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Review -A History and Introduction of synthetic dye and their usage

Madhuri R. Basutkar

Department of Post Graduate Studies and Research in Microbiology, Gulbarga University, Kalaburagi,- 585106, Karnataka.

Abstract: **Coloring industry is a huge industry, it having a wide history, earlier natural colors were using to dye a clothes or any material, but when natural dyes are replaced by synthetic dyes a actual problem had been started, the present review covers the history and types of synthetic dyes and out of all other ynthetic dyes a reactive azo dyes widely used was covered, finally usage of dye in textile industry and consumption of water for the dying had been reviewed.**

Keywords: **natural colors, synthetic dyes, textile industry.**

1. INTRODUCTION

Colors are the part of life, as the nature is itself color full gives pleasant to eyes and feel good, fresh, polite and respectful. But in present days it becomes reverse due to excessive use of synthetic colors leading to the environment pollution especially the hydrosphere. Introduction of harsh full recalcitrant and xenobiotic compounds into the environment (water) by the industries or companies like textile and dye manufacturing industries creating the negative effect on biosphere of water bodies and surrounding terrestrial life. Due to drastic development in agriculture, medicine, energy sources and chemical industries but it is necessary also in order to fulfill the needs and demands of the overgrowing human population. Almost all processes employed by man for the production of goods and services lead to the production of environmental pollutants. These pollutants are released into air, water and soil and have detrimental effects on the health of humans, plants, animals and microbes. Human endeavors for the production and improvement of goods and services cannot be absolutely stopped because these are needed by humans for their survival on earth. Alternatively, we must look for green processes - that lead to the production of eco-friendly products.

We must also focus our attention on ways for the eradication and reduction of the existing environmental pollution. Thus, for a sustainable human society, we need green chemistry and environmental remediation. A tremendous increase raised in the awareness of the toxic and carcinogenic effects of many polluting chemicals, which were earlier not considered hazardous substances (King *et al.,* 1997). Some of the synthetic chemicals are extremely resistant which cannot be degradable easily (Fernando and Aust, 1994). Many of the recalcitrant compounds are major environmental pollutants, such as municipal waste, pesticides, organochlorines, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, wood preservatives, synthetic polymers and synthetic dyes (Pointing, 2001). Most synthetic dyes are toxic and highly resistant to degradation due to their complex chemical structures (Lu *et al*., 2009). Synthetic dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetic and leather industries (Rafii *et al*., 1990; Kuhad *et al*., 2004; Couto, 2009). Since from 1856, different types and varieties of dyes have been produced worldwide with an annual production of over $7×10^5$ metric tons (Chen *et al*., 2003). Paper and pulp mills, textiles and dyestuff industries, distilleries and tanneries are some of the industries, which release highly colored wastewaters (Raghukumar, 2000). Textile industry is one of the greatest generators of liquid effluent pollutants due to the high quantities of water used in the dyeing processes (Kalyani *et al*., 2009). The traditional textile finishing industry consumes about 1000 Liters of water to process about 1 kg of textile materials (Couto, 2009).

Colorants

Colorants are the coloring agents or substances, generally colors are available in two forms one is natural and another which is artificial types. Artificial colors are being an organic compound or these coloring chemicals having the special character of absorbing the light in visible spectrum (400-700 nm) and gives maximum absorption peaks and highest wavelength peaks considered as λ max of the dye, each absorption in the spectrum helps in the identification of different dyes or colors (Booth and Gerald , 2000. **Table -**1). **Table 2.1:** Absorption spectrum of colors ((Booth and Gerald , 2000).

S. No.	Color Absorbed	Color Observed	Absorbed Radiation (nm)
1	Violet	Yellow green	350-435
2	Blue	Yellow	435-480
3	Green-blue	Orange	480-490
4	Blue-green	Red	490-500
5	Green	Purple	500-560
6	Yellow-green	Violet	560-580
7	Yellow	Blue	580-590
8	Orange	Green-blue	590-605
9	Red	Blue-green	605-750

Types and classification of dyes (Colorants)

Colorants are divided into two categories pigments and dyes. Pigments are insoluble in liquid medium or in an applicable solution. Dyes are coloring agents which having affinity towards the substrates and soluble in applicable solution further dyes are divided into two categories:

1. Natural dyes
2. Synthetic dyes.

Classification of dyes

Natural colorants are naturally occurring in nature which are made from using plants, roots, lichens, flowers etc. India has a rich biodiversity contains wide range of plants which are using as natural dyes. Earlier natural dyes were used in festivals like holi, Ganesh festivals and dying of cloths, coloring to the walls etc (Siva, 2007).

Archeological survey of India and historical evidence

At Indus valley civilization at Mohenjo-Daro and Harappa (3500 before years), natural matter was used to stain hides, decorate shells and feathers and in cave paintings, scientists have been able to date the black, white, yellow and reddish pigments were used. In Egypt, mummies have found with wrapped in dyed cloth, the earliest written record of the use of natural dyes.

The natural dye turmeric, the brightest of naturally occurring yellow dyes is a powerful antiseptic which revitalizes the skin, while indigo blue from the leaves of *Indigofera tinctoria* gives a cooling sensation (Vanker, 2000; Gulrajani, 1992).

Preparation of natural dye (color)

Natural dyes (color) were extracted from the different parts of the plants through fermentation, hydrolysis and oxidation process. The Table -2 showing the name of plants and their parts using in the preparation of different natural dyes (Siva , 2007).

Table-2: Usage of the plants for the production of natural dyes (Siva, 2007).

Color	Botanical name	Parts used
Red dye		
Safflower	*Carthamus tinctorius* L	Flower
Caesalpinia L. Alum	*Caesalpinia sappan*	Wood
Madder	*Rubia tinctorium* L.	Wood
Indian mulberry	*Morinda tinctoria* L	Wood
Kamala	*philippinensis* Muell	Flower
Yellow dye		
Teak	*Tectona grandis* L.f.	Leaf
Marigold	*Tagetes* sp.	Flower
Saffron	*Crocus sativus* L	Flower
Blue dye		
Indigo	*Indigofera tinctoria* L	Leaf
Water lily	*Nymphaea alba* L.	Rhizome
Black dye		
Custard apple	*Anona reticulata* L.	Fruit
Harda Retz	*Terminalia chebula*	Fruit
Orange dye		
Annota	*Bixa orellena* L.	Seed
Dhalia	*Dhalia* sp.	Flower
Lily	*Convallaria majalis* L.	Leaf

Synthetic dyes and their classification

Synthetic dyes have a wider and brighter color range, longer color permanence and are faster, easier and cheaper to produce compare with natural dyes. There are over 10,000 different types of synthetic dyes (McMullan *et al.*, 2001). Synthetic dyes were obtained from the distillation of coal tar and most of these are polycyclic aromatic in nature.

Chemical synthesis of synthetic dyes

Synthetic process needs various chemicals to prepare a synthetic dye, all process undergo the series of reactions which results in the formation of synthetic dye. Because of the complexity of the chemical process the dye is usually made in the batch quantities.

The first synthetic dye was Mauveine by Perkin in Germany in 1856, at the age of 14, since, from these the various research was made on synthetic production of dyes and Germany was called first synthesizer of synthetic dye and it only banned certain azo dyes in 1996 and became first country for the production and terminating of certain synthetic dyes (Fig.1 ; Zollinger, H, 2003)

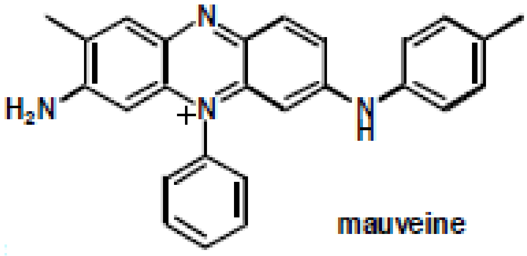


Figure 1: Chemical Structure of Mauveine

When we look to the history of synthetic dyes it starts from - In 1857- were industries begin to the synthesis of various dyes, collecting the required raw material for the productions of dye, they were aniline, benzene, nitric acid etc.

In 1856 – 1867 the complete synthesis of Mauveine has been done.

In 1858 – Different azo dyes were synthesized by Peter Gries and now azo dye s accounts for 60-70 % of dye in industrial application.

In 1869- Alizarian dye invented in England and France.

In 1871- Germany patented on various dyes.

In 1870- By Heinrich caro started industrial and academic cooperation group, through these group various conferences for the synthesis of dyes were taking place.

In 1870-1890- Different industrial laboratory established to synthesize new dyes.

The history of dyeing can be divided into two great periods, the "pre-aniline", extending to 1856 and the "post-aniline" period. The former was characterized by a rather limited range of colors that were based on dye-producing animals and plants. The main vegetable dyes available were extracted from madder root (Asia and Europe), producing a brilliant red and leaves of the indigo plant (India), yielding the blue dye still used today in jeans. Among the most important animal based dyes is the famous and expensive "Tyrian Purple" which was obtained from the small shellfish (Aljamali ,2015) and followed by post-aniline" period.

On occasion of 100 years celebration of synthetic dye manufacturers, two chemists of ICI Company (UK) named Stephen and Rattee tried to manufacture new dye stuff. Thus, they succeed to invent a new dye in 1956 which was named "REACTIVE DYE". This was manufactured for dyeing cellulosic fiber. The first three reactive dyes were Procion Yellow R, Procion Brilliant Red 2B and Procion Blue 3G. For this effort they were awarded gold medal of the society of dyes and colorists for the year 1960 (Chinta and Shrivastava, 2013).

Classification of synthetic dyes

Dye are classified based on the its usage, application, structure of dyes and based on the origin. From origin of dye- dye are classified into natural dyes, synthetic dyes, organic or inorganic. Further classification based on the dying processes - Acid dyes, Basic dyes, Direct or Substantive dyeing, Vat dyes, Reactive dyes, Disperse dyes, Azo-dye, Sulphur dyes, Fluorescent brightening agent. Classification based on by the chromopheric group-Acridine dyes, Anthraquinone dyes, Aryl metahne dyes, Azo dyes Cyanine dyes, Diazonium, dyes, Nitroso dyes, Phthalocyanine dyes, Quinoneiimine dyes (azine dyes, Indamins, Indophenols, oxazone, Thiazin), Thiazole dyes, Xanthate dyes (Booth and Gerald , 2000).

Based on application these are classified as Food, cosmetics, drug dyes, Laser dyes, Leather dyes.

Based on the chromopheric group presence dyes are classified which is listed in below (Table .3 Fig.2).

Table 3: Classification of dyes based on its chromopheric group (Zollinger, H, 2003)

Dye	Chromophore
Azo dyes	**N=N**
Nitro	$-NO_2$
Nitroso	-NO (or =N-OH)
Ethylene	C=C
Carbonyl group	C=O
Carbon nitrogen group	C=N
Carbon sulphur groups	C=O

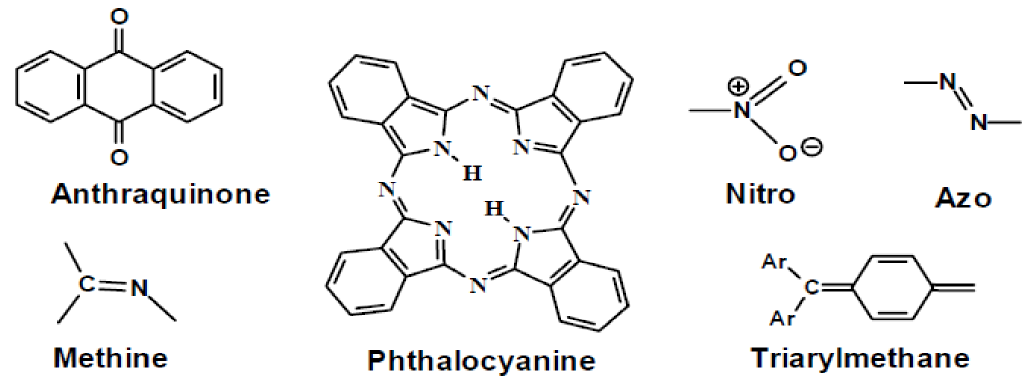
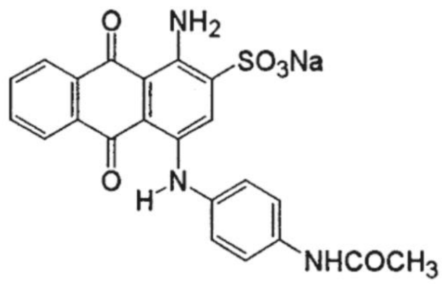


Fig. 2: Showing structure of different synthetic dyes which are classified based on cromophoric group (Zollinger, H, 2003)

Dyes are classified into process and application

I. Acid dyes

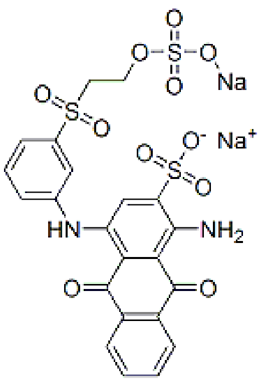
This is the largest class of dyes in the color index and is referred to as Acid dyes. Acid dyes are anionic compounds that are mainly used for the dyeing nitrogen-containing fabrics like wool, polyamide, silk and modified acryl and hey bind to the cationic ions of those fibers. Most of the acid dyes are azo, anthraquinone or triarylmethane compounds. The adjective 'acid' refers to the requirement of acidic condition for dyeing to fibers (Booth and Gerald , 2000).



Acid blue 40

II. Reactive dyes

The dyes, which containing the reactive groups are called as reactive dyes. In the Color Index, this is the second largest dye class, introduced in 1956. The reactive dyes form covalent bonds with -OH, -NH, or -SH groups of fibers. The reactive group is often a heterocyclic aromatic ring substituted with chloride or fluoride or vinyl sulphone. The hydrolysis of reactive group during dyeing lowers the degree of fixation of reactive dyes. These create the problem of colored effluent (Zollinger, H, 2003 ; Booth and Gerald , 2000).



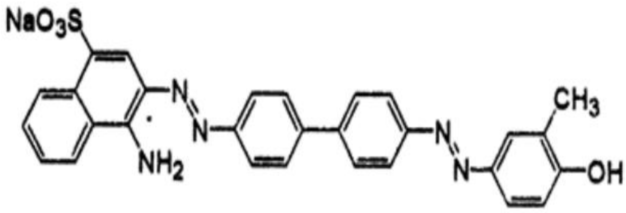
Reactive blue -19

III. Metal complex dyes

Many metal complex dyes are reported among the acid and reactive dyes. Metal complex dyes are the strong complexes of one metal atom (usually chromium, copper, cobalt or nickel). About 16% of the azo dyes listed in the color index are metal complexes (Klaus Grychtol and Winfried Mennicke , 2005) .

IV. Direct dyes

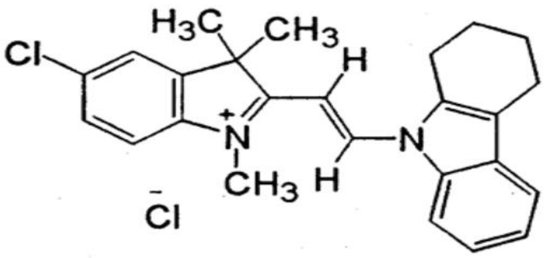
The direct dyes are the second largest dye class in the color index with respect to the amount of the dyes. Direct dyes are relatively large molecules with high affinity for cellulose fibers. Vander Waals forces make them bind to the fiber. They are mostly azo dyes with more than one azo bond or phthalocyanine, stilbene or oxazine compounds. About 1600 direct dyes are listed but only 30% of them are in current production (Hunger , 2003).



Direct orange- 25

V. Basic dyes

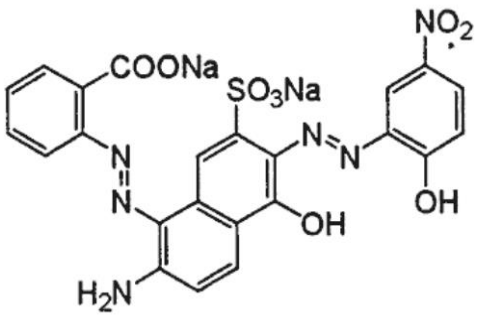
Basic dyes represent 5% of all dyes listed in the color index. They are cationic compounds and used for the dyeing acid-group containing synthetic fibers. Most of the basic dyes are diarylmethane, triarylmethane, anthraquinone or azo compounds (Hunger , 2003).



Basic yellow 23

VI. Mordant dyes

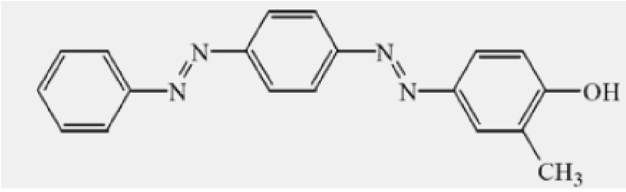
The dyes which required the mordant for dying it to fibers is called as mordant dyes. They are used for dyeing wool, leather, silk, paper and modified cellulose fibers. Most mordant dyes are azo, oxazine or triarylmethane compounds. The mordents are usually dichromate's or chromium complexes (Balter, 2009).



Mordant black 106

VII. Disperse dyes

Disperse dyes form the third largest group of dyes in the color index. Disperse dyes are scarcely soluble dyes, thus it required high temperature or chemical softeners for dying to synthetic fibers viz., cellulose acetate, polyester, polyamide, acryl, etc. They are usually small azo or nitro compounds, anthraquinones or metal complex azo compounds (Balter, 2009).



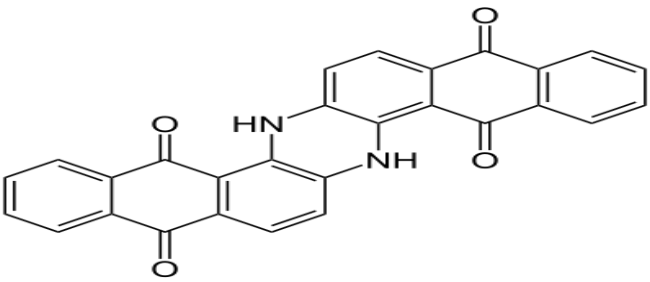
Disperse yellow 7

VIII. Pigment dyes

These are insoluble non-ionic compounds or insoluble salts retain their crystalline or particulate structure throughout their application. Pigment dyes (i.e., organic pigments) represent a small but increasing fraction of the pigments, the most widely applied group of colorants. About 25% of all commercial dye names listed in the color index is pigment dyes. Most pigment dyes are azo compounds or metal complex phthalocyanines or anthraquinone or quinacridone (Balter, 2009).

IX. Vat dyes

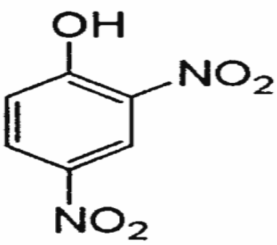
Vat dyes are water insoluble dyes that are widely used for dyeing cellulose fibers. Vat refers to the reduction of indigo plants through fermentation. The dyeing method is based on the solubility of vat dyes in their reduced form (Balter, 2009).



Vat blue-4

X. Sulphur dyes

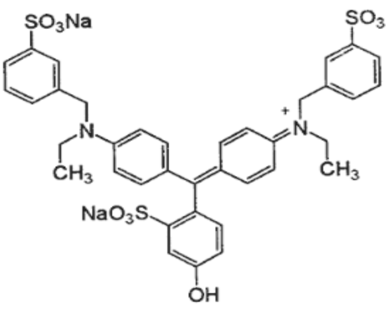
Sulphur dyes are complex polymeric aromatics with heterocyclic sulphur containing rings. This dye group represents about 15% of the global dye production. Dyeing with sulphur dyes involves reduction and oxidation comparable to vat dyeing. These dyes are mainly used for dyeing cellulose fibers (Klaus Grychtol and Winfried Mennicke , 2005).



Sulphur black 1

XI. Other dye classes

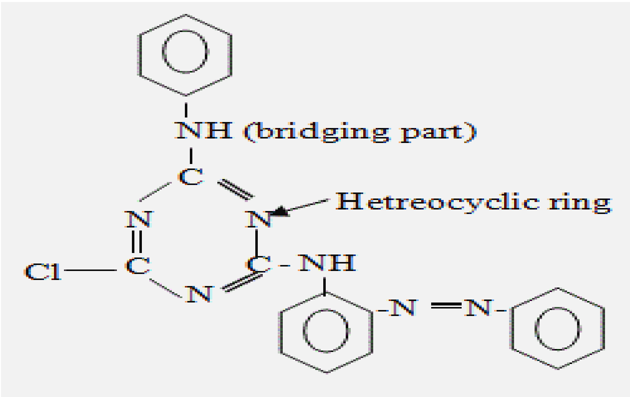
Apart from the dye classes mentioned above, the color index also lists food dyes and natural dyes. Food dyes are not used as textile dyes and the use of natural dyes viz., anthraquinone, indigoid, flavenol, flavones or chroman compounds that can be used as mordant, vat, direct, acid or solvent dyes in textile processing operations is very limited (Hunger, 2003) .



Food green 3

Reactive Azo Dyes and their classification

Reactive dye is the only class of dyes amongst all the classes of dyes which makes covalent bond with the fiber and becomes a part of it. This can be described as: Reactive dyes + Fiber = Reactive dye-Fiber (covalent bonding). If the general structure of a reactive dye is "R-B-X" then, R-B-X + Fiber = R-B-X-Fiber (Dyed fiber). Here, R = Chromophore Group (Azo, Anthaquinone, Phthalocyanine etc.) B = Bridging Group (Imino, Ethyl & Methyl, Oxide, Sulphide group) X = Reactive Group (-Cl, -Br, -SH, -OCH, etc) (Horst Tappe *et al*., 2000).



Chemical structure of Reactive dyes

Classification of Reactive Dyes

By depending on the chemical constitution reactive dyes can be classified as:

1. Chlorotriazine Dyes (CT)

2. Vinyl Sulphone Dyes (VS)

3. Heterocyclic Helogen Containing Dyes (HHC)

4. Mixed Dyes (MCT-VS)

By depending on application methods of temperature, reactive dyes can be classified as per : (Horst Tappe *et al*., 2000)

Cold brand reactive dyes

This type of reactive dyes is applied at low temperature i.e., at room temperature. They are highly reactive with fiber at this temperature.

Hot brand reactive dyes- This type of dyes is applied at a medium temperature around are 60ºC. Their reactivity is medium with fiber.

High Exhaust brand reactive dyes- This type of dyes has very low reactivity properties with fiber as against the reactivity with cold and hot brand reactive dyes. Dyeing is carried out around 80-90ºC.

Properties of Reactive dyes.

1. Reactive dye is anionic in nature.

2. Reactive dye is a water soluble dye.

3. They have better wash and light fastness properties.

4. They have better sustainability.

5. They form strong covalent bond with the cellulosic fiber in alkaline condition.

6. The electrolyte is must for exhaustion of dyes in the fiber.

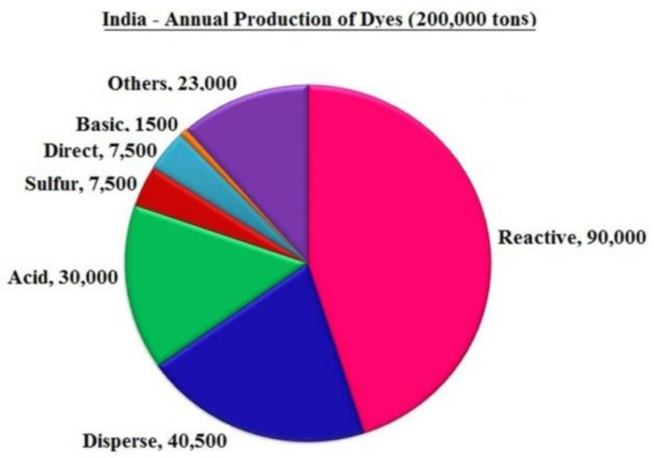
7. A certain amount of dyes is hydrolyzed during application (around 15-20%).

8. Wide range of color can be produced with reactive dyes.

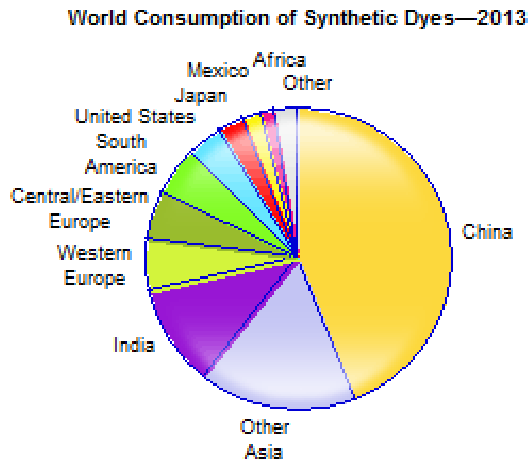
9. Comparatively cheaper in price.

Usage of dyes in textile industries

Around 10000 different dyes with an annual production of more than $7x10^5$ metric tons world-wide are commercially available (Mcmullan *et al.,* 2001) and 95% of dyes were used by textile industries, other industries like leather, paper and prints. It is estimated that 280,000 tons of textile dyes are discharged in textile industrial effluent every year worldwide (Jin *et al.*, 2007). In India, an average textile mill discharges about 1.5 million liters of contaminated effluent per day was recorded (Sani and Banerjee, 1999). Out of different synthetic dyes reactive dyes widely used it occupied first position and our India took 3rd position in the utilization of synthetic dye (Gupta *et al.*, 2014 ;Fig.3 a, b).



(a)



(b)

Out of other countries India has taken 3rd position in the consumption synthetic dye (Gupta *et al.*, 2014).

Fig. 3: Usage of dyes and consumption of synthetic dyes worldwide (FCCI-2013)

Usage of water in textile industries

Today the whole world is facing water crises because of unrestricted and excessive exploitation of water. The textile dyeing and finishing industry has created a huge pollution problem as it is one of the most chemically intensive industries on earth and the No. 1 polluter of water.

More than 3600 individual textile dyes are being manufactured by the Industry today. The industry is using more than 8000 chemicals textile manufacturing's includes dyeing and printing. Many of these chemicals are poisonous and damaging to human health directly or indirectly. Large quantities of water are required for textile processing, dyeing and printing. The daily water consumption of an average sized textile mill having a production of about 8000 kg of fabric per day is about 1.6 million liters. 16% of this is consumed in dyeing and 8% in printing. Specific water consumption for dyeing varies from 30 - 50 liters per kg of cloth depending on the type of dye used. The overall water consumption of yarn dyeing is about 60 liters per kg of yarn. Dyeing section contributes to 15% - 20% of the total waste water flow. Water is also required for washing the dyed and printed fabric and yarn to achieve washing fastness and bright backgrounds. Washing agents like caustic soda based soaps; enzymes etc. are used for the purpose. This removes the extra color and paste from the substrate. Water is also needed for cleaning the printing machines to remove loose color paste from printing blankets, printing screens and dyeing vessels (Wasif and Kone, 1996; Vijaraghavan, 1999). It takes about 500 gallons of water to produce enough fabric to cover one sofa. The World Bank estimates that 17 to 20% of industrial water pollution comes from textile dyeing and finishing treatment given to fabric. Some 72 toxic chemicals have been identified in water solely from textile dyeing, 30 of which cannot be removed. This represents an appalling environmental problem for the clothing and textile manufacturer. (Fig.4.a.b) showing the untreated colored effluent going to the water bodies and contaminating it.

Tamil Nadu (www.thehindu.com)

(a) Rivers of Tripura, Tamil Nadu **(b) Dye effluent discharged in Nallur**

Fig. 2.4: Discharge of untreated dye effluent in India

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