

ECO-FRIENDLY DYES AND DYEING

Asim Kumar Roy CHOUDHURY

KPS Institute of Polytechnic, Govt. College of engineering and Textile Technology, Serampore (W.B.) India
akrc2008@yahoo.in

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Dyeing and finishing processes for the textiles are practiced by human beings since ancient time. However, in recent years a lot of attention has put in these processes because of the awareness of sustainability and eco-friendly textiles and garments. Textile processes use many toxic dyes and chemicals. This waste water is discharged into fields, ponds or rivers without or improper effluent treatment. As a result, the workers and people coming in contact with discharge water suffer from various skin diseases and respiratory problems. The people are becoming more and more health conscious and demands for producing textile products through environment friendly and sustainable dyes and dyeing processes. Many carcinogenic and allergic synthetic dyes are banned now. Many dyes, though not banned yet, may not be completely safe. Most synthetic dyes are not biodegradable; they accumulate on lands and in river causing ecological problems. Dyes from natural resources such as vegetables, animals and minerals were popular before the invention of synthetic dyes. The efforts have been made to substitute harmful synthetic dyes with natural counterpart. However, natural dyes should be selected with caution – some are neither eco-friendly nor good performer. The present paper discusses the environmental impacts of conventional synthetic dyes and existing laws in this regard. The environmental benefits and possibility of revival of natural dyes have been discussed.

INTRODUCTION

Ecology studies the relationship between the living organisms and natural environment. This concept has important consideration in the field of textiles. This is done in order to ensure the human safety aspects of the clothing without compromising fashion and function.

In the eco-friendly environment, it is very important to assure that the human beings live in a world of hygiene and freshness. The necessities of human beings are not fulfilled with the provision of food, clothing and shelter alone, but it is important that the environment is clean and liveable with pure and safe air as well as water.

The sourcing of a truly sustainable fabric is difficult because there is very little transparency about the quality of dyes and chemicals used during dyeing and printing of fabrics, even in case of organic cloth. Synthetic dyestuffs are made of nasty chemicals and only a few of them are prohibited by laws due to their proven toxicity, which means that many dyestuffs with unsafe ingredients are still permitted and commonly used in conventional industrial dyeing.

Textile dyes are complex synthetic organic compounds. They are common industrial environmental pollutants during their synthesis and later during dyeing. For the textiles dyed or printed with synthetic dyes, one should look for suppliers whose products possess eco-labels issued by well-

known authorities like GOTS, blue-sign etc. The textiles dyed or printed with natural dyes should be mordanted (pretreated) with alum and never with chrome, copper or tin. A responsible natural dyer should disclose their mordanting information with no hesitation.

The large-scale production and extensive application of synthetic dyes create considerable environmental pollution, thereby destroying eco-friendly atmosphere. Legislations on air and water pollution are becoming increasingly stringent.

DYES

A dye is a natural or synthetic colouring substance which is used for dyeing or printing of textile, paper, leather and other materials so that the colour of the dyed or printed materials is not faded by washing, heat, light, or in other external conditions to which the material is commonly exposed. The dyes are generally applied from aqueous solution. The dyes can adhere to compatible surfaces by forming solution, covalent bond or in situ complexes with salts or metals, by physical adsorption or by mechanical retention [1, 2]. Dyes are classified according to their methods of application or by their chemical structures. A group of atoms in dye molecules called chromophores such as azo, anthraquinone, methine, nitro, arylmethane, carbonyl and others, are responsible for the colour of dye. In addition, substituents called auxochromes, such as amine, carboxyl, sulphonate and hydroxyl, withdraw and/or donate electrons thereby generate or intensify the colour of the chromophores [3].

BIODEGRADABILITY OF DYES

Dyes are stable against breakdown by microorganisms and most dyes do not biodegrade under the aerobic biological treatments, in a municipal sewage plant. Many dyes, including the azo dyes, degrade under anaerobic conditions and the aromatic amines thus formed have been found to degrade further aerobically. Therefore, the aerobic conditions of rivers and lakes should degrade the amines formed from the biodegradation of azo dyes if they accumulate in the river sediments. Due to this recalcitrant nature of

dyestuffs under aerobic processes, concern arose as to the toxicity of these compounds towards the microorganisms [4].

According to Cooper [5] 'monitoring by the authorities and regulatory bodies is by no means totally effective'. Some harmful dyes lead to algae overpopulating watercourses, preventing adequate levels of sunlight entering the water. This means flora cannot grow, oxygen levels in the water are reduced and the flora and fauna that are there already are suffocated. Salt pollutes freshwater courses, kills fish and makes soil too alkaline to support crops. There are a number of freshwater lakes that have been turned permanently saline by mixing with dyeing waste water. Dyes, especially dark ones, do not allow sunlight to penetrate into water. Thus, bacteria are inhibited from the task of breaking down waste components of the effluent water. Heavy metals and chlorine present in effluent may be toxic to aquatic organisms. Almost all dyes take a long time to break down and can be considered ecologically unsound or environmentally hazardous. And, of course, it all looks pretty unpleasant too.

The manufacture of synthetic dyes is a problem because they are made from finite non-sustainable resources, such as petroleum. Even with more sustainable dyes that are more inherently carbon neutral, such as plant based ones, there's room for improvement – they're used in factories that run off fossil fuels and require products and additional agents to be transported long distances.

Extensive tests indicate that the dyes are generally absorbed to the extent of 40-50% by the bio-mass and are thus partially eliminated in sewerage plants; practically no biodegradation takes place. The large dye molecules have high affinity for various materials and some are only sparingly water-soluble. Porter and Snider [6] showed that most of the textile dyes are non-biodegradable. Dyes should have a high degree of chemical and photolytic stability in order to fulfil the fastness requirements of textile materials. Due to such stability, they are not readily degraded under the aerobic conditions prevailing in the biological treatment plant. Therefore, unless dye is removed by chemical or physical means, it may pass with

discharge water and lead to public complaint even if the concentration of dye is as low as 1 mg/l. Unnatural colours like red and purple usually are of most concern – blue, green or brown colours are less objectionable.

The requirements of eco-friendly dyes and dyeing are:

- 1) Biodegradable dyes
- 2) Safe dyes - no harm to human being on use, non-toxic, non-carcinogenic
- 3) Eco-friendly auxiliaries used during dyeing.

DUSTING OF DYES

In wet processing one potential hazard presented by dyestuffs is the form of dust. Inhaled dust can block the respiratory tract and certain dyes may induce allergic reaction, which can severely restrict breathing. The problem can be minimised by employing dust masks and downdraught booths in the most affected areas, such as dye weighting and dissolving areas.

The dusting problem with some reactive dye powder brands can be avoided by working with granulated or liquid formulations. Cold-dissolving granular brands such as the Drimarene CDG (Clariant) dyes, are developed which are non-dusting, free-flowing grains that dissolve readily in cold water and offer ease of handling in automatic and metering devices [7].

Liquid brands present less of a health hazard to the dyehouse operative than do dusty solid brands. They are also more amenable to use in automated metering equipments. Liquid acid and direct dyes are easy to formulate, and several manufacturers provide simple aqueous solutions of acid and direct dyes. Reactive dyes are prone to hydrolysis in water, hence, it is not easy to prepare liquid formulations of reactive dyes. However, considering the advantages, tremendous efforts were made and liquid brands of more stable sulphatoethylsulphones and monochlorotriazines are now well established in the market. Liquid brands are essentially isotropic solutions of dye in water, often with additional agents like buffer, a cosolvent caprolactum or a solubility enhancer, such as urea and sometimes a polymer, to prevent or minimise solid deposition. During dye manufacture, those are standardised by adding inorganic salts like common salt or Glauber's

salt. However, the presence of inorganic electrolytes reduces the effective aqueous solubility of the dye, hence are to be removed before preparing liquid brands.

The removal may be made by physical means using membrane technology, viz. reverse osmosis, ultra-filtration, electrodialysis and multi-stage membrane processes. One of the chemical means for preparing dye solutions of low salt content is the preparation of insoluble calcium salt form of the dye, which can be washed to free salts, converted to soluble lithium salts with lithium sulphate and filtered to remove insoluble calcium sulphate. The other methods are:

- a) Use of salt-free intermediates.
- b) Avoidance of mineral acids in the preparation of dyes by utilising sulphonic groups in the diazotisation.
- c) Preparation of a salt-free acid form of dye which can be converted to a neutral derivative by reaction with an alkali metal hydroxide.

Some dyes form lyotropic liquid crystals in aqueous media and this effect can sometimes be utilised to prepare convenient, though more viscous, liquid brands.

Liquids, however, may settle in storage. The granular dyestuffs dissolve more readily than powders and they flow like liquids. Many dyestuffs are now available in granular form [8].

DYE CLASSES

The dyes may be classified according to the methods of application or dyers point of view as follows:

- 1) Direct dyes
- 2) Acid dyes including metal complex
- 3) Basic or Cationic Dyes
- 4) Chrome mordant dyes
- 5) Azoic dyes
- 6) Sulphur dyes
- 7) Vat dyes
- 8) Solubilized vat dyes
- 9) Reactive dyes
- 10) Disperse dyes
- 11) Pigment colours

Each of the above dye classes is suitable for one or more textile fibres and has characteristic fastness.

Higher fastness means lower amounts of dyes released during washing causing lesser water pollution.

Among above dye classes, acid, basic and disperse dyes have high exhaustion properties - hence, less polluting. Azoic and solubilizing vat are not used in large quantities. Pigment colours are water-insoluble and can be separated easily from effluent. Mordant dyes may be synthetic or natural. While synthetic mordant dyes are toxic and obsolete, many natural dyes cannot be applied without mordant. Those will be discussed later. Direct, vat, sulphur and reactive dyes are very popular for dyeing of cellulosic materials. They are used in huge quantities and consequently create enormous impact on environment. The characteristics of the above dye classes are discussed below.

Direct dye

Direct dyes are so-called because they dye cellulose 'directly', which benefits the environment by eliminating the need for a mordant (the chemical fixing agent). They're most often used for fashion clothing, and are popular because they are cheap, easy to apply, a few are light-fast, and available in a wide range of bright colours.

However, the dyeing with direct dyes requires salts, which hampers eco-friendliness. Energy is needed to heat the dyebath to boiling point. The waste water from this process contains salt, dye-fixing agents and about 5% to 20% residual dyestuff.

Some direct dyes are made from a nitrogen compound called azo dyes. They are usually red, brown, or yellow, and make up about half of the direct dyes produced. They are known to give off a range of carcinogenic amines and have hence been banned by several EU countries.

Vat dye

Certain dyes, such as indigo, are applied after alkaline reduction and are classed as vat dyes. The effluent from this process contains of residual dyestuff (between 5% and 20%), as well as reducing agents, oxidizing agents, detergents and salts. Among conventional dyes, vat dyes have least

impact on environment, while resistance to light and wash (i.e. fastness) are highest.

Sulphur dye

Sulphur dyeing is a relatively cheap method of obtaining good colour strength and acceptable fastness of dyeing. It's often used for low cost fabrics and garments such as working clothes. Environmentally speaking, it's free from heavy metals and other toxic materials, so it's not too bad when compared to reactive dyes, except for the fact that 90% of all sulphur dyes make use of sodium sulphide, which makes the effluent more toxic than any other's. This effluent from sulphur dyeing endangers life and possibly alters DNA of water-borne species, corrodes sewage systems, damages effluent treatment plants and possesses high pH and unpleasant odours. This effluent discharged from the sulphur dyeing contains about 30-40% of the unexhausted dye along with alkalis and salt.

Reactive dye

Reactive dyes form complex with textile fibres through covalent bonds, hence they do not merely remain as separate chemical entity within the fibre. These dyes are easy to apply and are available in a wide range of colour and provide wash-fast bright colours. Though the fixation or absorption rate of these dyes is poor (about 70% and above), these dyes are safer creating less waste water problem. Reactive dyes are applied at comparatively lower temperatures (30-70°C) than direct dyes (around 100°C) saving energy. But they require good amounts of salt and alkali. Like other dye classes, the fastness properties of reactive dyes are not dependant on structure and molecular size of dye. Consequently, reactive dyes may be simpler and smaller in molecular sizes which are brighter and richer, without hampering colourfast properties.

However, like other synthetic dyes, reactive dyes are also made from synthetic petrochemicals. The reactive dyeing requires large amount of salt (20%-80% of the weight of the material), alkali and water. The effluent from the reactive dye bath, contain high concentrations of salts, surfactants and defoamers in addition to unexhausted reactive dyes and are strongly alkaline. It's also quite expensive compared

to conventional dyes. As reactive dyes currently make up 50% of world's total dye consumption, more knowledge on how to improve upon this method is needed.

Fortunately, research is being undertaken in this area, and a number of companies have produced high exhaustion products that improve on its impacts. Reactive dyeing can be carried out at neutral pH without salt and alkali if cotton fabric is pre-treated with phosphate buffer (120 g per kg of fabric). The amount of water required is just half as compared to conventional method and the whole dyeing time is significantly reduced, resulting cost savings. The use of relatively low concentration of chemicals and high exhaustion of dyes results in lower pollution load of the effluent, making it a much greener alternative.

Phosphorus is a common constituent of agricultural fertilizers, manure, and organic wastes in sewage and industrial effluent. It is an essential element for plant life, but when there is too much of it in water, it can speed up eutrophication (a reduction in dissolved oxygen in water bodies caused by an increase of mineral and organic nutrients) of rivers and lakes. Soil erosion is a major contributor of phosphorus to streams [9].

Most laundry detergents contain approximately 35% to 75% sodium triphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$), hence, huge quantity of phosphate is already mixing with water during cleansing processes.

Bi-functional, also known as mixed dyes require shorter dye procedures. Because of their increased fixation properties, the salt requirement is reduced to almost half. As fewer chemicals are consumed, these are also less in the effluent.

The recently introduced hot dyeing Procion XL+ range utilizes the MCT reactive system in combination with conventional chromophores. Reactive dyes offer several environmental benefits, such as high fixation, easy wash-off and reduced use of energy, electrolyte and water. Very high bio-elimination is claimed – 60% in case of a bluish-red dye as against 18% or less for other commercial reactive red dyes [3].

Investigations were made to introduce a simpler method of heat fixation dyeing. In *Ecosteam* method,

introduced by Brückner in early 1980s, the fabric remains wet (instead of dried), condition known as *warm wet dwell*, before fixation. However, the method has not produced any major impact in the market. In the absence of urea, poor colour is obtained. On the other hand, urea can be avoided with DCT reactive dyes if a certain degree of humidity could be maintained around the fibre whilst fixation took place. Monforts and Zeneca have developed an even more environmentally sound process that it calls Econtrol. In Econtrol Thermex machine (Monforts), humidity is injected into the hot flue at the impulse of the computer, which would monitor and control the humidity level. In the *Econtrol process*, developed jointly by Monforts and BASF, the relative humidity content in the dryer is carefully controlled. It is demonstrated that in the hot flue drying, the minimum drying cost is achieved with humidity content of 10-20 vol%. The process is a continuous one, i.e. it happens 24 hours a day. Urea, sodium silicate, soda ash, sodium hydroxide or salt are eliminated from this process, and the amount of sodium bicarbonate required is about 5% of its previous levels. Excellent results are reported to have been achieved. The effluent contains between 4 and 5% of what is currently emitted by state-of-the-art technology. The machine is not very effective for less reactive MCT dyes.

Low-impact (less polluting) reactive dyes have been developed, which have been classified by the EU as eco-friendly. These dyes contain no heavy metals or other known toxic substances, and do not need mordants for fixation. Due to high cost of these dyes it is cheaper to reclaim the unexhausted dye from its effluent rather than to discharge; this is advantageous from environmental point of view. The water can also be recycled. The dyeing cycle is shorter than that for other dye processes, meaning lesser requirement of water, salt and chemicals are needed. The entire process normally occurs at a pH of around 7.0, meaning no acids or alkalis need to be added to the water. It's really hard to find out the names of these low-impact reactive dyes and who's using them, but the Dandelion Clothing Company seems to be one of the companies using them [10].

DYES IN THE EFFLUENT

According to an estimate in 1977 [11] about 40,000 to 80,000 tons of dyes and 1,500 to 1,800 tons of pigments are discharged in a year by the textile processing units due to incomplete exhaustion, washing operation, etc. After a lapse of 40 years, the above quantities must have increased many folds. About 15% of total world production of colorants is lost in the synthesis and processing of colorants. About 10-20% of dyes is lost in residual liquor due to incomplete exhaustion. For water-insoluble pigments, the loss is only 1-2%. One of the major factors determining the release of a dye to the environment is its degree of fixation on the substrate. The fixation, on the other hand, is clearly dependent on individual circumstances and governed by several factors including depth of shade, application method and liquor ratio. It is, therefore, impossible to give a definite set of figures. Although the dyes in general have low toxicity to aquatic life, the dyeing industry remains under severe pressure to reduce coloured discharge, as a very large quantity of dyes and pigments are discharged every day. Table 1 shows the percentage loss of dye in the effluent during dyeing with various classes of dyes. The wool and acrylic dyeing are trouble-free in this respect, as exhaustion is very high (>90%) when wool is dyed with acid dyes and acrylic with cationic dyes. The biggest problems occur during dyeing of cotton with reactive and sulphur dyes. The dyeing industry should move to total reuse of its water by several processes. The recovery and reuse of unused dye will be harder. However, constant efforts are being made and commercial systems are available to recover and reuse indigo e.g. Romicon and Dorr-Oliver in the USA [12].

HARMFUL DYEING ASSISTANTS

Different dye classes require different dyeing assistants or dyeing auxiliaries, some of them are not eco-friendly. The non-eco-friendly pollutants released after dyeing for various dye classes are listed in Table 2.

Adsorbable Organic Halides (AOX)

Adsorbable Organo-halogens (AOX) is a measure of the organic halogen load at a sampling site such as soil from a land fill, water, or sewage

waste. The test measures chlorine, bromine, and iodine as equivalent halogens, but the fluorine levels in the sample are not considered. Utilization of halogen containing materials in processes such as water treatment, bleaching, or even general synthesis to create the final product, generates a number of organic halides. These organic halides are released in wastewater from the oil, chemical, and paper industries and find their way to the consumer and eventually to a landfill or ocean fill. Within the soil, the halogen compounds resist degradation and often react with metal ions, resulting in non-degradable metal complexes, increasing soil toxicity and accumulating in the food chain of aquatic organisms. Up to 2000 ppm of these bio-accumulative organic chlorides were detected in fat of fish from the waters where bleaching effluents were disposed by paper mills where a 2% water concentration is considered toxic for the fish [13]. While strict regulations from the government have reduced the high level of past emissions, these compounds find their way to water sources through improper consumer disposal of items that contain chlorinated compounds. The presence of organic halides in natural water is considered as contamination or xenobiotic [14]. A xenobiotic is a foreign chemical substance found within an organism that is not naturally produced by or expected to be present within. It also covers substances which are present in much higher concentration than are usual. Consumption of these mutagenic or carcinogenic compounds could cause several abnormalities in development and reproduction in humans through long half-lives and mimicking hormone receptors.

The EU Drinking Water Directive (Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption concerns the quality of water intended for human consumption. Its objective is to protect human health from adverse effects of any contamination of water intended for human consumption by ensuring that it is wholesome and clean [15]. The consent limit is likely to be as low as 2 ppm and as such compounds containing these are to be used carefully. The products used in the textile industry causing AOX are:

- 1) Chlorine-containing bleaching agent.

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- 2) Shrink-proofing of wool with chlorine, the most promising alternate being permonosulfuric acid.
- 3) Insect-proofing agent for wool.
- 4) Some types of carriers used in dyeing with disperse dyes.
- 5) Certain chromophores or colour generating components of dyes.
- 6) Some classes of reactive dyes.

For reactive dyeing of cellulosic fibres, the demand for achieving virtually 100% dye uptake and

fixation is very high. The efforts are to be made to replace halogen groups with other groups. Alternately, it is necessary to develop after-treatments that liberate halogens from unfixed dye. Interestingly, organo-fluorine does not fix in AOX classification as the presence of fluorine is not detected in the test protocol due to formation of water-soluble silver fluoride. The manufacturers are thus likely to concentrate on reactive dyes containing vinyl sulfone and fluoro-heterocycles.

Table 1. Estimated Degree of Fixation of Various Dyes on Fibers [5]

Dye Class	Fibre	% Fixation	%Loss in Effluent
Acid	Polyamide	80-95	5-20
Basic	Acrylic	95-100	0-5
Direct	Cellulose	70-95	5-30
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Cellulose	80-95	5-20
Metal-complex	Wool	90-98	2-10
Disperse	Polyester	90-100	0-10

Table 2. Effluent composition after completion of dyeing with different classes of dyes

Dye class	Pollutants in the dyeing effluent
Direct dye	Salt, unfixed dyes (3-30%)
Reactive dye	Salt, alkali, unfixed dyes (5-30%)
Vat dye	Alkali, oxidizing agents, reducing agents.
Sulphur	Alkali, oxidizing agents, reducing agents.
Chrome	Acids, heavy metal, salts, unfixed dye
Basic dyes	Acids, unfixed dye (0-5%), cationic retarder
Metal Complex Acids	Unfixed dye (2-10%)
Disperse dyes	Acids, unfixed dye (~5%), carriers or accelerators (if used)

Considering the increasing costs of using and disposing of water, attention was moved towards non-aqueous dyeing systems. Unfortunately, most of the organic solvents suitable for the purpose are

chlorinated hydrocarbons, which are now subjected to absorbable organohalogen (AOX) controls.

TOXICITY OF DYES

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All synthetic dyes are not harmful. For example, fibre-reactive dyes are dyes that form covalent bond to the fibres like cotton, rayon, and soy. The dyeing with these dyes does not require harmful mordants.

The toxicity of a dye considers the structure of the dye rather than the dyeing process. Heavy metals containing dyes and cancer-producing dyes cause high impact and are objectionable. Dyes that cause allergic reactions are not considered low impact. Dyes that pass eco- standards such as bluesign, GOTS, OekoTex 100 and Cradle to Cradle and are compliant to the ZDHC MRSL have been assessed thoroughly for toxicity and should be chosen over dyes that have not.

Acute toxicity involves oral ingestion and inhalation; the main problems of acute toxicity with

textile dyes are skin irritation and skin sensitization, caused mainly by reactive dyes for cotton and viscose, few acid dyes for polyamide fibres and disperse dyes for polyester, polyamide and acetate rayon.

The reactive dyes which have proved to cause respiratory trouble and/or skin sensitization in workers on occupational exposure has been identified by ETAD and are listed in Table 3 [4].

In order to minimize the risk of exposure to these dyes, dye dust should be avoided. This may be achieved by using liquid dyes, low dusting formulations and by using the appropriate personal protective equipment.

Table 3. Reactive dyes classified as respiratory/skin sensitizers by ETAD

Hue	C I Name
Yellow dyes	Reactive Yellow 25, Reactive Yellow 39,
	Reactive Yellow 175
Orange dyes	Reactive Orange 4, Reactive Orange 12,
	Reactive Orange 14, Reactive Orange 16,
	Reactive Orange 64, Reactive Orange 67
	Reactive Orange 86, Reactive Orange 91
Red dyes	Reactive Red 29, Reactive Red 65,
	Reactive Red 66, Reactive Red 123,
	Reactive Red 219, Reactive Red 225
Violet dye	Reactive Violet 33
Blue dyes	Reactive Blue 114, Reactive Blue 205
Black dye	Reactive Black 5

After dyeing and fixation, reactive dyes have completely different toxicological properties because the reactive group is no longer present and the high wash fastness of the dyed fabric ensures that no dye is exposed to the skin of the wearer. Consequently, no cases of allergic reactions have been reported by consumers wearing textiles dyed with reactive dyes.

Disperse dyes, showing low perspiration fastness, are responsible for causing allergic reactions. Polyester dyed with disperse dyes does not in general pose a problem since the perspiration

fastness is high. However, problems can arise with polyamide or acetate rayon dyed with disperse dyes since the low perspiration fastness allows the dyes to migrate to the skin.

Water is used to wash, bleach and prepare the fabric for dyeing and it is used to clean and rinse the fabric after dyeing. Low impact dyes have a significantly lower environmental footprint as they require much less water, less rinsing and less thermal energy (lower dyeing temperatures).

Reactive dyes require salt to help them be attracted to cotton and alkali to fix them permanently onto the fabric. Levelling agents and wetting agents are used in the dye process as well.

Harmful chrome dyes

The chrome mordant dyes or chrome dyes for wool, almost universally applied by the after-chrome process (i.e. mordanting is done with chromium compound after dyeing). They are still important in the market place due to their extraordinary fastness properties and economy, especially in full shades of navy and black. However, the release of chromium is increasingly seen as a severe environmental problem. The male workers occupationally exposed to Cr(IV), have been found to have lower sperm count and decreased sperm mobility [16]. The draft regulations indicate that very little chrome (<100 ppb) in dyehouse effluent will be tolerated. This is unrealistic because a Cr(III) consumption of 10 mg per day in food is normal for good health and the natural content of Cr(III) in soil is about 200 mg/kg. Nevertheless, Cr(IV) is highly toxic, both to human and aquatic life and steps should be taken to eliminate Cr(IV) from the dyeing process. Efforts have been made to replace toxic dichromate with fibre substantive Cr(III)-organic acid, anionic complexes. The oxidative damage of wool with Cr(IV) will also be reduced. All chrome-dyed shades cannot be reproduced with reactive dyes – in deep navy and black shades on wool, reactive dyes cannot provide equivalent fastness because of lower degree of fixation.

The premetallized dyes are important for wool and nylon, but have similar problems as with chrome dyes. Many US mills have banned their use. However, in their absence it is difficult to obtain muted shades of required light fastness and levelness, especially on nylon [12].

Harmful azo dyes

Azo dyes are the largest group of colorants in terms of number of dyes and production volume, constituting 60-70% of all organic dyes produced in the world. The success of azo dyes is due to their ease and cost effectiveness for synthesis as compared to natural dyes. They have great

structural diversity, high molar extinction coefficient, and medium-to-high light and wash fastness properties.

Azo dyes are synthetic organic colorants that have been extensively used in numerous industrial applications, mainly because of their lower price and higher colour fastness. However, azo dyes are relatively resistant to degradation under aerobic conditions and they get readily reduced to form aromatic amines under anaerobic conditions. A number of aromatic amines thus formed have been found to be carcinogenic [17-18]. For this reason, the European Union has enacted legislation to prevent exposure to these hazardous amines, prohibiting the manufacture and sale of consumer goods containing certain aromatic amines originating from specific azo dyes [19]. According to this legislation, the concentration of any of these amines should not exceed 30 ppm in the finished articles or in the dyed parts thereof. Countries such as the United States have more restrictive laws about the content of these aromatic amines [20].

German ban of azo dyes

About 100 years some trade journals reported increased risk of bladder cancer for people working in dyestuff production. The cause of these malignant diseases was soon thought to be certain aromatic amines widely used in the production of synthetic dyes in those days.

Genotoxicity is the major long-term potential health hazard of certain textile dyes. This became apparent when a high incidence of bladder cancer was observed in plant workers involved in the manufacture of particular dyes during the period 1930-1960. The specific compounds involved were fuchsine, auramine, benzidine and 2-naphthylamine. Strict regulations concerning the handling of all known carcinogens have been imposed in most industrial countries, which have caused virtually all dye companies to cease production of these compounds.

Close study of the dyes has revealed that carcinogenicity is linked to specific types of dye intermediates or metabolites (decomposition product), such as benzidines. Whaley examined 1,460 dyes for evidence of hazardous nature, based on their molecular structure. The structures of 585

dyes (approximately 40%) were found or known. Based on an assessment of likely formation of degradation products on reduction, 55 percent of these known dyes were predicted to be hazardous, and 13 percent were predicted to be uncertain in terms of safety [4].

Azo dyes are by far the most important class of dye, accounting for over 50% of the world annual production. Not surprisingly, toxicity of azo dyes has been studied extensively. As early as 1895 increased rates in bladder cancer were observed in workers involved in dye manufacturing. Since that time, many studies have been conducted showing the toxic potential of azo dyes. The dye itself or its reduced degradation products may be carcinogenic.

Azo dyes contain one or more azo groups (-N=N-) in their chemical structure. During reduction with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), azo groups break into two amines, as shown in Figure 1.

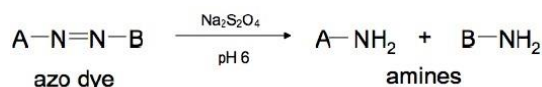


Figure 1. Reductive cleavage of azo dyes

Following the introduction in 1994 of the German Consumer Goods Ordinance that restricted the use of certain azo dyes in consumer goods, several other EU member states introduced similar but different regulations. For transparency and the maintenance of uniformity in the market, the European Parliament adopted the 19th amendment of the Council Directive 76/769/EEC relating to restrictions on the marketing and use of azo colorants. To protect human health, azo dyes, which break down to specific aromatic amines on reduction, are prohibited to use on consumer goods having regular skin contact. The EU Directive was in force from September 2002 and all EU member states adopted appropriate legal restrictions until 11th September 2003 [21]. The banned azo dyes are those which, on reductive cleavage of one or more azo groups, release one or more of the aromatic amines listed in the Directive's appendix, in detectable concentrations, i.e. above 30 mg/kg in the finished articles or in the dyed parts thereof,

according to the testing method BS EN 14362-1:2012 (British Standard).

The German Senate Committee for Testing of Occupational Hazardous Substances prepared and update MAK list (MAK = maximum workplace concentration) annually. Group III of the MAK list includes carcinogenic chemicals (for carcinogenic category 1 and 2 substances no maximum tolerable workplace concentration is specified, though).

Benzidine, the starting material for the popular benzidine dyes is at the top of MAK list. The epidemiological evidence shows that the following four aromatic amines have a carcinogenic effect in humans namely:

1. Benzidine
2. 2-naphthylamine
3. 4-aminodiphenyl
4. 4-chloro-o-toluidine

The above four amines are listed as "definitely carcinogenic in humans" in Category 1, Section III of the MAK list.

Twenty-two aromatic amines were banned, which are listed in Table 4. The figure 2 shows the chemical structures of 22 banned amines indicated by symbols "A" to "Y" as mentioned in Table 4 [22].

The textile workers handling benzidine dyes showed the presence of traces of free benzidine in the urine. Banned amines released in the human organism from azo dyestuffs can cause cancer. An increased incidence of bladder cancer among painters and dye factory workers who never came in direct contact with free MAK amines, but only with the azo dyes manufactured from the said MAK amines. Only after sufficient exposure with MAK dyes, human may suffer from cancer, i.e., when these dyes actually enter the human organism as a result of improper handling or low occupational safety standards for sufficient long time. The MAK Committee recommends that all azo dyes capable of releasing MAK amines on degradation should be avoided. German legislation has adopted this recommendation.

At the beginning of the 1990s, the German Senate Commission for testing for harmful substances recommended that the azo dyes should be treated in the same way as the amines on which

they are based, because the azo dyes can be split under certain physiological conditions to form carcinogenic amines. In a second amendment in 1994 to the Ordinance on Materials and Articles, the use of certain azo dyes is prohibited in the manufacture of materials and articles that are designed for more than temporary contact with the human body. The specific azo dyestuffs include those, which are known to be toxic or are suspected to release harmful aromatic amines.

Two German laws have been amended that apply specifically to textile processing activities. These are the Fourth Federal Emission Protection Ordinance and the ordinance on materials and articles. The German Legislation came in force from 30th June, 1996. The German ordinance on materials and articles has received worldwide attention because of its fundamental importance for the textile supply chain and probably the most widely discussed law in the textile sectors.

In 1994, the German Consumer Goods Ordinance was amended to ban specific azo dyes, triggering widespread discussion about textile ecology stating: "Azo dyestuffs which, on cleavage of one or more azo groups, release any of twenty listed amines should not be used in commercial production or treatment of consumer goods."

Approximately 70% of all dyes (belonging to various dye-classes) used in the textile industries are azo dyes. Due to the toxic nature or amine (banned)-releasing properties, about 25% of the azo dyes are already prohibited to manufacture and to use.

Textiles dyed with azo dyestuffs based on MAK amines do not represent a real health risk to the consumer. The dye first migrates from the textile to the skin, and then absorbed by the body through the skin. When fastness of the dye is high enough, no or little dye comes out from the textile goods. Hence, those MAK dyes can do little harm to the consumer.

Table 4. Aromatic amines derived from the azo dyes banned by Directive 2002/61/EC

Sr. No.	Symbols in figure	CAS number	Chemical name
1	A	92-67-1	4-aminobiphenyl
2	B	92-87-5	benzidine
3	C	95-69-2	4-chloro-o-toluidine
4	D	91-59-8	2-naphtylamine
5	W	97-56-3	o-aminoazotoluene
6	X	99-55-8	5-nitro-o-toluidine
7	E	106-47-8	4-chloroaniline
8	F	615-05-4	4-methoxy-m-phenylenediamine
9	G	101-77-9	4,4'-methylenediamine
10	H	91-94-1	3,3'-dichlorobenzidine
11	I	119-90-4	3,3'-dimethoxybenzidine
12	L	119-93-7	3,3'-dimethylbenzidine
13	M	838-88-0	4,4'-methylenedi-o-toluidine
14	N	120-71-8	p-cresidine
15	O	101-14-4	4,4'-methylene-bis-(2-chloro-aniline)
17	Q	139-65-1	4,4'-thiodianiline
16	P	101-80-4	4,4'-oxydianiline

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18	R	95-53-4	o-toluidine
19	S	95-80-7	4-methyl-m-phenylenediamine
20	T	137-17-7	2,4,5-trimethylaniline
21	U	90-04-0	o-anisidine
22	Y	60-09-3	4-aminoazobenzene

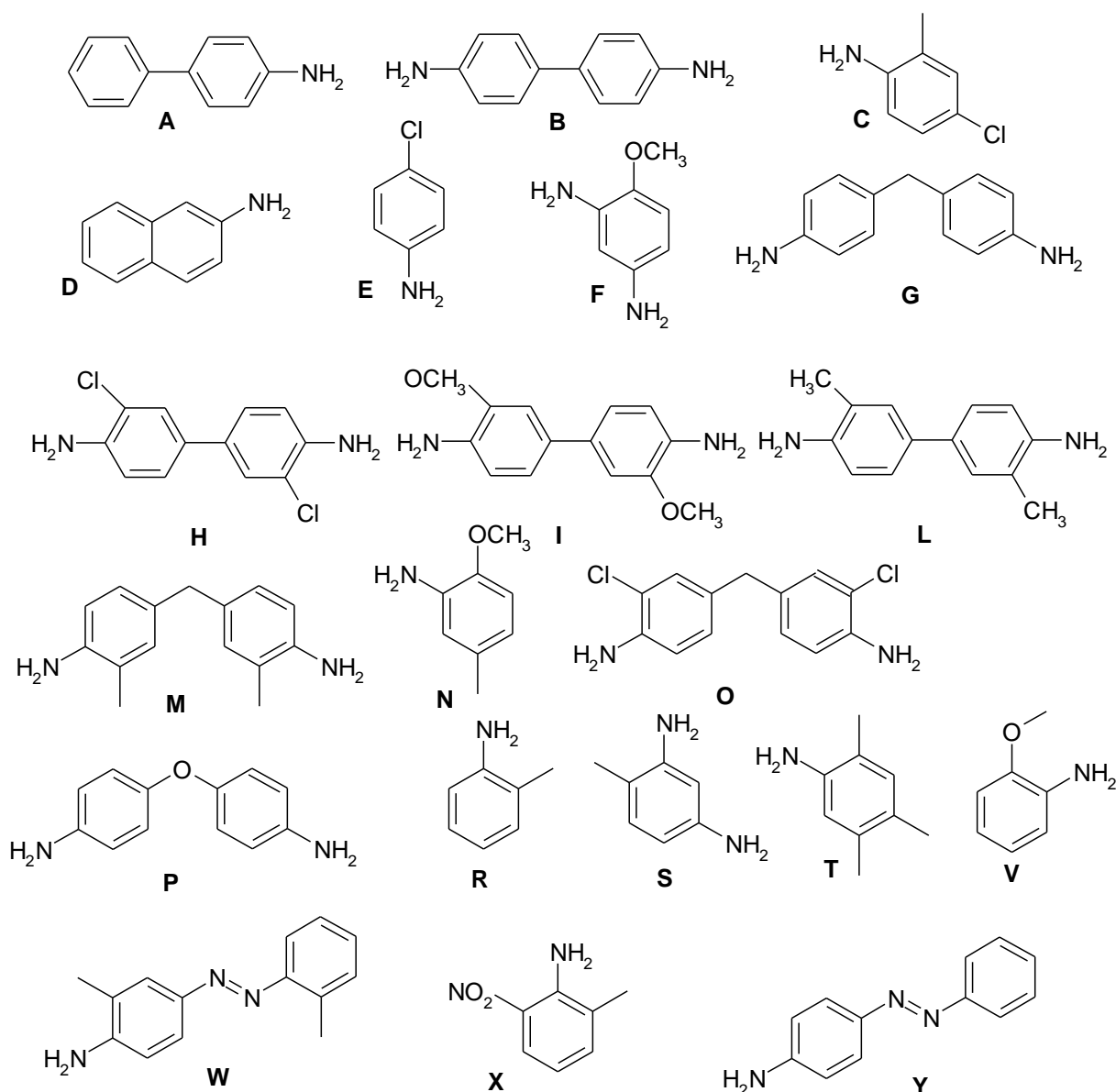


Figure 2. Chemical structure of 22 aromatic amines banned by German Senate

According to DIN 55493, pigments are colorants that are not bio-available because they are not soluble in the application medium. The Fifth Amendment in November 1996, excludes poorly

soluble pigments with a molecular weight of over 700. The decision on whether a pigment is prohibited is based on the official test method.

It must be remembered that not all azo dyes release banned amines. 70% of the total synthetic dyes produced for coloration are azo dyes. Among all azo dyes, only about 4 to 5% dyes release banned amines under certain conditions due to reductive cleavage and are, therefore banned. A proper study of the dyes is to be carried out by the user of the dyes before using in his production process. In general, banned amines may release from different colorant classes namely disperse, direct, acid, basic, reactive dyes and organic pigments.

The banned dyes belonging to various dye-classes are listed below:

Banned Direct dyes (amine releasing, 82 dyes)

- C.I. Direct Yellows 1 (22250*), 24 (22010), 48 (23660).
C.I. Direct Oranges 1 (22370), 6 (23375), 7 (23380), 8 (22130), 10 (23370), 108 (29173).
C.I. Direct Reds 1 (22310), 2 (23500), 7 (24100), 10 (22145), 13 (22155), 17 (22150), 21 (23560), 22 (23565), 24 (29185), 26 (29190), 28 (22120), 37 (22240), 39 (23630), 44 (22500), 46 (23050), 62 (29175), 67 (23505), 72 (29200).
C.I. Direct Violets 1 (22570), 12 (22550), 21 (23520), 22 (22480).
C.I. Direct Blues 1 (24410), 2 (22590), 3 (23705), 6 (22610), 8 (24140), 9 (24155), 10 (24340), 14 (23850), 15 (24400), 22 (24280), 25 (23790), 35 (24145), 53 (23860), 64 (22595), 75 (24411), 76 (24411), 151 (24175), 160 (-), 173 (-), 192 (-), 201 (-), 215 (24115), 295 (23820).
C.I. Direct Greens 1 (30280), 6 (30295), 8 (30315), 8:1 (-), 85 (30387).
C.I. Direct Browns 1 (30045), 1:2 (30110), 2 (22311), 6 (30140), 25 (36030), 27 (31725), 31 (35660), 33 (35520), 51 (31710), 59 (22345), 79 (30056), 95 (30145), 101 (31740), 154 (30120), 222(30368), C.I. Direct Blacks 4 (30245), 29 (22580), 38 (30235), 86 (24115), 91 (30400), 154 (-).
Direct dyes (without C.I. No.) - (23820), - (30230).

Banned Acid dyes (amine releasing, 24 dyes)

- C.I. Acid Orange 45 (22195)
C.I. Acid Reds 4 (14710), 5 (14905), 24 (16140), 73 (27290), 85 (22245), 114 (23635), 115 (27200), 116 (26660), 128 (24125), 148 (26665), 150 (27190), 158 (20530), 167 (-), 264 (18133), 265 (18129), 420 (-).
C.I. Acid Violet 12 (18075), Brown 415 (-).
C.I. Acid Blacks 29 (-), 94 (30336), 131 (-), 132 (-), 209 (-).

Banned Acid dyes (poisonous, 2 dyes)

- C.I. Acid Oranges 156 (26501), 165 (28682)

Acid dyes (carcinogenic, 4 dyes):

- C.I. Acid Red 26 (16150), Violets 17 (42650), 49 (42640), (without C.I.No.) - (16155).

Banned Basic dyes (carcinogenic, 8 dyes)

- C.I. Basic Yellows 2 (41000), 21 (48060).
C.I. Basic Reds 9 (-), 12 (48070).
C.I. Basic Violet 16 (48013).
C.I. Basic Blues 3 (51004), 7 (42595), 81 (-).

Banned Basic dyes (amine releasing, 3 dyes)

- C.I. Basic Reds 42 (-), 111 (-).
C.I. Basic Brown 4 (21010).

Banned Azoic dyes (poisonous, 3 Components)

- C.I. Azoic Diazo Components 20 (37175, Blue BB), 24 (37155, Blue RR), 41 (37165, Violet B).

Banned Azoic colors (amine releasing Components, 8 Nos.):

- C.I. Azoic Blue 37.
C.I. Azoic Diazo Components 11 (37085, Red TR), 12 (37105, Scarlet G), 17 (37270, Orange R), 29 (37255, Red GTR), 48 (37235, Blue B), 112 (37225, Corinth B), 113 (37230, Dark Blue R).

Banned Disperse dyes (carcinogenic, 1 dye)

- C.I. Disperse Blue 1 (64500).

Banned Disperse dyes (allergenic, 26 dyes):

C.I. Disperse Yellows 1 (10345), 3 (11855), 7 (26090), 9 (10375), 23 (26070), 39 (-), 49 (-), 54 (47020), 56 (-), 64 (47023).
C.I. Disperse Oranges 1 (11080), 3 (11005), 76 (-), 149 (-).
C.I. Disperse Reds 1 (11110), 11 (62015), 15 (60710), 17 (11210), 151(-).
C.I. Disperse Blues 3 (61505), 7 (62500), 26 (63305), 35 (-), 102 (-), 106 (-), 124 (-).

Other Banned Dyes

C.I. Developer 14 (76035, Developer B)
C.I. Ingrain Blue 2/2(74160, Phthalogen Brill. Blue IF3G, Brill. Blue 3G)

* the values represent the Colour Index International

Testing methods for banned amines

The monitoring of the presence of banned amines in finished products requires highly sophisticated laboratory testing. To ensure accurate results, samples must be tested in an ISO 17025 accredited laboratory covering the analysis of banned amines under its accreditation scope. The points to remember before testing a sample for banned amines:

- All components of an article must be tested.
- All colours present in the article must be tested.
- An undyed fibre or fabric need not be tested, e.g. full white fabric treated with an optical brightening agent need not be submitted for banned amines test.

The different standard test methods are mentioned in Table 5.

Table 5. Testing methods for the presence of banned amines in dyed fabrics

Substrate Type	Test Method
Textile	ISO 14362-1:2017 (https://www.iso.org/standard/68330.html) GB/T 17592-2011: Translated English of Chinese Standard. (GBT 17592-2011) by Wayne Zheng. www.ChineseStandard.net , 10-Mar-2015
Textile (for 4-aminoazobenzene)	ISO 14362-3:2017 (https://www.iso.org/standard/68331.html) GB/T 23344-2009: Translated English of Chinese Standard. by Wayne Zheng. www.ChineseStandard.net , 10-Mar-2015
Natural Leather (All amines except 4-aminoazobenzene)	ISO 17234-1: 2015 https://www.iso.org/standard/61791.html GB/T 19942 - 2005 (China). http://www.gbstandards.org/
Leather (for 4-aminoazobenzene)	ISO 17234-2: 2011 https://www.iso.org/standard/53716.html

The most important steps of the textile test method are:

- 1) Take 1.0 g textile sample carefully. For a rich pattern sample, a sample must be taken for each shade and each is analysed separately.
- 2) The sample is stored for 30 minutes at 70°C.
- 3) Treat with 3.0 ml of sodium dithionite solution (200g/L)

in citrate buffer (pH 6) in a closed vessel at 70°C for 30 min.

- 4) After cooling, the extract is passed over a silica column and eluted with 80ml of t-butylmethylether on Extrelut 20 (Kieselguhr, Merck).
- 5) The ether solution is carefully concentrated in a rotary evaporator to around 1 ml

- 6) Dissolve solvent-free residue in 2 ml methanol.
- 7) The extract is analysed for the 20 listed amines using one of the following methods:
 - Thin layer chromatography (TLC),
 - Gas capillary chromatography (GC),
 - High-pressure liquid chromatography (HPLC) or
 - Capillary electrophoresis (CE).
- 8) Prepare qualitative results by at least two independent chromatographic separation techniques.

Quantification of amines, if present, is performed using HPLC/diode array detector (DAD) or chromatograph with mass spectrometer (GC-MS) (with internal standard).

Compared to earlier methods, the validated analytical method differs as follows [23]:

- Only azo colorants and certain susceptible pigments are cleaved.

The following are not cleaved:

- Polyurethanes
- Amine or amide compounds in non-azo dyestuffs
- azo pigments.

False positive findings, therefore, can be practically eliminated.

The existing limit value is not a legal one. It only exists for analytical reasons and called recognition threshold value. It is defined as 30 ppm of arylamine per kilogram of homogeneously coloured sample.

Low Impact Dyes

Most dyes require water and energy to work. Most of them also work in the presence of assisting chemicals such as salt, soda ash, acids, levelling agents etc. The specific chemicals are dependent on the type of dye and the type of fabric being dyed [24].

Low impact dyes are identified by the following features:

- a) Do not contain toxic chemicals like heavy metals such as chrome, copper and zinc
- b) Do not require any toxic chemical mordants to fix them to the fibre.

- c) Require less rinsing and

- d) Have a high absorption rate in the fabric (~70%).

Such dyes, therefore, have a lower impact on the environment. From effluent point of view, basic dyes on acrylic, metal-complex dyes on wool and disperse dyes on polyester are comparatively less harmful to the environment as they are highly exhaustive (Table 1).

The problem of coloured effluent is mainly encountered while dyeing cellulosic fibres, which account for almost 50% of the total fibre consumed by the textile industry. The table shows that as much as 50% of reactive dyes used may be lost to the effluent.

The dyes are not truly water pollutants since the biological effects are negligible. However, some azo dyes e.g. benzidine-based direct dyes easily reduce to colourless more toxic primary organic amines.

The environmental problems posed by the dyes are rather moderate in their impact, but great complexities arise due to the variation in chemical structures and properties of a few thousand dyes in use. The problem is enhanced by the fact that many auxiliaries used during dyeing, such as cationic fatty acid polymers, quaternary mono-, di- and tri-alkyl ammonium salts, are not biodegradable and are difficult to remove.

Low-salt reactive dyes

During dyeing with reactive dyes is the use of large quantities of inorganic salts to suppress the negative charge at the fiber surface. Multifunctional reactive dyes are developed to achieve high substantivity and reactivity. For low salt application, two ranges of reactive dyes namely Cibacron LS (Ciba) and Remazol EF (EF = environmentally friendly, Dystar) are developed. An alternative approach to enhance substantivity is the modification of cellulose by amination.

Effluent control authorities will eventually demand low-salt dyeing of cellulosic materials. High electrolyte concentration in discharge water is undesirable, as increased salinity in river upsets the delicate balance of aquatic flora and fauna. This is particularly objectionable in situations where

discharge of dyehouse effluent can give rise to build-up of salinity, for example with discharges to fresh water lakes. Sodium chloride is an electrolyte commonly used, but the alternative sodium sulphate is even more harmful, as it attacks concrete pipes and also has been associated with increased acidity of waterways. Reactive dyes, in particular, use very high concentrations of salt, so are under the most scrutiny. The sodium and potassium salts of polycarboxylic acids have shown some promise as alternatives to sodium chloride, but their use is likely to prove too costly.

Efforts have been made to produce reactive dyes demanding less salt during application. The most notable of these is the Cibacron LS range (LS = low salt), which utilizes several different reactive groups in a number of arrangements. The bulk of the dyes are bi-functional, usually bismonofluorotriazines.

Other groups or their combinations are also used, including MFT and MCT in combination with VS as well as trifunctional (MCT/bis VS) dye. The ability of these to function effectively in the presence of reduced salt reflects their high affinity for cellulose, which is partly due to the large molecular size of these dyes. Flat dye molecules with hydrogen bonding sites increase affinity for the substrate. Hoechst introduced low-salt reactive dyes, Remazol EF range. These are probably selected dyes from conventional VS range.

Improving the substantivity of cellulose towards anionic dyes will greatly reduce the need for electrolyte in the dyebath and improve dyebath exhaustion, serving less residual dye in dyehouse effluent. Several chemical modifications of cellulose are reported. Introduction of amino groups into cellulose structure produces a fibre that may be considered analogous to wool. Unlike cellulose, wool has a natural substantivity towards anionic dyes, especially under acidic conditions [25].

The following points were noted during modification of reactive dyes.

- No of sulphonic groups in chromophore are optimized to give required solubility but high substantivity.

- Bridging groups between chromophore and reactive group allows molecular flexibility i.e. easy diffusion.
- Control of reactivity: Introduction of two fluorine groups with a very high reactivity. (Chlorine is replaced by Fluorine).
Example of this type dye is Cibacron LS dye.

Eco-friendly sulphur dyeing

Disadvantages of Sodium sulphide (Na_2S) used in sulphur dyeing are:

- Cheap but bad smell.
- Toxic.
- pollutes water in sea/river and destroys marine life
- High COD.

International standard for discharge limit of sodium sulphide is 2 ppm.

Solutions to sulphide problem are:

- Recovery of sulphides from effluent. But it requires costly equipment.
- Replacement of sodium sulphide

Sodium sulphide may be replaced by glucose as reducing agent. However, the limitations of glucose are:

- Highly unstable compared to sodium sulphide.
- Works only at high pH of 11-12.
- Quantity of glucose required is about 2 times for black and 2.5 times for Navy on the weight of dye.
- Less yield of dye.
- Narrow range of reduction conditions.
- Costly

The dyeing method with glucose is done as follows:

- Sulphur dye is pasted with Turkey red oil (or suitable dispersant), soda ash equal to the quantity of dye is added. The pH is maintained at 11-12, and then glucose 2.5 times of dye (2% at and above 8%) is added.
- The reduction is done at 70°C for 20 minutes, followed by dyeing at boil for 1 hour, followed by oxidation and soaping.

Ibrahim and others [26] made to search for an eco-friendly reductants and oxidants for complete

substitution of the hazardous ones along with finding out proper conditions for attaining better knitted sulphur dyeing. The study indicates that:

- 1) The extent of coloration is governed by both the type of reductant as well as dye/reductant ratio, i.e. Liquid glucose (ratio 1/1) > glucose (ratio, 1/1) > molasses (ratio 1/4), as well as the knitted fabric structure i.e. Pique > rib > milton;
- 2) The depth of shade can be improved by raising the dyeing temperature up to 80°C for 45 min., at a material-to-liquor ratio 1/10, in presence of 30g/l common salt;
- 3) The extent of sulphur dyeing is determined by the nature of oxidant, i.e. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ > H_2O_2 > none;
- 4) After treatment with cationic softener results in higher softness along with better washing and rubbing fastness; and
- 5) The dyeing as well as fastness properties of the obtained sulphur dyeings depend on the sulphur dye category.

Hydrol is obtained during manufacture of glucose as waste product. It is a homogeneous, dark brown liquid produced during crystallization of glucose hydrate from solutions starch. It contains 65-66% dry material, of which 68-72 % is reducing substances and 5-6 % is salt (including 2% sodium chloride). About 70% of the reducing substances, mainly glucose ferments.

Hydrol is used to produce nutrient mediums, ethanol, and composite feeds, as well as in tanning leather. It has same potential as sodium sulphide. It contains 50% reducing sugars. It is cheaper than glucose. 65 % of Hydrol and 25 parts of caustic reduce 100 parts of sulphur dye at 80°C at pH 10 [27].

NATURAL DYES

Dyeing is an ancient art which predates written records. Its practice could be traced back during the Bronze Age in Europe. Primitive dyeing techniques included sticking plants to fabric or rubbing crushed pigments onto cloth. The dyeing method with natural dyes improved with time and techniques. The natural dyes from crushed fruits, and other plant materials were boiled into the fabric when some fastness to light and water tests were achieved [28].

Natural dyeing processes of India were documented in a book by Mohanty et al. [29]. Chandramouli [30] published a book on natural dyeing processes of India. Dyes traditionally used in the Scottish Highlands were reviewed by Grierson et al. [31]. Buchanan [32] presented a detailed account of dye plants used for natural dyeing of textiles such as alkanet, annatto, chamomile, coreopsis, madder, safflower, indigo, and so on, and methods for dyeing of textiles with these colorants.

Popular ancient natural dyes include madder (roots of the *Rubiatinctorium*), blue indigo (leaves of *Indigoferatinctoria*), and saffron yellow (plant, *Crocus sativus* L). The most famous and highly prized colour through the ages was Tyrian purple, noted in the Bible, a dye obtained from the spiny dye-murex shellfish. One of the most unlikely "marriages" ever arranged is the one between the Chinese silk moth, *Bombyx mori*, and Mediterranean sea snails of the murex family. This snail produces a pigment (colouring matter) that, when brought together with silk, led to the world's longest-lasting fashion statement. Murex first gained fame as the basic ingredient in "Tyrian purple," a dye named for the city of Tyre, located in what is today Lebanon. More than 3,000 years ago, Tyre was the centre from which the seafaring Phoenicians controlled a trade in luxurious murex-dyed silks. Centuries later, the dye was known as "royal purple" or "imperial purple" because Roman and Byzantine emperors decreed that only members of the imperial family could wear the colour.

Until the seventh century, Tyrian purple was prepared by the Phoenician, when Arab conquerors destroyed their dyeing installations. A bright red called cochineal was obtained from an insect native to Mexico. All these produced high quality dark colours. Until the mid-19th century all dyestuff were made from natural materials mainly vegetable and animal matter [33].

Natural dyes were solely used for coloration of textile products till the midst of nineteenth century. The first synthetic dye mauvine was invented by Perkin in 1856. Since then demand for synthetic dyes became ever-increasing as they were affordable, easily producible and were available in different colours possessing good colour-fastness

and most of them are easy to produce. As a result, with a distinct lowering in the cost of synthetic dyestuff, the natural dyes were virtually neglected at the beginning of twentieth century. The textile industry is accountable for using and producing majority of dyes and pigments, most of which are made synthetically.

Zollinger [2] reported the use of over 10,000 different dyes and pigments industrially and over 7×10^5 tons of synthetic dyes annually worldwide. Global trends show that the dyes and organic pigments are expected to grow 6.0% per year to \$19.5 billion in 2019. There is increased demand for organic colorants in textiles and plastics, while increasing global construction activity results in larger demand in paints and coatings. Future dyes and pigments should meet increasingly stringent performance standards and from end-user preferences for more environmentally friendly products.

Majority of demand growth occur in developing countries. Increasing number of the middle-class families, particularly in the Asia/Pacific and Africa/Mideast regions, will accelerate in global consumer spending benefitting important dye and organic pigment markets for textiles and plastic products. The textile market accounted for over half of global dye and organic pigment demand in 2014. It will be the primary contributor to increased demand going forward while growing plastic output will expand demand for organic pigments. Dye and organic pigment consumption will remain concentrated in the Asia/Pacific region, the site for the majority of global textile and consumer plastic product manufacturing. Though China is the most dominant consumer of dyes and organic pigments globally, rapid growth will also be experienced in Asian markets in countries like Bangladesh, India, and Vietnam as textile and plastic producers continue to move production to these countries with the low labour costs. Consumers more and more prefer for new, unusual fast textile colours and yet are environmentally friendly will boost growth in value demand as textile producers increasingly turn to these newer, higher value products [34].

A new approach for upgrading the dyeing properties of cotton knits with natural dyes as well as

to enhance both the UV-protection and antimicrobial functions of the obtained dyes was investigated by Ibrahim and others [35]. The mordant was deposited in situ as a metal oxide onto and/or within the fabric structure followed by dyeing. This resulted in a dramatic improvement in the colour strength as well as the fastness properties.

It is of great concern that the production and application of synthetic dyes release vast amount of waste and unfixed colorant causing serious health hazard and disturbing the eco-balance of nature. Nowadays, people become more and more aware about eco-friendly natural dyes owing to their better biodegradability and higher compatibility with the environment. They are non-toxic, non-allergic to skin, non-carcinogenic, abundant and renewable.

Unfortunately, the knowledge required for sourcing and extracting such dyes and mordents are no longer available and extensive research work is required to identify suitable plants minerals, etc. In Zambia for example, there is a wealth of plants available for producing natural dyes but due to lack of knowledge of the process involved in harvesting and processing the plants are utilized to a low extent. In some countries such as India, Nigeria and Liberia, where this research has been carried out, or where there exists a tradition of natural dyeing, natural dyes and mordants are used to a great extend [36].

The discussion about possible replacement of synthetic dyes by natural dyes is often not based on scientific facts, but clouded with other considerations about toxicity of synthetic dyes, particularly during production, and the recent craze for using natural products. A systematic study [37] showed that the large-scale use of natural dyes is not feasible and the present processes of application of natural dyes need optimization from the point of view of economy and ecology. Considerable variations occur from batch to batch and the recipe formulation and tone adjustments are more difficult than synthetic dyes. Frequent redyeing adds to the cost.

Natural dyes do not always mean safe. In fact, the toxicological properties of synthetic dyes are very well tested scientifically and safety data sheets are available for each dye. Similar study in case of

natural dyes is not available. Many of the natural dyes are quite safe but few are toxic. Logwood, for example, is a natural dye, capable of producing a range of colours such as violets, blue-greys, and the best natural black, depending on the mordant used. However, the active ingredients, hematein and hematoxylin, are toxic when inhaled, absorbed through the skin, or ingested. As much care should be taken with this natural dye as with any of the harmful synthetic dyes [4].

Mordants

Few natural dyes are fast with fibres. But most of the natural dyes require mordants for their application. The mordants are substances which are used to fix dye to the fibres. They improve the dye uptake into the fabric and also wash and light fastness of dyes in dyed fabric. The term "mordant" is derived from the Latin word "mordere", meaning "to bite". Some natural dyes, indigo for example, will fix without the aid of a mordant. These dyes are known as substantive dyes. Other natural dyes such as madder and weld, have limited fastness and the colour will fade with washing and exposure to light. They require the use of mordant before, during or after dyeing in order to achieve require colour strength and fastness.

Traditionally, mordants were found in nature wood ash or stale urine may have been used as an alkali mordant, and acids, could be found in acidic fruit or rhubarb leaves (which contain oxalic acid) for example. Conventionally, most natural dyes require chemical mordant like alum, copper sulphate, iron or chrome for their fixation. In the absence of such auxiliaries, colour build-up and/or fastness will be poor. However, nowadays the use of these chemicals is objectionable due to their toxic nature. Mordants are prepared in solution, often with the addition of an assistant which improves the fixing of the mordant to the yarn or fibre. The most common used mordant is alum which is usually used with cream of tartar as dyeing assistant. Other mordants are:

- Iron (ferrous sulphate)
- Tin (stannous chloride)
- Chrome (bichomate of potash)

- Copper sulphate
- Tannic acid
- Oxalic acid

However, some natural dyes can produce multiple shades with different mordants such as:

- Iron is used as a "saddener" and is used to darkens colours.
- Copper sulphate also darkens but can give shades which are otherwise very difficult to obtain.
- Tin brightens colours
- Tannic acid, used traditionally with other mordants, will add brilliancy.
- Chrome is good for obtaining yellows
- Oxalic acid is used for extracting blues from barries
- Cream of tartar is used to give lustre to wool [33, 36].

Alum and ferrous sulphate are relatively safe mordants compared to copper and chromium. However, still they have to be used carefully. A dose of 30 grams alum is fatal for an adult; the fatal dose for a child is, of course, far less, depending on body weight, may be as little as 3 grams. Iron is toxic in overdose according to the United States FDA, but it will not harm the environment when disposed off. Tin and copper mordants have to be used with care. Chrome mordant is toxic and has both human and environment toxicity. It is a known human carcinogen. Chrome can produce very bright yellows, but it is not worth the risk of cancer, other illnesses, and even death. Many eco labels have fixed the optimum limits for these mordants particularly copper (50 ppm), tin and chromium (2 ppm) to be released in the environment [4].

Protective clothings are always used when working with mordants with utmost care of inhaling the fumes. The mordant may be added before, during or after dyeing (called pre, simultaneous and post mordanting respectively), although in most cases mordanting is done prior to dyeing. It is best to follow the instruction given in the recipe being used or experiment on a sample before carrying out

the final dyeing. These chemical mordants are usually obtained from specialist suppliers or from chemist. Where this is prohibitive, due to location or cost, natural mordant can be used. There are a number of plants and minerals which will yield a suitable mordant but their availability will be dependent upon your surrounding [36] some common substitutes for a selection of mordant are listed below.

- Some plants such as mosses and tea contain small amount of aluminium. This can be used as a substitute to alum. It is difficult to know however, how much aluminium will be present and experimentation may be necessary.
- Iron water can be used as a substitute to ferrous sulphate. This can be made simply by adding some rusty nails and a cupful of vinegar to a bucket full of water and allowing the mixture to sit for a couple of weeks.
- Oak galls or sumach leaves can be used as a substitute to tannic acid.

Mordants are applied by the following three methods:

- Premordanting; samples were pretreated with the solution of different chemical and natural mordants. This method is suitable for dyes which have more or less substantivity towards the fiber.
- Post mordanting: dyed silk fabric were taken out of the dye bath, squeezed and treated with solution of different chemical and natural mordants. This method is suitable for dyes which have poor substantivity towards the fiber.
- Simultaneous mordanting and dyeing of silk sample: Silk is dyed with dye extract as well as different chemical and natural mordants simultaneously. This method is suitable for dyes which are stable and do not precipitate in the dyebath in the presence of dye.

Sources of Natural dyes

Natural dyes are extracted from various sources namely:

- 1) Specialized plants and animal sources

Many plants and some animals' are potentially rich in natural dye content. Various parts of plants like roots, stems, bark, leaves, fruits and seed contains colouring matter. The depth and shade will vary according to time of year.

2) By-products (lac dye)

The lac industry produces lac dye as a by-product which is extracted from effluent. (Lac is a by-product of insect coccus lacca)

3) Attempt has also been made to synthesize natural dye having similar structure.

4) Genetic modification of certain fungi produces anthraquinone dye.

Fustic, safflower, madder, and various other types of natural sources have been known to be used to dye various natural fibres like wool, cotton, silk, etc. since man first started colouring his clothes. By mid-19th century there was a vast range of colours that could be obtained.

Two hundred years or more ago, production of crops such as indigo (and woad), weld and madder was based on labour-intensive agronomy and time-consuming downstream manufacturing processes for preparing the dye were necessary. The trade of natural dyes began to decline in the second half of the 19th century and now 100 years later, many of the dyes that were once commonplace are little known and difficult to obtain. Many of the plants have not been cultivated for their dyes on any commercial scale for the last 100 years. Indeed, the original cultivation variety in Holland had been lost; a new variety of similar characteristics has been recently developed.

Cochineal cultivation, which was discontinued in Central America, has survived in Peru and Canary Islands. Despite this success, the reestablishment of some of the old sources of these dyes is not possible and many old dyes are rarely seen. Newer sources are gradually becoming available. Biotechnological routes, like use of microorganisms and cell cultures, are being utilized for manufacture of natural dyes like indigo, alizarin, etc. Although such dyes as madder, cochineal, fustic, Brazil wood, sanders wood, cutch, indigo, logwood and weld are

obtainable; they are relatively expensive and retailed in small amounts.

The current worldwide awareness about environment has again revived interests in natural dyes. Synthetic colorants have been cited as causing skin complaints, illnesses and cancer. Some natural dyes have low level of toxicity as well. Certain natural dyes may have detectable mutagenic effects.

Some traditional mordants used in dyeing of natural dyes, such as certain salts of tin and chromium, may be objected on environmental grounds. Aluminium and iron are relatively innocuous; they are naturally abundant and can produce excellent results in dyeing.

What attracts people to textiles coloured with natural dyes may be one or a combination of factors, including a preference for naturalness, environmental friendliness, harmonising natural shades or just for novelty.

In recent years, considerable research work is being carried out in various institutes, on the standardization of the process for the extraction and application of natural dyes. Efforts are also being made for simplifying and modifying the existing dyeing techniques to improve the fastness properties, particularly washing.

Present requirement of natural dyes is about 10,000 tons, which is equivalent to 1% of the world's synthetic dye consumption.

Natural dyes as such are sustainable as they are renewable and biodegradable but they cannot fulfil the huge demand from the textile sector in view of the preferential use of land for food and feed purposes. For production of natural dyes from natural resources may result in deforestation keeping endangered species at stake. For these reasons, the Global Organic Textiles Standard (GOTS) permits the use of safe synthetic dyes and prohibits the use of natural dyes from endangered species. In general, the shortcomings of natural dyes are much less significant than the tremendous environmental advantage they offer.

Just because the dye itself is natural, it doesn't mean that the crop is sustainable. Pesticides may

have been used on the crop and it may be genetically modified or irrigated unsustainably. Some colours come from forest products, depleting valuable natural resources. Also, other substances used in the colouring process may well be environmentally damaging. Mordant is not required for cutch, while madder, cochineal, weld and many other natural dyes require mordants. Indigo is a vat dye, requiring dissolving in alkaline solution before use. Also, the amount of water used, considered to be the biggest environmental impact of dyeing, hasn't been considered. The effluent from the natural dyeing process may be just as harmful as that in case of synthetic dyes. And despite being natural, these dyes aren't necessarily safe, as in the case of poison ivy and toxic mushrooms. Proper training and supply of health and safety equipment are necessary.

The use of natural dyes will almost certainly make the garment more expensive, firstly, because large quantities of land and raw material are required to obtain the same depth of colour that a synthetic one would obtain. Both the cultivation and application of natural dyes are time-consuming, thereby increasing cost of dyeing. Natural dyes take time at least twice than that synthetic dyes to get a result, and using natural dyes on vegetable fabric will be costlier still, as it is difficult to get good colour build-up on them than animal fibres are, and slower, longer treatments often give better results.

Classification of Natural dyes

They are classified by various ways namely [38]:

- (a) Based on sources of origin [39]
- (b) Based on solubility
- (c) Based on substantivity
- (d) Based on colours formed with various mordants
- (e) Based on chemical constitution
- (f) Classification according to the method of application

Classification based on sources of origin

Depending on the source of origin, natural dyes are of three groups:

- a) Vegetable/Plant Origin
- b) Insect/Animal Origin
- c) Mineral Origin

Vegetable/Plant Origin

Most of the natural dyes belong to this category. The colorants derived from various plant parts such as flowers, fruits, seeds, leaves, barks, trunks, roots, etc. fall in this category. In India there are nearly four hundred fifty dye yielding plants.

Insect/animal Origin

Cochineal (carminic acid), Kermes (kermesic acid), Lac (*Laccifer lacca/Kerria lacca*, laccaic acid) and Tyrian purple (mollusks) dyes are obtained from dried insects. They are well known for dyeing purposes from ancient times.

Natural colorants obtained from plants and animals are discussed in detail later in chemical structure basis classification with examples.

Mineral Origin

Various pigments from inorganic metal salts and metal oxides belong to this category of natural dyes. The most important mineral pigments of various colours are as follows:

Red Pigments

Cinnabar, Red Ochre, Red lead and Realgar are some of the examples of red pigments originate from minerals.

Yellow Pigments

Yellow Ochre (Ram Raj), Raw Sienna, Orpiment and Litharge (Massicot) are source for yellow pigments.

Green Pigments

Terre-Verte (Green Earth), Malachite and Verdigris are examples of green pigments.

Blue Pigments

Ultramarine Blue and Azurite are blue pigments.

White Pigments

Chalk (White Lime), White lead and Zinc White.

Black Pigments

Charcoal Black, Lamp Black, Ivory Black, Bone Black, Graphite, Black Chalk and Terre-noire (Black).

Classification based on solubility

Based on solubility, natural dyes are classed into two groups namely:

- a) Soluble and
- b) Insoluble natural dyes.

Soluble: They can be dissolved in water and applied.

Insoluble: They have no solubilizing group hence temporary solubilizing group is introduced e.g. Indigo.

Classification based on substantivity

Based on substantivity, natural dyes can be classified into two groups:

- a) Substantive and
- b) Adjective natural dyes.

Substantive dyes can dye the fibrous materials directly without mordant. e.g. Turmeric.

Adjective dyes can dye the fibrous materials which are mordanted. e.g. logwood. Mordants create affinity of the dyes toward fibrous materials

The substantive dyes require no pre-treatment to the fabric (e.g. indigo, orchil, turmeric, etc.). The adjective dyes can only dye mordanted material or with the addition of a mordant to the dyebath (e.g. logwood, madder, cochineal, fustic, alizarin, etc.)

Classification based on colours formed

Based on colors formed with various mordants, natural dyes can be classed into two groups namely:

- a) Monogenetic and
- b) Polygenetic natural dyes.

Monogenetic: Produce only one colour irrespective of mordant present in the fibre.

Polygenetic: Produce different colours with different mordant (e.g. logwood, alizarin, fustic and cochineal).

Classification based on the method of application

Substantive dyes can further be classified as direct (for cotton, e.g. turmeric, safflower; for wool and silk e.g. safflower), acid (for silk and wool, e.g. saffron, lac), basic (for silk and wool, e.g. berberine).

Non-substantive dyes can be bound to a material for which it otherwise has little or no affinity by the addition of a mordant, a chemical that increases the interaction between dye and fibre. This classical definition of mordant dyes has been extended to cover all those dyes which can form complex with the metal mordant. Most of these dyes yield different shades or colours with different mordants.

Vat dyes

Vat dyes are insoluble in water, however they can undergo reduction into soluble leuco form which has an affinity for fibre or textile to be dyed. Re-oxidation of the leuco vat dyes converts them again into 'insoluble form' with retention of original colour. Only three natural dyes belong to vat dyes: indigo, wood and Tyrian purple.

Direct dyes

Direct dyes are water-soluble organic molecules which can be applied as such to cellulosic fibres such as cotton, since they have affinity and taken up directly. Direct dyes are easily applied and yield bright colours. However, due to the nature of chemical interaction, their wash fastness is poor, although this can be improved by special after-treatment. Turmeric, annatto, harda, pomegranate and safflower are examples of natural direct dyes.

Acid dyes

Acid dyes are also another type of direct dyes for polyamide fibres like wool, silk and nylon. These dyes are applied in acidic medium and they have either sulphonic acid or carboxylic acid groups in the dye molecules. At least one natural dye, saffron has been classified as acid dye. This dye has two carboxylic acid groups.

Basic dyes

These are also known as cationic dyes. These dyes on ionization give coloured cations which form

an electrovalent bond with the carboxyl group of wool, silk and acrylic fibers. Basic dyes are applied from neutral to mild acidic condition. Berberine has been classified as basic dye. Structurally, this dye carries a non-localized positive charge which resonates in the structure of the dye, resulting in poor light fastness.

Disperse dyes

These are water insoluble dyes which dye polyester and acetate fibres. The principle of disperse dyeing is recent one as compared to the age of natural dyeing. However, in view of their structural resemblance and solubility characteristics it is felt that some of the natural dyes such as lawsone, juglone, lapachol and shikonin can be classified as disperse dyes.

Chemical composition

Natural dyes can be classified into various classes on the basis of their chemical constitution [39-42]. A few are discussed below and shown in Figure 3:

- 1) Indigoids (Figure 3 a)
- 2) Berberine (Figure 3 b)
- 3) Carotenoids (Figure 3 c)
- 4) Quinonoids (Figure 3 d)
- 5) Flavonoids (Figure 3 e)
- 6) Dihydropyran-based Dyes (Figure 3 f)
- 7) Betalains (Figure 3 g)
- 8) Tannins (Figure 3 h)

Indigoids

Indigo and Tyrian purple are most important natural dyes and are most primitive natural dyes. Natural indigo is a dye having distinctive blue colour with long history and is regarded as one of the most important and valuable of all colouring matters [42-43]. Indigo is extracted from *Indigofera* spp. (*Indigofera tinctoria*), *Polygonum tinctorium* (dyer's knotweed), *Perisicaria tinctoria*, and *Isatis tinctoria* (woad). But nowadays large percentage of indigo (Several thousand tons per year) is produced synthetically. The dye Tyrian purple (C.I. 75800)

also known as Tyrian red, royal purple and imperial purple is a bromine-containing reddish-purple natural dye, derived from the hypobranchial glands of several marine predatory sea snails in the family *Muricidae*. This dye has excellent light fastness properties [44].

Berberine

It (natural yellow 18; C.I. 75160) is an isoquinoline alkaloid with a bright yellow color, is the only natural dye belonging to this class [45]. Some

important berberine yielding dye plants are *Berberis aristata*, *Berberis vulgaris*, *Phellodendron amurense* [46], and *Rhizoma coptidis* [47].

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

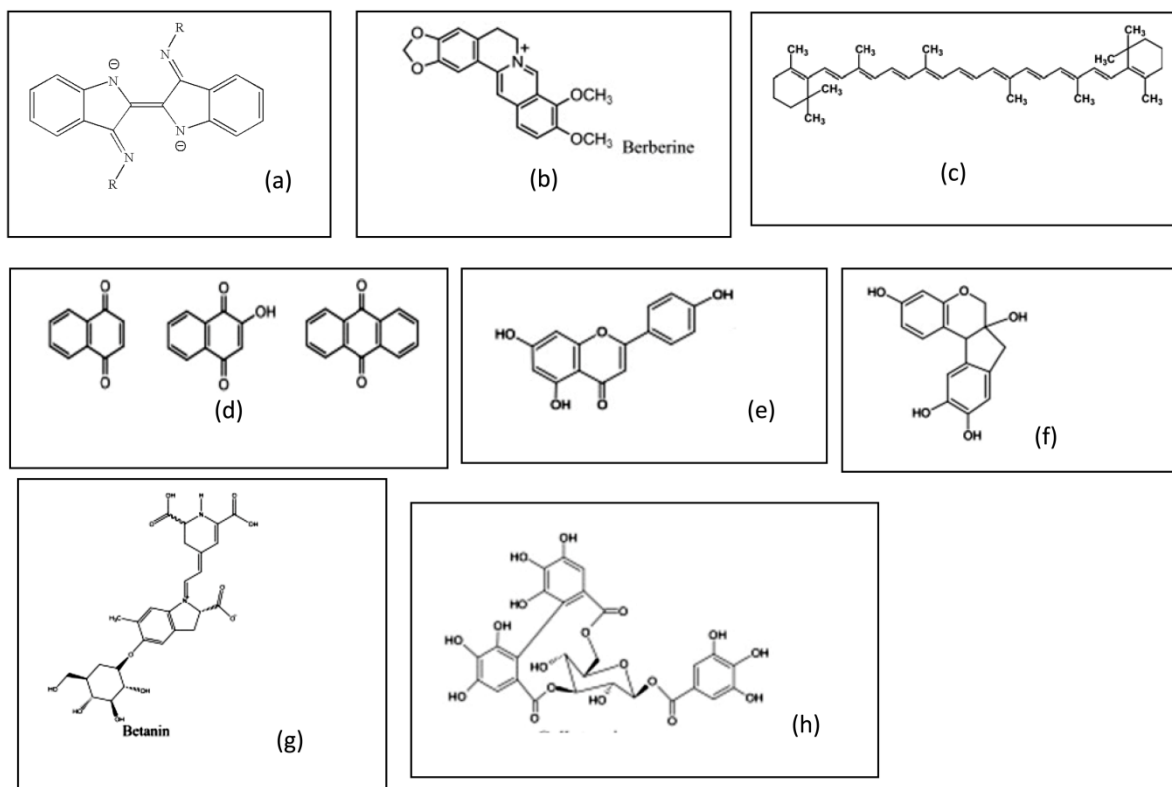


Figure 3. Chemical structures of various chemical classes of natural dyes: a) Indigoids, b) Berberine, c) carotenoids, d) flavonoids, f) dihydropyran based, g) betalain and h) Tannins

Carotenoids

Carotenoids also called tetraterpenoids are brightly colour natural organic pigments found in the chloroplast and chromoplast nearly in all families of plants and some other photosynthetic organisms. Only plants, fungi and prokaryotes can synthesize carotenoids [48]. The colour of the carotenoids is due to the presence of long conjugated double bonds. They absorb light in the 400–500 nm region of the spectrum and this give rise to yellow, orange

and red colour. *Bixa orellana*, *Crocus sativus*, *Curcuma longa*, *Nyctanthes arbor-tristis*, and *Cedrela toona*, are some of carotenoids source plants.

Marigold (*Tagetes* spp.) is a bright yellow flower-yielding plant. It is commonly used for making garlands and floral decorations. It is available in different colors including yellow, golden yellow, orange, and the like. Quercetagetol, two of its glycosides and lutein are responsible for the colour

marigold. It dyes wool and silk in deep yellow colours with good fastness properties. Cotton can be dyed with this dye in combination with mordants to get fast colors. Cotton fabrics are first pretreated with tannic acid/tannin-containing mordants and then followed by metallic mordants before dyeing.

Quinonoids

Quinonoids [41] are widely distributed and occurs in large numbers in nature ranging from yellow to red. Chemical structures of naturally occurring quinones are more diverse than any other group of plant pigments. On the basis of chemical structure these dyes are further classified as benzoquinones, α -naphthoquinones and anthraquinones. The natural resources for quinonoids class; subclass anthraquinonoids and naphthoquinonoids are *Carthamus tinctorius* in Safflower, *Chlorophora tinctoria* in Gaudich, *Lawsonia inermis/ Lawsonia alba* in Henna or Mehendi, *Juglans regia* in Walnut, *Plumbago capensis* in Chitraka/ Chita, *Drosera whittakeri* in Sundew, *Tabebuia avellanedae* in Taigu/ Lapachol, *Alkanna tinctoria* in Ratanjot/Alkanet, *Lithospermum erythrorhizon* in Tokyo Violet/Shikone, *Dactylopius coccus* in Cochineal, *vermilio/Coccus ilicis* in Kermes, *Laccifer lacca/ Kerria and lacca/Coccus lacca* in lac, *Rubia tinctorum*, *Rubia cordifolia* in Indian Madder, *Rheum emodi* in Himalayan rhubarb, *Oldenlandia umbellata* in Chay Root, and *Morinda citrifolia* in Al/surangil/ ach [38, 42].

Madder called as, the “queen of natural dyes.”, belongs to anthraquinone. It is the red colour producing natural dyes from the plants of various *Rubia* species. The dye is obtained from the roots of the plant. The main colouring constituent of European madder *Rubia tinctorum* is alizarin. The yield of roots from the 3-year-old plant is between 3–5 tons per hectare and about 150–200 kg of dye. The use of natural Indigo declined after the manufacture of synthetic indigo. Similarly, the demand for natural madder declined after the invention of synthetic alizarin by the BASF. *Rubia cordifolia* is known as Indian madder, manjishth, or manjeet, and its coloring matter is a mixture of munjistin and purpurin. The dye is not only present

in root, but also present in the stems and other parts of the plant.

It was shown that the glycosides are the main contributor to the dyeing components of both Iranian and Turkish madder, and the molar adsorption of these two compounds is much greater than the aglycon, alizarin, which is often referred to as the main dye component of *R. tinctorum*. Comparative work using sorption isotherms for the purified 1:1 ruberythric acid:lucidin primeveroside mixture and alizarin demonstrates that chemical differences in these compounds results in different adsorption mechanisms onto mordanted wool [49].

Dye is usually extracted by boiling dried root chips or stem pieces with water but sometimes, these are merely steeped in cold water for few hours. It produces brightly coloured insoluble complexes or lakes with metal ions present in the mordanted fabric. Alum is widely used to get pink and red shades. A mixture of alum and iron produces purple shades. Alum is used as the principal metallic salt along with other mordants to develop a range of red shades. Dyed materials possess good fastness properties [50].

Safflower belongs to benzoquinone. It is an annual herb known to have originated in Afghanistan. It is mainly cultivated for oil from its seeds which are rich in polyunsaturated fatty acids. The safflower florets were traditionally used for extracting dye which was valued for its bright cherry-red colour. It contains two colouring matters, a water-soluble yellow present in abundance (26-36%) which was not used as a dye and the scarlet red water-insoluble carthamin present only to the extent of 0.3–0.6 %. Even smaller quantities of the yellow amorphous colouring matter may affect the pure pinkish shade imparted by the red dye and hence, the same is to be removed completely from carthamin before dyeing. Safflower has been employed to give cherry-red direct dyeing on silk and cotton. The dye is extracted from dried safflower florets by continuously washing it with acidulated water to remove all the water-soluble yellow colouring matter. The residue containing insoluble red dye is partially dried and moulded into cakes for use in dyeing or it is extracted with a sodium carbonate solution and precipitated by dilute acids.

Versatile safflower when used with different acids and alkalis, can give off yellow, orange, red and pink shades. However, it is a weak dyeing agent and requires a great deal of dyestuffs. The washing and light fastness of the dye is poor. Yellow dye has now also been used to dye mordanted cotton [50].

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

Flavonoids

Flavonoids [38] provide the largest group of plant dyes ranging in colors from pale yellow (isoflavones) through deep yellow (chalcones, flavones, flavonols, aurones), orange (aurones) to reds and blues (anthocyanins). Various plant sources of flavonoid dyes [51] are *Reseda luteola* (Weld), *Allium cepa* (Onion), *Artocarpus heterophyllus/Artocarpus integrifolia* (Jackfruit), *Myrica esculenta* (Kaiphal), *Datisca cannabina* (Hemp), *Delphinium zaili* (Yellow Larkspur), *Gossypium herbaceum*, *Sophora japonica/Styphnolobium japonicum*, *Butea monosperma/Butea frondosa* (Flame of the forest/Palas), *Mallotus philippinensis* (Kamala), *Bignonia chica/Arrabidaea china* (Carajuru/Puca), *Commelina communis*, and *Pterocarpus santalinus* (Red Sandalwood).

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

Alum mordant produces an orange yellow known as saffron yellow.

Dihydropyran-derivatives

These pigments (Figure 3 f) comprise of brazilin (C.I. 75280) from brazilwood (*Caesalpinia sappan*) and haematoxylin (C.I. 75290) from logwood (*Haematoxylon campechianum*).

Brazil Wood/Sappan Wood: A red dye is obtained from the wood of *Caesalpinia sappan*, a small tree

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

Diarylol methane

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

Betalains

These are a class of water soluble nitrogen containing plant pigments of the order Caryophyllales which comprise of the yellow betaxanthins and the violet betacyanins. *Opuntia lasiacantha* and *Beta vulgaris* (Beet root) are common natural sources for betalains class of colorants [52].

Tannins

These are astringent vegetable products found in most of the vegetable kingdom. Tannins are obtained from the various parts of the plants such as fruit, pods, plant galls, leaves, bark, wood, and roots. Tannins are defined as, water soluble phenolic compounds having molecular weights between 500 and 3000. Tannins are usually classified into two groups-hydrolysable (pyrogallol) and condensed tannins (proanthocyanidins). The hydrolysable tannins are polyesters of a sugar moiety and organic acids, grouped as gallotannis and ellagitannins which on hydrolysis yield gallic acid and ellagic acid, respectively [53].

Tannins are primarily used in the preservation of leather. Tannins are used in glues, inks, stains and mordants. Tannins are also used for heavy metal removal in surface water treatment. Tannins play very important role in dyeing with natural dyes by improving the affinity of fibers towards different dyes. By mixing with different natural dyes it gives different shades like yellow, brown, grey and black. *Acacia catechu* (Cutch), *Terminalia chebula* (Harda), *Punica granatum* (Pomegranate/Anar), *Quercus infectoria* (Gallnut), are plant sources for tannins [53-54].

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

Black and brown dyes

Oak galls are rich in tannin and are used for mordanting. They can also be used to get a brown colour. Catechu or cutch obtained from the heartwood of *Acacia catechu* is used to dye cotton, wool, and silk to brown color directly. It is also rich in tannins and can be used to get black color with iron mordant. Black color can also be obtained from many yellow and red dyes by iron mordanting. Famous logwood black color having very good fastness properties was obtained by using iron mordant and the extract of logwood obtained from the heartwood of the tree *Haematoxylon campechianum* found in Mexico and the West Indies [50].

The major types of natural dyes and their origin have been tabulated by Hill [55] as shown in Table 6.

Presently efforts are being made to apply natural dyes on various synthetic fibers, but so far this has met with limited success [37].

Mohanty *et al.* [56] reported dyeing of cotton and silk with babool, tesu, menjinstha, henna, indigo, marigold etc. with different mordants. Applying different mordants on certain natural dyes a variety of shades like black to brown and green to yellow to orange can be obtained.

Dyeing method

As usual, the amount of natural dye to be taken is normally expressed as % shade. It denotes the amount of dye (in grams) to be taken for each 100 g of textile material during dyeing. As natural dyes are mostly used in raw or partially purified form, the amount of dye required may be 10–30 %, whereas the amount can be reduced to 5-10 % for the purified dye extracts. The quantity of mordant depends on the depth of shade required. Deeper shades require larger quantity of mordant.

The amount of water to be taken in the dye bath is expressed in the recipe as the material-to-liquor ratio (MLR). The MLR denotes the ratio of the weight of the material in gram and the quantity of water in ml required for dyeing.

As natural dyes differ in their chemical constituents, their dyeing procedures also differ but their basic dyeing process is similar. There may be different optimum temperature, time, and pH of dyeing but the basic steps remain the same. Many natural dyes are dyed at near boiling temperature on cotton. Wool and silk are dyed at a lower temperature although some dyes may dye cotton also at lower temperature. Normally natural dyes are applied under neutral pH but some natural dyes require acidic pH and some others may need alkaline pH. For dyeing animal fibres wool, pashmina, and silk, generally 1–2 % of acetic acid is added during dyeing. The material to be dyed is pretreated with mordant or it is introduced into the dyeing bath at room temperature. The temperature is then raised slowly to ensure uniformity of dyeing. The dyeing is carried out for a minimum period of one hour so that the dye penetrates well inside the textile material. It is essential that the textile material should be agitated or moved or agitated in the dye bath during dyeing. In dyeing machines, movement of the material is well controlled, but in manual or hand dyeing, the fabric is to be continuously stirred in the dye bath, otherwise uneven dyeing may result. If delicate fabrics such as pashmina is to be dyed, the dye bath should not be stirred continuously otherwise the fabric structure will be destroyed. In such cases, a high material-to liquor ratio (at least 1:100) is to be maintained so that the fabric is completely immersed in the dye liquor during dyeing

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and dyeing is uniform. For simultaneous dyeing and mordanting, the required quantity of mordant is also added to the dye bath. After the dyeing is over, the dyed material is removed and allowed to cool down for some time and then washed with water. Some traditional dyers leave the material in the dye bath itself to cool and then remove the material for washing. The washed dyed material is then soaped with a hot soap or nonionic detergent solution to

remove loosely held dye and is again rinsed with water and air dried in shade. Natural colours are sensitive to alkali. Hence, soda ash should be avoided during washing. In industries excess water after washing is removed by hydro-extractors. If post-mordanting is to be carried out, the washed material is taken up for post-mordanting without soaping and soaping is carried out after post-mordanting.

Table 6. Major Types of Natural Dyes and Their Origin

Chemical class	Coloring matter	Origin	Color obtained
Vat dyes			
Indole	Indigotin	Woad, indigo	Blues
Quinone	Juglone	Walnut	Browns
Mordant dyes			
Anthraquinones	Alizarin	Madder roots	Reds, oranges, browns
	Pseudopurpurin	Madder roots	Reds, oranges, browns
	Munjistin	Munjeet stems	Reds, browns, maroons
	Laccaic acids	Lac insects	Reds, purples, Maroons
Flavoid tannins	Catachin	Cutch	Browns, grays
Saffron, Flavone	Luteolin	Weld	Yellows, khaki
Flavonol	Quercetin	50% of all plants	Yellows, khaki
Anthocyanins	Cyanidin	Elderberries	Purples
Neoflavanoidones	Haematoxylin	Logwood	Violets, blacks
	Brazilin	Brazilwood	Reds, purples
Isoflavanoid	Pterocarpin	Sanderswood	Oranges
Direct dyes			
Cartinoid	Curcumin	Turmeric	Yellows
	Crocin	Saffron, gardenia	Yellows
Alkaloid	Berberine	Mahonia wood	Yellows
Orinol	Orcein	Orchil	Purples
Benzoquinone	Carthamine	Safflower	Pinks
Reactive dyes			
Depsides	Atranorin	Lichens	Fawns
Despidones	Salazinic acid	Lichens	Browns

When cotton materials are dyed with dyes such as madder which do not have affinity to it without mordant, the material must be pre-mordanted. After dyeing the material may be further post-mordanted to get different shades and improvements in fastness properties. A post-dyeing treatment with tannins and alum can help in improving the fastness to washing [50].

Industrial application

As the application of natural dyes is tedious, in the present form it is not acceptable as industrial practice. The dyeing processes are very lengthy and hence, they are uneconomic to conduct in industrial dyeing machines and become labour-intensive. Also the availability of many natural dyes is also not sufficient as in many cases a proper supply chain is

not in place. The range of fast shades is limited. They are not suitable for working in mixtures and not amenable to shade matching and prediction with the help of computerized colour-matching systems. Therefore, these dyes are mostly used by craftsmen, hobby groups, and NGOs only on the cottage level. Today's high cost of purified natural dyes makes their industrial use an impractical proposition [50].

Advantages of Natural Dyes

- Minimal impact on environment – As of natural origin, natural dyes are not harmful to the environment. This makes it very appealing to the consumers. Natural dyes are biodegradable and disposing them do not create pollution.
- Renewable – Natural dyes are obtained from renewable sources assuring no harm to the environment.
- Chemical reactions - no or little chemical reactions are involved during dye preparation.
- Disposal - No disposal problems.
- Natural shades – If you're going for a soft hue or soothing shade, natural dyes can help you achieve that look.
- Safe – Some natural dyes, such as carmine found in lipsticks, will not cause harm or health problems when ingested.

Disadvantages of Natural Dyes

- Cost – A larger amount of natural dyes may be needed in order to dye a specific amount of fabric as opposed to synthetic dyes. For instance, one pound of cotton may be dyed with just five grams of synthetic dye, whereas 230 grams of natural dye are needed to dye the same amount of material. Since that is the case, using natural dyes is more expensive than synthetic dyes.
- Standardization - Difficult to standardise and to blend.
- Poor brightness and fastness properties – Colour pay-off from natural dyes tends to fade quickly. More so, quality may not be as consistent as what synthetic dyes can deliver.
- Availability – Another issue with natural dyes is their availability. It can be difficult to produce because the availability of raw materials can

vary from season to season, place, and species, whereas synthetic dyes can be produced in laboratories all year round.

- Fixation - Inadequate degree of fixation.
- Lengthy dyeing procedure.
- Reproducibility - poor reproducibility of shade.
- Solubility- Poor solubility in water and tedious extraction procedure may be necessary.
- Harmful Effects – Natural dyes can also be harmful to some extent. Logwood has ingredients, hematein and hematoxylin, that can have harmful effects when inhaled, ingested, or absorbed through the skin. Bloodroot, another natural dye source, can cause irritation and inflammation when inhaled. More so, natural dyes may need mordants for application. While these substances help the dye stick to fabrics, they can also be toxic. Example of mordants used in natural dyes are aluminium, copper, iron, and chrome [57].

Textile dyeing and finishing in a green way can be achieved by using chemical-free dyes made from plants, marine invertebrates (like sea urchins and starfish), algae, bacteria, and fungi. These herbal dyes are not only bio-degradable but also possess medicinal properties. Plants, fruits, barks, stems, minerals, and herbs are used to make fabrics with anti-bacterial, anti-inflammatory, and anti-allergic fabrics. However, it is difficult to get all desirable shades and to get good color fastness properties.

CONCLUSIONS

After the advent of synthetic dyes and their immediate acceptability throughout the world, the use of natural dyes in textile coloration industries slowly became a thing of the past. Extraction of the colorant from biomass depends on the extraction technique employed and, it can be noted that the full range of colours might not yet be available for further application. Considerable weaknesses associated with the use of bio-colorants are poor reproducibility, poor cost effective, inadequate degree of fixation, and low colour fastness properties. These drawbacks of natural dyes can be overcome with the use of environment-friendly mordants which are permissible up to some levels for textile dyeing. Environmental concerns and eco-protection has created the revival

interest of R&D in the use of bio-colorants worldwide. Environmental awareness and pollution concerns implied ban on azo dyes made from benzidine and

other 21 aromatic amines because of their carcinogenicity [58].

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