary according to the age, part of the plant, and agroclimatic conditions, and it is important to know the dye content in order to get reproducible shades. While procuring the dye materials, pricing should match the dye content and when powdered dye materials or extracts are used, these should be authentic. Thus determination of dye content as well as characterization of dye material is important in the case of natural dyes. Absorption spectroscopy is very successfully used for measuring the dye content of synthetic dyes but has limited applicability for natural dyes as these dyes are usually not a single chemical entity but a mixture of closely related compounds and in many cases there are no clearly defined absorption maxima. A literature survey shows that the earliest attempts to characterize the natural dyes were made in the context of identifying the dyes present on historical textiles kept in museums or those found in archaeological excavations. Different techniques including high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), high-performance thin-layer chromatography (HPTLC), UV visible, and mass spectroscopy have been employed for this purpose [13, 46]. However, there are no certification bodies or any testing agencies that can certify or characterize and identify the commercial natural dyes or the fabrics dyed with natural dyes although such fabrics fetch higher prices. As a result, some unscrupulous elements in the trade tend to mix natural dyes with cheap synthetic dyes or try to pass off the fabrics dyed with synthetic dyes as those dyed with natural dyes. It is quite common to find people trying to market fabrics dyed with synthetic alizarin or indigo as dyed with natural dyes. Therefore development of process protocols for quick identification and characterization of natural dyes is very important for the sustainability of true natural dyed textiles. TLC and HPTLC techniques can be easily employed for quick identification of natural dyes by comparing with chromatographic fingerprints of authentic natural dye samples. Many organizations have worked in this direction and in authors' lab HPTLC fingerprints of root and stem samples of *Rubia cordifolia* and *Rubia sikkimensis* were also developed which are presented in Fig. 8.

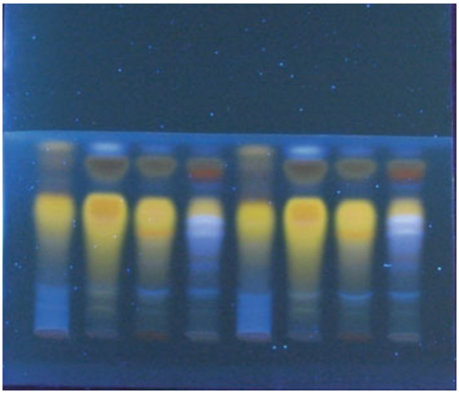


Fig. 8 HPTLC fingerprints of *Rubia* spp. root and stem

Establishment of some certification system such as those followed for organic crop products would be very helpful in this regard as that can ensure both authenticity and quality because often the fastness properties of natural dyed materials are not satisfactory due to improper dye application procedures. Such a certification system has been established in Turkey under the DOBAG project where the University of Marmara is ensuring the quality of each natural dyed carpet having the DOBAG tag.

8 Present Scenario and Sustainability Issues in Usage of Natural Dyes

Presently natural dyes are not in use for mainstream textile processing. Only about 1 % of the total textiles produced are dyed by using natural dyes [20]. Traditional dyers, enthusiasts, and hobby groups are the main users of natural dyes who work at the cottage level. Some small industries are also using natural dyes and there are a number of companies who are manufacturing and selling natural dyes both as finely ground plant material as well as purified extracts. Sustainability is a complex multidimensional concept concerning the environment, economy, human health, and social impact. It aims to meet the needs of the present generation without compromising the ability of future generations to meet their needs. According to Hill [23] greater emphasis on using natural dyes in the textile industry can make a valuable contribution to the environmental sustainability in the twenty-first century. Various sustainability issues involved in the present status of usage of natural dyes and in its further promotion are discussed in this section.

8.1 Renewable and Biodegradable

Natural dyes are obtained from natural resources, mainly different parts of the plants which unlike petroleum resources are renewable. Some of the dyes including turmeric, safflower, marigold, and indigo are obtained from annual plants and thus are renewed annually. Many dyes derived from flowers and fruits and seeds of trees such as myrobolon, tesu or flame of the forest, annatto, and the like, also are renewed annually. Tree leaves are also a sustainable and renewable source, provided these are harvested in a scientific manner and quantity and frequency of leaves removed from each tree does not exceed its renewal potential. The removal of leaves is not as harmful to the plant as the stripping of bark [39]. Deciduous tree leaves are again annually renewable. Bark and wood are not sustainable sources in the sense that removing these without harming the tree is difficult. However, these can be obtained as by-products from the timber industry and new plantings of such plant materials need to be made to ensure sustainability. Some dyes such as safflower florets, onion skin, and pomegranate rind, among others are an agricultural by-product and other than the collection and transportation costs, no other investment is needed in their use as natural dyes. Pomegranate rinds are an agroprocessing by-product. Temple waste flowers also offer an inexpensive source of natural dyes [58]. Lac is an industrial by-product as it is recovered from the washwaters of the shellac-processing industries. Exploration of ways and means to utilize these resources for enhancing the availability of natural dyes is much required as that would also provide additional income and empower the farmers and small scale entrepreneurs.

Natural dyes are biodegradable as they are derived from natural materials and can be easily degraded by microbial action. The dye molecule on its own is weakly colored and is susceptible to the action of light and water. It is due to the complex formation with the mordant that deep coloration is obtained and good resistance to the action of light and water in terms of improved fastness to light and washing is achieved. However, in the case of synthetic dyes, the dye molecule in itself is designed to have brilliant color and good resistance to the action of light and water. It is the good performance of these synthetic molecules as a dye on textiles that makes them difficult to degrade thus making the treatment of the effluent containing their residual amounts extremely difficult.

8.2 Easy-to-Treat Effluent

As natural dyes are biodegradable, and complex chemical auxiliaries and extreme pH conditions are not used in the dyeing process, effluent produced during their usage is considered to be easily treatable and expensive elaborate effluent treatment plants needed for synthetic dyes are not required. Data presented by Henriques and Shankar [22] confirmed it. The effluent produced by using different natural dyes was found to have a BOD value of 40–85 mg/L only which was less than the limit of 100 mg/L prescribed by the Central Pollution Control Board (CPCB), Government of India. It also had no color and its TSS and TDS levels were much below the levels reported for various classes of synthetic dyes. Most parts of the TDS also consisted of various plant nutrients such as potassium, calcium, sulphate, and the like and hence were successfully used for irrigation of plants. Earlier, it was reported in a pilot-level study conducted on the dyeing of cotton with dye extracted from dried chrysanthemum flowers, that COD of the dye effluent was reduced by almost 75 % within a day upon simple storage and by next day its level came down to below 20 mg/L which was the limit prescribed by the CPCB, India in respect of BOD for discharge into inland water bodies 49]. A reduction in pollution load with plant-based dyes in comparison to the application of synthetic dyes even with latest dyeing techniques has been reported by Bechtold et al. [5]. Thus these dyes are advantageous to the rural artisans practicing traditional craft forms in remote areas as they can use locally available resources for coloration of textile materials. As they do not have access to complex effluent treatment solutions, easy biodegradability of these dyes reduces the risk of polluting the local water resources and offers a clean production model.

8.3 Promote Vegetation and Carbon Fixation

As natural dyes are mostly derived from plant parts, higher usage of natural dyes would lead to the planting of more dye-bearing plant materials which would lead to higher carbon fixation in the form of biomass synthesized by these plants. Generally only a part of the plant is used for dyeing purposes and that too contains at most 5 % of dye. Therefore for every kilogram of natural dye produced, some other useful products can also be obtained if purified dyes containing only the specific dye components are isolated. Also, if the enormous quantity of biomass produced is composted, it would help in improving soil fertility and agricultural production and thus further increase the carbon fixation. The UNDP-sponsored project implemented in India during 1998–2001 listed more than 100 promising natural dye materials, many of which were suitable for revegetation of wastelands [3]. Thus cultivation of dye-yielding plants may be practiced for the greening of the wastelands and thereby enhancing the carbon fixation. The SPINDIGO (sustainable production of plant derived indigo) project implemented in Europe in the beginning of this century involving 10 institutions from five countries found that production of plant- (woad-) derived high-purity indigo is a viable alternative and such indigo can meet about 5 % of total indigo consumption in Europe. Farmers can be given seeds and agronomic packages for improved indigo content of the produce and cultivation of indigo can provide a good source of income to the farmers. Similarly, farmers in the other parts of the world can grow dye-yielding crops and trees that would enhance their income and also help in promoting vegetation and hence carbon fixation. Similar observations were made in respect to other dye-yielding plants such as weld and madder also in other projects implemented in the European Union during the first decade of this century. However, due to problems with the consistency of raw plant products, actual commercial production of such crops for industrial-level application could not pick up.

8.4 Status in GOTS

All natural dyes except those derived from a threatened species are recommended for coloration of organic textiles according to the latest (3.0) version of Global Organic Textile Standards (GOTS). However, it is also specified that all dyed textiles should fulfill the norms with respect to restricted heavy metal content and colorfastness requirements and their production should not lead to environmental contamination. Therefore, not all natural dyes would be able to fulfill these criteria. Natural-dyed textiles where chrome or tin is used as mordant would not be able to pass the test for restricted heavy metal content and those with copper mordant would need careful monitoring to ensure compliance. Also natural-dyed fabrics not matching up to required levels of fastness to rubbing, perspiration, washing, or light are also not eligible for this certification. At the same time, all safe synthetic dyes that do not contain the banned aromatic amines or prohibited heavy metals are also allowed provided the effluent meets the criteria prescribed by the local regulatory bodies. This does not confer any special status to natural-dyed textiles. A separate sublabel for natural-dyed textiles in this standard would have been of much help in promoting the cause of natural dyes as it would have provided incentives to those practitioners of natural dyes who would have been able to meet the technical performance specifications and environmental requirements.

8.5 Availability and Supply Issues

Availability and supply of natural dyes is of major concern from the sustainability angle. At the present level of world textile production, natural dyes can only replace a fraction of total textile dye consumption. The tedious process of color extraction and seasonal availability of natural dye sources are the reasons hindering their use in textile coloration. In order to reduce the problem and to ensure ready availability of natural dyes, they have to be converted into ready-to-use soluble powders or liquid concentrates just like synthetic dyes. By converting into powder form, the shelf-life of natural dyes can also be increased. Many companies in the United States, India, and China are presently selling natural dyes as both raw material powders and ready-to-use extracts and these can be ordered on the Internet. Ready-to-use dyes are, however, very costly. It is possible to exploit the by-products and waste material from the food processing industry such as pomegranate rinds, onion skins, grape skins, and the like for extracting natural dyes as the problem of ready availability at a place gets solved and the costs can be reduced. A collection and supply mechanism for some agro by-products such as safflower florets as also for forest products such as myrobolon fruits, tree leaves, and so on needs to be established to increase their availability. Some important dye plants including madder and indigo can be cultivated on marginal and wastelands to enhance their availability and good income for cultivators. Better agronomic practices and high color-yielding varieties with respect to such plants need to be developed to make the production economical. Some initiatives in this direction were undertaken in Europe some years back whereby it was observed that cultivation of plants such as woad, weld, madder, and so on for producing dyes is economically feasible but guidance for growers and establishment of forward linkages in the form of processing units is needed. Land availability for growing natural dyes is, however, limited in view of the first preference to food and fodder crops and therefore microbes offer tremendous potential for the supply of natural colorants. Biotechnological tools can be of great help in this regard by identifying and transferring the dye-producing genes into fast-growing harmless microbes. Due caution about the safety and toxicological aspects, however, is needed.

8.6 Danger of Deforestation Due to Indiscriminate Exploitation

Promotion of natural dyes without ensuring the increased availability of dye-bearing resources carries the danger of overexploitation. It is in this context that GOTS prohibits the use of dyes and auxiliaries from the bioresources on the endangered list. Many dyes are obtained from tree bark, wood, and roots and it is difficult to obtain them without damaging the plant. Harvesting only a small portion or obtaining these materials as a by-product from the timber industry may be sustainable but indiscriminate harvesting and tree cutting to get these materials for dyeing purposes is sure to damage trees and lead to deforestation. It takes a number of years for a tree to grow, therefore unless these trees are planted in greater numbers before harvesting the existing ones biodiversity would be greatly endangered. Although leaves are a more sustainable resource than bark or roots, frequent indiscriminate harvesting of leaves may also cause damage to the trees. Use of flowers has the danger of disturbing the natural pollination and reproduction cycle of plant species. Harvesting of fruits and seeds does not affect the plants but care should be taken to use only such fruits and seeds that are not eaten by animals and birds otherwise their natural food sources would be lost. It is observed that many tribal people who live on the edges of the forest area have learned to live in harmony with nature. They fulfill their needs by obtaining forest produce only to the extent required for their needs and leave the rest undisturbed. This balance may be disturbed by the lure of money from the sale of dye resources which may lead to deforestation unless the people are trained in sustainable harvesting of dye plants and such harvesting is closely monitored to prevent overexploitation at the instance of dye manufacturers. Such efforts were made in an ICEF-funded project in India [22] where tribal people were trained in sustainable harvesting of dye-bearing tree leaves. They were further trained in the drying of these leaves and these dry leaves were then supplied to a natural dye manufacturing unit that in return provided them with cooking gas cylinders which eliminated the cutting of forest trees for firewood by these people leading to improved forest cover rather than deforestation.

8.7 Use of Non-Eco-Friendly Metallic Mordants

The use of metallic mordants during natural dyeing often puts a question mark on the eco-friendliness of natural dyes. Only a small amount of these metal salts gets fixed onto the textiles and the rest is discharged as effluent which leads to the contamination of land and water resources. However, it has been observed that out of the five metallic mordants traditionally being used for natural dyes, alum and iron are environmentally safe and these have not been restricted by any eco-regulations. In fact they are used for effluent treatment of synthetic dyes. Out of the remaining three mordants, chromium as Cr VI is very toxic, hence should not be used. Tin should also be avoided; copper may, however, be used judiciously as it has a higher tolerance limit in various eco-regulations. Of course the effluent should contain as low an amount of the mordant as possible to avoid pollution problems. Creation of awareness about this aspect among traditional dyers using natural dyes is important to make the naturally dyed textiles eco-friendly. Use of standing baths for these mordants can minimize the pollution problems but it would require working out the exact amount exhausted onto the fibers so as to facilitate replenishment. Traditional recipes need to be reworked for maximizing the mordanting bath exhaustion so that lower quantities can be used and there is less mordant to be discharged as effluent. Use of some auxiliaries such as formic acid or cream of tartar can improve the uptake of metal ions by the animal fibers and a pretreatment with tannin substances can improve the metal ions pick-up by cellulosic materials. At the same time, it should also be ensured that the amount of restricted metals on the fabric is within the prescribed eco limit. Extensive reworking of mordanting and dyeing recipes is also needed so that the required level of fastness properties could be achieved while maintaining heavy metal mordant content within the limits suggested by eco-regulations. In order to make natural dye sustainable, it would be very important if metallic-salt–based mordants can be replaced with natural mordants. Several research studies have attempted to use tannin-based natural substances such as myrobolan, tannic acid, and pomegranate rind as natural mordants in place of metallic mordants and these were found to be effective in improving the fastness properties. Thorough research and transfer of research results to actual users is necessary to stop the usage of non eco-friendly mordants.

8.8 Unsuitable for Industrial Set-Up

Natural dyes presently are not suitable for industrial set-up due to the tedious application process of raw natural resources. These materials are not compatible with many industrial dyeing machines hence the dyeing process becomes labor intensive. Also the availability of many natural dyes is also not sufficient as in many cases a proper supply chain is not in place. A range of shades with good fastness properties is limited. They are not suitable for working in mixtures and not amenable to shade matching and prediction with the help of computerized color-matching systems. Therefore these are mostly being used by practitioners of craft forms, hobby groups, and NGOs only on the cottage level. Today's high cost of purified natural dyes makes their industrial use an impractical proposition.

8.9 Cost Considerations

Presently the cost of dyeing textiles with natural dyes is much higher in comparison to the cost of dyeing with synthetic dyes due to several reasons. First the application procedure is lengthy and complicated. Most of the dyeing is done by hand hence it is labor intensive. The dye yield of colorants is not good and a much larger amount is needed to get good shades, whereas synthetic dyes are intensely colored and a much smaller amount is sufficient to produce good coloration. The cost of the dye material itself may be more as sometimes it is already in use for other purposes such as traditional medicine, food ingredients, and the like. Only few dyes have a similar application technique so that if two dyes are needed to produce a shade, dyeing has to be carried out twice which increases the cost. Also due to the small level of operations, economy of scale is not achieved. However, if the hidden cost of the use of synthetic dyes in terms of pollution caused and its detrimental effects on the environment or the investments made and expenditure incurred on effluent treatment is also considered, the gap substantially narrows down. According to the study conducted by Nayak [34] under the ICEF-funded project executed in India, the hidden environmental cost for synthetic dyes works out to be Rs. 410/kg of dye and if this cost is to be incurred by synthetic dye manufacturers, production of these dyes would become unsustainable. According to the same study, the cost of dyeing textiles in blue, black, and yellow shades with natural and synthetic dyes is almost comparable and only the cost of dyeing red is slightly higher for natural dyes when environmental cost is also taken into account. Natural dyed textiles presently sell at a premium, but this is only a partial compensation towards the environmental health and social benefits associated with the use of natural dyes.

8.10 Human Health and Safety Aspects

As textiles are worn next to the skin, the substances present on these can get absorbed by the skin and affect the health of the wearer. Skin irritation and contact dermatitis have been reported for some synthetic dyes and the use of azo dyes made from carcinogenic amines has been banned by legislation in many countries. Production of synthetic dyes involves the use of many toxic and hazardous chemicals and harsh conditions, and adequate protection measures for the workers and proper effluent treatment and disposal systems are needed. Many natural dyes, on the other hand, have been used as medicines in traditional medicine systems; it is therefore likely that textiles dyed with these dyes may have a beneficial effect on health. People using naturally dyed textiles have reported their positive effects on health although detailed systematic studies on this aspect have not been conducted. Care, however, is required when new dye sources are introduced and detailed toxicological studies have to be undertaken to establish their safety to humans and environment. Also, the production process of these dyes does not use harsh chemicals and uses mild conditions, therefore there is no adverse effect on the health of the workers. On the contrary, it may have a positive effect on health in view of the therapeutic and medicinal value of dye-bearing plant materials. The presence of pesticide residues in natural dyes from the usage of pesticides to control insects and pests and content of restricted heavy metals in dyed material from the soil or from the mordanting process during dyeing are aspects that need monitoring from the human health viewpoint.

8.11 Social Issues

Synthetic dyes seem to be cheaper today but according to the study by Nayak [34] if their impact on the environment and health of people is considered, their cost increases by almost INR 410 per kg of dye. It is common knowledge that dyeing operations in developing countries are mostly carried out in small-scale industries that discharge highly polluted effluent in nearby water bodies or land with no or little treatment resulting in heavy contamination of surface and groundwater in areas having a large concentration of dyeing units as reported in places such as Tiruppur and Pali in India. This contaminated water was unfit for human or animal use and people in the surrounding area had to fetch water from long distances and at huge costs causing them immense hardship. This water was not even fit for irrigating crops, resulting in fertile agricultural land turning barren and farmers being deprived of their livelihoods. It was observed in the study conducted by Rajkumar and Nagan [43] that untreated and partially treated effluent discharged in the river Noyyal by textile dyeing units for the past 20 years has accumulated in the soil and water at many locations and has affected the groundwater, surface-water, soil, fish, and the natural ecosystem in the Tiruppur and downstream area and it would require remedial measures and many years after stoppage of pollution for their restoration. According to the estimates of PWD, Coimbatore, about 25-crore INR would be required for restoring the 40-km stretch of River Noyyal [34]. Thus cheaper synthetic dyes come with huge social and economic and environmental costs.

9 Future Prospects and Conclusion

Brief information about natural dyes, their sources, application procedures, and various advantages and disadvantages of using them was discussed in this chapter. Although many disadvantages such as poor fastness properties and use of banned metal salts and the like can be easily overcome by research and awareness, others such as nonreproducibility of shades and improving the availability would need higher research and industrial investments.

Presently an approximately 1 % share of textiles is only being dyed with natural dyes mostly in the cottage sector by traditional artisans, enthusiasts, and small entrepreneurs. Selling of natural dye-bearing materials and their purified extracts is, however, being done at a small industry level. Many manufacturers in the United States, India, China, and other countries are engaged in this activity and their products are available on the Internet. The tedious application process and nonreproducibility of shades and insufficient availability are some of the factors responsible for their nonadoption in mainstream textile processing. However, at the present level of dye resource availability, their adoption by the textile industry is not desirable also as that would result in an environmental disaster by way of loss of biodiversity and depletion of forest cover in spite of the tremendous environmental advantage offered by them in terms of the lower pollution of the effluent if used properly. This advantage can be utilized by the traditional artisans in preserving their surroundings from the ill effects of pollution caused by synthetic dyes as they do not have access to expensive effluent treatment plants needed for synthetic dyes. A clean production model offered by natural dyes is a better alternative for them. The benefits of research conducted on the development of improved application techniques for better fastness and environmental compliance should reach these people so that they can earn their livelihoods and the consumer also get the benefit of truly environmentally friendly textiles. The availability of natural dyes needs to be increased in a sustainable manner by utilizing the by-products and wastes from agriculture and agroprocessing industries and judicious collection of forest produce. This may be supplemented by growing important dye-bearing plants on wastelands and marginal lands thus providing an alternative cash crop to cultivators. Establishment of proper characterization and certification protocols for natural dyes would definitely improve consumer confidence in natural dyed textiles and would benefit both producers and users. If natural dye availability can be increased by the above-described measures and the cost of purified dyes can be brought down with a proper certification mechanism, there is a huge scope for adoption of these dyes by small-scale dyeing units as they lack the resources to install and operate expensive effluent treatment plants needed to bring the synthetic dye effluent within the limits set by regulatory authorities. If at any time in the future, the availability of natural dyes can be increased to very high levels by biotechnological interventions such as tissue culture or genetic engineering resulting in mass production of these dyes by microbes at low cost, then only can their usage become sustainable for mainstream textile processing. At the level where scientific developments stand today, natural dyes are a sustainable option only for small-scale applications and they can complement synthetic dyes as an eco-friendly option for the environment-conscious consumer and a means of providing livelihood to various stakeholders of the natural dye value chain.

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