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Lizamoni Chungkrang

Department of Textiles and
Apparel Designing, Faculty of
Community Science Assam
Agricultural University, Jorhat,
Assam, India

Environmental friendly synthesis of natural dyes and pigments

Lizamoni ChungkrangDOI: <https://doi.org/10.22271/chemi.2020.v8.i5ag.10677>**Abstract**

Natural dyes comprise those colorants (dyes and pigment) that are obtained from vegetable, animal or mineral matters without chemical processing. These dyes are used in coloration of textiles, food, drugs and cosmetics. Small quantities of dyes are also used in coloration of paper, leather, shoe polish, wood, cane, candles and such other products requiring coloration. This article attempts to reviews the chemical constitutions of natural dyes and discussed about the available colour shades of natural dyes.

Keywords: Natural dye, coloration, chemical constitutions, colour shades etc.

Introduction

Presently there is a great demand for the use of natural colours throughout the world. All this happened due to the excessive use of synthetic dyes which is estimated around 10, 00,000 tones per annum (Gulrajani, 1999) [6], whose production and application release vast amount of waste and unfixed colourant causing toxic, pollutantive and also the non-treatments of effluent contained in the waste waters of the dyeing process has led to horrendous (extremely unpleasant) results (Anliker, 1977; Yahagi *et al.*, 1975; Khanna and Das, 1991) [2, 25, 13]. Government of Germany was the first to take initiative to put ban on azo-dyes for manufacturing, dyeing and importing textiles and other consumer goods dyed with these dyes from January 1, 1995 by the act of German Legislation (Consumer Goods Ordinance). Netherlands followed a ban with effect from August 1, 1996 on similar lines. European Union is likely to impose ban on these toxic dyes shortly. India has also banned the use of specific azo-dyes and under notification "sufficient legal teeth" had been given for taking panel action against those who use these dyes (Kapoor and Pushpangadan, 2001; Singh *et al.*, 2006) [11, 21]. The synthetic dyes are produced with high conversion of raw materials, while natural dyes are isolated from plants or animals and are not chemically modified except perhaps they may be oxidized or reduced. According to the Society of Dyers & Colourist's Colour Index (3rd edition) defines natural colouring matters as 'the natural dyes and pigments comprise of all colours obtained from animal and vegetable matter with no or very little chemical treatments (Gulrajani and Gupta, 1992) [7, 8]. The natural dyes are used in coloration of textiles, food, drugs and cosmetics. Small quantities of dyes are also used in coloration of paper, leather, shoe polish, wood, cane, candles and such other products requiring coloration (Gulrajani, 2001) [5]. Worldwide the use of natural dyes for the colouration of textiles has mainly been confined to craft, dyers and printers.

Classification of Natural dyes

The natural dyes are further classified in various ways (Ong, 2001; Moses and Venkatchalam, 2001; Agarwal and Gupta, 2004; Mondal *et al.*, 2004; Mukherjee *et al.*, 2005) [19, 16, 1, 15, 18].

Classification according to the chemical structure

Indigoids: Two of the most important natural natural dyes which have the indigo structure and are as follows

Indican: Chemically indicant is indoxyl D-glucoside having molecular formula $C_{14}H_{17}NO_6$. It occurs in the leaves of *Indigofera tinctoria* and *Isatis tinctoria*

Corresponding Author:**Lizamoni Chungkrang**

Department of Textiles and
Apparel Designing, Faculty of
Community Science Assam
Agricultural University, Jorhat,
Assam, India

(Mukhopadhyay and Bhattacharyya, 2001) ^[17]. Indican dye produces the variety of colours starting from blue to a deep rich blue, light gray to black, turquoise blue, peacock blue to green according to the dyeing process and ingredients used.

(Indican)

Tyrian purple: Structurally Tyrian purple is 6,6-dibromo indigo, which is extracted from the mollusc *Murex brandaris*. Due to low yield, the dye was quite costly and mainly used for the dyeing of clothes of Royal people such as British Emperor.

(Tyrian purple)

Dihydropyrans: Most important numbers are haematin and its leucoform haemotoxylin, principal colour bodies of heartwood of *Halmotoxylon campechianum*. Brazilwood is closely related in chemical structure to logwood.

Brazilin: Brazilin, a red colouring matter, soluble in water and alcohol is isolated from *Caesalpinia sappan*, which belongs to the family Cassalpinaceae. When it is used in combination with indigo it produces purple shades.

(Brazilin)

Haemotoxylin: This pigment occurs in *Haematoxylon campechianum* of family Leguminosae and is commonly known as logwood. It provides various shades by mordanting with different mordants such as chromium, tin, iron etc.

(Haemotoxylin)

Flavonoids: Flavonoids are benzo- γ -pyroni derivatives, which resemble coumarins and are ubiquitous in photosynthesizing cells. They occur as aglycones, glycosides

and methylated derivatives. Structurally flavonoids resemble the nucleosides, isoaloxa-zinc and folic acid and thus possess physiological activity.

Flavonal: The flavonals are the hydroxylated flavones, which contain hydroxyl group at position - 3 and are widely distributed in the plant kingdom usually in the form of glycosides. The pigments of this group give yellow colours which are deeper than those obtained from flavones but they are not so fast to light, undoubtedly due to their great sensitivity to oxidation.

(Flavone)

Quinones: Quinones refer to a class of organic compounds which contain at least one cyclic ring system having saturated ketone groups. The simplest quinone is para benzoquinone, which is easily converted to hydroquinones on reduction. When para benzoquinone is attached to one more benzene nucleus at 2,3-C, they are called as naphtha quinones while the quinones, which are attached to benzene nucleus on either side of quinone structure are called anthraquinones.

Benzoquinones: Benzoquinones have not been isolated from plant kingdom. The synthetic compounds have limited application as textile dyes. There is a red dye extracted from the flower of safflower (*Carthamus tinctorius*). Safflower florets contain principally two colouring matters, carthamin, which is scarlet red and insoluble in water and safflower yellow which is soluble in water (Kamat and Alat, 1990) ^[10].

(Carthamin)

Anthraquinones: Anthraquinone is not found in nature, although it had been prepared by Laurent as early as in 1835 by oxidation of anthracene with nitric acid. The term 'anthra' refers to the Greek word for coal from which anthracene was originally obtained. Anthraquinone is one of the most valuable intermediates in the manufacture of dyestuffs. It comprises of a greater number of dyes having outstanding fastness properties than any other group of dyes, therefore, it is in great demand.

(Anthraquinone)

Naphthaquinones: The majority of the naphthalene derivatives found in nature are quinones and most of these are plant products. Naphthaquinones can exist in three isomeric forms. A group of closely related polyhydroxy derivatives is found in certain species of sea urchin and a few others are elaborated by micro-organisms.

(Naphthaquinones) (Anon, 1996)

Carotenoids: Carotenoids are also called tetraterpenoids. They are brightly coloured natural organic pigments found in the chloroplast and chromoplast nearly in all families of plants and some other photosynthetic organisms (Chandrika, 2009; Gulrajani and Gupta, 1992) [4, 7, 8].

Carotenoids are yellow to red pigments of aliphatic, alicyclic or aromatic structure composed of isoprene units. They have the molecular formula, $C_{40}H_{56}$.

They are insoluble in water, acids and alkalies but soluble in chloroform, ether and fats. Many carotenoids are unstable to air, heat and to acids and alkalies. The carotenoids can be identified by the colour reactions.

Bixin: Bixin is a yellow component occurring in *Bixa orellana* fruits commonly known as Annatto, which belong to the family Bixaceae.

(Bixin)

Lutein: It is the main constituent of the flowers of *Tagetes erecta* commonly known Genda or Marigold (Asteraceae). It dyes both silk and wool in variety of deep and fast colours with different mordants, 1% of marigold dye solution give colours ranging from bright yellow; yellow ochre, yellow brown, olive brown, gray green and bright orange.

(Lutien)

Nyctanthin: Nyctanthin is a yellow pigment, which belongs to the carotenoids. It has been isolated from *Nyctanthes arbor-tristis* commonly known as Harshingar belonging to the family Oleaceae and *Cedrela loona* of Meliaceae. The pigment is used to dye wool, silk and cotton and provide magnificent orange-yellow called saffron yellow.

(Nyctanthin)

β -carotene: It occurs in *Helianthus annuus* commonly known as Sunflower or Surajmukhi in Hindi, belonging to the Asteraceae family. The flowers are a good source of yellow dye.

(β -carotene)

Aurones and chalcones

Butein: Butein is isolated from the flowers of *Butea monosperma* of family Leguminosae, commonly called as Palas or Tesu. The flowers of this tree have traditionally been used for dyeing turbans in a yellow colour basanti and also a colour during the Holi festival of Hindus. Colours obtained range from orange yellow, ochre to brown depending on the mordants used.

(Butein)

Rottlerin: This dye is an orange-red powder from *Mallotus philippensis*, which occurs as a glandular pubescence on the pods and is gathered by shaking the ripe capsules in canvas bags. The colouring matter of Kamala comprises of several chalcones; rattlerin and isorottlerin, which constitute 11% of the weight of powder. It is used for dyeing silk and wool and a rich yellow colour of great beauty is obtained.

(Rattlerin)

Alkaloids: Alkaloids are generally defined as physiologically active basic compounds of plant origin, in which at least one nitrogen atom forms part of a cyclic system. Some alkaloids are liquids, which are soluble in water. Most of the alkaloids are optically active (laevorotatory) and generally contain one or two nitrogen atoms usually in the tertiary state in a ring system also possess oxygen.

Berberine: Berberine accompanied by its hydroxylated derivatives occurs in roots, bark and stem of *Berberis aristata* which is commonly known as Kilmora, Rasaut in Hindi belong to the family Berberidaceae. The bark and roots of this plants species yield a fluorescent yellow dye, fast to washing. It is considered to be one of the best yellow dyes in India.

(Berberine)

Diaroyl methane: It is isolated from the rhizomes of *Curcuma langu* of Zingiberaceae. Curcumin dyes wool and silk yellow, when comes into contact with an alkali, turns red. Curcumin is the only natural pigment belonging to this class. It is diferuloylmethane. Curcumin occurs in turmeric in three stereo-isomeric forms termed as curcumin I (60%), II (24%) and III (14%).

(Curcumin)

Chlorophyll: These are green coloured pigments, which occur in plants. Chloroplasts are only found in parts exposed by light, they occur abundantly in green leaves and in green parts of the shoot. Chlorophyll is a mixture of two pigments – chlorophyll ‘a’ ($C_{55}H_{72}O_5N_4Mg$) (blue black) and chlorophyll ‘b’ ($C_{55}H_{70}O_6N_4Mg$) (dark green). Chlorophyll gives a green solution in organic solvents and is not soluble in water even under prolonged boiling.

Based on colour shade

Red: The Colour Index lists 32 red natural dyes. Among them the prominent members are madder (*Rubiatinctorum*), manjistha (*Rubiocordifolia*), Brazil wood/sappanwood (*Caesalpineasappan*), Al or morinda (*Morindacitrifolia*), cochineal (*Coccusacti*) and lac dye (*Coccuslacca*). Most of the red colourants are found in the barks or in roots of the plant or camouflaged in the bodies of the dull grey insects (Yusuf *et. al.*, 2017; Vankar, 2000) [26, 24].

Blue: The color index lists only four blue natural dyes, these are Natural Indigo, sulphonated Natural Indigo, Kumbh (Manipur) and the flowers of Japanese ‘Tsuykusa’ used mainly for making awobana paper (Sinha *et. al.*, 2012). The only viable choice among the blue natural dyes is Indigo. Natural indigo is obtained by fermenting the leaves of various species of *Indigofera*, running off the liquor and oxidizing it to precipitate the dye. Woad (*Isatis tinctoria* L.) is another important source of indigo. The plant is grown mostly in North Europe and British Isles.

Yellow: Yellow is the most common color in the natural dyes. However most of the yellow colorants are fugitive. The color index lists 28 yellow dyes. Some of the important are obtained from barberry (*Berberisaristata*), tesu flowers (*Buteamonosperma*) and kamala (*Mallotusphilippensis*) (Gulrajani *et. al.*, 1992; Paul *et. al.*, 1996) [7, 8, 20]. The other sources of natural yellow colour include turmeric, kamela, tesu, marigold, larkspur, harshingar, annatto, berberis, and dolu.

Green: Plants that yield green dyes are rare. Both woad (*Isatistinctoria*) and indigo have been used since ancient times in combination with yellow dyes to produce green shades. Woollen cloth mordanted with alum and dyed yellow with dyer’s green weed was over dyed with woad and, later with indigo, to produce the once-famous Kendal green. Soft olive greens are also obtained when textiles dyed yellow are treated with iron mordant.

Orange: Dyes that create reds and yellows can also yield oranges. The sources for a natural orange dye are barberry, annatto, sweet pepper blood roots etc. (Tayade and Adivarekar, 2013; Kamel *et. al.*, 2007) [23, 12].

Black and Brown: The colour index lists six black natural dyes like roots of iris plant, lac, carbon, and caramel (Yusuf *et. al.*, 2017; Hao *et. al.*, 2006) [26, 9]. When it comes to natural brown, there is virtually no limit to the natural sources for that. Cutch is an ancient brown dye from the wood of acacia trees; particularly *Acacia catechu* is used for dyeing of cotton in brown hue.

Conclusion

Natural dyes are available in nature with various hues and tones, mostly used to coloration of textiles, food, drugs and cosmetics. The colours produced by natural dyes are soothing to eyes, earthly, warm and highly appealing. Scientific implementations should be focused to adopt modern technologies for making natural colorants as a compatible with synthetic colorants to make a greener world.

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