Chemistry of Natural Dyes

Padma S Vankar

Padma S Vankar is at the facility for ecological and analytical testing in IIT, Kanpur.

Nature expresses itself in a wide spectrum of colours all around us. The alchemy of colours started from an early time. Indians have been forerunners in the art of natural dyeing. The advent of synthetic dyes caused rapid decline in the use of natural dyes, which were completely replaced by the former within a century. Earlier understanding of dyeing techniques and their applications was empirical and was not backed by scientific reasoning. Natural dyeing had developed essentially as a folk art. However, in recent times the dyeing technique is interpreted on sound scientific principles, and the interaction between the dye and the dyed material is well understood. From our recent work, we have tried to explain the nature of bonding in certain dyes by looking at their structures and using metal ions for chelation.

Sources of Natural Dyes

There are primarily four sources from which natural dyes are available.

Specialised plant and animal sources: Many plants and some animals have been identified as potentially rich in natural dye contents, and some of them have been used for natural dyeing for quite some time. Various parts of plants like roots, stems, barks, leaves, fruits and seeds may contain colouring matter which can be exploited. Normally natural dyes are extracted from the roots, stems, leaves, flowers, fruits of various plants, dried bodies of certain insects and minerals. Some plants may have more than one colour depending upon which part of the plant one uses. The shade of the colour a plant produces will vary according to time of the year the plant is picked, how it was grown, soil conditions, etc. The minerals in the water used in a dye bath can also alter the colour. Some natural dyes contain natural mordants.

By-products (especially lac dye): The lac industry gives lac dye as a by-product, which is extracted from the effluent. Similarly, from *Cassia tora*, used in gum manufacturing, a brown dye is obtained as a by-product.

Chemical synthesis: This involves synthesis of dyes with molecular structures identical to those of natural dyes. We have tried to make such synthesis environmentally less hazardous by using microwave technology.

Tissue or cell culture by DNA transfer biotechnology: Certain fungi such as *Drechslera* and *Trichoderma* produce anthraquinone derivatives as secondary metabolites. As anthraquinones are a very important class of dyes, exploiting the fungi would be advantageous over their chemical synthesis. If genetic modifications can be achieved, it is possible to develop fungi that produce substituted anthraquinones.

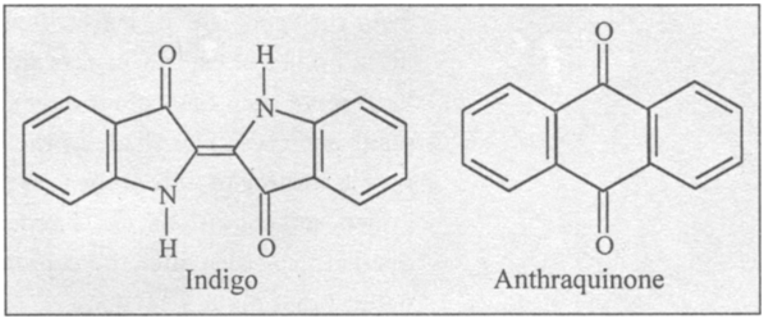
Classification of Dyes

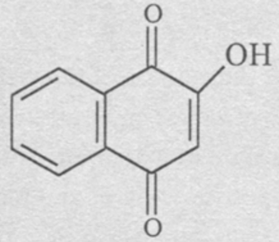
Dyes are classified based on their structure, source, method of application, colour, etc. We briefly describe below two types of classification.

Based on Chemical Structures

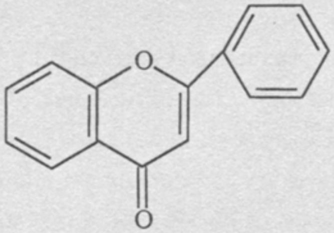
Indigoid dyes: This is perhaps the most important group of natural dyes, obtained from *Indigofera tinctoria*.

Anthraquinone dyes: Some of the most important red dyes are based on the anthraquinone structure. They are obtained both

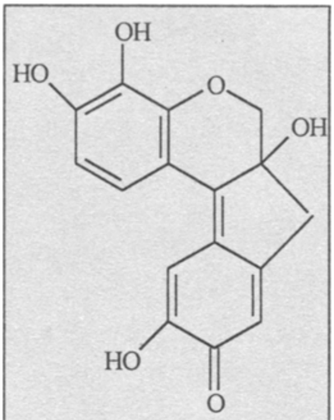




α-hydroxynaphthoquinone



flavone



Dihydropyran

from plants and insects. These dyes are characterised by good fastness to light. They form complexes with metal salts and the resultant metal-complex dyes have good wash fastness.

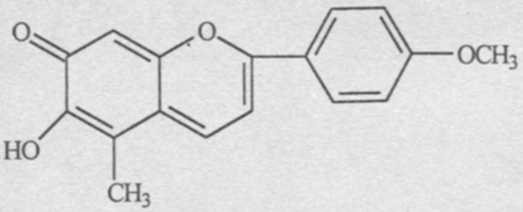
Alpha-hydroxy-napthoquinones: The most prominent member of this class of dyes is lawsone or henna, obtained from *Lawsonia inermis*.

Flavones: Most of the natural yellow colours are hydroxy and methoxy derivatives of flavones and isoflavones.

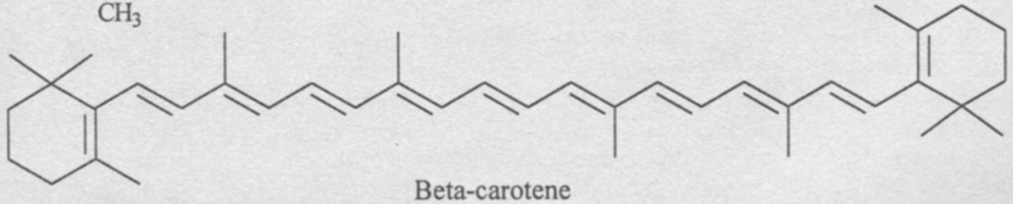
Dihydropyrans: Closely related to flavones in chemical structure, are substituted dihydropyrans like the one shown here.

Anthocyananidins: Carajurin obtained from *Bignonia chica*.

Carotenoids: In these the colour is due to the presence of long conjugated double bond. Annatto and saffron are examples of this.



Anthocyananidin



Beta-carotene

Based on colour

Various natural dyes could present all the colours of the visible spectrum. The natural colour and hue of a dye can be altered by treating with metal salts. If the dye is of plant origin, the colour may vary depending on the soil properties, part of the plant, season of harvesting, cultivation practices, etc (*Table* 1).

Red colour: Most red dyes are found in roots or barks of plants or camouflaged in the bodies of dull grey insects. Unlike the wide abundance of yellow, the sources of red colour are limited. Cochineal is an important red dye and it is the brightest of all the available natural red dyes. Manjith and Kusumbar among the vegetable sources and lac and Kermiz among the animal sources give red colours.

Yellow colour: Yellow is the liveliest and perhaps the most abundant colour in nature. The plants which yield yellow dyes outnumber those yielding other colours.

Mordants

Dyes do not combine directly with the material they are in-

Table 1. Sources of Different Coloured Dyes.

Colour	Botanical Name	Parts used	Mordant
Red Dyes			
Safflower	*Carthamus tinctorious*	Flower	---
Caesalpina*	*Caesalpinia sappan*	Wood chips	Alum
Maddar	*Rubia tinctorium*	Wood	Alum
Lac*	*Coccus lacca* (insect)	Twigs inhabited by these insects	Stannic chloride
Yellow Dyes			
Bougainvillea*	*Bougainvillea glabra*	Flower	Tin
Golden rod	*Solidago grandis*	Flower	Alum
Teak	*Tectona grandis*	Leaves	Alum
Marigold	*Tagetes species*	Flower	Chrome
Parijata	*Nyetanthesar bortristis*	Flower	Chrome

Table 1 continued...

Colour	Botanical Name	Parts used	Mordant
Blue Dyes			
Indigo	*Indigofera tinctoria*	Leaves	---
Woad	*Isatis tinctoria*	Leaves	---
Suntberry	*Acacia nilotica*	Seed pods	---
Pivet	*Ligustrum vulgare*	Mature berries after frost	Alum and iron
Water lily	*Nymphaea alba*	Rhizomes	Iron and acid
Black Dyes			
Lac*	*Coccus lacca (insect)*	Twigs inhabited by these insects	Ferrous sulphate
Alder	*Alnus glutinosa*	Bark	Ferrous sulphate
Rofblamala	*Loranthus pentapetalus*	Leaves	Ferrous sulphate
Custard apple	*Anona reticulata*	Fruit	---
Harda	*Terminalia chebula*	Fruit	Ferrous sulphate
Brown Dyes			
Caesalpina*	*Caesalpinia sappan*	Wood chips	Ferrous sulphate
Bougainvillea*	*Bougainvillea glabra*	Flower	Ferrous sulphate + acid/ neutral
Balsam*	*Impatiens balsamina*	Flower	Alum
Marigold	*Tagetes species*	Flower	Chrome
Black berries	*Rubus fructicosus*	Berries	Iron
Green Dyes			
Tulsi*	*Ocimum sanctum*	Leaves	Ferrous sulphate
Bougainvillea*	*Bougainvillea glabra*	Flower	Alum + Base and Ferrous sulphate+Acid
Canna*		Flower	Alum and Ferrous sulphate
Lily	*Convallaria majalis*	Leaves and stalk	Ferrous sulphate
Nettles	*Urtica diocia*	Leaves	Alum
Orange/Peach Dyes			
Bougainvillea*	*Bougainvillea glabra*	Flower	Stannous chloride + Acid; Alum + base
Balsam*	*Impatiens balsamina*	Flower	Tin
Dahlia	*Dahlia* species	Flower	Alum / chrome
Annatto	*Bixa orellana*	Seeds	

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* The sources marked with an asterix have been used by us for the first time for dyeing cotton fabric mainly by utilising ultrasonic energy in the dye bath. We have even attempted to dye synthetic fabric terrycot with lac dye.

tended to colour. Natural dyes are substantive, requiring a mordant to fix to the fabric, and prevent the colour from either fading with exposure to light or washing out. These compounds bind the natural dyes to the fabric. They are of three types.

Metallic mordants: Metal salts of aluminium, chromium, iron, copper and tin are used.

Tannins: Myrobalan and Sumach are the commonly used tannins employed as mordants in the dyeing of textile fibres.

Oil mordants: Oil mordants are used mainly in the dyeing of turkey red colour from maddar. The main function of the oil mordant is to form a complex with alum used as the main mordant. The sulfonated oils, which possess better metal binding capacity than the natural oils due to the presence of sulfonic acid group, bind to metal ions forming a complex with the dye to give superior fastness and hue.

Limitations of Natural Dyes

Tedious extraction of colouring component from the raw material, low colour value and long dyeing time push the cost of dyeing with natural dyes considerably higher than with synthetic dyes. In case of sappan wood, prolonged exposure to air converts the colourant brasiline to brasilein, causing a colour change from red to brown. To overcome this drawback we used a sonicator, and found that the dye extraction was much faster. Some of the natural dyes are fugitive and need a mordant for the enhancement of their fastness properties. Some of the metallic mordants are hazardous.

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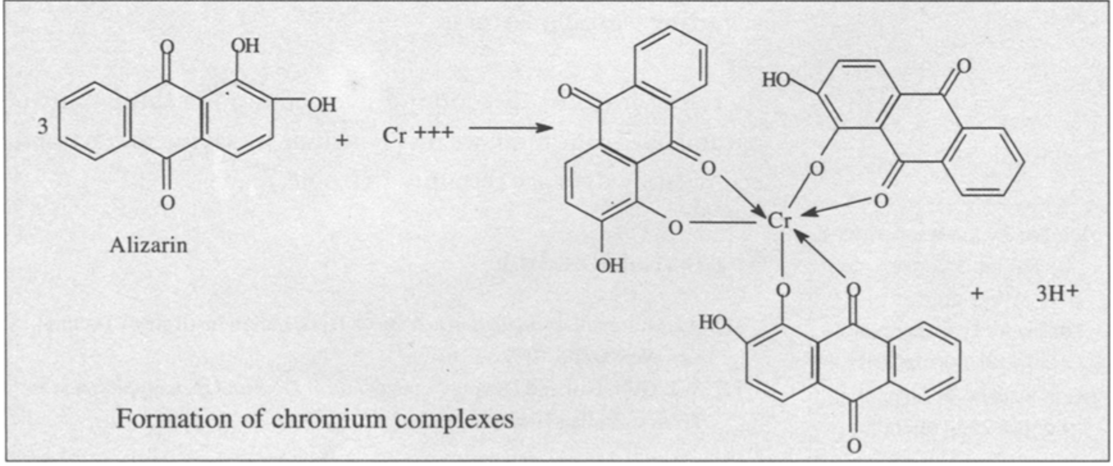
Bonding

Natural dyes work best with natural fibres such as cotton, linen, wool, silk, jute, ramie and sisal. Among these, wool takes up dyes most easily followed by cotton, linen, silk and then the coarse fibres such as sisal and jute. Nearly all of them require some sort of a mordant. The trick is to choose the right dye from the right source that gives not only beautiful tones, but colourfast shades as well.

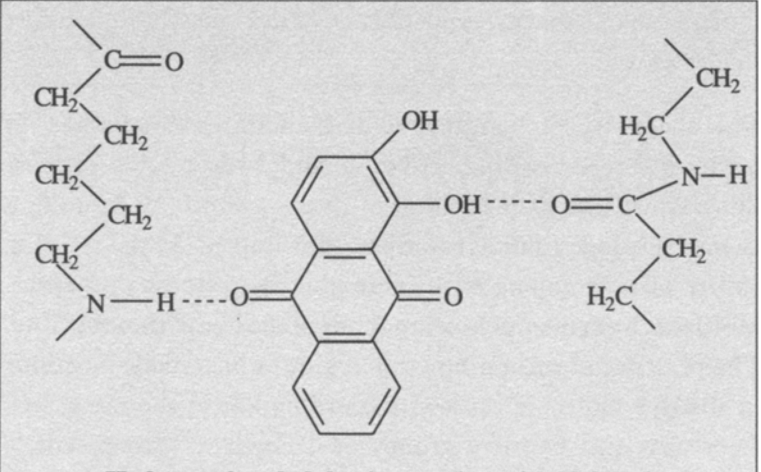
The chemistry of bonding of dyes to fibres is complex. It involves direct bonding, H-bonds and hydrophobic interactions. Mordants help binding of dyes to fabric by forming a chemical bridge from dye to fibre, thus improving the staining ability of a dye along with increasing its fastness properties. Mordants form insoluble compounds of the dye within the fibre. The presence of certain functional groups in suitable positions in the dye molecule causes its coordination to the metal ion. Generally, two hydroxy groups or a hydroxy group with a carbonyl, nitroso or azo group in adjacent positions are responsible for coordination. The mordant dyes produce a wide range of hues of remarkable resistance to wet treatments, but the shades lack brilliancy.

An example is the chromium-alizarin complex. A chromium ion can combine with alizarin by covalency and co-ordinate valency to form the 'Lake'. Chromium, being trivalent, combines with three molecules of alizarin.

The fibres made of proteins, such as wool and silk, retain the dye through hydrogen bonding between the polypeptide linkages and the dye. An example of alizarin is given to show the nature of bonding with Nylon-6, which also has peptide linkages.



Formation of chromium complexes



Hydrogen bonded dye interaction with Nylon-6

Improving the Quality of Natural Dyes

Poor light fastness of some of the natural dyes is attributable to photooxidation of the chromophore. We have tried to prevent/ minimize such photooxidation by forming complex of the dye with transition metal. We have improved the washing fastness of natural dyes by treatment with eco-friendly mordants such as alum, stannic chloride, stannous chloride and ferrous sulphate. We have also used tannins with mordants. Treatment with metal salts alters the light absorption characteristics of tannins in addition to making them insoluble in water with the fabric acquiring washing fastness.

As research in the direction of overcoming the limitations of natural dyes continues, we may conclude by saying that natural, eco-friendly dyes are certainly welcome.

Address for Correspondence
Padma S Vankar
Incharge
Facility for Ecological and
Analytical Testing(FEAT)
Indian Institute of Technology,
Kanpur 208 016, India.

Suggested Reading

[1] **M L Gulrajani, *Introduction to Natural Dyes*, Indian Institute of Technology, New Delhi, 1992.**
[2] **M L Gulrajani and Deepti Gupta, *Natural Dyes and their Application to Textiles*, Indian Institute of Technology, New Delhi, 1992.**