

## CHAPTER 2

### REVIEW OF LITERATURE

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#### 2.1 Natural dyes

##### 2.1.1 Introduction

Natural dyes have presumably been utilised ever since humans began producing textiles. Natural dye usage has been documented as early as 2600 BC in China, as well as in numerous other cultures. The dyes were utilised for cave paintings, garment decoration, and shell embellishment. Indigo, Heena, Tyrian Purple, Madder, and Brazilwood are among the most ancient naturally occurring colors in use today (Siva, 2007).

Considerable investigation has been dedicated to synthetic dyes, resulting in their economical manufacturing with desirable fastness characteristics. As a consequence, natural dyes are considerably diminished to an insufficient degree in comparison to synthetic dyes. The environmental safety of textile production with natural ingredients is widely acknowledged. In addition to imparting color, natural dyes also include therapeutic benefits. Many dyes exhibit anti-bacterial and anti-fungal properties and lower the risk of cancer (Siva, 2007).

In recent years, a segment of environmentally conscious consumers has created the demand for environment-friendly products. This has led to increased demand for natural dyes, and many industries have started using them. Over the last two decades, research in the area of natural dyeing has been going on. Besides the dyeing of textiles, natural dyes are used in food, medicines, leather dyeing, and other items.

All the local craftsmen/artisans are extracting the dyes and dyeing as per their skills. Besides that, many organizations are producing the dyes. Some Indian companies are Satal Katha, Sam & Ram, Amma Herbal, D. Manohar Lal, etc. (Gulrajani, 2001).

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. Natural dyes have been grouped 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 (Saxena & Raja, 2014).

Optimization of mordanting (Tutak, Acar, & Akman, 2014), dye extraction (Goodarizian & Ekrami, 2010), dyeing processes (Farooq, Ali, Abbas, Zahoor, & Ashraf, 2013), finishing of textiles like UV protection (Gnanavel & Ananthakrishnan, 2014), antimicrobial effect (Mirjalili & Karimi, 2013); printing with natural dyes (Ibrahim Bahtiyari, Benli, Yavaş, & Akca, 2017; Özgüney, Seçim, Demir, Gülümser, & Özdoğan, 2015), use of natural dyes in digital printing with padding method (B. Patel, Agrawal, & Patel, 2003), application on synthetic fibers (Ebrahimi & Parvinzadeh Gashti, 2016; Eser, Aktas, & Onal, 2016) are some of the areas where research is going on for natural dyes. It is also true that much more research impetus is required to make it competent with respect to synthetic dyes. There is ample scope for research on natural dyes in agriculture production, processing, and dyeing (Gulrajani, 2001).

### **2.1.2 Historical Perspective**

The first written records of natural dyeing were found in China, dated 2600 BC. Historical sources indicate that these were utilised in Europe throughout the Bronze Age and the Indus Valley culture. It is hypothesised that in 3500 BC, madder was utilised at Mohenjo Daro and Hadappa to dye textiles.(Siva, 2007). Indigo dye which is still the favorite for many, is as old as 5000 years old and used by our ancestors in East Asia, India and Egypt. Many dyed textiles in Egyptian tombs prove natural dyeing methods (Satyanarayana & Chandra, 2013). Madder, widely available in many parts of the world, is found on the clothes of mummies and confirmed by chemical tests (Aberoumand, 2011).

Indian scriptures describe the use of natural colors. Dyeing and printing of textiles have been a part of Indian tradition to create beautiful textiles and costumes. Great Rasayan-Shastri (chemistry experts) have been working on natural dyes and their color fastness. The color and design of Indian textiles have been of supreme quality, and the world has always appreciated them.

Many of the popular dyes and pigments like Patang, Saffron, Catechu, Dhao, Myrobalan, Madder, Pomegranate, etc., were used during the Mughal reign (1556-1803)

using metallic mordents with good fastness properties (Yusuf, Shabbir, & Mohammad, 2017).

Seventy samples of traditional textiles were collected from the Calico Museum, Ahmedabad, to identify natural dyes using thin-layer chromatography (TLC). They found the type of natural dyes used for their respective material. It was found that Suranji, Manjeet, Pomegranate, Myrobalan, Catechu, Indigo, etc., were used to dye the fabric (Kharbade & Agrawal, 1988).

Traditional textiles of India are appreciated for the use of natural dyes in the form of dyeing, printing, and weaving. Teli Ruma, an Ikat textile, is produced in Chirala, a town in Telangana state of India, in terracotta red and black colors by the use of natural dyes. Alizarine, iron, and alum were used to create the red and black color on textiles. Patola is a prestigious weaving from Gujarat state of India, where warp and weft yarns are tie-dyed to produce many colors and patterns. A traditional scarf (chunni) called piliya from Rajasthan state is a costume for young mothers. The fabric is dyed using turmeric powder to produce a yellow color and anti-inflammatory properties. Indigo is widely used in solid, tie-dyed, and printed traditional textiles in Rajasthan state, Gujarat state, and other parts of India. Kalamkari is a block-printed cotton textile from Andhra Pradesh that uses Alum, Jaggery, Alizarine, Myrobalan, Cow dung, seeds, etc.

### **2.1.3 Advantages and Limitations**

Natural dyes have been used in textiles and other items for centuries. Many textiles dyed using natural dyes had good fastness properties, but the process was skill-based and complex. Later, with the introduction of synthetic dyes, the use of natural dyes declined rapidly. The advantages and disadvantages of natural dyes are mentioned below to understand the dyes in a better way:

#### **Advantages of Natural dyes**

- Natural dyes are used traditionally and connect us with the culture, tradition, and heritage
- These are obtained from natural resources and the process of extraction is simple in most of the cases

- No disposal problem is associated with the use of natural dyes because of biodegradability. In some cases, these materials increase the fertility of the land, e.g., Indigo, Harda
- Different shades are produced using the same dye with different mordants, which increases the color gamut of these dyes
- The shades produced by natural materials are soft, soothing, and unique. The shades are harmonic and sometimes enhance with usage
- Besides coloration, some natural dyes impart anti-microbial, medicinal, UV protective, and other properties. These materials are beneficial in skin-related diseases. Specific end usable natural dyed fabric range can be created
- Natural dyes can be applied on natural as well as on many synthetic fibers
- The process of natural dyeing is labor intensive and creates job opportunities
- In general, natural dyes do not stain other fabrics during laundry

#### **Limitations of Natural dyes**

- Natural dyes are produced using natural resources, so the material varies with crop, season, location, etc. Hence, the non-standardization leads to reproducibility issues. Subsequently, the standardization of dyeing recipes becomes very difficult
- Dyestuff extracted from natural resources has a deficient color proportion and requires a high amount of raw material, which leads to an increase in dyeing cost
- The dyeing process requires skill and involves many steps for good color fastness properties
- Limited exhaustion and color fastness properties
- Use of mordents increases the dyeing cost and sustainability issues
- The extent of research on natural dyes is very limited and requires extensive research for competition with synthetic dyes

#### **2.1.4 Classification of Natural Dyes**

Many natural dyes from different sources have different properties and produce a range of colors. The properties and constitution depend on the source from where we get the dye. We can classify them in many ways as follows:

- Classification based on Source
- Classification based on Color
- Classification based on Application methods
- Classification based on Structure

## **1. Classification based on Source**

### **(A) Plant/Vegetable Origin**

A large number of known natural dyes are obtained from plants only. It is to be noted that not all the pigments obtained from plants are used for dyeing of textiles. Different parts of the plants, like roots, bark, leaf, fruit, wood, seed, flower, rinds, hulls, husks, etc., are used to obtain the natural dyes. There are nearly four hundred fifty varieties of dye-yielding plants in India. Many of the popular dyes of earlier times are still in use. These dyes are now commercially available due to a reinduction of interest in natural dyes. Indigo is one of the most popular dyes in this category. Amongst red dyes, Madder, Brazil Wood, Morinda, and Safflower are the popular dyes even now. In yellow dyes, Turmeric, Saffron, Barberry, Pomegranate, Myrobalan, Marigold, Kamala, Onion, Weld, and Dolu have been popular dyes for a very long time. Catechu is an ancient dye that produces a brown color and Annatto produces orange color. Black is obtained by iron mordanting of many yellow and red dyes (Saxena & Raja, 2014).

### **(B) Animal/Insect Origin**

Some of the dyes are obtained from the dried bodies of insects. In many cases, red is obtained from them. Cochineal, Kermes, and Lac are the most popular dyes in this class. Cochineal dye is obtained from the female insects when dried under the sun and grounded. The main coloring component in Cochineal is Carminic acid, which produces Crimson red on animal fibers with excellent color fastness properties. Lac is obtained from the hardened secretion of the insect *Kerria lacca*. Tyrain purple, produced from one of the very costly dyes in this class, gives a purple color (Saxena & Raja, 2014).

### **(C) Mineral Origin**

Various pigments, including red, yellow, green, blue, white, and black, are obtained from inorganic metal salts and metal oxides. Some minerals are cinnabar, red ocher, yellow ocher, gypsum, charcoal, and malachite.

The primary sources of red colors include Cinnabar, Red Ocher, and Red lead. Cinnabar produces bright scarlet to brick-red color and is a form of mercury sulphide (HgS). A red ocher called Geru in Hindi was used to dye the robes of monks (Yusuf et al., 2017).

Yellow colors include Yellow Ocher, Orpiment, Litharge, and Raw Sienna. Yellow Ocher is due to the presence of many hydrated forms of iron oxide. Orpiment produces a deep orange-yellow color (Yusuf et al., 2017).

In other colors, Green colors include Malachite, Verdigris, and Terre-Verte as primary sources. Ultramarine blue and Azurite produce blue colors. Chalk and charcoal are examples of white and black pigments, respectively (Yusuf et al., 2017).

#### **(D) Microbial and Fungal Origin**

Various bacteria have produced many colors. Some fungus has also been used for dyeing silk and wool with excellent washing fastness. Lichens also produces violet and purple shades (Saxena & Raja, 2014).

## **2. Classification based on Color**

Mother Nature gifts various tones of red, yellow, brown, and other colors. Amongst these, red and yellow are available in abundance. This classification gives color-wise details, including source, habit, part used, botanical name, and coloring component (pigment). However, the color may vary with the change in pH and mordant, but the color mentioned is the common one produced by the material. The details of all the color is mentioned in tables below. (Gulrajani, 2001; Patil, Rao, & Wasif, 2012; A. K. Samanta, Datta, & Datta, 2015, Saxena & Raja, 2014)

#### **(A) Dyes for Red/Similar Colors**

It is the most prominent color in the gamut of natural dyes. Different materials produce many tints and tones of red. Colors like Madder, Sappanwood, Lac, and many more have been used since ancient times. Madder has been producing good colorfast textiles. Many of these are anthraquinone-based dyes. Some of the most important red color dye details are mentioned in Table 2.1

**Table 2.1:Details of Red/Similar Color Natural Dyes**

<b>Common Name</b>	<b>Color</b>	<b>Source</b>	<b>Part Used (if plant source)</b>	<b>Botanical Name</b>	<b>Pigment (Coloring Component)</b>
Annatto	Orange, Red	Shrub	Pulp surrounding the seed	<i>Bixa orellena</i>	Bixin, Norbixin
Henna	Orange	Shrub	Dried leaves	<i>Lawsonia inermis L.</i>	Lawsone
Red Sandalwood	Red	Tree	Bark	<i>Pterocarpus santalinus L.</i>	Santalin
Madder	Red	Herb	Whole Plant	<i>Rubia tinctorum</i>	Purpurin
Beetroot	Red	Herb	Fruit root, leaves	<i>Beta vulgaris</i>	Betanin
Sappan Wood	Pink	Tree	Wood chips	<i>Caesalpinia sappan</i>	Brazilein
Lac	Red	Insect: Laccifer lacca	-	<i>Kerria lacca</i>	Laccaic Acid
Red Cabbage	Purple	Leafy Vegetable	Leaves of cabbage	<i>Brassica oleracea</i>	Ruburobrassicin
Hibiscus	Red	Shrub	Flower	<i>Hibiscus rosa sinensis</i>	Rhamnazin

**(B) Dyes for Yellow/Similar Colors**

The most common color in natural dyes is Yellow. The CI index has listed more than 28 yellow natural dyes. Marigold, Kamala, Tesu, Himalyan Rhubarb, and Pomegranate are some of the most used materials for yellow color. These materials have different coloring components. Wool, Silk, Cotton and other materials are conveniently dyed using this class of dyes. Some of the important details of the yellow dye are mentioned in Table 2.2.

Table 2.2: Details of Yellow/Similar Color Natural Dyes

Common Name	Color	Source	Part Used (if plant source)	Botanical Name	Pigment (Coloring Component)
Indian Barberry	Yellow	Bush	Root, Bark	<i>Berberis aristata</i>	Berberine
Kamala	Yellow	Tree	Fruit, flowers	<i>Muell.</i>	Rottlerin
Palash/Tesu	Yellow/Orange	Tree	Dried flowers	<i>Butea monosperma</i>	Butrin
				( <i>Lam</i> ) <i>Taubert.</i>	
Safflower	Yellow/Red	Small Tree	Flower	<i>Carthamus tinctorious L.</i>	Carthamin
Turmeric	Yellow	Herb	Rhizomes	<i>Curcuma longa L.</i>	Curcumin
Pomegranate	Yellow	Tree	Flower, Rhind of fruits	<i>Punica granatum L.</i>	Petargonidon 3,5,diglucoside
Mango	Yellow	Tree	Bark and leaves	<i>Mangifera indica L.</i>	Euxanthic acid
Himalayan Rhubarb/Dolu	Yellow/Brown	Herb	Rhizomes and Roots	<i>Rheum emodi</i>	Chrysophanic acid
Marigold	Yellow	Herb	Flower	<i>Tagetes erecta</i>	Quercetin
Onion	Yellow	Vegetable	Skin	<i>Allium cepa</i>	Delphinidin
Haldu/Kadam	Yellow	Tree	Wood	<i>Haldina cordifolia</i>	Adinin
Aloe Vera	Yellow	Herb	Plant	<i>Aloe vera (L.)</i>	Emodin

### (C) Dyes for Blue/Similar Colors

Indigo is mainly used to obtain a blue color for textiles. Indigo provides very good fastness properties. Woad is another material that produces a blue color similar to Indigo. Due to different application processes, these Vat dyes cannot be mixed in a single bath with other dyes. Industries, designers, and other hobby groups extensively use indigo dye. Tyrian purple is another vat dye obtained from sea snails. It is costly and gives a purple shade. Details of these blue dyes are mentioned in Table 2.3.

**Table 2.3: Details of Blue/Similar Color Natural Dyes**

Source	Color	Habit	Part Used	Botanical Name	Pigment
Indigo	Blue	Shrub	Leaves	<i>Indigofera tinctoria L.</i>	Indigotin
Woad	Blue	Herb	Leaves	<i>Isatis tinctoria L.</i>	Indigotin
Tyrian Purple	Purple	Sea Snails		<i>Hexaplex trunculus</i>	Kermesic acid

**(D) Dyes for Brown and Other Colors**

Myrobalan, Catechu, Babool, and many other materials produce a brown color. Some of these materials are rich in tannins and provide good fastness properties. Green color can be achieved using mulberry leaves and gives a unique shade. Some of the brown and other dyes details are mentioned in Table 2.4.

**Table 2.4: Details of Brown/Similar Color Natural Dyes**

Source	Color	Habit	Part Used	Botanical Name	Pigment
Myrobalan	Brown/Yellow	Tree	Root, seeds, fruit, Bark	<i>Terminalia chebula</i>	Allagic acid
Black Catechu/Katha	Brown	Tree	Bark	<i>Acacia catechu</i>	Catechin
Bark of Acacia/Black Babool	Black/Brown	Tree	Seed pod	<i>Acacia - nitotica</i>	Catechin
Marking Nut tree	Black	Tree	Seeds	<i>Semecarpus anacardium L.f.</i>	Bhilawanol
Walnut	Brown	Tree	Hulls, shells, bark, and leaves	<i>Juglans regia L.</i>	Juglone
Mulberry plant	Green	Tree	Leaves	<i>Mulberry leaves</i>	Maclurin or morin

### **3. Classification based on Application methods**

The application methods for natural dyes are similar to those used for synthetic dyes. However, it becomes difficult to classify them in a particular dye class. The affinity of most natural dyes is very limited and needs certain treatment to achieve desirable results (Gulrajani, 2001).

Mordant dyes are capable of attaching to a material with which they would normally have little or no affinity. This attachment is made possible by introducing a mordant, a chemical that enhances the interaction between the dye and the fiber. The traditional definition of mordant dyes has been expanded to include all dyes that can form a complex with a metal mordant. These dyes produce various tints or colors when combined with different mordants (Yusuf et al., 2017).

Indigo, Woad, and Tyrian Purple belong to the vat dyes category as they are applied in the same method as synthetic vat dyes. Turmeric, Annatto, Safflower, Pomegranate, and Harda are examples of direct dyes as they are applied directly on cotton fabric. These are water-soluble and easily dyeable (A. K. Samanta, Agarwal, Singhee, & Datta, 2009).

Acid dyes can be easily applied on polyamide fibers like wool, silk, and nylon in an acidic medium. They have either sulphonic acid or carboxylic acid groups in their structure (Yusuf et al., 2017).

Berberine is a dye that can be classified as a basic dye and forms an electrovalent bond with wool and silk fibers. Structurally, this dye carries a nonlocalized positive charge, which resonates in the structure of the dye, resulting in poor light fastness (Yusuf et al., 2017).

Many natural dyes can be classified into disperse dye category. These dyes are sparingly soluble in water and can dye hydrophobic fibers. The procedural and structural resemblance may lead these dyes into the disperse dye category. The classification of some natural dyes based on application properties is mentioned in Table 2.5.

**Table 2.5: Classification of some natural dyes based on application properties (Gulrajani, 2001).**

S. No.	Botanical name/ source	Common name	Dye class
1.	<i>Indigofera tinctoria</i>	Indigo	Vat
2.	<i>Rubia tinctorum</i>	Madder	Mordant/Disperse
3.	<i>Rubia cardifolia</i>	Manjeet	Acid/Mordant/Disperse
4.	<i>Ceasalpinia sappan</i>	Sappanwood	Mordant/Disperse
5.	<i>Lucifer lacca</i>	Lac dye	Acid/Mordant
6.	<i>Berberis aritata</i>	Berberine	Basic
7.	<i>Butea frondosa, monosperma</i>	Tesu	Mordant/Disperse
8.	<i>Mallotus philippensis</i>	Kamala	Mordant/Disperse
9.	<i>Rheum emodi</i>	Dolu	Mordant/Disperse
10.	<i>Quercus infectoria</i>	Gall nuts	Acid/Mordant
11.	<i>Acacia catechu</i>	Katha	Acid/Mordant/Disperse

#### 4. Classification based on Structure

Natural dyes have a mix of similar chemical structures. Table 2.6 shows the broad classification of structures in natural dyes.

**Table 2.6: Classification of some of Natural dyes based on Structure**

Class	Coloring Compound	Species	Common Name	Shades Obtained
Anthraquinone dyes	Alizarin	<i>Rubia tinctorum</i> and <i>R. cordifolia</i>	Manjistin, Manjistha, Indian Madder	Red
Indigoid dyes	Indican	<i>Indigofera tinctoria</i>	Neel(Indigo)	Blue
Alphanaphthoquinones	Lawsone, Juglone	<i>Lawsonia inermis</i>	Henna, shells of unripe walnuts	orange
Flavonoids	Flavones and Isoflavones	<i>Curcuma longa</i> , <i>B. monosperma</i>	Turmeric, testu, kapila	Yellow, deep yellow
Di-hydropyrans	Haematian and its leuco form, haematoxylin	<i>Haematoxylum campechianum</i>	Logwood, Brazil wood, and Sappan	Violet-Purple, Red

			wood	
Anthocyanidins	Anthocyanins	<i>Hibiscus rosa sinensis</i>	Shoe flower, china rose, Jaswand	Red, Violet, blue
Carotenoids	Lutein, b-Carotene	<i>Tagetes erecta</i>	Marigold	Yellow

### Color Index for Natural dyes

Dyes and pigments are described by a color index and classified by application and chemical class. Natural dyes are also classified in this way. The dyes are arranged according to the hue in the application class and assigned a separate section. These are classified as Yellow, Orange, Red, Blue, Green, Brown, and Black colors. Red, Yellow, and Brown have the maximum number of dyes. Blue has the minimum number of dyes (Chakrabarti & Vignesh, 2011).

### 2.1.5 Extraction Methods

Natural dye sources contain a major portion of other constituents and a small portion of color. The majority of materials contain 2-5% coloring material on weight. Fibers, protein, carbohydrates, tannins, and many other matters are present in natural sources. Hence, the process of extraction is a complex process. Various extraction methods are used depending on the nature of the source. Different solvents are used based on the polarity of the compound. Many methods are used, such as aqueous extraction, solvent extraction, microwave assistance, fermentation, enzymatic, and supercritical fluid extraction. Many of these methods give good yields (Saxena & Raja, 2014; Yusuf et al., 2017).

#### Aqueous Extraction method

Water has been used to extract dyes from various sources and has been the easiest method for ages. Soaking the material and heating process are used repetitively to get the maximum dye. The extraction method is very simple, but it also has some limitations. Mainly, water-soluble dyes can be extracted through this method. The dye yield produced by this method is limited, and the water requirement is very high. For dye standardization, we may check the optical density of the dye solution. The extraction conditions may be optimized for high color yield.

### **Solvent Extraction method**

Many natural coloring materials are soluble in organic solvents such as acetone, chloroform, methanol, or other solvents. The possibility of a water/alcohol mixture can lead to good color yield due to the extraction of water and alcohol-soluble dyes. Adding acid or alkali to the solvents can also improve the extraction. As the solvents can be easily removed, purification becomes very easy. Generally, the processing temperature is low and does not impact the dye. Limitations of this method include the presence of toxic residual solvents and the fact that the extracted material is not easily water-soluble.

### **Ultrasonic and Microwave-Assisted Extraction method**

Ultrasound and microwave can be used in aqueous or solvent methods to increase the rate of the extraction process. Ultrasound and microwave can reduce solvent requirements with reduced extraction time and temperature. This method has been used to extract annatto and butterfly pea flowers.

### **Supercritical Fluid Extraction method**

A supercritical fluid extraction procedure has been used to extract natural materials using CO<sub>2</sub>. The cost of dye extraction is high, with low color yield. The major advantage of this method is that the extracted material is purified and majorly used in food and pharmaceutical industry applications.

In the case of the dyeing process being done later, the extracted dye can be converted into a powder form of high-concentration solution. Drying can be done using many different methods, such as spray drying, drying with a vacuum, and freeze-drying.

### **2.1.6 Mordants**

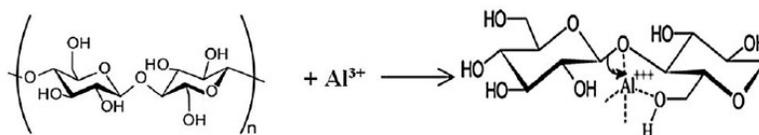
Mordants are compounds that have an affinity for the fiber and the dyes. They create complex between them and enhance the fastness properties in many cases. Mordants become more critical in the case of cellulosic fibers as these fibers have limited affinity compared to protein fibers.

Mordants can be classified into three types: Metallic, Oil, and tannin mordants.

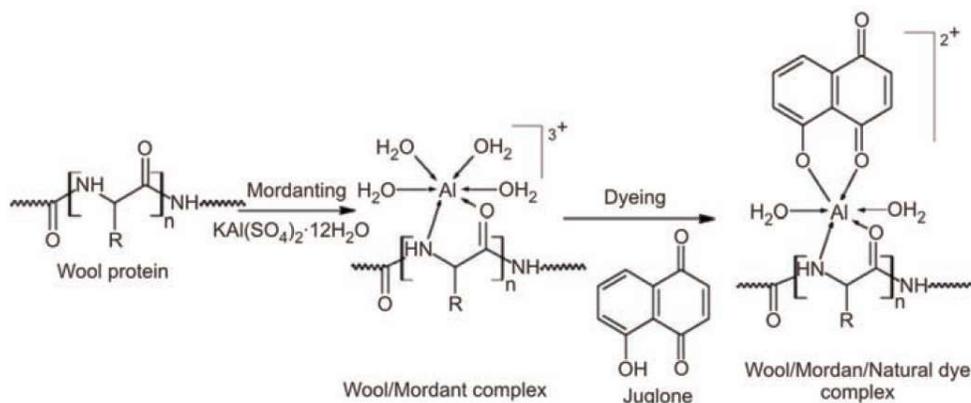
**(A) Metallic Mordants**

Salts of many metals like aluminum, chromium, iron, tin, and copper are used. The compound includes alum, copper sulphate, ferrous sulphate, potassium di-chromate, stannous & stannic chloride, and many others. The dyers have used these compounds. Metallic mordants can create ecological issues, so their use has certain restrictions. Alum and iron salts are considered safe mordants as they are abundantly present in our environment. Alum, Potassium di-chromate, and stannous chloride brighten the fabric, and copper and ferrous sulphate create a dull effect on the fabric. Alum is used in the form of potash, sodium, and ammonia alum; out of these, potash alum is mostly used. Figure 2.1 Shows the cotton mordanting using alum with coordinate bond formation. It shows the chelation between cellulose and alum. In the case of wool mordanting with alum, the mechanism of complex formation between wool, alum mordant, and juglone dye is shown in Figure 2.2. Iron salts are used as a mordant in the form of ferrous sulphate. The color obtained with ferrous sulphate is generally blackish in tone.

Tannin pre-treated fabric absorbs much more iron than the fabric treated only with iron salt. Fermented iron turns blackish and has been traditionally used. Copper sulphate or blue vitriol is used as a mordant and improves the light fastness of dyed fabric. Stannous and Stannic chloride are preferred on cotton tannin pre-treated fabric. Chromium is used as potassium di-chromate. From an environmental point of view, chromium and copper content have to be below 0-2 ppm as per GOTS standards.



**Figure 2.1: Cotton Mordanting with Alum (Repon, Islam, & Mamun, 2017).**



**Figure 2.2: Complex formation between wool, alum mordant, and juglone dye (Haji & Nasiriboroumand, 2018).**

### (B) Oil Mordants

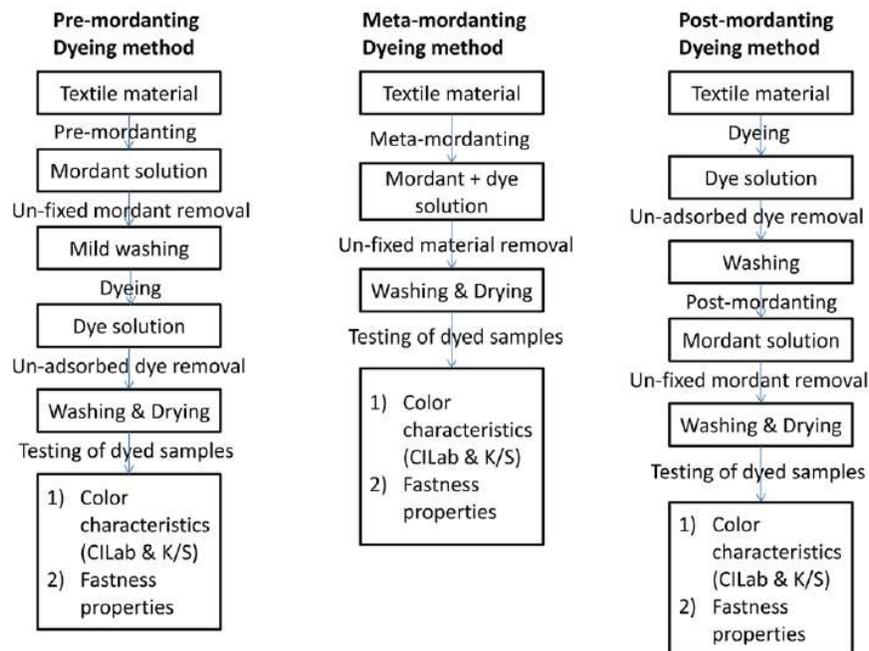
Oil can be used to make a complex with alum, increasing alum retention on cotton fabric. The carboxylic group of fatty acid reacts with metal salts and converts to  $-COOM$  (M-Metal). Oils treated with concentrated acid produce sulphonated oils, which leads to better binding capacity. Sulphonated oils are called Turkey Red Oil (TRO) (Prabhu & Bhute, 2012; Shukla & Dhuri, 1992).

### (C) Tannins

Tannin-treated cotton fabrics can easily absorb all types of metallic mordants. Tannins can be obtained from various species, such as bark, wood, fruit, pods, leaves, galls, etc. Names of some of the tannin-containing compounds include myrobalan, oak galls, sumac, and Pomegranate rind. Myrobalan is widely used as a tannin source containing yellowish-brown matter, giving the yellow color to textiles. Tannins can be classified as two hydrolyzable tannins and condensed tannins. From available sources, acacia catechu, eucalyptus, and myrobalan have maximum tannin content (Shukla & Dhuri, 1992).

### Mordent Application Methods

Mordants can be applied on textiles using pre-mordanting, meta-mordanting and post-mordanting method. The Figure 2.3 shows the type of application methods for mordanting and dyeing.



**Figure 2.3: Type of Application Methods for Mordanting and Dyeing (Yusuf et al., 2017).**

### 2.1.7 Mixed or Compound shades of natural dyes

Teli, Sheikh, Mahalle & Labade (2012) reported a study of self and mixed shades of catechu and heena on cotton and silk using harda as a natural mordant. The analysis was encouraging as the results showed a wide range of shade gamut. The effect of pH on the color depths of different dyes in compound shades was also examined. Other shades were possible to obtain at different pH. The fastness properties remained unchanged even with the combination of dyes.

Teli, Valia & Agrawal (2014) reported a study of mixed shades of Indian madder and sappanwood on cotton and silk fabrics using alum and ferrous sulphate as mordants. Mixed shades were developed by increasing the proportion of sappanwood at the cost of madder, the samples treated with alum mordant showed darker and brighter shades, and samples treated with ferrous sulphate showed deeper but duller shades of red on both cotton and silk, with good wash and light fastness ratings.

Teli, Valia & Kolambakar (2014) studied the coloration properties of natural indigo on wool fabric top dyed with marigold using alum as a mordant with a pre-mordanting technique. Wool fabric was first dyed with natural indigo as per the conventional process,

which does not require any mordant. Then, dyed wool was treated with alum and then dyed with the extract of waste natural marigold flowers to get a compound shade effect. Results were encouraging as a wide range of shades of green and acceptable fastness ratings for washing and light were obtained.

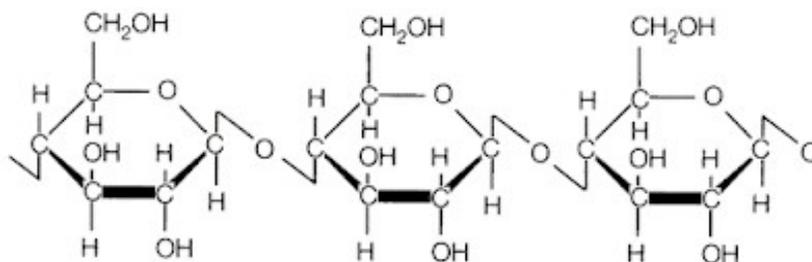
Teli & Ambre (2015) reported the study of mixed shades of marigold and sappanwood on cotton and silk fabrics using alum and ferrous sulphate as mordants. Mixed shades were developed by increasing the proportion of sappanwood at the cost of marigold; the samples treated with alum mordant brighter shades ranging from yellow, reddish-orange, and orange to red, and samples treated with ferrous sulphate showed deeper but duller shades of grey and greyish brown on both cotton and silk with a good wash and light fastness ratings. Dyed samples were also subjected to wash and light fastness. The results achieved were satisfactory. Thus the study indicates that a wide range of shade gamut can be obtained by dyeing the compound shades of natural dyes.

## 2.2 Cotton

Cotton fibers are the hair of the plant *Gossypium hirsutum* seed. The typical composition of raw cotton is shown in Table 2.7. A major component of the fiber is cellulose material. A hollow cylindrical structure emerges when the fiber develops within the seed.

**Table 2.7: Typical Composition of Raw Cotton**

Component	Approx. Amount (%)
Cellulose	86.9
Oils, waxes	0.7
Pectins	1.1
Carbohydrates	0.5
Proteins	1.2
Salts	1
Water	6.7
Other	1.9



**Figure 2.4: Chemical Structure of Cotton**

(<https://www.onlinetextileacademy.com/chemical-structure-of-cotton-fibre/>)

The product remains after removing the unwanted natural impurities in cotton, as the main constituent is cellulose. Cellulose is a water-insoluble polysaccharide with an empirical formula  $(C_6H_{10}O_5)_n$ . The chemical structure of cotton is shown in Figure 2.4. Cellulose is essentially a poly (1,4) (3- D glucopyranose). Each glucopyranose ring in cellulose contains three free hydroxyl groups, one primary at C6 and two secondary at C2 and C3. In the case of cotton dyeing, the hydroxyl groups present are responsible.

In the case of synthetic dyes, cotton fabric is dyed using direct, sulphur, vat, reactive, and azoic dyes. Each dye class has its application methods, dyeing characteristics, and fastness properties, thus its advantages and disadvantages. Each category's application and performance properties differ significantly in their pros and cons.

### Natural Dyeing on Cotton

Cotton, an entirely cellulosic fiber, is offered in an extensive variety and quality profile worldwide. Cotton-based textiles are generally subjected to a preliminary procedure that includes bleaching, desizing, and scouring before using synthetic colors. Cottage-level dyers and craftspeople frequently employ the below mentioned conventional technique of pre-processing cotton fabric and combining it with natural colors in diverse global places (A. K. Samanta et al., 2009).

1. Soak the fabric overnight in dung (cow dung, camel dung, etc.)
2. Next day morning-Washing the fabric properly
3. Steaming
4. Steeping in alkaline lye (mixture of water, oil, and alkali)
5. Rinsing
6. Repeat the step 4 & 5 for 3-7 days
7. Washing and drying

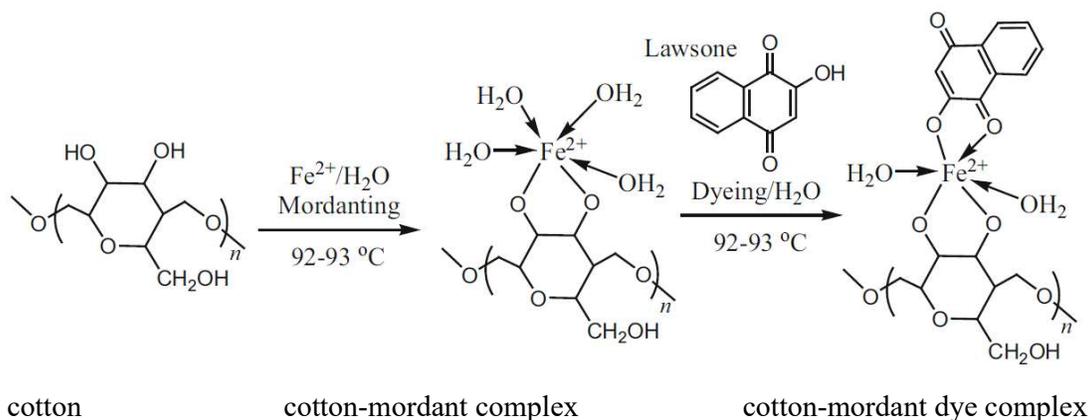
8. Galling-Soaked in a solution of harda
9. Drying
10. Mordanting with alum/tamarind seed powder
11. Dyeing with different materials
12. Drying
13. Finishing

However, the above process is lengthy and may not be feasible for industrial-scale dyeing. The preparatory process may be followed per standard industry standards. Based on the research done so far and optimization, the following processes with conditions are followed for cotton dyeing. The dyeing conditions may vary according to the type of dyeing material, shade depth, and machinery used.

- Dyeing time varies from 30 -120 minutes, depending on the dyeing material
- Dyeing temperature, 70- 100°C
- Material to liquor ratio-1:20 -1:40 or higher as per machine used
- Dye: Raw material: 10-50% (own)

After dyeing, the dyed samples are given a hot and cold wash and soaping with 2g/L soap solution at 60 °C for 15 min, followed by repeated water wash and line drying.

Figure 2.5 shows the plausible cotton-mordant-dye complex, where Lawsone is an example. The same mechanism is followed in the case of any other dye.



**Figure 2.5: Cotton-Mordant-Dye Complex (Lawsone as an example) (Yusuf et al., 2017).**

A study used Onion (*Allium cepa L.*) on cotton and other materials in pre and simultaneous mordanting conditions. The most effective pH for cotton dyeing was 2,4,7, higher than the desired pH of 8 or higher. The author showed that the bonding between dye and cotton does not happen in the alkaline pH range (Onal, 1996).

In one of the studies, the dyeing of cotton with natural colorant, natural mordant, and other natural fixing agents was investigated. Extracted natural dye was used in the dyeing by pre-, simultaneous, and post-mordanting processes. Cowdung was used as a mordant for six different types of natural colorants. Simultaneous mordanting was found to be the most effective process with optimum dyeing conditions found as neutral pH, 60 mins, and 60 degrees C (Kalapriya & Gurumallesh Prabu, 2020).

Pan, Chattopadhyay & Day (2003) did a study on dyeing jute using natural plant colors. The raw jute fabric underwent bleaching and mordanting processes using varying concentrations of potash alum. Subsequently, the jute fabrics that had been treated with a mordant and bleached were individually dyed using jackfruit leaf and marigold flower petals. The findings indicated that jute fabrics treated with a 10% potash alum pre-mordant exhibited superior dye absorption and fastness to washing. The brightness index values of these samples, which were treated with potash alum as a mordant, were lower than untreated jute fabrics dyed with the same dyes.

In a study by Shah & Patel (2012) it was found that viscose rayon fiber can be effectively dyed to get a natural black color. The natural color exhibits similar color strength and tensile strength characteristics as the manufactured black color. The natural black dyed viscose rayon fiber exhibits comparable fastness properties to other dyes examined in this study. Therefore, the black color derived from *Terminalia chebula* can be effectively employed for dyeing viscose rayon fiber when environmental friendliness is a top priority.

B. H. Patel & Shah (2010) stated that the Pad-Dry-Steam procedure allows for the successful application of natural dyes on the cotton substrate without the need for treatment with metallic salts. The three fundamental colors, yellow, red, and blue, can be combined to create several secondary colors using wet-on-wet padding techniques. These secondary colors exhibit excellent overall fastness capabilities.

It may be concluded from the above that in the case of natural dyeing, we have many variables to take care of, namely pre-mordanting, simultaneous, and post-mordanting, type of mordant, pH, and other dyeing parameters. Researchers are working in almost all possible directions, allowing us to go forward with natural dyeing. In the case of cotton, the process is multi-step and lengthy, where skilled people can get good results.

### **2.3 Compatibility of dyes**

Most of the dye producers provide the tones and hues of the three primary colors. They try to give as many tones as possible by changing the structure of the dye. Three colors are generally required to dye a fabric for any color standard. If the dyer is lucky enough, single dyeing or combining two dyes may obtain the same tone, but this phenomenon is rare. Mainly, the dyer would require three primary colors. The dyer's task of mixing the dyes and getting a shade out of them is difficult. The dyer has to check the compatibility of the dyes being mixed. The optimum dyeing conditions may be different for different dyes. The other dyes' fastness properties may differ, or the mixture may change the tone during the dyeing cycle. The shade's reproducibility is a crucial matter of concern for the dyer. There is scope for improvement through better compatible dyes (Sivaramakrishnan, 2014). During dyeing, the color of the goods will then gradually become deeper, but since the dyes are absorbed in the same proportions throughout the process, the hue does not change, and the goods will always be on shade (Broadbent, 2001).

If all the dyes in the mixture are exhausted at the same time and the hue remains the same with time and depth, then the dyes are referred to as 'compatible' for that specific combination in those dyeing conditions used (Bhatt & Chaturvedi, 1986; Kamel, Shakra, & Zayatie, 2001; Pai, Shah, & Gandhi, 1990; Shukla & Dhuri, 1992). A combination of dyes with optimal compatibility behaves as a homogeneous dye, with no color alteration by the fiber during the dye uptake process (Rao, Chapatwala, & Gandhi, 1988). The term "Compatible recipe" refers to dye recipes of this nature.

Also, if the dyes in the mixture are compatible, then:

- The duration of the dyeing process may decrease
- The level of reproducibility may enhance
- The probability of achieving uniform dyeing is enhanced, and the quantity of leveling agent needed may be reduced compared to that needed for incompatible colors.

The AATCC technical manual (1989) defines compatibility as **"the propensity of individual dye components in a combination shade to exhaust at similar rates resulting in a build-up of shade that is constant or nearly constant in hue throughout the dyeing process."**

In this way, several dyeing parameters that define the compatibility of dyes are mentioned in the literature. Many researchers have attempted to define the different methods for compatibility.

### **Factors Affecting the Dye Compatibility**

The factors that contribute to optimal dyeing behavior in terms of compatibility are as follows (Vaidya & Dayte, 1984):

- Dye's state in a liquid solution.
- The interaction among the dyes in the combination.
- The rate at which the dye is absorbed onto the fiber's surface.
- Diffusion rate inside the fiber phase.
- The affinity of dyes for the substrate in a combination and the saturation value.
- Competition among dyes for binding sites on the fiber.

In addition to the circulation of liquor, the packing of goods, the concentrations of solutions, the additives, auxiliaries, etc., in the dye bath also contribute to some extent (Baldwinson, 1985). He emphasized the importance of conducting compatibility studies in dye houses using settings that closely resemble the bulk methods. The behavior of a dye combination in a specific dyeing process may be unpredictable, yet it may show compatibility when used in a different set of conditions. Therefore, it is necessary to establish compatibility ratings based on the specific dyeing conditions (Vaidya & Dayte, 1984).

## **2.4 Introduction to Computer Color Matching**

Achieving precise color matching and texture imitation, particularly in textiles with different fibers and blends, is crucial for apparel applications. The complexity increases when exact color matches with acceptable color fastness are required for different materials exposed to washing, rubbing, light, and perspiration. The passage highlights the imperative for professionals in dyeing, printing, and molding to comprehend the theory of color measurement and quantification for diverse applications. Consumer concerns regarding

accurate color matching in lifestyle products further drive manufacturers to develop meticulously matched products. These concerns are resolved by the measurement of color using a spectrophotometer, also called a computer color matching (CCM) system.

### **Applications of Computerised Color Matching (CCM) and Measurement Systems**

1. The quantification of tristimulus values, either by measuring the reflectance at the wavelength of maximal absorption or by using the K/S measurement of transmittance. This aids in quantifying and assessing color. The CIELAB color space is illustrated in Figure 2.6.
2. The CIELAB equation calculates the overall color difference, represented as  $\Delta E^*$ . A representation of the CIE color difference space diagram accompanies this calculation. The shade sorting, which involves determining if a dyed shade meets the quality standards, assesses color variations between different batches or lots.
3. The values are expressed in terms of the degree of darkness and lightness ( $\Delta L^*$ ), the degree of redness and greenness ( $\Delta a^*$ ), and the degree of yellowness and blueness ( $\Delta b^*$ ).
4. This involves anticipating new computer-aided color-matching recipes/formulations with the lowest cost and the closest metameric match. This is achieved by utilizing a pre-set stored database of specific dyestuff data of primary shades.
5. Batch correction or automatic correction of shades using human or computerized adjustments. Expansion of the match projection through batch adjustments and the utilization of dyeing waste solution.
6. Perform a purity/quality test on the incoming dyes using computer-aided color measuring equipment.
7. The whiteness, yellowness, and brightness indices of a bleached textile substrate can be determined using many standard scales such as the CIE scale, Hunter Lab scale, ASTM-E-313 scale, and Stansby scale.
8. The efficiency of optical brightening agents (OBA) can be predicted using this technique by comparing their performance under UV light and without UV light settings.
9. This aims to provide a more precise and quantitative assessment of color fastness grade for color fading (P. Samanta, 2022).

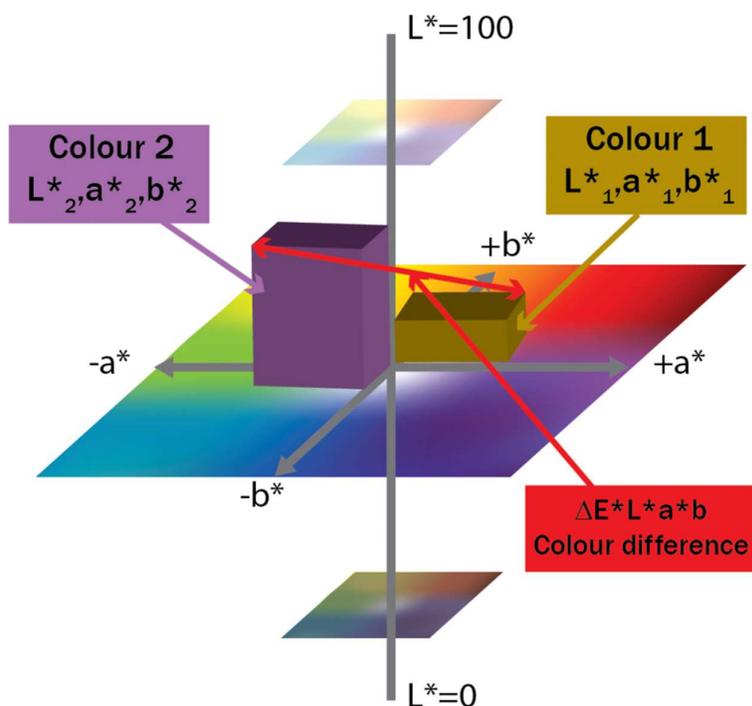


Figure 2.6: CIELAB Color Space Diagram

(<https://s3-us-west-2.amazonaws.com/courses-images/wp-content/uploads/sites/2782/2017/12/04183636/delta-E-in-Lab-1024x1016.png>)

#### Details of CIE Color Coordinates and Color Differences

CIE Color Coordinate / Color difference	Detail
$L^*$	CIELAB lightness
$a^*, b^*$	CIELAB $a^*, b^*$ coordinates
$C^*_{ab}$	CIELAB chroma
$h_{ab}$	CIELAB hue angle
$\Delta L^*$	CIELAB lightness difference
$\Delta a^*, \Delta b^*$	CIELAB $a^*, b^*$ difference
$\Delta C^*_{ab}$	CIELAB chroma difference
$\Delta h_{ab}$	CIELAB hue angle difference
$\Delta H^*_{ab}$	CIELAB hue difference
$\Delta E^*_{ab}$	CIELAB color difference

The value of 'L' ranges from '100' to '0'. The value of 'L' is '100' for pure white and '0' for pure black. If the value of 'a' is positive, the color is red, and the color will be green in case of a negative value of 'a'. If the value of 'b' is positive, the color is yellow, and the color

will be blue in case of a negative value of 'b'. If both 'a' and 'b' are zero, it indicates achromatic color. The color can vary between neutral shades of light grey, dark grey, black, or white, depending on the 'L' value.

If the value of both 'a' and 'b' are positive, the point is located in Quadrant I. The colors red, orange, and yellow are located in Quadrant I. If 'a' is negative and 'b' is positive, the point is in Quadrant II. The colors greenish yellows and greens are located in Quadrant II. When both 'a' and 'b' are negative, the point is located in Quadrant III. Greens, Bluish green, and Blues are in Quadrant III. When the value of 'a' is positive, and the value of 'b' is negative, the point is located in Quadrant IV. The colors blue, violet, and red are located in Quadrant IV.

The chroma or saturation 'C' refers to the distance between an achromatic point and a color. It is determined using the following equation, which involves the variables 'a' and 'b.'

$$C^*_{ab} = [(a^*)^2 + (b^*)^2]^{1/2}$$

CIELAB hue angle,  $h_{ab}$  equals :

$$h_{ab} = \arctan (b^*/a^*)$$

It's value shall be as follows:

If  $a^*$  and  $b^*$  are both positive -  $h_{ab}$  from  $0^\circ$  to  $90^\circ$

If  $b^*$  positive,  $a^*$  negative -  $h_{ab}$  from  $90^\circ$  to  $180^\circ$

If  $a^*$  and  $b^*$  are both negative -  $h_{ab}$  from  $180^\circ$  to  $270^\circ$

If  $b^*$  negative,  $a^*$  positive -  $h_{ab}$  from  $270^\circ$  to  $360^\circ$

CIELAB color difference equals:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

Color tolerance levels in terms of  $dL^*$ ,  $da^*$ ,  $db^*$ , and  $dE^*$  is as follows:

$$dL^* = 0.7 \text{ to } 1.2$$

$$da^* = 0.6 \text{ to } 1.0$$

$$db^* = 0.6 \text{ to } 1.0$$

$$dE^* = 1.0 \text{ to } 1.5$$

The mentioned limits are liable to change as per end-product requirements.

### **Kubelka - Munk Theory**

The foundation of Computer Color Matching mainly relies on the theory proposed by Kubelka and Munk in 1931. This theory explains how radiant light is scattered and absorbed in a turbid medium by considering its reflectance.

$$K/S = \frac{(1 - R)^2}{2R}$$

The term 'K/S' is often used to denote the function of reflectance, which is often represented as  $f(R)$ . K represents the absorption coefficient when the concentration is at its unit value. The symbol S represents the scattering coefficient when the concentration equals one unit.

$$K/S \text{ Mixture} = C_1(K/S)_1 + C_2(K/S)_2 + C_3(K/S)_3 + \dots$$

The property of K/S being additive means that it can be combined or added together. The  $C_1$ ,  $C_2$ , and  $C_3$  are the respective concentrations of individual dyes in the mixture.

Therefore, the property of K/S exhibits additivity, whereas reflectance does not exhibit additivity. The rate constant (K/S) shows a direct relationship with the concentration of the dye, but only up to a specific concentration known as the saturation point.

### **Database Preparation for Recipe Prediction using Computer Color Matching (CCM)**

Developing a dyestuff database for dyeing specific textile fabrics with selected types and classes of dyes is an intricate process which involves carefully selecting substrate, dye class, and manufacturers/suppliers. To facilitate computer-aided color measuring and matching systems, a comprehensive dyestuff database is constructed by subjecting control bleached cotton or alternative textile fabric samples to the dyeing process using each chosen dye at varying concentration levels (typically 5-8). Subsequently, the dyed samples are measured for reflectance values at diverse wavelengths, which are meticulously stored for future use (P. Samanta, 2022).

The primary objective is to establish a categorized data repository based on dye class or company, encompassing different dye types tailored for specific substrates according to a standardized dyeing protocol. The system is designed to segregate data efficiently into distinct files within a computerized processor for streamlined retrieval. The precision of color measurement assumes paramount importance, considering variables such as folding, sample orientation, and color difference index values.

Achieving optimal efficacy necessitates rigorous control over laboratory dyeing machines and processes concerning dyeing variables. Prior to the execution of accurate calibration dyeing, standardization is imperative. The responsibility lies with laboratory dyers and colorists to maintain precision in color data and dyestuff databases, which are categorized for different companies, substrates, and specific dye classes.

One suggested approach for ascertaining the appropriate concentrations is multiplying the maximum concentration of each dye that may be utilized by a sequence of factors, resulting in a total of eight to twelve samples. Consider, for instance, applying a dye in the concentration range of '0' percent to '1' percent. The factor values for the greatest concentration, which is 3 percent, are as follows: 0.025, 1.1, 1.0, 0.8, 0.6, 0.5, 0.3, 0.2, 0.1, 0.05, and 0.25. This will result in the following concentrations: 0.075 percent, 0.3 percent, 0.15 percent, 1.8 percent, 1.5 percent, 0.9 percent, 0.6 percent, and 0.3 percent. Minor adjustments to the concentrations may be made to facilitate the dyeing process. However, concentrations below 0.05 percent are not advised owing to the increased risk of inaccuracy. The aforementioned method can also be implemented using units other than %. Following an analysis of the samples, it may be required to eliminate certain concentrations in order to permit further dyeing in regions where the behavior of the dye has not been precisely established (Butts, 2003).

## **2.5 Research Review**

The dyes were chosen for the study based on the background and introduction. Many researchers have attempted to work on various areas of these natural dyes. Many researchers have done extensive work for the compatibility check of the dyes. The compatibility assessment methods and the work done using those methods were studied.

The following research review areas are included in this chapter:

1. Research review related to Natural dyes used in the present study
2. Research review related to Compatibility Assessment Methods
3. Research review related to Compatibility of dyes in combination

### 2.5.1 Research Review related to Natural Dyes Used in the Present Study

Dye materials Pomegranate, Marigold, Madder, Annatto, Sappanwood, Babool, Katha, and Rhubarb dyes were selected for the study.

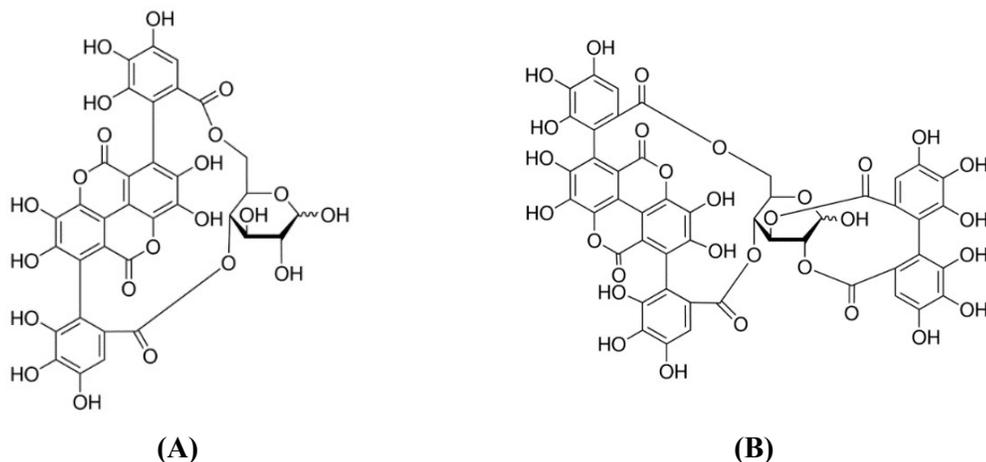
#### Pomegranate

This dye is high in tannin (19 to 26%), so it works effectively with cotton and other plant fibers, although it can also be used for dyeing wool and silk. The Pomegranate peels are dried under the sun and then grinded, which is used to dye the material. A picture of dried Pomegranate peels and their powder is shown in Figure 2.7. Using Pomegranate without a mordant will produce fawn-colored yellow, whereas utilizing a mordant will produce golden yellows. With the addition of iron mordant, greens, greys, and blacks can be produced. It can be over-dyed with indigo to create dark greens. Pomegranate peels are commonly used in contact dyeing (Eco prints). Unripe fruits produce yellow hues, while ripe fruits produce golden yellow shades. The structural features of Pomegranate possibly resemble a direct dye. (Rachel & Kumar, 2018; Samanta, Agarwal, Singhee, & Datta, 2009).



**Figure 2.7: Pomegranate dry peels and its powder**

The Pomegranate peel, scientifically known as *Punica granatum L.*, has been found to contain tannins. The hydrolysate may be gallic acid and ellagic acid. The yellow coloration of the substance is attributed to the presence of Punicalagin and Puniclin, both of which are classified as tannins due to their chemical composition. The structure of Punicalagin and Puniclin are shown in Figure 2.8: Tannin Derivatives in Pomegranate peel; (A) Punicagalin; (B) Punicalin (Botteri et al., 2022) (Botteri, Miljković, & Glogar, 2022).



**Figure 2.8: Tannin Derivatives in Pomegranate peel; (A) Punicagalin; (B) Punicalin (Botteri et al., 2022)**

In a study by Botteri et al. (2022), extract derived from pomegranate exhibits a peak absorption at a wavelength of 400 nm, specifically within the yellow region of the electromagnetic spectrum. This spectral characteristic is indicative of the presence of punicalin within the extract. The presence of punicalin in the aqueous extract of pomegranate was verified through analysis in the ultraviolet region of the spectrum, where peaks were observed at 256, 278, and 360 nm.

In the same study as above, onion peels and pomegranate peels that give yellow color and its tones, were used to dye the cotton yarn. The influence of pre-treatment was studied using different mordants, including alum with the pre-mordanting method. Mordanting was performed using 5 % alum at 50°C for 30 mins. The dyeing was carried out at 60°C, for 60 mins, and at pH 4. Samples treated with natural dye extracted from pomegranate peel exhibit a more prominent yellow coloration than those treated with natural dye derived from onion peel. The results mentioned above can be attributed to the pomegranate's classification as a tannin-based dyestuff, which possesses the characteristic of serving as a mordant due to the presence of tannin. Notably, the utilization of pomegranate dye is attributed to its natural substantive properties, rendering it a fitting option for cotton material. Pomegranate peel with alum mordant gives good to average overall fastness properties.

As natural dye, thyme and pomegranate fruit peel might be utilised well without the addition of mordants, which are mostly metal salts that are hazardous to the environment and human skin. The application of pre-mordanting significantly enhanced the colour efficiency (K/S) of cotton textiles dyed with pomegranate fruit peel and thyme. (Davulcu, Benli, Şen, &

Bahtiyari, 2014). In the same experiment as above on dyeing cotton fabric with pomegranate peel, The fabric was pre-mordanted with alum. The dyeing parameters were temperature 100°C, pH 7, and time 60 min. The K/S for the mordanted fabric was significantly higher than the unmordanted fabric, with a similar effect on L\*a\*b\*h\* values. Anti-bacterial activity tests showed a 90% reduction in bacterial activity on unmordanted cotton-dyed fabric with pomegranate (Davulcu, Benli, Şen, & Bahtiyari, 2014).

Tutak, Acar, & Akman (2014) showed that the waste pomegranate peel extract can dye the wool fabric properly. Pomegranate dyed fabric had a K/S range of 6.63 to 23.05, and the color fastness results obtained were moderate to high. Samples dyed using iron sulphate mordant gave good light fastness properties (5-6 rating). Mordant iron sulphate gave good light fastness (rating 5-6). The SEM images of the dyed fabrics demonstrated a smooth surface profile.

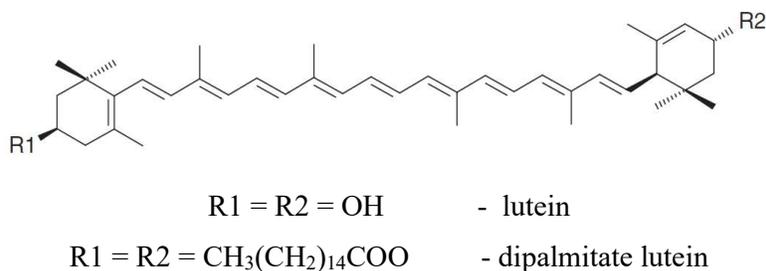
### Marigold

The yellow flower, which is considered to be auspicious, is utilized to create garlands and embellishments. The coloration comprises a blend of hues ranging from golden yellow to yellow and orange. Marigold, scientifically known as *Tagetes erecta*, has been the subject of numerous research studies. This method's utilization for household and business textile dyeing dates back to earlier times and exhibits significant potential for future expansion. This can be applied to various fabrics, such as cotton, wool, silk, and other materials. The pigment is obtained from desiccated blossoms and employed to color the pretreated fabrics. Mordants are utilized when required to confer desirable fastness characteristics and tonal variation. The obtained color yield and fastness properties are deemed satisfactory. The marigold flowers and powder are shown in Figure 2.9. The structural features of marigold possibly resemble a mordant dye (Haque, Hannan, & Masud Rana, 2015).



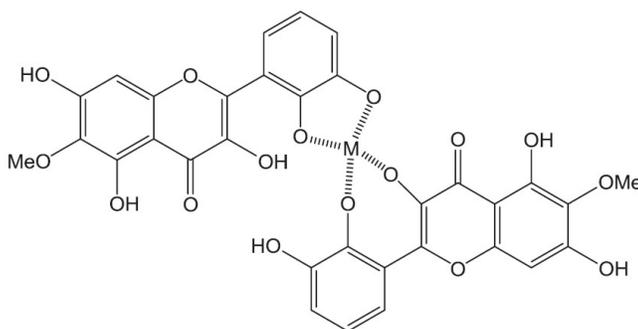
**Figure 2.9: Marigold flowers and powder**  
(<https://www.indiamart.com/proddetail/marigold-extract-12179719530.html>, accessed on 12/12/2023)

The predominant pigment found in marigold is the asymmetric carotenoid all-trans-lutein (xanthophyll). Marigold orange flower extract that has been freshly produced does not include free lutein. Instead, it comprises several lutein di-esters, the principal esters of which are dipalmitate (Figure 2.10) and myristate palmitate. Due to their natural occurrence in human foods and yellow to orange-red coloration, xanthophylls have the potential to serve as a food colorant (Farooq, Ali, Abbas, Zahoor, & Ashraf, 2013).



**Figure 2.10: Lutein Structure in free and esterified forms**

In contrast to silk and wool, the Tagetus dye extract exhibited a diminished attraction for cotton fibers. Fastness was increased using metal mordants that produced an insoluble combination with dye molecules, Figure 2.11 illustrating a typical metal salt-M (Sultana & Uddin, 2007).



**Figure 2.11: Proposed dye-metal mordant complex in Marigold**

The findings of Farooq et al. (2013) indicate that the parameters involved in the processes of extraction and dyeing have a noteworthy impact on the color attributes and overall quality of cotton textile materials. The study determined that the optimized conditions for the marigold flower extraction were MLR of 1:20, an extraction time of 90 minutes, and a temperature of 100°C. Similarly, the optimized parameters for dyeing were found to be a M:L ratio of 1:30, a dyeing time of 1 hour, a temperature of 90°C, and a salt concentration of

60 g/L of Na<sub>2</sub>SO<sub>4</sub>. Pre-mordanting with alum was checked for optimum temperature and concentration, and it was found that K/S was higher at 90°C than at 60°C. The mordant concentrations, 5%, and 10%, had negligible effect at 90°C.

In a study by Jothi (2008), 100% cotton and silk fabrics were dyed under normal dyeing conditions using Marigold flower. They also studied their fastness properties and spectral data were using a spectrophotometer. The fastness results were satisfactory. It was concluded that most metal salts exhibited the highest K/S due to the coordinate complex formation with dye molecules (Jothi, 2008).

The same author as above experimented using pre-mordanted method with alum and other metallic mordants on cotton and silk fabrics using marigold flowers. The color parameters and fastness properties were measured. Dyeing was done using the conventional method at neutral pH for cotton and pH 4 for silk fabrics. Moderate to good color fastness properties are obtained using aluminum, copper, and iron mordants (Jothi, 2008).

### **Madder**

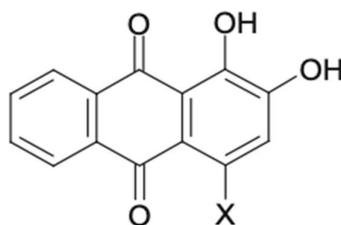
The durability and desirability of red dyes derived from Madder (*Rubia tinctorum L.*) have led numerous researchers to employ this plant in the natural dyeing of textiles. It is used to dye cotton, wool, silk, nylon, and other textiles. The madder roots and powder are shown in Figure 2.12. The Madder dye comprises 23 organic components structured based on anthraquinone structure. These components predominantly consist of hydroxyl groups, with some carboxyl groups. The intensity of the Madder color is associated with these components. Different species of Madder exhibit distinct variations in the type and quantity of anthraquinone structures present, which are contingent upon the specific breed and age of the plant. Thus, identifying the variety and quantity of these constituents makes it possible to distinguish the Madder plant species to some extent. The presence of alizarin compound in the root of Madder has been noted, and its primary function in the dyeing process is to form complexes with different metallic mordants (Sadeghi-Kiakhani, 2015). The structural features of Madder possibly resemble a mordant/disperse dye (Gulrajani, 2001).

Madder with C.I. name natural red 8 is based on the anthraquinoid structure, and the compound name is Alizarine. The chemical structure of Alizarine is shown in Figure 2.13. According to existing literature, it has been suggested that Madder predominantly contains a

yellow dye substance at approximately one year of age, with the red dye substance emerging during the subsequent year of growth. The utilization of various mordants and dye concentrations can produce red hues through the application of Madder dye. The color of Madder dye can be altered to multiple shades such as red, pink, orange, lilac, and brown based upon the mordant employed (Devi Priya & Siril, 2022).



**Figure 2.12: Madder roots and its powder (Devi Priya & Siril, 2022)**



**Figure 2.13: Chemical structure of Alizarin (X=H) and Purpurin (X=OH)**

In a study by Sadeghi-Kiakhani (2015), a measured quantity of dried madder root was subjected to extraction with distilled water utilizing laboratory HT dyeing equipment. The conventional methodology involved a mass-to-volume ratio of 1:20 for the madder plant and water, respectively. The extraction process was conducted at a temperature of approximately 100°C for 120 minutes. Subsequently, the solution underwent filtration through filter paper, resulting in a clear solution. The characteristics of madder natural dye on wool and nylon yarns with regards to dyeing, fastness, and adsorption isotherm were assessed. The study involved the initial mordanting of wool and nylon using aluminum sulphate, followed by dyeing with natural dye extracted from madder root. The research further sought to determine and compare the rates of dyeing and equilibrium times. The results indicate that nylon exhibited a greater rate of dye absorption and attained equilibrium in a relatively shorter duration. The affinity of madder organic dye to nylon showed a gradual rise compared to

wool. Overall, the colorimetric and fastness properties of madder natural dye were superior on nylon compared to wool.

Devi Priya & Siril, (2022) studied the effect of mordants and mordanting methods on bleached cotton poplin fabric using madder, where the extraction was done using an aqueous method. Different mordants, including alum, at 5% owf, were applied using pre-mordanting, simultaneous mordanting, and post-mordanting methods. The dyeing was done at pH 7.5 and 95°C for 45 minutes. Various hues of red were obtained using alum mordant in three mordanting methods. The dye uptake on cotton fabric was highest using alum in pre-mordanting and myrobalan in post-mordanting methods, while it was lowest in the simultaneous mordanting method for all the mordants. The color fastness rating shows an average to the good rating for all the mordants except copper sulphate for wash color fastness.

Mijas, Josa, Cayuela, & Riba-Moliner (2022) studied the dyeing of hemp/cotton fabric using *Rubia tinctorum L.* using alum mordant with and without the use of tannin as a first mordant. For selected samples, the first mordanting of tannin was done at 8% owf at 50-60°C for 1 hr, followed by twice alum mordanting. For other samples, alum mordanting was done twice at 15% owf and 10% owf, respectively, at 50-60°C for 1 hr. Dyeing was done with 8% owf of the madder extract powder at 60°C for 1 hour. It was found that the samples treated with tannin had a yellowish/brownish tint after mordanting. Delta E values were higher for tannin-treated samples than for untreated samples. On the other hand, the results showed that the tannin–alum combination was effective. The color fastness test shows a marginally higher rating for samples mordanted with tannin.

### **Annatto**

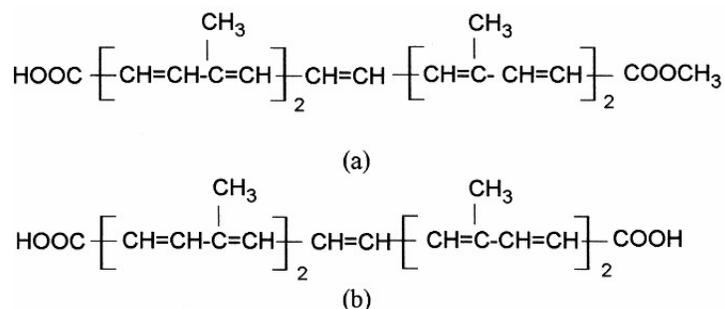
The Bixaceae family includes the little tree known as Annatto (*Bixa orellana*). It originated in tropical America and eventually spread to other tropical nations throughout the globe after acclimatization. The fruits have a capsule or pod morphology and are enveloped by soft thorn structures. The physical characteristics of the pods exhibit a range of sizes and shapes, featuring rounded and elongated forms with pointed ends. The pods' interior is typically partitioned into two sections containing 10 to 50 tiny seeds comparable to grape

seeds. The dye is found exclusively on the outer surface of the seeds. When the pulpy section of the tree's seeds is macerated, coloring material may be extracted. Figure 2.14 shows the Annatto tree and its seeds (Das, Maulik, & Bhattacharya, 2007; Veríssimo et al., 2003).

Although the pulp is high in tannin, it also includes a combination of carotenoids, the two main components of which are bixin and nor-bixin. Nor-bixin which has two carboxylic acid groups in its composition. Figure 2.15 shows the structure of bixin and nor-bixin. Butter, margarine, cheese, dairy goods, cookies, and chocolate all employ annatto as an edible coloring. In the case of dyeing on textiles, this substance does not fall under the category of mordant dyes but instead belongs to the class of direct dyes (Haque et al., 2015). It can be utilized without the need for a mordant. The presence of mordant results in an increase in both color depth and brightness. The color index of Bixa is C.I. natural orange 4 (C.I. 75120).



**Figure 2.14: Annatto Tree and Annatto Seeds (Silva, Zobot, Náthia-Neves, Nogueira, & Meireles, 2018)**



**Figure 2.15: Coloring components of Annatto (a) bixin and (b) nor-bixin**

In an experiment by Saha & Sinha (2012), aqueous extraction method was used for Annatto seeds and optimized for the quantity, temperature, time, and pH using the optical density of extraction. It was found that the extraction increased with the increase in temperature and was highest at 100°C. Regarding the time optimization, absorbance increased with the increase in time and maximum at 150 min at 100°C. Dye extraction was higher in the basic medium than in any other medium, indicating that the extraction is affected by the pH of the bath. It was observed that the concentration of the solution increases and is maximized at 3gm in 100 ml of water at 424 nm wavelength.

Das et al. (2007) found that the process of dyeing silk and wool with annatto has been effectively achieved at a pH of approximately 4.5. Annatto exhibits a significant affinity towards both protein fibers. The light and washing fastness of silk and wool dyed with annatto in the absence of salts is observed to be between 2-3. The efficacy of salt application, specifically magnesium sulphate and aluminum sulphate, about the wash fastness and light fastness properties of fibres treated with annatto was investigated. Results indicate that applying these salts before, after, or during the annatto treatment did not significantly improve these properties. However, using ferrous sulphate prior to the annatto treatment resulted in a one-point increase in both light and wash fastness ratings. The pre-application of ferrous sulfate on protein fibers such as wool and silk, followed by dyeing with annatto, results in a well-balanced enhancement of color uptake, light, wash fastness, and color retention upon repeated washing.

### **Sappanwood**

*Caesalpinia sappan L.* is a tree species classified under the Leguminosae family. The tree is usually referred to as the Sappan wood tree or Brazil wood tree. The Tamil term for it is "Pathimugam". The wood had a long-standing tradition of treating tuberculosis, diarrhea, dysentery, skin infection, and anemia among individuals. The heartwood of *Caesalpinia sappan* contains a crimson pigment known as "Brazilin" (Kannathasan & Kokila, 2021). The structural features of Sappanwood possibly resemble a mordant/disperse dye (Samanta et al., 2009).

Brazilin is the main dye found in the closely associated brazilwood tree, which is responsible for naming the country of Brazil. Besides brazilin, its oxidized product, brazilein,

is also reported in this plant. A photograph of its plant, powder, and chromophore structures is shown in Figure 2.16. Brazilin produces highly intense crimson and maroon red hues, and the wood is seemingly abundant: a single amount can often be used for numerous dyeing sessions.

Sappanwood is remotely associated with logwood and exhibits comparable dyeing properties. When applied on an alum mordant, it yields vibrant cherry red colors. However, these colors are known to be light-sensitive and will fade if exposed to sunlight. Applying a copper mordant creates vibrant and long-lasting shades of mulberry purple. The substance is pH-sensitive, and the addition of soda ash will cause the color to change towards purple or a pleasing steel blue on cotton that has been treated with copper.



**Figure 2.16: Sappanwood plant, powder (a), chromophore structure brazilin (b)**

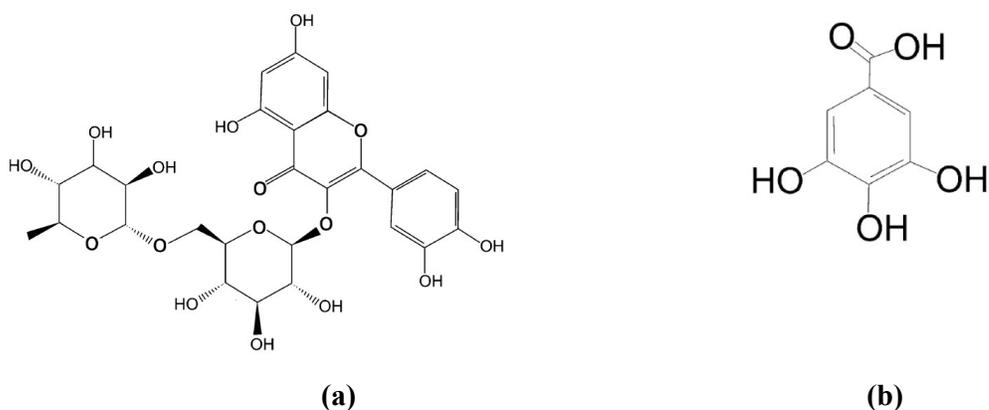
### Babool

The bark of the Babool tree (*Acacia nilotica*) is rough and dark brown or reddish brown wood. It has golden yellow flowers with long white thorns. The babool bark and its powder are shown in Figure 2.17. The tree's bark produces brown dye, which is used to dye many textile materials. The Babool bark extract comprises a relatively low percentage range of common tannins such as gallic acid, ellagic acid, and gallotannin derivatives, estimated to be between 9% to 16.5% based on its dry weight. The extract contains various coloring compounds, including quercetin, isoquercetin, catechin, epicatechin, epi-catechin-di-gallate, and tri-gallate (Dhanania, Singhee, & Samanta, 2021). The chemical structure of the main coloring component is shown in Figure 2.18. The structural features of Babool possibly resemble a direct or reactive dye (Samanta et al., 2009).

The Babool bark is found to be very useful in dyeing cotton, silk, wool, and nylon fabric and has good fastness properties (Patel, Agarwal, & Patel, 2002). It produces shades of black, brown, and khaki using different mordants and dyeing conditions (Rajeswari, 2020). Babool dye on cotton has been successfully used with the padding technique (Patel et al., 2002).



**Figure 2.17: Babool Bark and its powder** (<https://www.etsy.com/in-en/listing/1057905764/100-original-natural-remedies-babool>, dated 25/04/23, 7:10AM)



**Figure 2.18: Poly-phenolic complex as chromophore from babool bark (a) and Gallic acid (b)** (Sinnur, Samanta, & Verma, 2018)

Dhanania, Singhee, & Samanta (2021) experimented on babool extraction using an MLR of 1:30, a temperature of 60°C, a time of 45 minutes, and a pH of 6. Cotton fabric pre-mordanted with gallnut was subjected to dyeing using an aqueous extract of babool bark under different dyeing conditions, including variations in dye concentration, pH, MLR, time, and temperature. The optimal conditions include a dye concentration of 40%, an MLR of 1:20, a dyeing time of 30 minutes, and a dyeing temperature of 100°C. These conditions result in the highest surface color strength and satisfactory color fastness to light, washing, rubbing/crocking, and perspiration. FTIR spectroscopy has verified the creation of a hydrogen-bonded adduct between cotton fibers and gallnut bio-mordant. This has led to the development of a larger, insoluble adduct of color moieties originating from the gallnut bio-

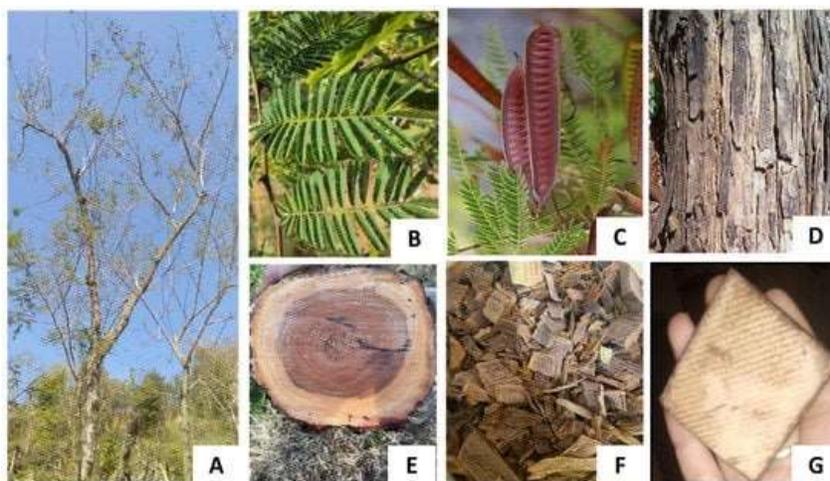
mordant and the natural dye of the babool bark. These moieties have been deposited and fixed onto the cotton fabric through hydrogen bonding. Using babool bark to dye gallnut pre-mordanted cotton fabric results in a uniform dark orangish-brown coloration with commendable color fastness and UV protection properties, as evidenced by a UPF value of 35. This approach of mordanting, dyeing, and finishing cotton yields a textile product with desirable UV protection properties.

### **Katha**

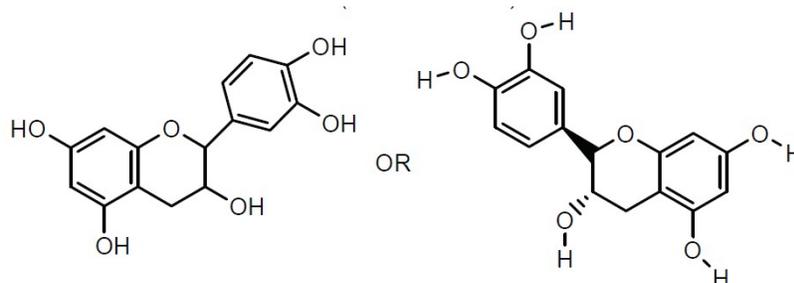
‘Catechu’ is obtained from the heartwood of a catch tree (*Acacia catechu*) and belongs to the Leguminosae family. It is mainly found in the Indian sub-Himalayas and is called *Katha* in Hindi. The powder is a natural dye derived from the *Acacia catechu* tree's wood, steeped in warm water until a syrupy liquid is obtained. The substance undergoes a process of drying and is subsequently converted into a fine powder. Different parts of *Acacia catechu* are shown in Figure 2.19. This phenomenon is prevalent in various regions, including Indonesia, India, Burma, and Peru. Catechu from India is a reliable source of brown hues that are resistant to fading (P. P. Singh, Sharma, & Chatterjee, 2020).

The chief coloring component present in catechu is ‘Catechin,’ with the molecular formula  $C_{15}H_{14}O_6$ , which contains many similar compounds, including gummy matter as mentioned in Figure 2.20. The structural features of *Katha* possibly resemble acid/mordant / disperse dye (Gulrajani, 2001).

Its high tannin content and coloring component make it suitable for textile dyeing. Due to its high tannin content, it can be used as a mordant for cellulosic fabric. It is known for its brown color and different hues and tones when used with different mordants and dyeing conditions. It produces a dark brown, fawn, or golden brown with good wash-fastness properties (Samanta, Datta, & Datta, 2015). It has a yellowish-brown color on cotton, wool, and silk materials. It turns grey-brown with iron and olive brown with copper mordant (Ibrahim, Mashaly, El-Hawary, Kamel, & El-Alfy, 2017; Samanta et al., 2015). Catechu is known for its medicinal properties. As per traditional Chinese medicine, Catechu has astringent, neutral, and bitter properties. It has anti-microbial activities, anti-inflammatory, anti-cancer, UV protection, and many other properties on dyed textiles.



**Figure 2.19: Different parts of *Acacia catechu*: (A) whole tree, (B) leaves, (C) fruits, (D) bark, (E) transverse section of wood, (F) heartwood chips, (G) concentrated extract (Kumari et al., 2022)**



**Figure 2.20: Structure of Catechin**

A study by Zerín & Foissal (2016) involved dyeing woven fabrics made of 100% cotton using *Acacia catechu*, a natural dye. The extraction of catechu was done using 10% w/v catechu and water and boiling for 2 hours. The process of mordanting involves three distinct methods: pre-mordanting, post-mordanting, and simultaneous mordanting during the dyeing process. The mordants employed in the process were alum and copper sulphate. In this investigation, a mordant solution with a concentration of 3% was used at a liquor ratio of 1:40. The mordanting process was done at a temperature of 80°C for a duration of 30 minutes in all mordant types - pre-mordanting, post-mordanting, and simultaneous mordanting. This study demonstrates that Catechu produces a variety of brown tones on cotton that can appeal to many discerning consumers. On cotton that has been catechu-dyed, it has been discovered that mordanting processes can affect the intensity of brown colors. Reflectance was found to be larger when no mordanting was conducted, whereas the K/S value was found to be greater

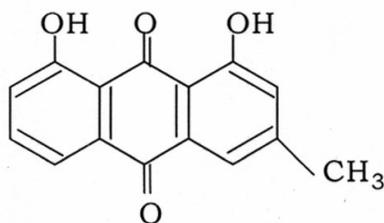
when mordanting was performed beforehand. In Catechu dyeing, the K/S and color fastness values for alum and copper sulphate were found similar.

Woolen fibers can be effectively dyed a vibrant brown color with catechu extract. Changing the mordanting agents under the same dyeing conditions altered the color. Woolen fibers were mordanted with ferrous sulfate stannous chloride, and their combination displayed a subtle change in hue and tone. Reasonably good fastness, durability, and antimicrobial activity demonstrated by catechu-dyed substrates suggest that catechu could be a promising antimicrobial dye after improved formulations and also supports the development of textiles with antimicrobial properties for use in the hospital and hotel fields, in addition to the conventional apparel applications. It can serve as an alternative to the synthetic and toxic antimicrobial agents currently on the market. These results demonstrate conclusively that using catechu's extracted natural colorants as dyeing materials significantly facilitates the production of high-quality antibacterial fabrics with subtle natural colors.

### **Himalyan Rhubarb**

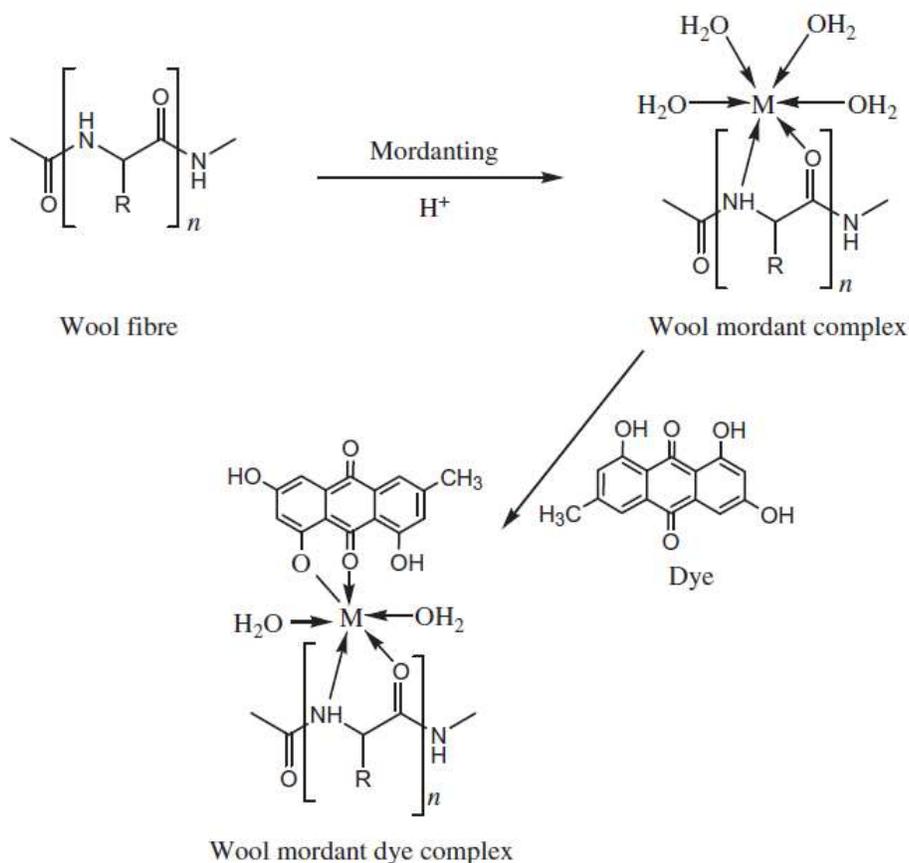
The botanical name for Himalyan Rhubarb is *Rheum emodi* and *dolu* in Hindi. It is a stout found at an altitude of 2800-300 mt in India. It is majorly used in medicines, especially in Ayurvedic and Unani systems of medicine. Its roots are used for the coloration of textile materials and contain several anthraquinone derivatives. Besides its coloration properties, Rhubarb is known to exhibit anti-oxidant, UV protection, and anti-microbial properties (Zhou, Zhang, Tang, & Zhang, 2015).

The primary chromophore found in Rhubarb is chrysophanic acid, whose structure is depicted in Figure 2.21. Rhubarb can be used to dye various textiles, including silk, wool, cotton, and some artificial textiles. The dye is pH sensitive, and changes color with pH, mordant type, and mordant concentration. It produces brown, yellow, yellowish green and reddish brown shades (M. A. Khan, Shahid-ul-Islam, & Mohammad, 2017; S. A. Khan et al., 2012). The fastness properties obtained depend on the type of mordant used and are generally in the moderate to good range.



**Figure 2.21: Chrysophanic Acid – Chromophore in Rhubarb**

Figure 2.22 graphically illustrates the predicted chemical interaction or metal complex creation that takes place among the wool, a metal ion, and a natural color derived from Indian rhubarb.



**Figure 2.22: Proposed Complex Formation for Wool-Mordant-Rhubarb**

### 2.5.2 Research Review related to Compatibility Assessment Methods

Methods to find the compatibility of a combination of dyes need to check different aspects of color parameters. Various methods have been developed to check the compatibility

by different authors. These include methods such as dip test, plotting  $\Delta L$  versus  $K/S$  or  $\Delta C$  versus  $K/S$ , using diffusion coefficient values, and finding relative compatibility rating (RCR), a newer method for compatibility check. Most of the methods used do far used for the synthetic dyes (Garg & Chattopadhyay, 2019).

The conventional and prevalent approach for evaluating compatibility involves visually measuring the extent of tone build-up in a succession of dyeing processes. These procedures are lengthy and complicated and rely on assessing the concentration of dyes rather than the intensity of color on the fiber (Datye & Mishra, 1984).

Neale & Stringfellow (1943) conducted a study on the absorption spectra of direct dyes, individually and in combination, in an aqueous phase. They discovered that the spectra of certain combinations exhibited non-additive properties. The researchers deduced from the spectral pattern of direct dye mixtures that the lack of additivity in the spectra can be ascribed to the reciprocal interaction of dyes in the solution.

In 1947, Lemin & Vickerstaff (1947) conducted a comprehensive analysis of direct dyes and their combinations. They noted that the optical density values of the observed spectra of the mixtures were greater than the computed spectra for all wavelengths. Furthermore, there was a significant disparity between the actual absorption spectra of the mixtures and the computed spectra. Their measurements led them to conclude that the absorption of combinations of direct dyes on cotton when using large amounts of liquid cannot be anticipated based on data from individual dyes. Hofmann, McDowell, & Weingarten (1968) employed a comparable approach to assess the compatibility of disperse dyes. Harwood, McGregor, & Peters (1972) utilized this method specifically for cationic dyes, while Johnson, Patel, & Peters (2008) employed the method to determine the compatibility of direct dyes.

Sultana & Uddin (2007) checked the compatibility of dyes using a dip test. In this test, small pieces of cotton of equal weight are dyed in the same bath with a mixture of dyes. At various intervals, a small dyed sample is removed from the bath and replaced by an identical piece of undyed fabric. A series of dyed samples arranged in order of increasing dyeing time will have gradually decreasing color depth, but the invariant hue when the dyes used are compatible.

Determination of the compatibility of reactive dyes was done using the chromatic diagram by M. Singh, Bhattacharyya, & Gupte (2006). It was assessed from the nature of plots of Chromaticity Co-ordinates (y against x). Compatibility is observed if the dominant wavelength of all the dyed samples taken out at various time intervals during dye fixation falls between the difference of 10 or less than 10 nm.

In 1975, Walsh established the exhaustion values as a measure of the exhaustion rate in a dip test to determine the compatibility of disperse dyes on polyester. The exhaust value (EV) refers to the number of dips in 10-minute intervals needed to exhaust a significant amount of color from the bath. The total time of exhaustion in the case of disperse dyes is determined by the concentration. Therefore, the approximate adjusted exhaust value (AEV) for any concentration can be calculated by multiplying the concentration (C) by the exhaust value (EV). The formula for AEV is the product of EV and C. The assessment of the AEV of the dyes in a dyeing recipe provides a measure of their compatibility or incompatibility. The approach for testing the compatibility of disperse dyes in dyeing polyester was also employed by Bhatt & Chaturvedi (1986) and Mittal, Thakore, & Shah (1987).

In another study by Hoffmann (1988), dyeing experiments were conducted, and the degree of exhaustion was analyzed at different intervals to evaluate the compatibility visually. A separate investigation was conducted to examine the depletion rates of cationic dyes at different concentrations. From these measurements, both the diffusion and affinity factors were determined and subsequently used to establish the compatibility value Z.

$$Z = \text{Constant} \cdot K_{\text{ads}} \cdot \sqrt{D}$$

$K_{\text{ads}}$  represents the Langmuir partition coefficient of adsorption, which measures the affinity factor. D, on the other hand, refers to the diffusion coefficient. The determination of the constant Z offers a means of assessing the rate at which a dye is absorbed in a combination. Dyes sharing the same Z value were determined to be mutually compatible.

Mclaren (1976) devised an objective method with a view to answer the doubts and disputes caused by the earlier methods of assessing compatibility because of its subjective nature. With the introduction of color measurement systems, a series of compatibility tests can be assessed by measuring, e.g., the hue angle. Compatible mixtures will have approximately same hue angle through out the dyeing process.

Hansford, Seaman, & Shore (1982) state that when a dye recipe includes dyes with different dyeing rates, any unevenness resulting from temperature increase becomes apparent as variations in hue. The quantitative expression of any discrepancy between real and ideal behavior can be achieved by measuring the variation in hue between the extracted patterns at different intervals.

Datye & Mishra (1983, 1984) introduced a technique that involves plotting the lightness (L) versus the chroma (C) for dyeing nylon, polyester, and acrylic fibers. This technique utilizes different combinations of dispersion dyes. The qualitative demonstration of the compatibility level of a specific mixture can be achieved by observing the proximity or complete alignment of plots for dyes that share a close resemblance in color.

Shukla & Dhuri (1992a) similarly endorsed the approach and determined that for combinations of dispersion dyes with comparable colors, evaluating compatibility based on the increase in chroma is a good method. They proposed a technique that relies on the accumulation of the overall dye quantity expressed as K/S values, which provides almost identical information.

Samanta et al. (2015) assessed the compatibility by plotting  $\Delta L$  versus K/S or  $\Delta C$  versus K/S. It is generally used for compatibility assessment of two dyes for two sets of the progressive depth of shade developed for a binary mixture of dyes. It is done by varying the temperature and time of dyeing for one set and varying the total dye concentrations of the binary mixtures of dyes in another set to judge whether the two sets of curves for shade buildup run alike or not. A plot of  $\Delta L$  versus  $\Delta C$  and  $\Delta L$  versus K/S gives better results than other methods because it assumes that there is no interaction between dyes and no change in the rate of dyeing in the presence of another dyestuff, which is not true. A plot of  $\Delta L$  versus  $\Delta C$  and  $\Delta L$  versus K/S would require a precise temperature-controlled machine for progressive shade buildup. This method is time-consuming and subjective.

Sultana & Uddin (2007) studied the compatibility of certain reactive dyes on cotton in the different textile industries in Bangladesh. A three-step process was used, including measuring the extinction coefficient, measuring the concentration at a different dyeing stage, and measuring the color strength before and after wash.

### **2.5.3 Research Review related to Compatibility of Dyes in Combination**

Many researchers have assessed the compatibility of dyes using the methods mentioned above. The assessment was done majorly in the area of synthetic dyes for different classes of dyes like direct dyes, reactive dyes, disperse dyes, etc. The outcomes of some of those studies are mentioned in this section. Later, few researchers attempted to assess the compatibility of natural dyes. Some of those studies are also mentioned.

Direct dyes vary widely in their dyeing behavior, giving compatibility problems. The compatibility of direct dyes depends on the rates of dyeing, migration and the salt sensitivity of the dyes. Hue differences as dyeing proceeds are much more apparent than depth differences. Incompatible dyes also tend to give unlevel dyeings. They have different rates of migration and degrees of fiber penetration because of dissimilar diffusion rates, and they change fabric hue during dyeing because of differences in their overall rates of absorption. For reactive dyes, we need to mix dyes with the same type of reactive group having the same substantivity. For cationic dyes, the key parameters determining the compatibility of dyes can be the fiber saturation value (Broadbent, 2001).

Haque et al. (2015) conducted research on the auxiliaries present in the dye bath, which may also affect the compatibility of dyes. Compatibility analysis of reactive dyes is done by exhaustion-fixation and adsorption isotherm on knitted cotton fabric. Red RR, Blue RR, and Yellow RR dyes were analyzed. The exhaustion % of Red RR and Blue RR was uniform, but the exhaustion % of Yellow RR decreased with the increase of shade %. The difference in their fixation was significant in deeper concentrations. Increasing the amount of electrolyte gives better results, especially for deeper shades. It was also found that a decrease in the alkali amount in a dye bath and a reduction in the washing temperature increases the compatibility of these dyes.

Zolotareva & Belenkii (1969) conducted studies with non-continuous wool dyeing using acid dyes with different leveling abilities in six mixtures consisting of two components. The absorption spectra of the individual dyes were found to be cumulative, resulting in the absorption spectrum of the mixture. This suggests that the dyes do not undergo any chemical reactions during the dyeing process. The rates of dye absorption were quantified, and the consistency of the color intensity was evaluated using visual observation and spectrophotometric analysis. The findings revealed that the rate of absorption of components

varies. They suggested that only dyes that exhibit minimal or no alterations in color are appropriate for utilization in combinations.

Collishaw, Glover, & Bradbury (1992) found that using dyes with comparable profiles in combination assures that they are fully employed, spread evenly, and fixed as a single dye, resulting in a consistent color angle throughout the process. Hence, while selecting dyes for binary and ternary shades, it is crucial to examine the compatibility of the individual profiles and any potential impact of dye-dye interaction. The researchers analyzed the behavior of individual colors in mixture using cell transmission measurements. The suggestion is to choose dyes that have been molecularly engineered to have compatible profiles. This will minimize sensitivity to both assignable and random variables in the production environment, resulting in better dyeing performance in exhaust application.

Shukla & Dhuri (1992a) dyed the polyester fabric by immersing it in a combination of three disperse dyes that had similar shades, all falling within the red-yellow range of the color spectrum. The dyes were mixed in equal amounts and applied at various depths. The spectrophotometer was used to measure the color of the dyed samples. The obtained data were then utilized to investigate the compatibility of dyes in a mixture. The researchers determined that the dyes exhibited improved compatibility when applied at a depth of 1.5% (o.w.f.) or lower. The technique of K/S values proved valuable for a pragmatic dyer in assessing the compatibility of dyes with comparable hues in mixtures.

Shukla & Dhuri, (1992b, 1993a) investigated the impact of a non-ionic leveling agent on the mixtures containing three disperse dyes, which were dyed at varying depths (1.5, 3.0, and 4.5%). The spectrophotometric method was used to measure the color coordinates of the dyed samples in comparison to the undyed substrate. A non-ionic leveling agent enhances the compatibility of dispersion dyes when mixed at any concentration. The impact of auxiliaries on the compatibility of dispersion dye mixtures was also investigated.

In their study, Shukla & Dhuri (1993b) examined the compatibility of a combination of disperse dyes in equal quantities, which had similar hues, on polyester fabric. They assessed the compatibility at various applied depths, both with and without a leveling agent. The assessment was done by plotting the hue angle against the K/S values. The plots demonstrated the usefulness of displaying the enhancement in dye compatibility at greater depths due to the inclusion of a non-ionic leveling agent.

Shukla & Dhuri (1993c) utilized three distinct binary combinations created by combining disperse dyes of similar hues onto polyester fabric at a total depth of shade of 4.0%. The binary mixtures were evaluated qualitatively by analyzing the variations in CIELAB color coordinates, specifically in relation to the undyed substrate. Various plots were built to visualize these differences. The hue angle and K/S values were measured as well. The compatibility behavior of three binary combinations, both with and without a leveling agent, has been elucidated based on the molecular mass and color strength of the constituent dyes.

In their study, Kamel, Shakra, & Zayatie (2001) conducted dyeing experiments on cotton using combinations of 3 direct dyes. The objective was to determine the parameters that influence the color properties exhibited by a single dye when combined with other dyes. They noticed that some colors overpower others in mixtures while others enhance the transmission of their own color qualities and diminish the impact of other dyes.

Shahparvari, Safi, Safapour, & Gharanjig (2018) studied the compatibility of natural dyes on Aluminum pre-mordanted woolen yarn. The diffusion coefficient was calculated, and compatibility was checked. The dyes were a walnut green shell, cochineal, and weld. The following equation has been used to check the compatibility:

$$\log \frac{C_{t,1}}{C_{0,1}} = K \cdot \log \frac{C_{t,2}}{C_{0,2}}$$

$C_{t,1}$  and  $C_{t,2}$  denote the concentration of each dye in the dye bath at time  $t$ . Besides,  $C_{0,1}$  and  $C_{0,2}$  show the concentration of each dye in the dye bath at the beginning of dyeing or time=0, respectively.  $K$  is a constant that defines the degree of compatibility and ranges between '0' and '1', with '0' as incompatible and '1' as excellent compatibility. It was found that the exhaustion of each dye in single dyeing is different from the exhaustion in the dyeing mixture. The order for compatibility is as follows: cochineal-weld > walnut green shell-cochineal > walnut green shell-weld.

It was observed by Kumar Samanta & Agarwal (2009) that the use of a mixture of turmeric and madder on cotton in case of simultaneous mordanting shows a synergistic effect in color development than that for single dye application; a 50:50 ratio of turmeric and madder gives the best results. For the combined dye application, it is observed that in the case

of the simultaneous mordanting method, turmeric, when combined with either madder or red sandalwood gives better color strength, while myrobolan shows the reverse trend.

Samanta et al. (2009) experimented on bleached jute fabric using a binary and single mixture of aqueous extracts of red sandalwood and the another five natural dyes in varying amounts. Manjistha (MJ), Jackfruit wood (JFW), Marigold (MG), Sappan wood (SW), and Babool (BL) are the five dyes utilised. Different amount of these were combined with red sandalwood (RSW). The compatibility, colour fastness, and colour characteristics of these dye mixtures were evaluated. In lieu of standard ways of compatibility check, the author of this study has developed a more recent approach based on a contemporary index known as CDI. By varying the proportions of binary dye mixtures applied to the same fabric, the empirical index 'CDI' was calculated using the magnitudes of respective  $\Delta E$ ,  $\Delta C$ ,  $\Delta H$ , and Metamerism Index (MI) values. The sign and direction of these values were not considered when determining the value of the index.

$$CDI = \frac{\Delta E \times \Delta H}{\Delta C \times MI}$$

The closer the CDI values for a different proportion of a mixture of dyes applied on the same fabric under a similar dyeing condition, the higher the compatibility will be. A relative compatibility rating (RCR) is proposed in accordance with CDI values. The scale of compatibility (RCR) is 0-5; zero is the least compatible, and 5 is excellent compatibility. As per the RCR system, the order of compatibility was found to be as RSW: MJ>RSW:MG>RSW:JFW>>>RSW:BL>>>RSW:SW.

In a similar study as above by Samanta, Agarwal, & Datta (2008), bleached jute fabric that had been pre-mordened with 20% myrobolan and 20% aluminium sulphate was dyed by altering the proportions of binary mixtures comprising aqueous extracts of jackfruit wood (JFW) and other natural dyes such as mariegold (MG), sappanwood (SW), manjistha (MJ), and babool (BL). The compatibility was determined using both the traditional and modern approaches (by finding RCR). The order of relative degree of compatibility of these binary pairs of natural dyes applied on pre-mordanted jute was found to be JFW:RSW  $\geq$  JFW: BL  $\geq$  JFW : MJ >>> JFW: MG >>> JFW : SW.