Dyes: Classification, Pollution, and Environmental Effects

Said Benkhaya, Souad M'rabet, Hassane Lgaz, Abderrahim El Bachiri, and Ahmed El Harfi

Abstract There are a wide variety of textile dyes including reactive, direct, vat, sulfur, disperse, basic, and acid dyes. Therefore, the classification of dyes has become mandatory due to the increase in the annual global production of these compounds. They can be classified according to their chemical compositions (azo, anthraquinone, nitroso, nitro, indigoïde, cyanine, phtalocyanine, and triphenylmethane) or according to their field of application to different substrates such as textile fibers, paper, leathers, and plastics. In our new investigation, we have been able to describe the different families of textile dyes according to their chemical structures (chromophoric/auxochromic), application methods in the textile industry, and their Color Index (**C**.**I**). The presence of these dyes in the liquid effluents from washing textiles cause a negative impact on the balance of the aquatic environment, which requires prior treatment of these effluents.

Keywords Textile dyes · Azo dyes · Reactive dyes · Color index · Chromophoric/Auxochromic · Aquatic environment

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1 Introduction

The mauveine, the first synthetic dye, was discovered by chance by William Henry Perkin in 1856, then 18 years old [16]. It was obtained from aniline (obtained from coal tar) by the action of sulfuric acid in the presence of potassium bicarbonate and made it possible to dye the silk purple. The first so-called “Azo” dyes were discovered in Great Britain in 1860. They quickly ousted aniline-based dyes, which had poor light resistance. But it was the German industry (Badische Anilin und Soda Fabrik: BASF) that made the biggest contribution to the rise of the dye industry [101].

A dye is a colored substance, natural or synthetic, which interacts with the medium into which it is introduced and colors it by dissolving and dispersing therein. These dyes constitute a real industry and a capital of modern chemistry, thanks to their chemical stability, ease of synthesis, and variety of colors. They have two specific properties: color and the ability to be fixed to solid substrates such as textiles, by dyeing or printing techniques. In general, dyes are widely used in printing, food products, cosmetics, and in particular in the dyeing of textile substrates (fibers, leathers, furs, woods, plastics, elastomers, etc.). In addition, they can be used in the field of research, in order to reveal small transparent structures by microscopy [19].

An enormous amount of synthetic dyes is used annually in the textile, leather, plastics, paper, and dye industries due to their coloring properties [29]. This results in a large amount of colored wastewater, unsuitable for recycling without proper treatment. Dyes are ubiquitous and persistent environmental contaminants due to their large-scale production and numerous areas of application [16]. Azo dyes are among the most widely used dyes in several industrial applications such as cosmetics, the paper industry, and the textile industry, all of which generate effluents loaded with residual coloring substances [16, 15]. Like most dyes, azo dyes have been shown to have an adverse effect on aquatic organisms and humans, and lead to brain, central nervous system, carcinogenicity, and mutagenicity dysfunction in humans [17]. This is because they contain many toxic substances such as aromatics and heavy metals and could reduce the transmission of sunlight. Wastewater containing dyes from textile industries is a serious problem due to the complex chemical structures of the dyes, their high pH, high chemical oxygen demand, and high temperature which make the degradation of dyes very difficult when they occur. They are present in any type of complex matrix [111]. Therefore, the emergence of true textile wastewater treatment is of great ecological interest around the world.

However, the objective of this review is to describe the different classes of textile dyes, including their chemical structures, their chromophoric, auxochromic, color index (C.I), and their application in the textile industry. Finally, we pointed out the impact of these dyes on aquatic environments.

2 Chemical Structure of Textile Dyes

Dyes have a unique chemical structure for each color. These structures are classified in the ChemSpider database under the data collection "NCSU Max Weaver Dye Library" [89]. The chemical structure of a textile dye is made up of three components: skeleton, chromophore groups (responsible for its color), auxochrome (promotes fixation on the substrate), and solubilizing groups (responsible for the solubility in water or organic solvents), Fig. 1 [16, 15].

An auxochrome is a functional group that contains isolated electron pairs that increase the intensity of the color, and are also important parts of dyes [3, 15, 39]. Table 1 shows some examples of auxochrome and chromophore groups [5, 16, 39, 118, 150, 151].

Table 2 shows the classification of textile dyes according to their chromogen [16, 15, 93, 129, 133].

Therefore, textile dyes have a unique chemical structure for each dye. This structure is made up of two main parts: The chromophore responsible for its color and the auxochrome which improves the capacity of this chromophore to absorb light. They

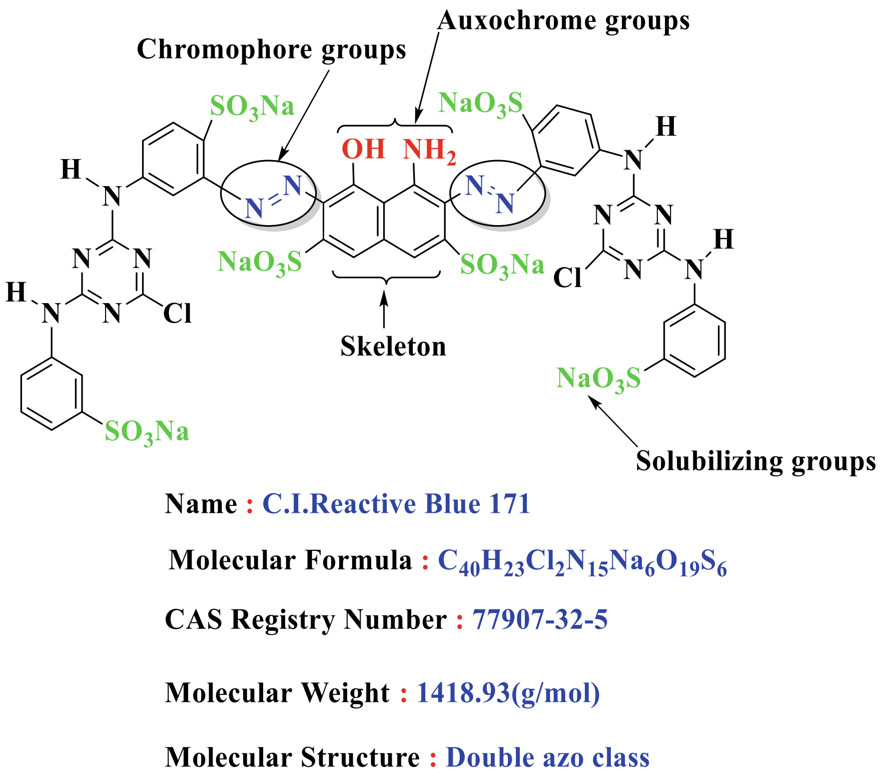
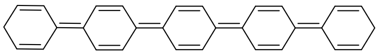


Fig. 1 Chemical structure of a textile dye (S. Benkhaya)

Table 1 Chromophore and auxochrome examples (S. Benkhaya)

Chromophore group		Auxochrome group	
Azo	– N=N–	Hydroxyl	– OH
– Carbonyl – Carboxylate	– C=O – R′CO2R (R and R′ ≠ H)	– Amino – Ammonia	– NH2 – NH3
– Nitro – Sulfonate	– N=O – RSO2OH	– Aldehyde and/or – Carboxylic acid – Sulfonic acid	– CHO – COOH – SO3H
Quinoid		Methyl mercaptan	– SCH3

themselves fail to introduce color, but when it is present with the chromophores in an organic compound, it intensifies the color of the chromogen.

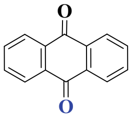
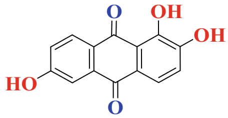
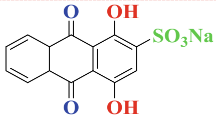
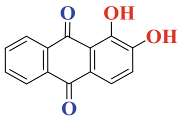
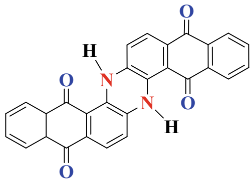
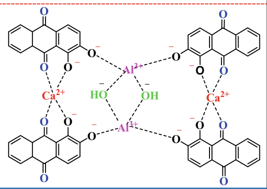
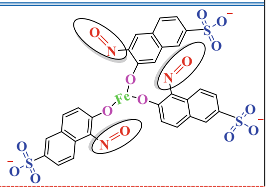
3 Classification of Textile Dyes

Dyes are organic chemicals containing aryl rings to delocalize electrons. They are mainly classified based on their structure, source, color, and method of application in the color index [16, 64].

3.1 Azo Dyes

Azo dyes have one or more than one azo groups (–N=N–) in their chemical structures (Ahmed et al. 2020) [158]. More than 70% of the dyes used in the world belong to the azo group, and they are also the most common dyes (60–70%) used for dying textiles (Alexander and Joseph Thatheyus 2021). They are widely used in a variety of industries, textile, pharmaceutical, paper, non-linear optical systems, medical and biomedical fields, etc. [62, 136, 142]. They contain an amino or dialkylamino group, and undergo a pronounced color change in different solvents and pH [77]. Azo dyes based on heterocyclic moiety are known for their excellent coloring properties, tinctorial strength, fastness, and thermal stability [120]. These dyes are generally characterized by chemical groups capable of forming covalent bonds with textile substrates [16, 15]. They represent more than 50% of synthetic dyes used worldwide [159]. They cover the whole spectrum, but mainly yellow, orange, and red dyes [1]. The azo group is responsible for the color of the dye [87]. Cleavage of the azo bond can lead to products containing aromatics, carcinogenic to humans and other organisms [11]. These dyes represent the largest class of industrially synthesized organic dyes [142]. They are one of the most widely used synthetic dyes due to their

Table 2 Classification of textile dyes according to the chromogen (S. Benkhaya)

Chromogen	Colour Index Generic Name	ColourIndex Constitution Number	CAS No	Structural formula of dye
 Anthraquinone	C.I. mordant red 4	C.I.58240	82-29-1	
	C.I.Pigment Violet 5	C.I.58055	22297-70-7	
	C.I.MordantRed 11	C.I.58000	72-48-0	
	C.I.Pigment Blue 60	C.I.69800	81-77-6	
	C.I. Pigment Red 83	C.I. 58000:1	22.6.12	
—N=O Nitroso	C.I. acid green 1	C.I. 10020	19381-50-1	

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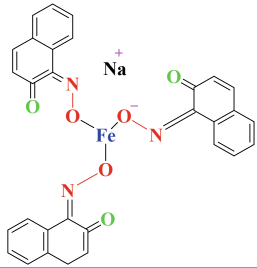
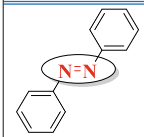
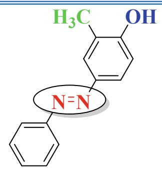
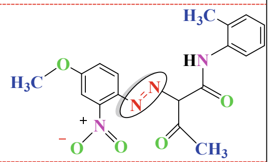
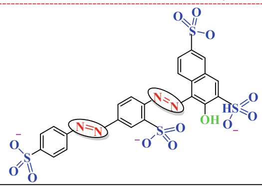
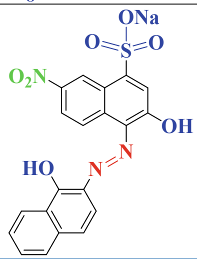
cost-effectiveness and stability under a wide range of pH, temperature, and light conditions [139]. Figure 2 shows some chemical structures of azo dyes.

The synthesis of an azo compound is based on the appropriate oxidation/reduction reaction or diazotization/coupling reaction in the presence of a diazonium salt and a coupling component. Figure 3 shows the process for the synthesis of an azo compound [16, 15]. Penthala et al. [115] synthesized azo and anthraquinone dyes according to the reactions shown in Figs. 4, 5, and 6.

Table 2 (continued)

	C.I. Pigment Green 8	C.I. 10006	15.8.2	
 Azo	C.I.Solvent Yellow 10	C.I.11840	621-66-9	
	C.I.Pigment Orange 1	C.I. 11725	11.1.1	
	C.I. Acid Red 112.	C.I. 27195	12.300.10	
	C.I. Mordant Black 11.	C.I.14645	17.300.2	

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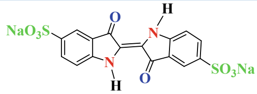
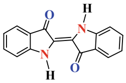
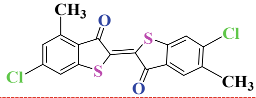
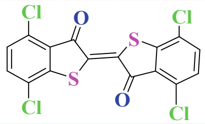
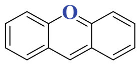
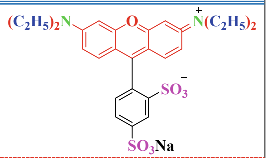
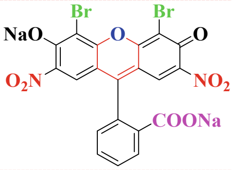
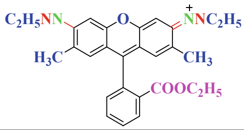
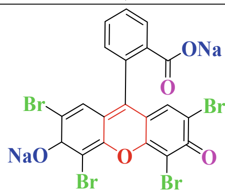
For their part [121] synthesized azo dyes containing a thiazole group. The dye synthesis routes are illustrated schematically in Fig. 7. Concerning Ghanavatkar et al. [59], they synthesized heterocyclic azo dyes according to the synthesis scheme mentioned in Fig. 8.

Table 2 (continued)

	C.I.Acid Blue 74	C.I.73015	860-22-0	
 Thioindigoid	C.I.Pigment Red 181	C.I. 73360	12.181.1	
	C.I.Pigment Red 88.	C.I. 73312	12.88.1	
 Xanthene	C.I. acid red 52	C.I. 45100	3520-42-1	
	C.I.Acid red 91.	C.I.45400	548-24-3	
	C.I.Basic Red 1.	C.I. 45160	70.1.28	
	C.I.Pigment Red 90	C.I.45380:1	29.3.1	

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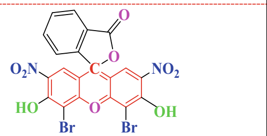
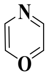
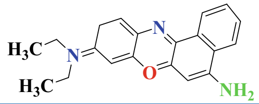
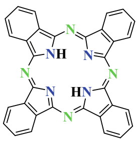
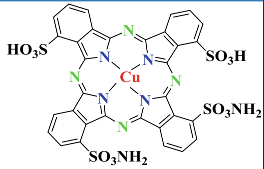
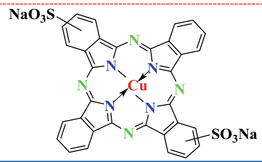
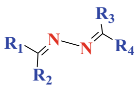
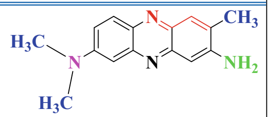
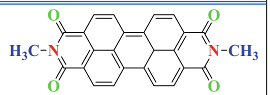
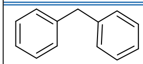
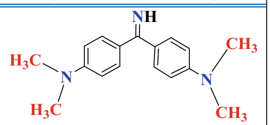
3.2 *Reactive Dyes*

Reactive dyes are soluble anionic dyes which, in solution, are repelled by the negatively charged surface of cotton fiber [85]. The first commercial reactive dyes for cotton were based on the dichloro-s-triazine reactive group [85]. Reactive dyes are

Table 2 (continued)

	C.I. Acid red 91	C.I. 45400	-	
 Oxazine	C.I. basic blue 12	C. I. 51180	3625-57-8	
 Phthalocyanine	C.I.direct blue 199	C.I. 74190	12222-04-7	
	C.I.Direct Blue 86	C.I.74180	1330-38-7	
 Azine	C.I. basic red 5	C. I. 50040	553-24-2	
Perylene	C.I. Pigment Red 179	C.I. 71130	12.179.1	
 Diphenylmethane	C.I. basic yellow 2	C.I. 41000	2465-27-2	

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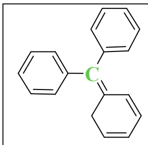
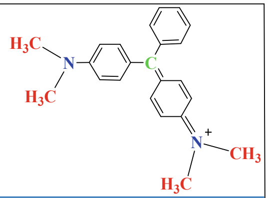
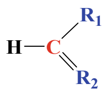
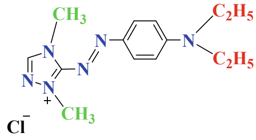
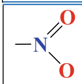
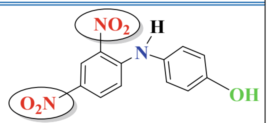
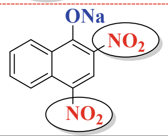
widely applied due to their brilliant colors, excellent long-term colorfastness properties, vivid colors, high photolytic stability, and a variety of profile shades [28, 114, 135]. These dyes are also known for their high solubility in water and low degradability [65]. Reactive dye is the most important class of dyes for cellulosic fibers and is also used today for protein fibers such as wool and silk [130]. The application of reactive dyes to the cellulosic fiber requires large amounts of salt like common salt (NaCl) or Glauber's salt (Na_2SO_4) to reduce the electrostatic repulsion between the anionic dye and the anionic cellulosic material [6]. These compounds are classified as azo and anthraquinone dyes based on their complex aromatic molecular structure [7]. These are the second largest classes of dyes [104, 143]. They are capable of forming a covalent bond with the amine or sulfhydryl groups of proteins in textile fibers [16].

Table 2 (continued)

 Triphenylmethane	C.I. basic green 4	C.I. 42000	2437-29-8	
 Methine	C.I.Basic Red 22	C.I.11055	12221-52-2	
 Nitro	C.I.Sulphur Blue 11	C.I.53235	1326-98-3	
	C.I.Acid Yellow 24	C.I. 10135	10142-54-8	

We can list three groups of reactive dyes: Azo, Anthraquinone, and Phthalocyanine [86].

This class of dyes were developed on the basis of direct dye; the structural difference between them is that reactive groups in reactive dye molecules form covalent bonds with cellulose fibers, which overcomes the disadvantage of the weak wet fastness of direct dye [131]. The rate of fixation is 50–70% for monofunctional reactive dyes and 70–85% for bifunctional reactive dyes, even under optimized dyeing conditions [47]. The dyeing of reactive dyes when dyeing cellulosic substrates leaves between 20 and 60% of the dyes unbound [37]. Reactive dyes left in the effluent cannot be reused as they become unreactive due to hydrolysis [68]. Reactive dyes which carry the azo group are present in wastewater from textile dyers at concentrations ranging from 5 to 1500 mg l^{-1} due to their poor attachment to fabrics (Gottlieb et al. 2003). These dyes are major threats to the environment because they have mutagenic properties and also affect the discoloration kinetics [4, 16]. Some chemical structure reactive dyes and the color index (**CI**) number are represented in Table 3 [44].

Zhang et al. [156] have synthesized five green anthraquinone reactive dyes according to Fig. 9. A new reactive azo dye containing heterofunctional reactive groups was synthesized by Siddiqua et al. [134]. The synthetic steps include condensation reaction, diazotization, and coupling. Figure 10 shows the overall reaction sequences.

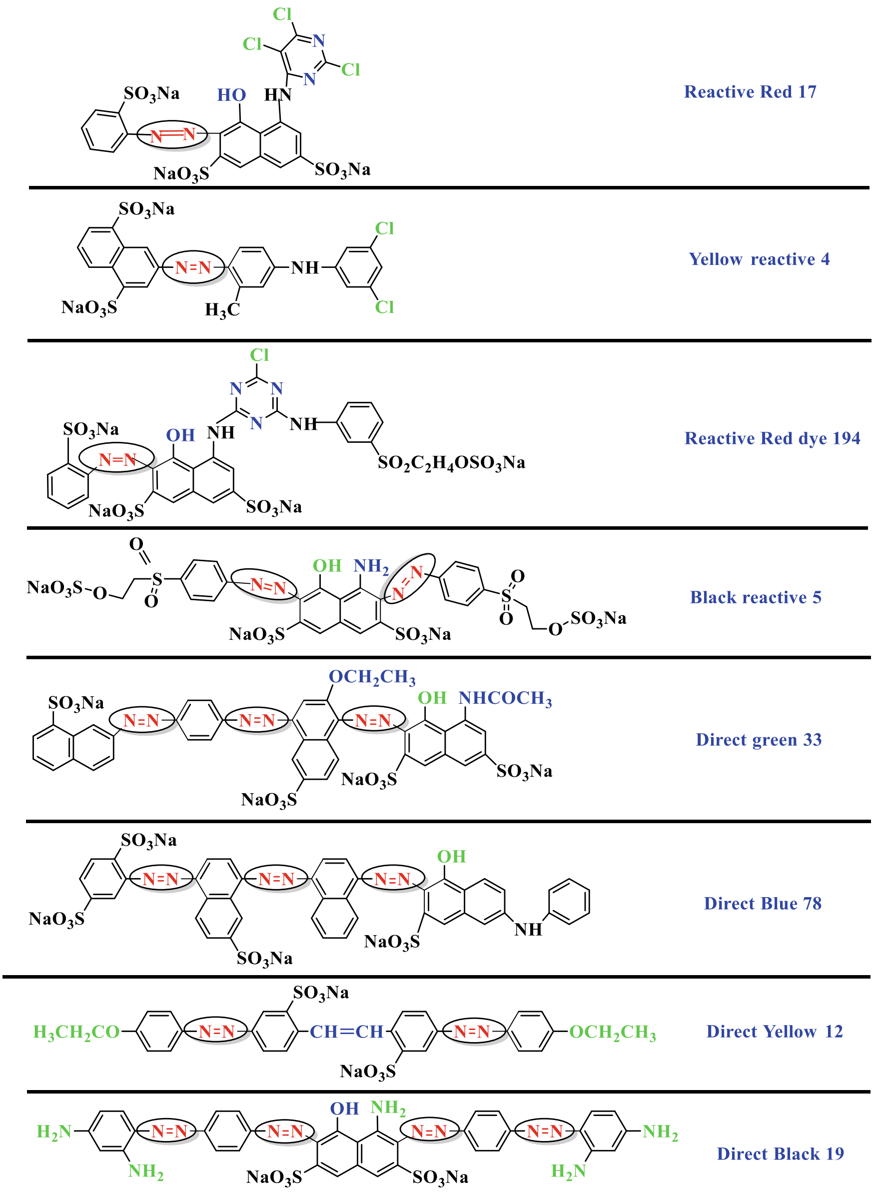


Fig. 2 Structures of some azo dyes and names (S. Benkhaya)

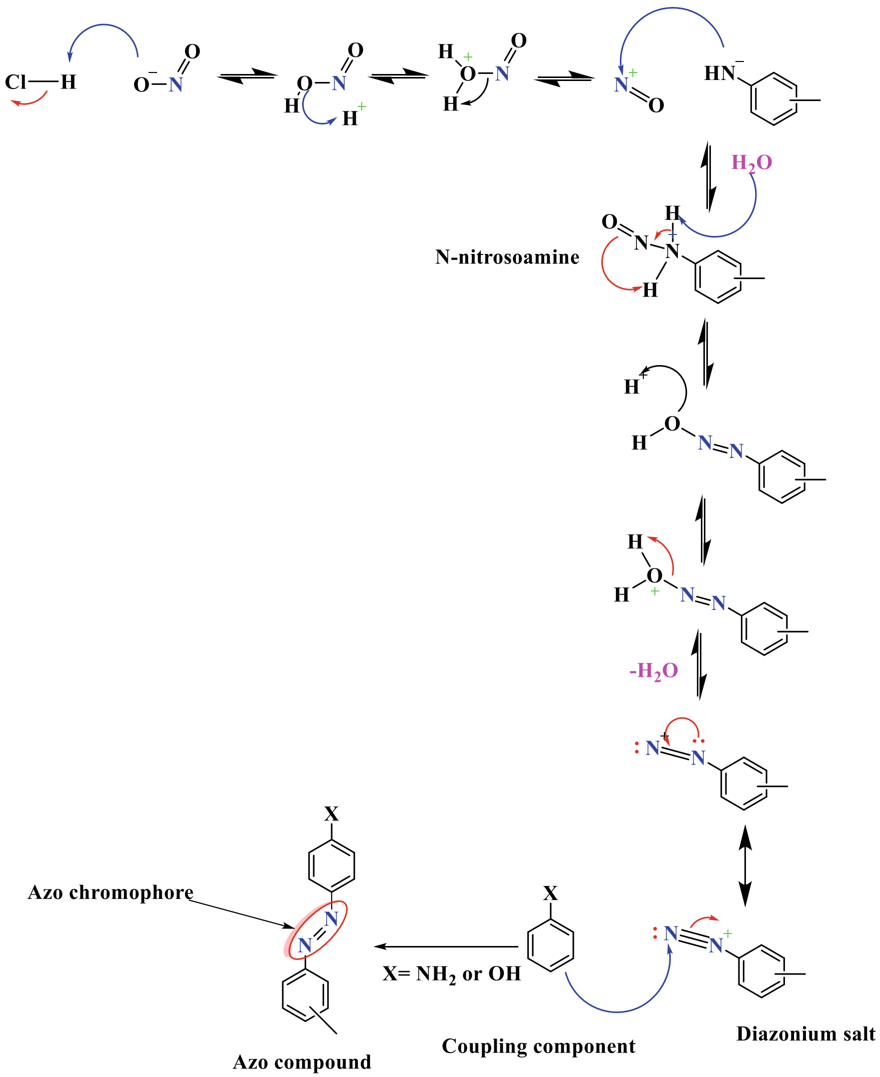


Fig. 3 Synthesis process of an azo compound (S. Benkhaya)

3.3 *Vat Dyes*

The annual consumption of vat dyes has been around 33,000 tonnes since 1992 with 15% of the total consumption of textile dyes [81, 124]. Vat dye is the most popular among dye classes used for the coloration of cotton [90]. They represent 24% of the cellulose fiber dyestuff market by value [90], and their application on nanofibers has not been investigated to date [84]. In addition, around 120,000 tonnes of vat dyes

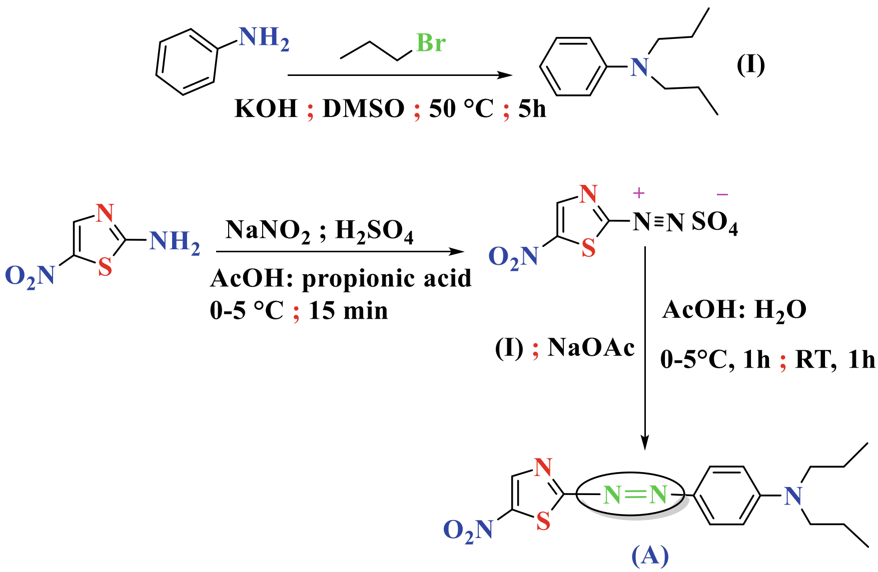


Fig. 4 Synthesis of azo dye (**A**) (S. Benkhaya)

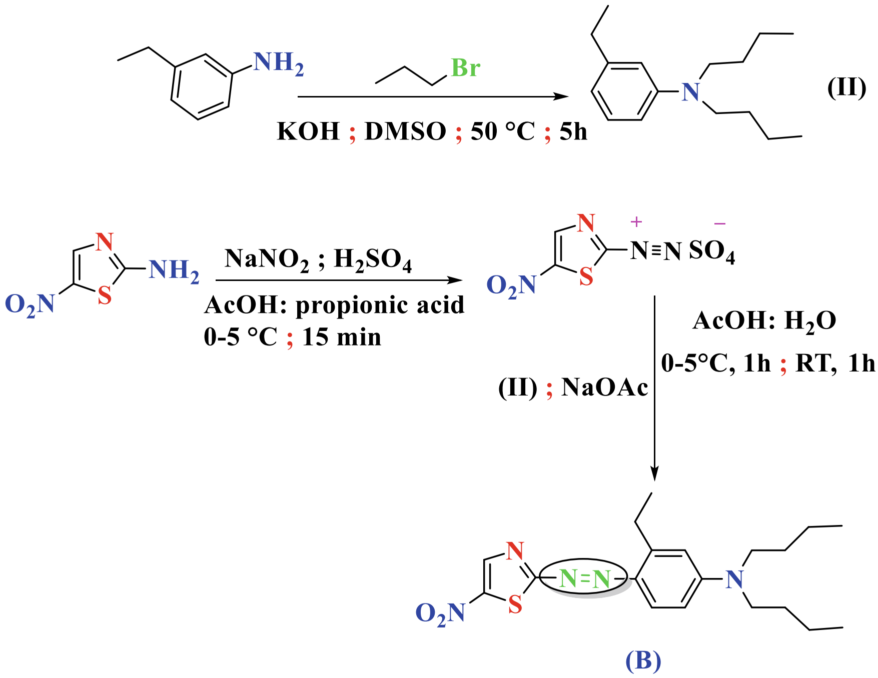


Fig. 5 Synthesis of azo dye (**B**) (S. Benkhaya)

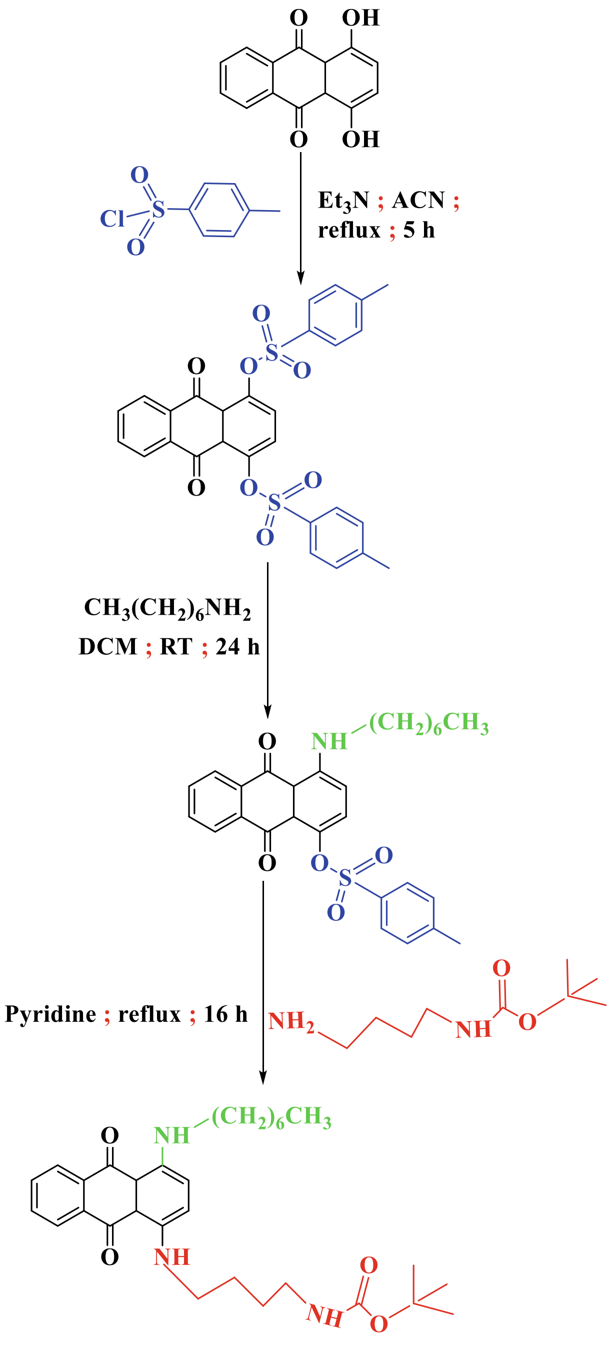


Fig. 6 Synthesis of anthraquinone dye (S. Benkhaya)

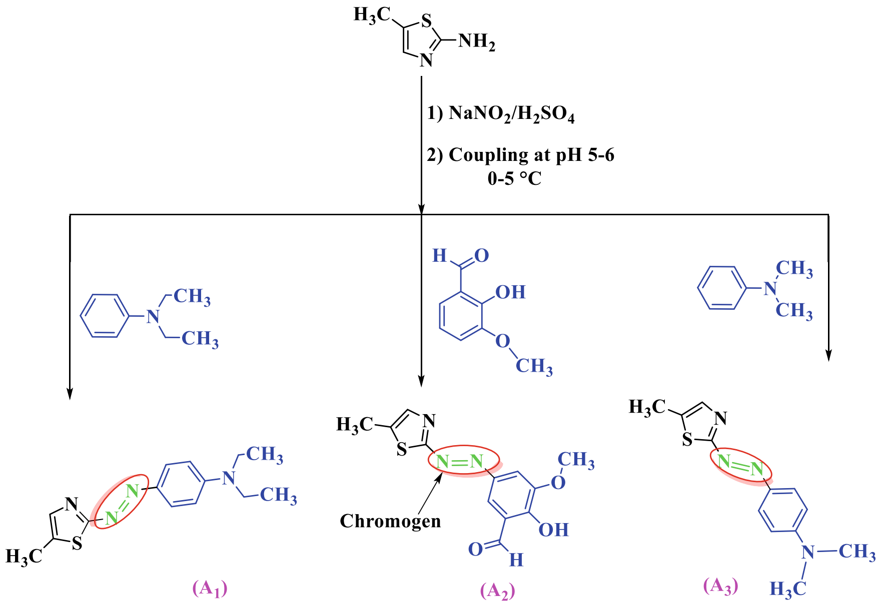


Fig. 7 Synthesis route for the preparation of azo dyes $\mathbf{A_1}$, $\mathbf{A_2}$, and $\mathbf{A_3}$ (S. Benkhaya)

are used each year [20]. Most vat dyes require a reducing agent to solubilize and are soluble only in their reduced (oxygen-free) form [8] Fig. 11 illustrates the reaction of reduction/oxidation of vat dyes. The reduced form of the vat dye exhibits affinity to cellulose fibers and thus becomes exhausted from the dye bath [12]. Vat dyes have some significant advantages over other dyes, viz., color value, reproducibility of color, fastness properties are usually better and the dyeing is easier to wash-off [35].

Table 4 shows the two most popular vat dyes in the textile industry "Vat Yellow 1 (**a**) and Vat Black 25 (**b**)" with their color index number, color, wavelength (λ_{max}), and chemical structure. Figure 12 illustrates some vat dyes [84, 70, 123]. A new vat dye (Vat Yellow 2) was synthesized according to the reaction scheme illustrated in Fig. 13 [144].

3.4 Sulfur Dyes

The first sulfur dye was prepared in 1873 by Croissant and Bretonnière [71]. Global production of these dyes has been estimated between 110,000 and 120,000 tonnes per year [109]. They play an important role in the textile dyeing industries [107]. Sulfur dyes are one of the most popular dye classes for cellulosic fibers and their blends, being widely used to produce inexpensive, medium to high depths [22]. They are widely used to produce economical black, blue, brown, and green shades on medium

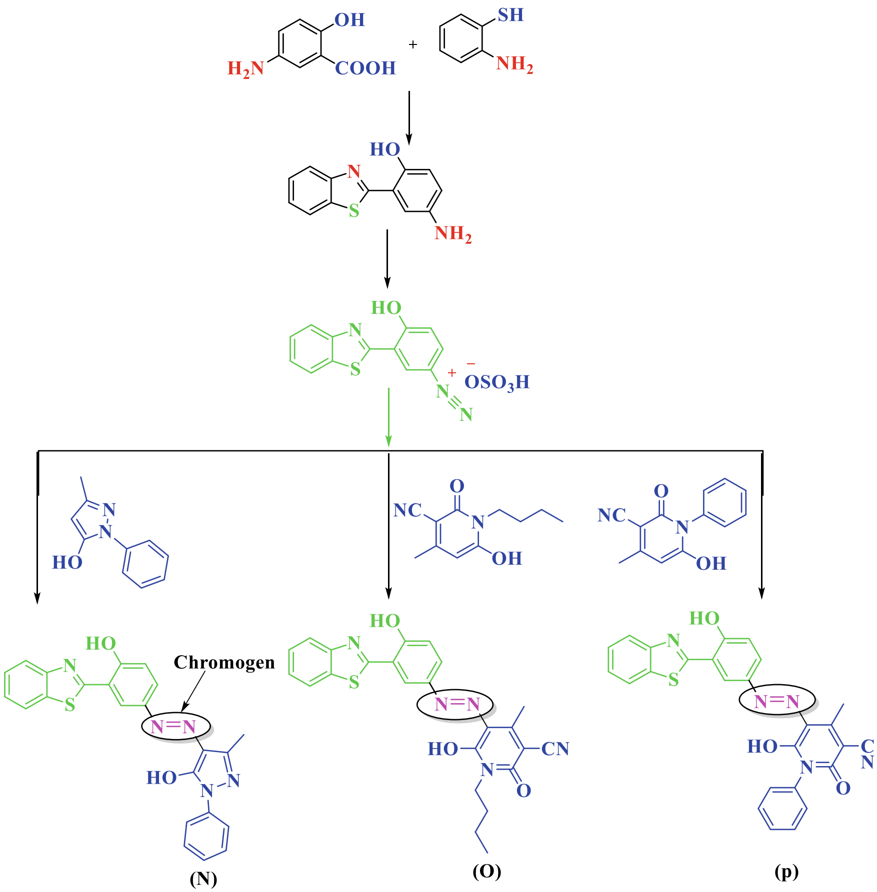
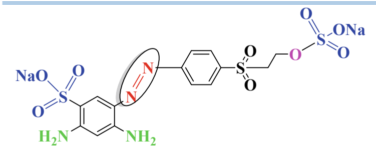
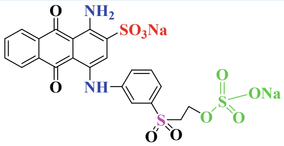
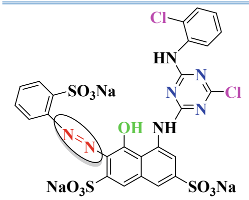
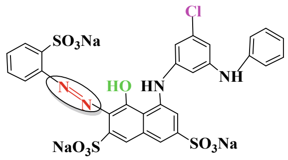
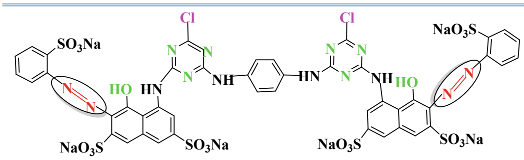
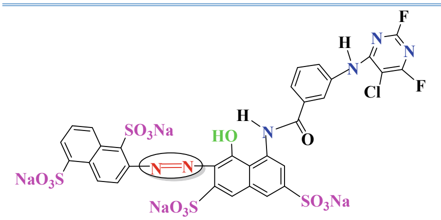


Fig. 8 Synthesis of heterocyclic azo dyes (S. Benkhaya)

to high depth cellulosic fibers [149]. Many sulfur dyes contain sulfide heterocyclics such as benzothiazole, thiazone, and thianthrene in their chemical structures [137]. Sulfurized vat dyes are produced by a sulfurization process which is used for other sulfur dyes, but are reduced with $Na_2S_2O_4$ and applied as vat dyes [34].

Stolte et al. [140] demonstrated that sulfur dyes are high molecular weight dyes obtained by the sulfurization of organic compounds. These dyes are commonly used for cellulose. The use of sulfur dyes on cellulosic fibers with sodium sulfide as an effective reducing agent is still known to be a traditional and inexpensive dyeing process [108]. Sulfur dyes on nylon 6,6 showed excellent resistance to moisture and rubbing, while lightfastness of the dyes was poor [23]. Sulfur dyes are converted to sodium-derived leuco by reduction using sodium sulfide [140]. Leuco sulfur dyes on cotton were enhanced by the application of two commercial cationic fixing agents when applied as a post-treatment using both the Pad-Dry and Pad-Flash Cure methods

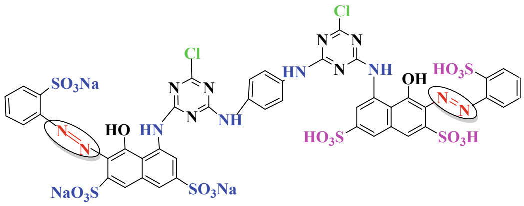
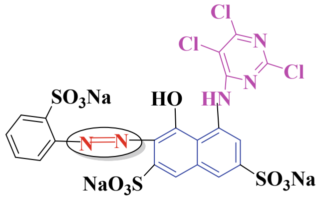
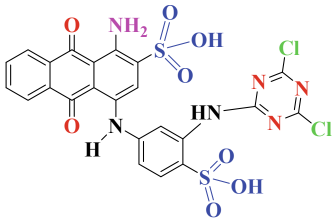
Table 3 Chemical structures of some reactive dyes (S. Benkhaya)

Chemical structure	CI no
	**ReactiveYellow 201**
	**ReactiveBlue19**
	**Reactive RR24**
	**C.I. Reactive Red 3**
	**C.I. Reactive Red 120**
	**C.I. Reactive Red 147**

(continued)

[21]. Table 5 illustrates some sulfur dyes with color index number and Cas Registry Number [41].

Table 3 (continued)

	**C.I. Reactive Red 120.**
	**C.I. Reactive Red 17**
	**Reactive Blue 4**

3.5 Acid Dyes

As the name suggests, they are "acids", and the molecule has one or more acid functions ($\mathbf{SO_3H^-}$ and **COOH**) [13]. They are anionic sulfonated dyes, and their acid nature explains their affinity for the basic functions of fibers, such as polyamides [13]. The usage of acid dyes constitutes about 30–40% of the total consumption of dyes, and they are applied extensively on nylon, cotton, wool, silk, polyamides, and leather [63, 103]. They are usually applied at acidic pH [16]. Mainly, the acid dyes are more stable in an acidic medium and hence a majority of the applications were carried out in a weakly acidic bath of pH 4.5–5 [132]. These dyes, especially sulfonic acid ones, are widely used in the textile, pharmaceutical, printing, leather, paper, and other fields, thanks to their bright colors and high solubility [153]. As a representative element of this family of dyes, mention may be made of the red congo. The acid dyes were divided into three groups because according to their application properties and variable strength, (i) the first group has little affinity under neutral or weakly acidic conditions, (ii) the second group of dyes escapes on the nylon in the pH range from 3.0 to 5.0, and (iii) the third group has a strong affinity for nylon under neutral or weakly acidic conditions (pH 5.0–7.0) [38]. Examples of these dyes are shown in Fig. 14 [43]. Sun et al. [141] have synthesized some surfactant-type acid dyes. The

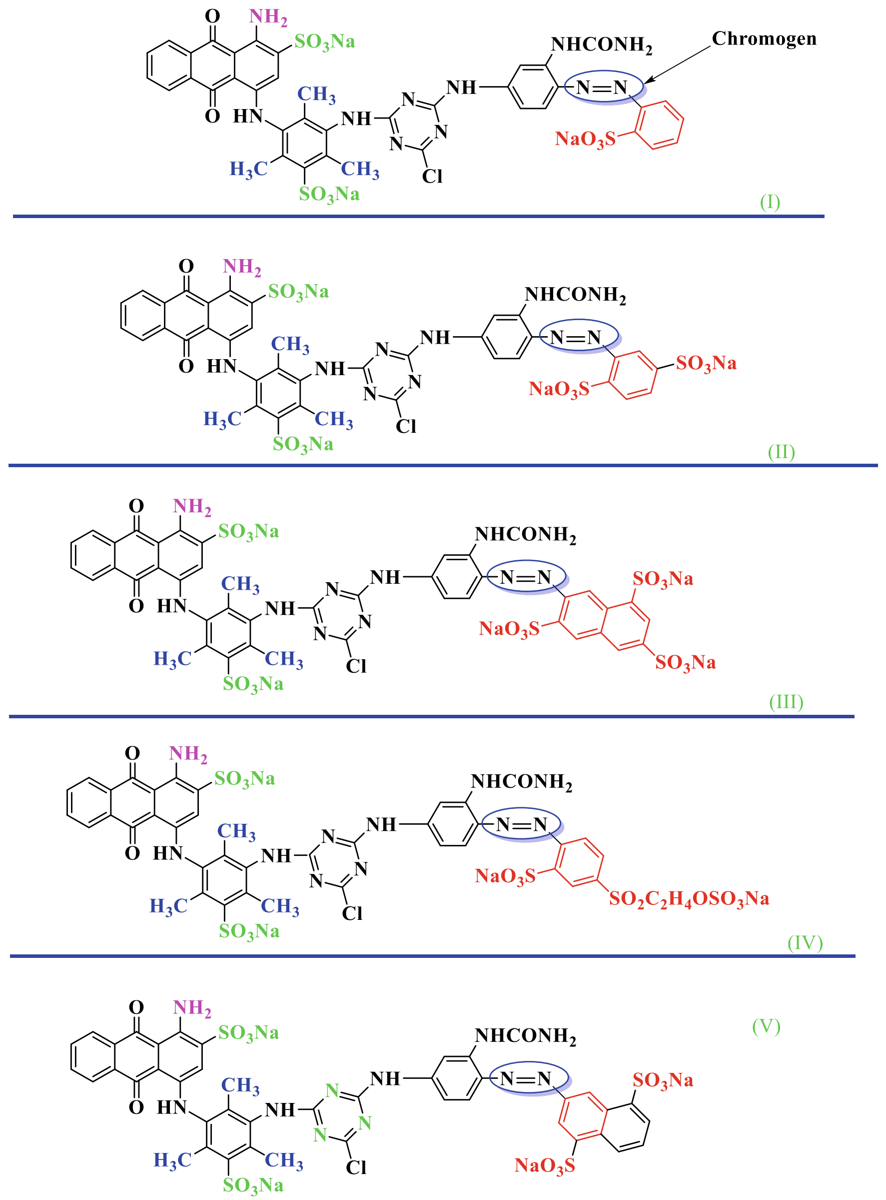


Fig. 9 Green anthraquinone reactive dyes (I–V) (S. Benkhaya)

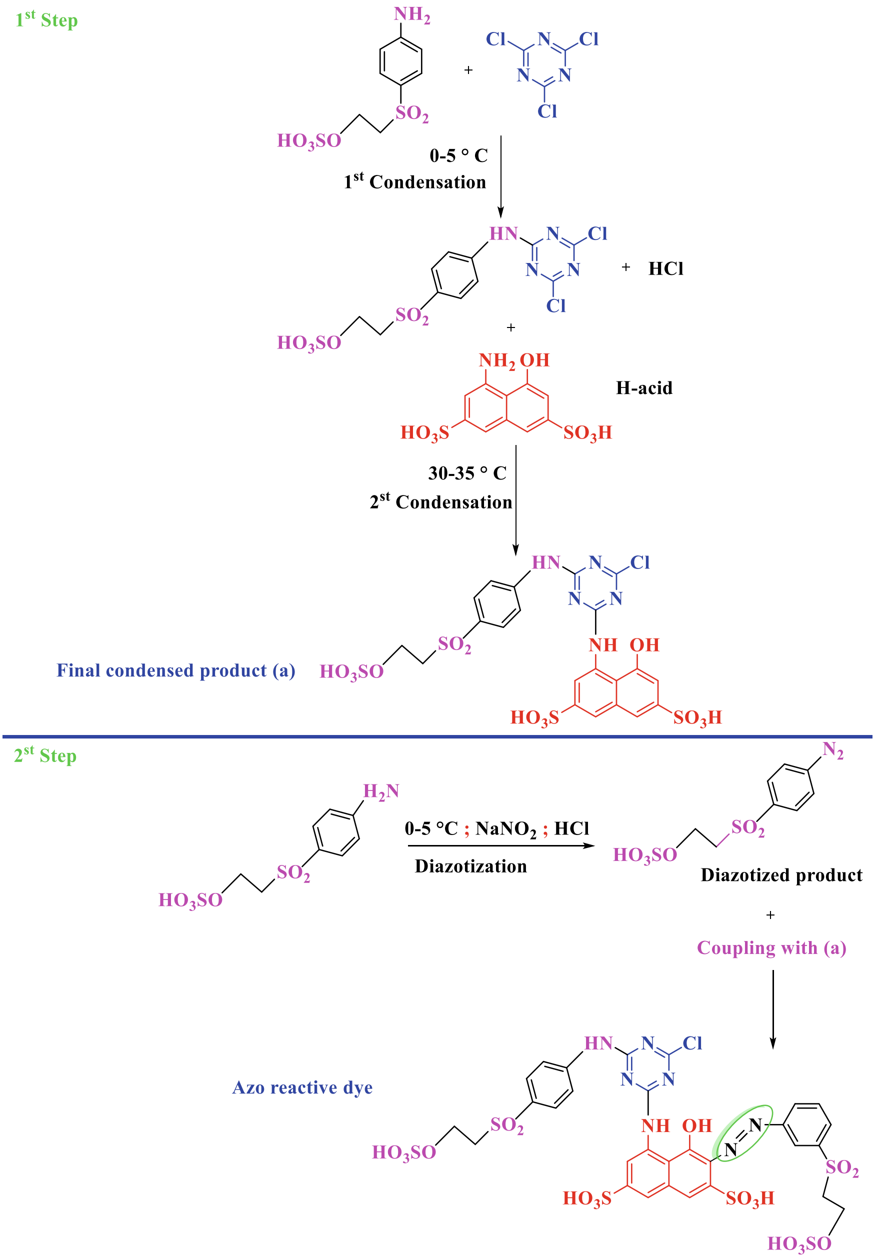


Fig. 10 Synthesis scheme of azo reactive dye (S. Benkhaya)

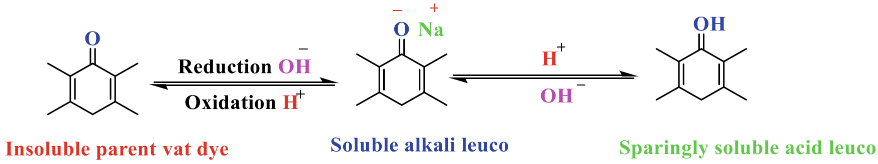
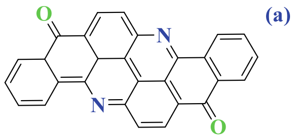
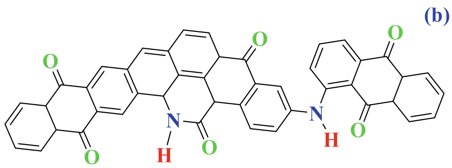


Fig. 11 Reduction/oxidation of vat dyes (S. Benkhaya)

Table 4 Physico-chemical characteristics of Vat Yellow 1 (**a**) and Vat Black 25 (**b**) (S. Benkhaya)

Color index no.	Color	(λ_{max})	Chemical structure
70600	Yellow	587	
69525	Darkblue	675	

synthesis route is described in Fig. 15. Figures 16 and 17 show different possible acid dye structures according to (**n**).

3.6 Disperse Dyes

Disperse dyes are for their part the most common type of dyes, and their total production was around 366,500 tonnes. They are synthetic dyes and are applied to hydrophobic fibers from an aqueous dispersion. Disperse dyes are among the persisting class of dyes due to their recalcitrant nature and non-biodegradable behavior [78]. They represent around 44% of the total dye production [117, 157]. These dyes are frequently insoluble or poorly soluble in water, and are non-ionic in character [40]. Disperse dyes are colored, non-ionic aromatic compounds that commonly contain azo and nitro groups, and are widely used for dyeing synthetic fibers [53].

Among disperse dyes, azo disperse dyes have attracted particular attention and they have been widely applied for dyeing natural and synthetic fibers [92]. Heterocyclic azo dyes are as disperse azo dyes which exhibit good tinctorial strength, large molar extinction, and brighter dyeing than those obtained from aniline-based intermediates [105].

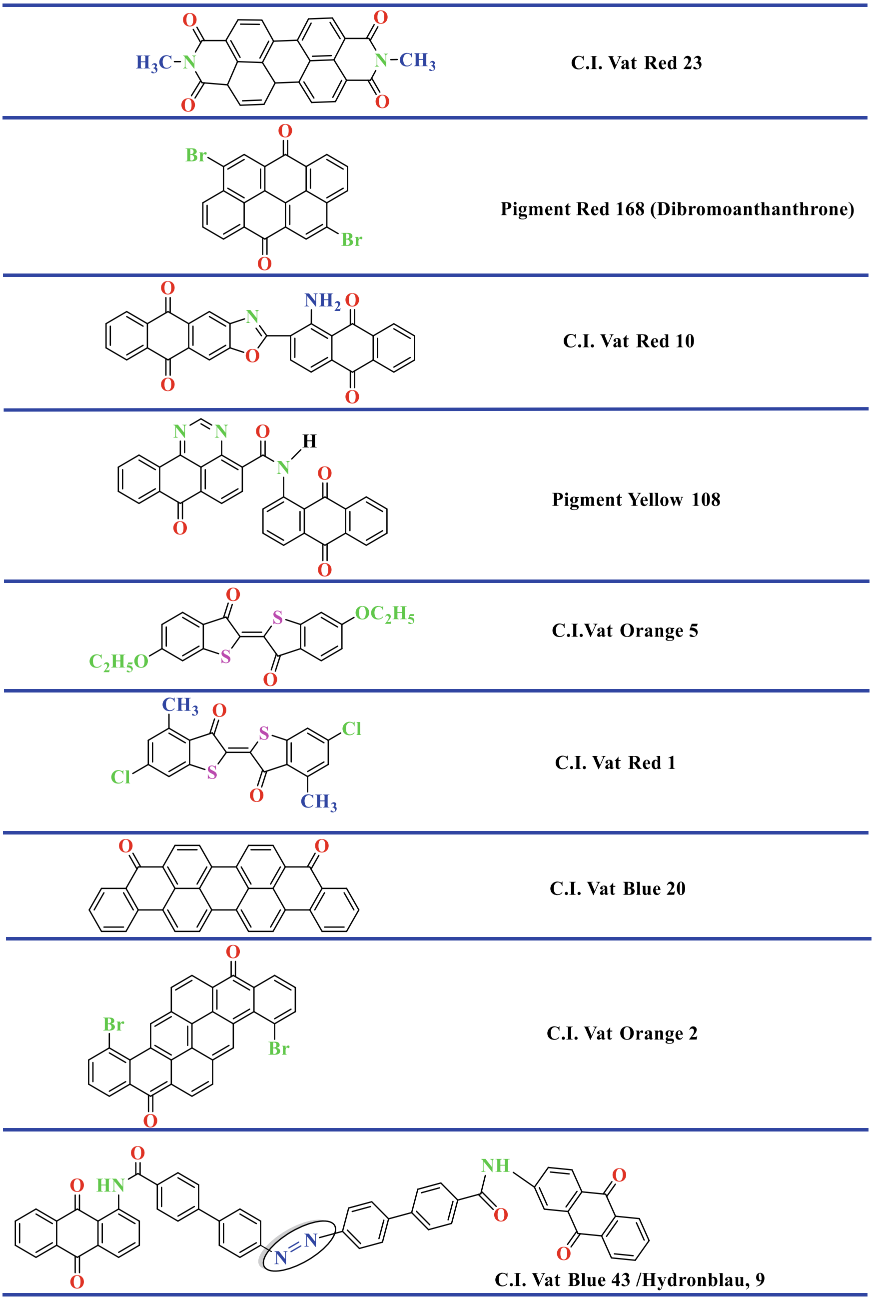


Fig. 12 Some examples of vat dyes (S. Benkhaya)

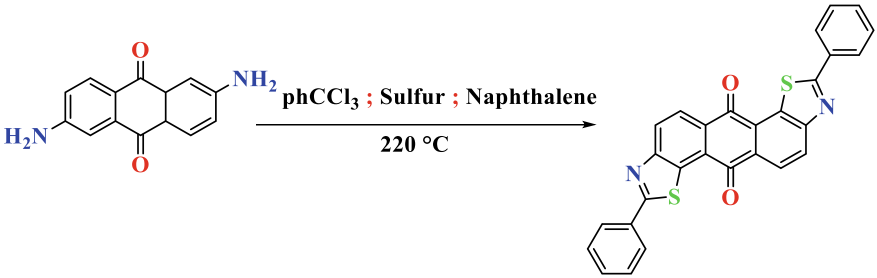
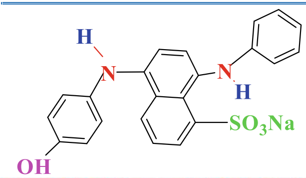
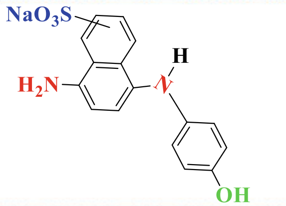
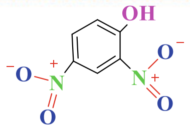
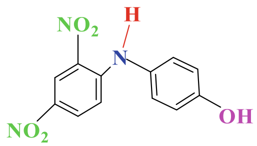


Fig. 13 Synthesis of Vat Yellow 2 (S. Benkhaya)

Table 5 Chemical structures of some sulfur dyes (S. Benkhaya)

Chemical structure	Color Index no	CAS Registry Number
	CI 53570	12262-33-8
	C.I.53540	1327-69-1
	C.I 53185	1326-82-5
	CI 53235	1326-98-3

In addition, aryl hydrazone dyes were used as efficient disperse dyes for high-temperature polyester dyeing which shows a high affinity with high color strength [10]. For polyester dyeing with disperse dyes, less water cleaner dyeing without additives is always the best and desired goal for researchers [55]. In the dyeing polyester with these dyes, ultrasonication decreased the size of dye particles [69]. Typical disperse dye structures are illustrated in Fig. 18. Phthalimide disperse dyes

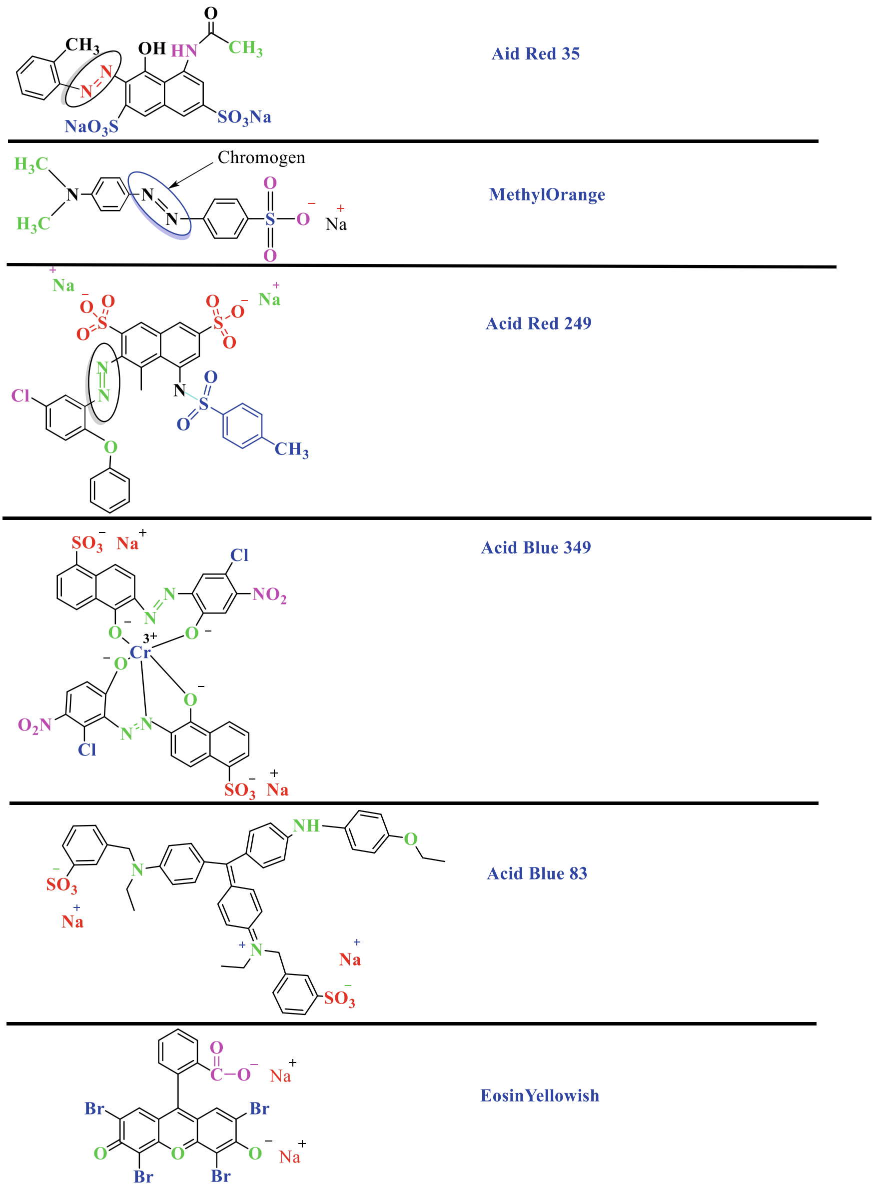


Fig. 14 Examples of the acid dyes (S. Benkhaya)

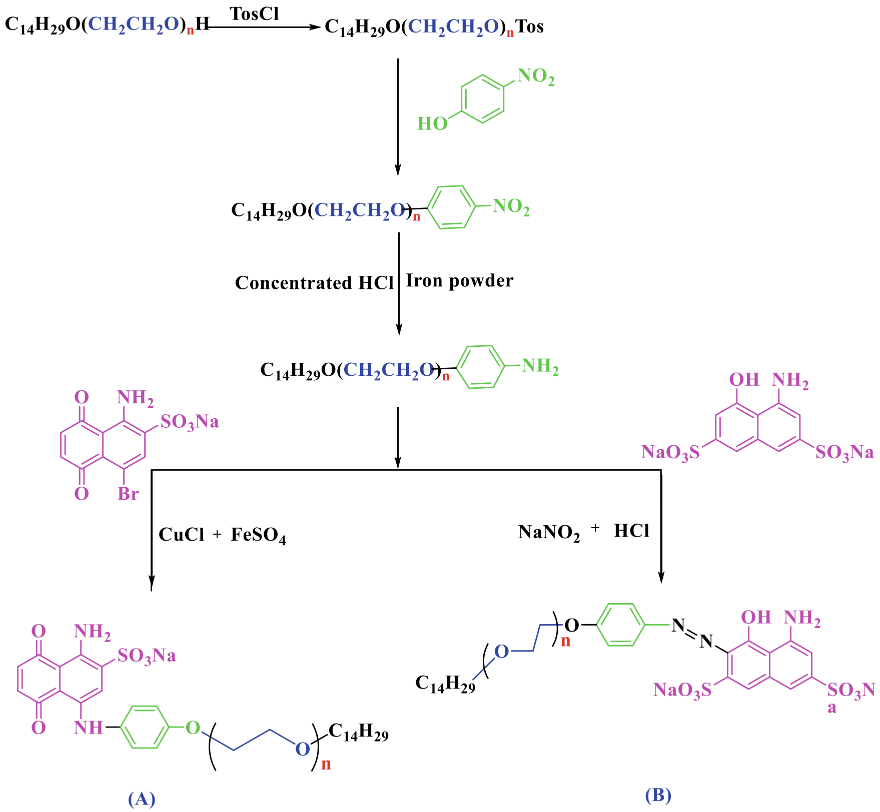


Fig. 15 The synthesis of acid dyes (**A**) and (**B**) (S. Benkhaya)

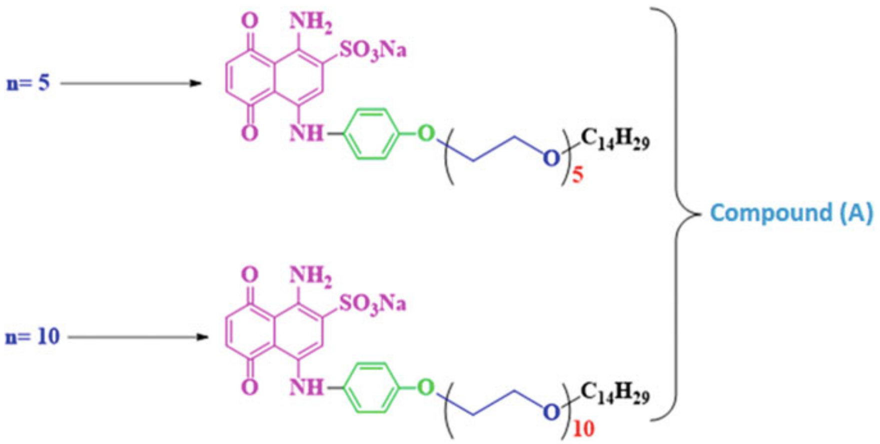


Fig. 16 Structure of compound (**A**) according to (**n**) (S. Benkhaya)

Fig. 17 Structure of compound (**B**) according to (**n**) (S. Benkhaya)

(Dye **1**, Dye **2**, and Dye **3**) were synthesized by Yizhen et al. [155] according to Figs. 19 and 20.

Karci and Bakan [80] have synthesized diazo pyrazole disperse dyes (Dye **4** and Dye **5)** from 5-amino-4-arylazo-3-methyl-1-phenylpyrazoles (aminoarylazopyrazoles), according to the reaction scheme shown in Fig. 21. Figure 22 shows different structures of Dye 4 and Dye 5 according to X substitution.

Maliyappa et al. synthesized a novel substituted aniline-based heterocyclic dispersed azo dyes coupling with 5-methyl-2-(6-methyl-1, 3-benzothiazol-2-yl)-2, 4-dihydro-3H-pyrazol-3-one [99]. The schematic representation of the synthesized dispersed azo molecules (Dye **6**) is shown in Fig. 23. Figure 24 shows different possible dispersed dye structures (Dye **7**) according to R_1 and R_2 substitutions.

Maliyappa et al. [98] have synthesized some new dispersed azo dyes. The general route for the synthesis of 6-substituted benzothiazole-based disperse azo dyes (Dye **8**) is described in Fig. 25. Figure 26 shows different possible structures (Dye **9**) according to R substitution.

3.7 Basic Dyes

Basic dyes are typically hydrochloride salts, so the formation of cations by loss of $Cl^-$is reasonable [138]. They include monoazoic, diazoic, and azine compounds [110]. Basic dyes have high brilliance and intensity of colors and are highly visible even in a very low concentration [73]. They are commercially available as chlorides and other water-soluble salts, and, on the other hand, they were treated with tannin or antimony potassium tartrate to yield insoluble colorants, i.e. pigments [128]. Cationic dyes commonly known as basic dyes are widely used in acrylic, nylon, silk, and wool dyeing [45, 146]. Basic dyes are used without adding any salt during the dying process [102]. They are easily decomposed when irradiated with light due to their poor photo-stability, owing to which their color intensity reduces and might even result in a color change [152]. Some basic dyes with their chemical structures and Color Index Generic Name are shown in Fig. 27 [14, 61, 95, 102, 126, 45].

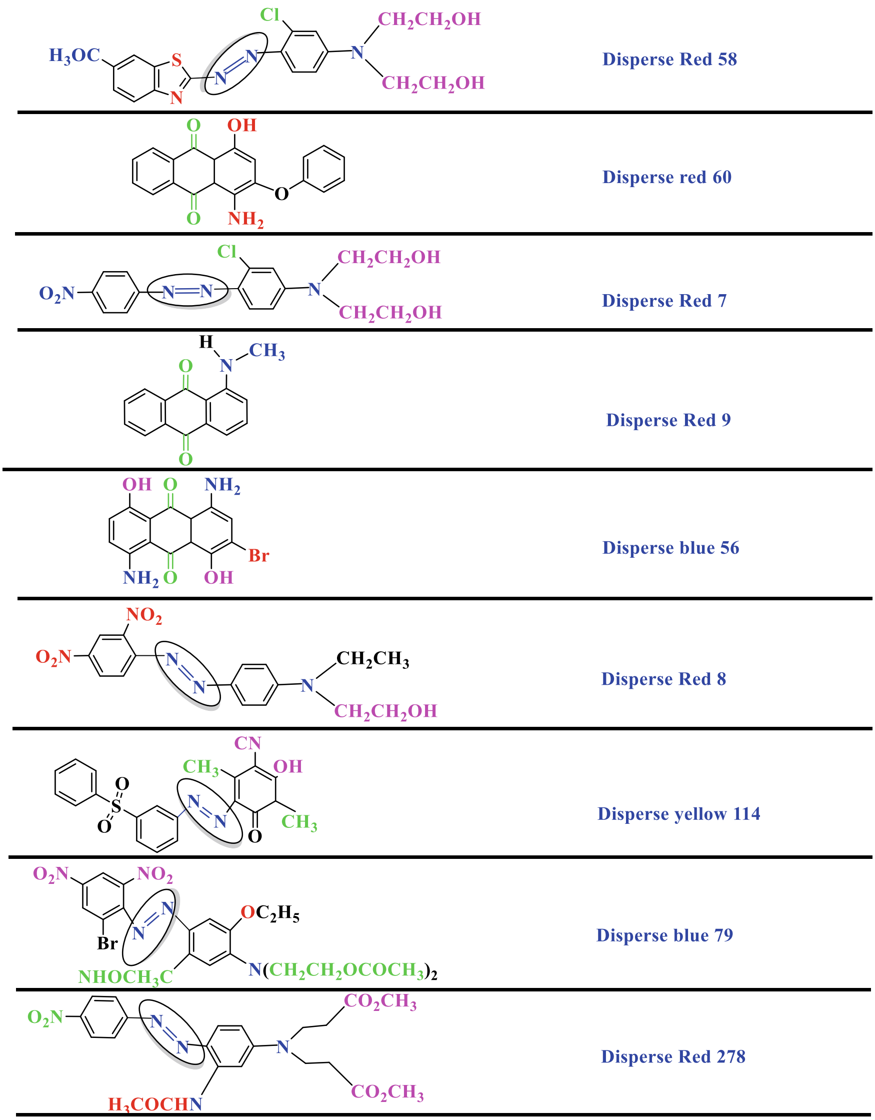


Fig. 18 Chemical structures of some disperse dyes (S. Benkhaya)

3.8 Direct Dyes

Direct dyes are water-soluble and anionic in nature. They are widely used in dying industries due to their easy application and economic factors [57]. The usage of direct dyes increased from 53,848 tonnes in 1992 to 181,998 tonnes in 2011 (237.98%) [58].

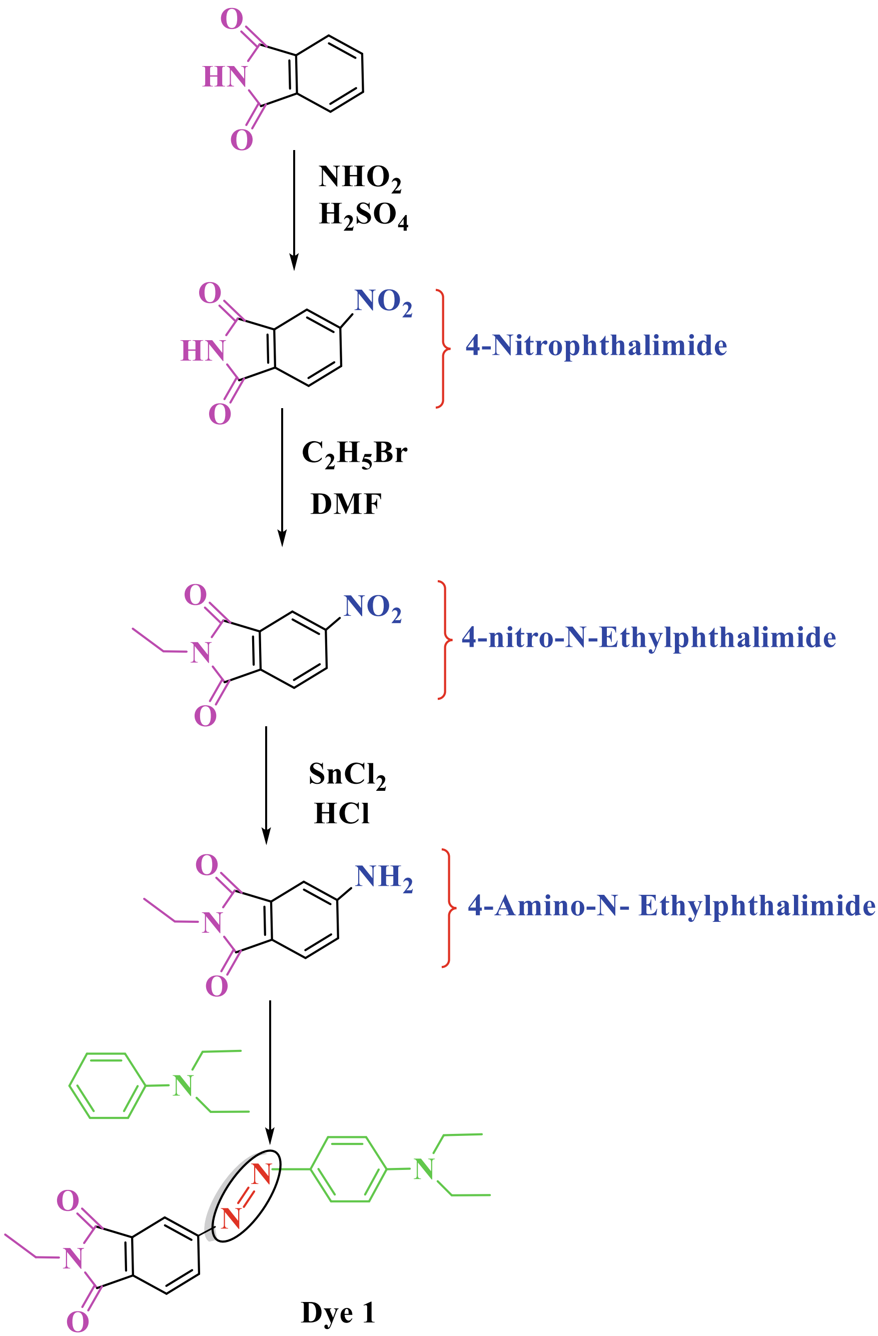


Fig. 19 Synthesis of dispersed azo dyes (Dye **1**) (S. Benkhaya)

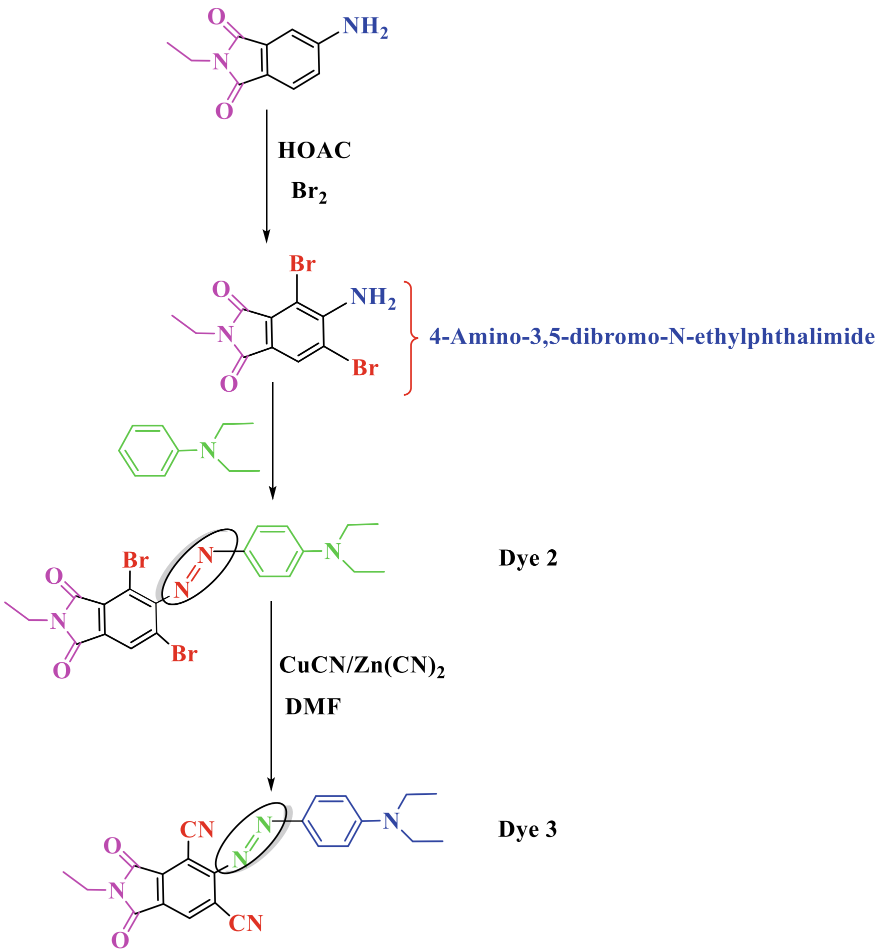


Fig. 20 Synthesis of disperse dyes (Dye **2** and Dye **3**) (S. Benkhaya)

They are structurally very similar to reactive dyes, in that both dye types are essentially long, planar, anionic molecules solubilized by one or more ionized sulfonate groups [26, p. 8].

In addition, they are classified according to many parameters such as the chromophore, the properties of solidity or the characteristics of application [91, 97]. The main types of chromophores are azo, phthalocyanine, dioxazine, and other smaller chemical classes such as formazan, anthraquinone, quinolone, and thiazole. Although these dyes are easy to apply and have a wide range of shades, their resistance to washing is only moderate; this has led to their replacement by reactive dyes which have much higher resistance to humidity and washing properties on cellulosic substrates. Figures 28 and 29 showed some structures of direct dyes [9, 24, 25, 67,

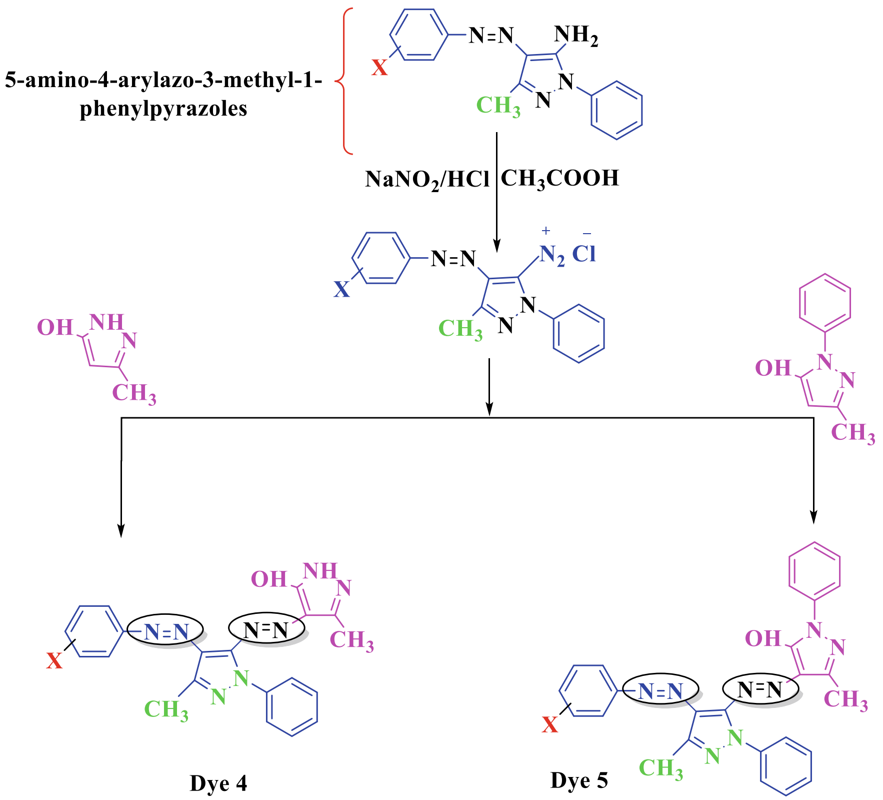


Fig. 21 Synthesis of disperse diazo pyrazole dyes (Dye **4** and Dye **5**) (S. Benkhaya)

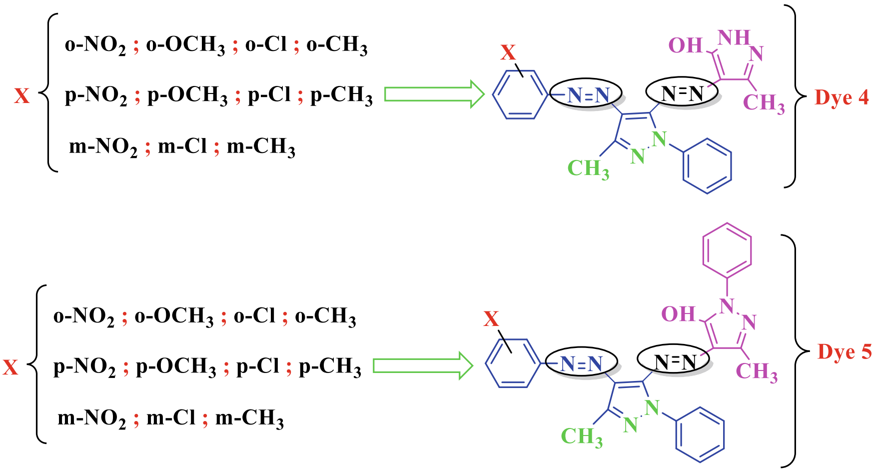


Fig. 22 Structure of disperse diazo pyrazole dyes Dye **4** and Dye **5** according to X substitution (S. Benkhaya)

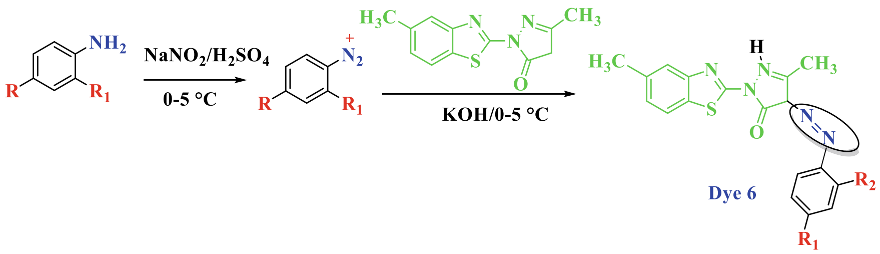


Fig. 23 Synthesis route for the dispersed azo dyes (Dye **6**) (S. Benkhaya)

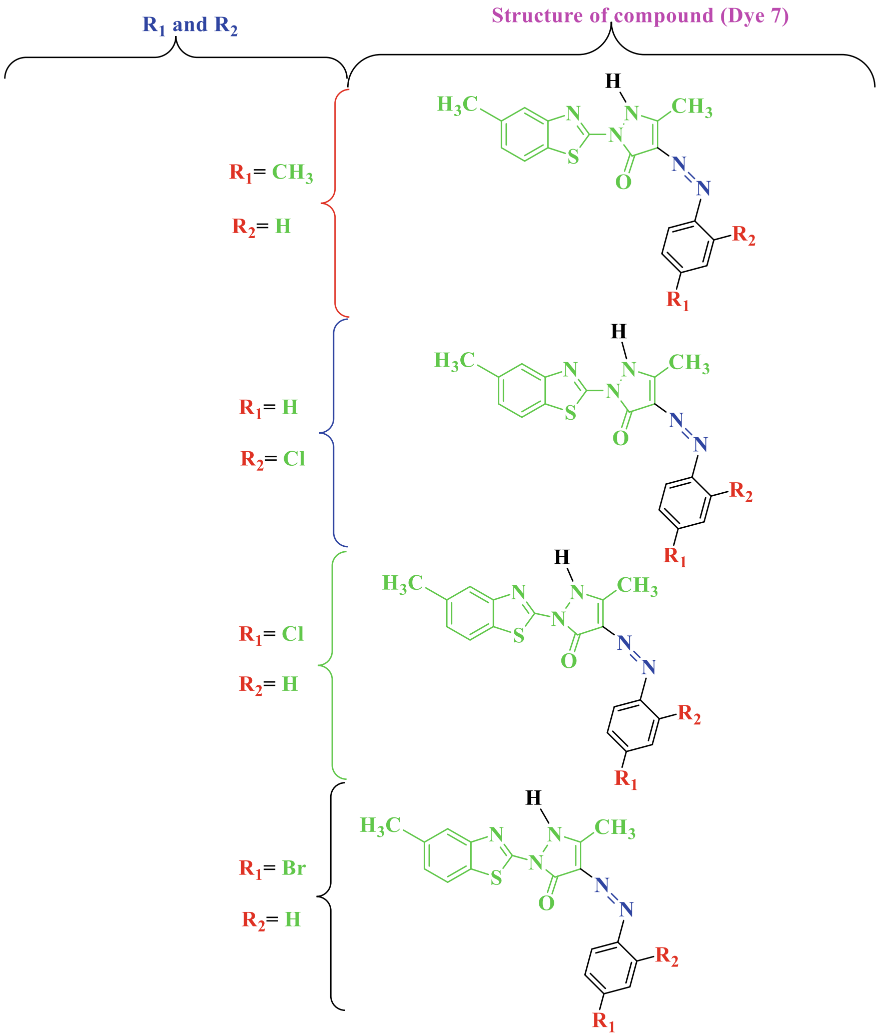


Fig. 24 Different structures of dispersed dyes (Dye **7**) (S. Benkhaya)

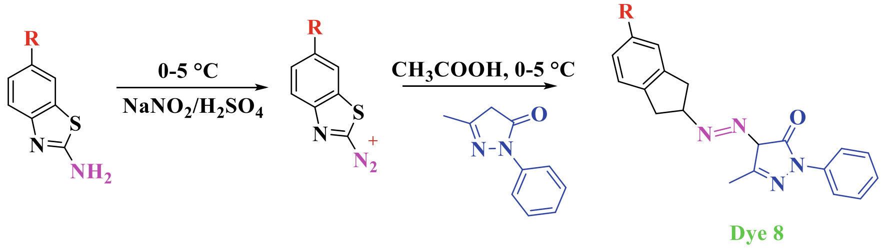


Fig. 25 The synthetic pathway of disperse azo dyes (Dye **8**) (S. Benkhaya)

106, 119]. Table 6 groups the classification of textile dyes according to their various application methods and their characteristics [15].

4 Dyes and Color Index Numbers

In the Color Index, each dye or pigment is presented with two numbers referring to the basis of the coloristic and chemical classification [160]. Color Index Name and Color Index Constitution Number have been developed for identifying the dyes [16, 127, 145]. So, the most important reference work dealing with the classification of dyes and organic/inorganic pigments (Fig. 30) [64] is the Color Index, Fig. 31 [16, 39]. It provides useful information for each dye and pigment on the methods of application and on the range of fastness properties that may be expected [39]. Reactive Red 6, which is a member of mono azo dyes, has been given as a representative example to illustrate the color index classification, Fig. 32.

5 Pollution and Environmental Effects

The textile industry produces large quantities of strongly colored wastewater with a high load of inorganic salts, dyes, pigments, chemical products, heavy metals (Pb, Cr, Ar), etc. [88, 94]. It is estimated that approximately 3,106 L of wastewater is produced after the treatment of approximately 20,000 kg of textiles per day [118]. The toxicity of liquid textile waste can come from either the metallic part of the dye molecule, such as chromium in acid dyes or copper in direct dyes, or other materials used in the process of tincture, such as traces of mercury present in various chemical reagents [112]. Heavy metal contents of less than 100 mg/l have been reported in the case of non-metallic dyes. In the case of metallic dyes and metallic salt dyes, the reported metal levels are considerably higher [72]. About 72 toxic chemicals have been identified in textile effluents, and it is estimated that approximately 200 million liters of effluents are produced annually worldwide by the textile industry

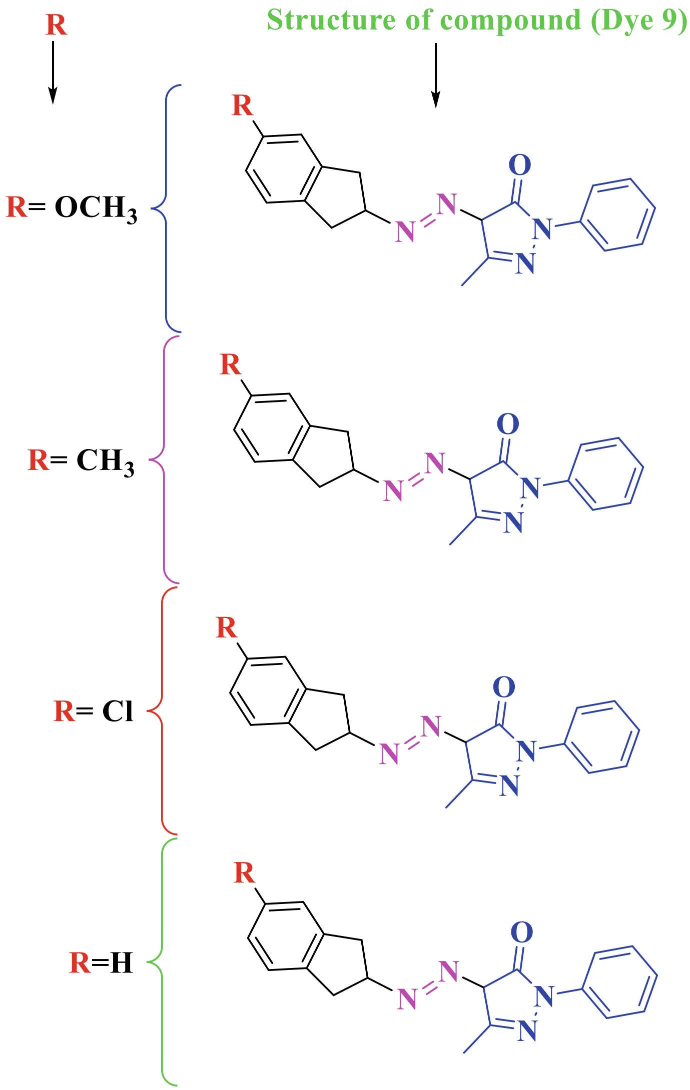


Fig. 26 Different structures of disperse azo dyes (Dye **9**) (S. Benkhaya)

[56]. More about 40% of textile dyes contain organically bound chlorine, which is a known carcinogen [60, 79, 83].

It has been reported that approximately 100 tons/year of dyes are rejected into the aquatic environment with a consumption of greater than 104 tons/year coming mainly from the textile industry [18]. During the dyeing process, not all dyes are attached to the fabrics. There is always a part of the unfixed dye which is washed away with water and which constitutes the main pollutant in textile effluents. The

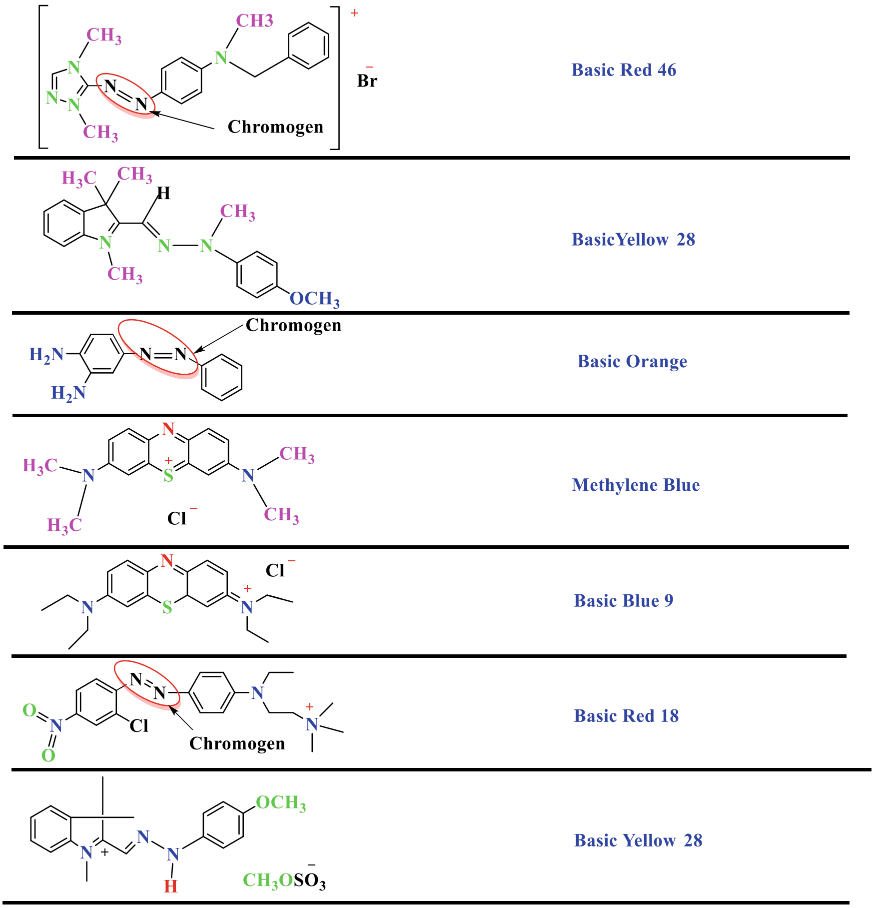


Fig. 27 Some chemical structures of basic dyes (S. Benkhaya)

reactive dye is a non-fixed water-soluble dye applied to cotton fabrics, and it spills 50–90% into the textile effluent [2]. Azo dyes have complex structures and show high resistance toward natural, biological, and physical degradation [154]. Most of the dyes are non-biodegradable and toxic, and they hinder light transmittance, which disturbs the ecosystem cycle, and dye-removal water treatment becomes more critical [100].

These dyes have harmful effects on the environment as well as on human health. Some dyes are toxic and/or carcinogenic, and the biodegradation of many dyes yields aromatic amines, which may be carcinogenic or otherwise toxic [82]. In aquatic environments, dyes affect photosynthetic activities by preventing the penetration of oxygen and light [49]. Despite this, most textile wastewater is characterized by high values of physico-chemical and biological parameters (temperature, salinity, pH, biological oxygen demand, chemical oxygen demand, biotoxicity, a large amount

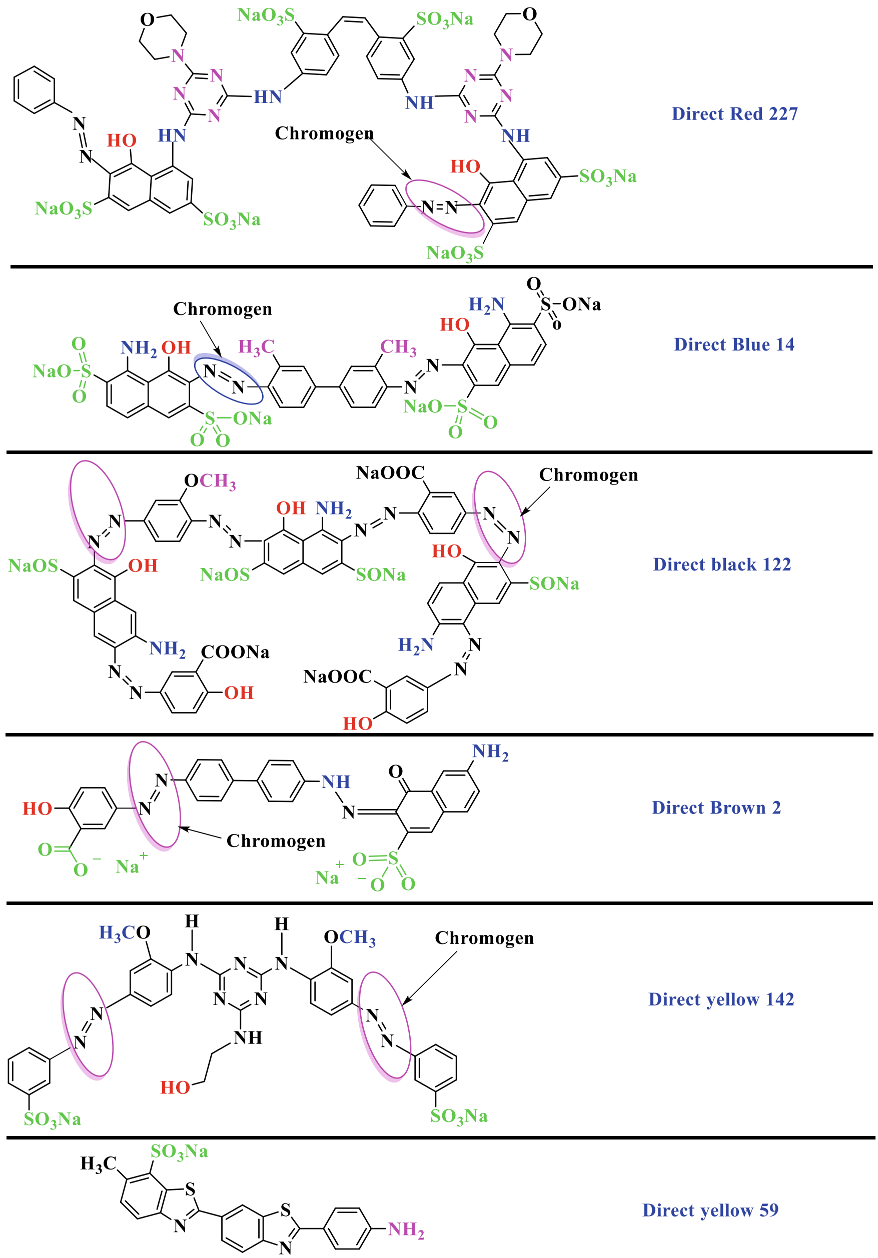


Fig. 28 Some chemical structures of direct dyes (S. Benkhaya)

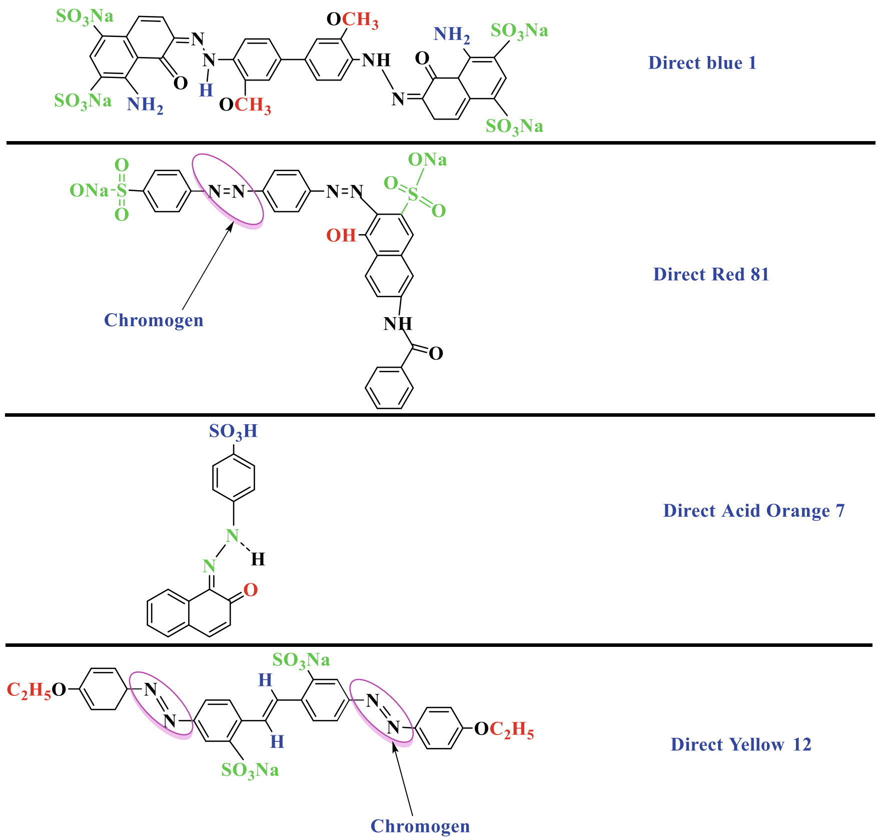


Fig. 29 Some chemical structures of direct dyes (S. Benkhaya)

of suspended solids, etc.) [102]. In addition, textile wastewater is characterized by high values of physico-chemical and biological parameters (temperature, salinity, pH, biological oxygen demand, and chemical oxygen demand) [50]. There are also organometallic compounds [42] which have harmful effects on the aquatic flora and fauna and, consequently, on the environment and humans in particular [48, 54]. In addition, colored water causes a scarcity of light essential to the development of aquatic organisms. Some studies have shown that certain dyes and surfactants can lead to the inhibition of biological systems and be toxic to fish [122].

Until now, a wide range of biological and physico-chemical techniques such as membrane filtration processes, ozonation, coagulation/flocculation, adsorption, and electrochemical oxidation have been used to remove dyes from their substances. Waste effluents [113]. Obviously, each of these techniques has its own advantages and limitations, and therefore, the implementation of an appropriate method is a decision-maker's choice based on cost–benefit analysis. Among the different water

Table 6 Classification of textile dyes [16, 74, 75, 125] (S. Benkhaya)

Dye class and examples	General description	Chemical structure	Properties and fixation degree (%)	Applications and loss in effluent (%)
Acid: – Acid blue 25 – Acid red 57 – Methyl orange	The degree of colorfastness for the size of the dye molecule [148]	Anthraquinone, nitroso, azine, azo, xanthene, nitro, and triphenylmethane	– Anionic, water soluble – 80–95% (Polyamide)	– Polyamide 70–75%, wool 25 to 30%, silk, wool, paper, nylon, inks, leather, inkjet printing and cosmetics, etc. [36] – 5–20% (Polyamide)
Reactive: – Reactive black 5 – Reactive yellow 2	Fixing of the reactive dye requiring a temperature above 60 °C	Anthraquinone, phthalocyanine, azo, oxazine, formazan, and basic	– Anionic, water soluble – 50–90% (Cellulose)	– Use of reactive dyes mainly in the dyeing and printing of cotton fibers – 10–50% (Cellulose)
Direct: – Direct orange 34 – Direct violet – Direct black	Relatively inexpensive direct dyes, available in a full range of shades but with a high color gloss [30, 31]	Phthalocyanine, azo, nitro, benzodifuranone, and stilbene	– Anionic, water soluble – 70–95% (Cellulose)	– Cellulose fibers, cotton, viscose, paper, leather, polyamide, silk, wool, and rayon – 5–30% (Cellulose)
Basic: – Basic brown – Basic yellow 28 – Basic red 9	The cheapest basic dyes [32]	Anthraquinone, azo, hemicyanine, cyanine, oxazine, azine, triarylmethane, acridine, diazahemicyanine and xanthene	– Cationic, water soluble – 95–100 (Acrylic)	– Synthetic fibers, wool, paper, polyester inks, leather, and acrylic – 0–5% (Acrylic)
Vat: – Green 6 – Vat blue – Indigo	Vat dyes are known for better colorfastness and their application to nanofibers [84]	Indigoids and anthraquinone (including polycyclic quinones)	Colloidal, insoluble	They have an affinity for cellulose, cotton, rayon viscose, and wool
Sulfur: – Sulfur black – Sulfur blue dye – Phthalic anhydride	Sulfur dyes have no well-defined chemical structures [33, 36]	Indeterminate structures	Colloidal, insoluble	Sulfur dyes are inexpensive and are used mainly for dyeing cellulosic textile materials or mixtures of cellulose fibers and rarely silk [36, 109]

(continued)

Table 6 (continued)

Dye class and examples	General description	Chemical structure	Properties and fixation degree (%)	Applications and loss in effluent (%)
Disperse: – Disperse red – Disperse yellow – Disperse orange – Disperse blue	Dispersed dyes are poorly water-soluble compounds, they disperse in water because their commercial formulations contain surfactants necessary for the dyeing process [147]	Anthraquinone, azo, benzodifuranone, and nitro	– Very low water solubility – 90–100% (Polyester)	– Polyester, polyamide, plastic, acetate, nylon, and acrylic – 0–10% (Polyester)

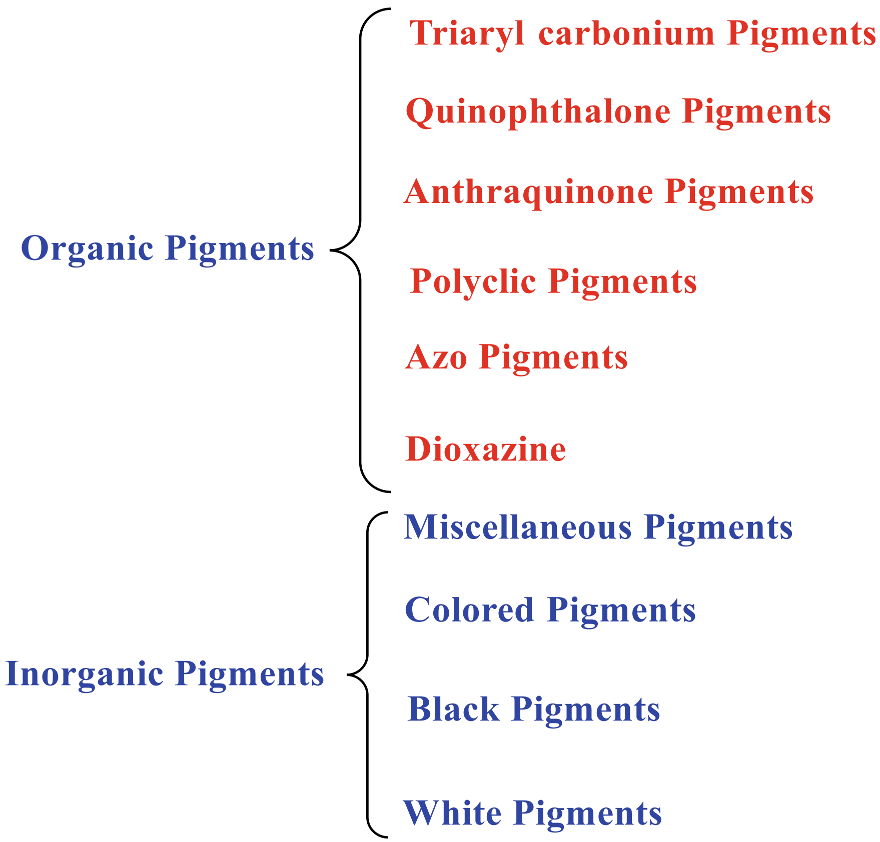


Fig. 30 Classification of organic and inorganic pigments (S. Benkhaya)

purification techniques available, membrane technology has received a lot of attention and it is one of the innovative ideas of water treatment, due to its energy saving, its moderate capital and maintenance expenditure, high efficiency, and ease of use [76]. Ultrafiltration (UF) is a pressure-driven membrane separation process that separates on the basis of molecular diameter. It is a quick and easily applicable method for fractionation and concentration steps in pure water production and water and wastewater treatment [52]. Figure 33 presents a summary of the toxics used in various processes in the textile and dye industries, different classes of textile dyes and their health effects, and sources of metals in textile effluents and dyes and base metals found in different classes of dyes).

Chemical structure	Range
Nitroso	10000-10299
Nitro	10300-10999
Monozo	11000-19999
Disazo	20000-29999
Trisazo	30000-34999
Polyazo	35000-36999
Azoic	37000-39999
Stilbene	40000-40799
Carotenoid	40800-40999
Diphenylmethane	41000-41999
Triarylmethane	42000-44999
Xanthene	45000-45999
Acridine	46000-46999
Quinioline	47000-47999
Methine	48000-48999

Chemical structure	Range
Thiazole	49000-49399
Indamine	49400-49699
Indophenol	49700-49999
Azine	50000-50999
Oxazine	51000-51999
Thiazine	52000-52999
Sulfur	53000-54999
Lactone	55000-55999
Aminoketone	56000-56999
Hydroxyketone	57000-57999
Anthraquinone	58000-72999
Indigoid	73000-73999
Phthalocyanine	74000-74999
Natural	75000-75999
Oxidation bases	76000-76999
Inorganic pigments	77000-77999

Fig. 31 The main colorant categories and C.I. constitution numbers (S. Benkhaya)

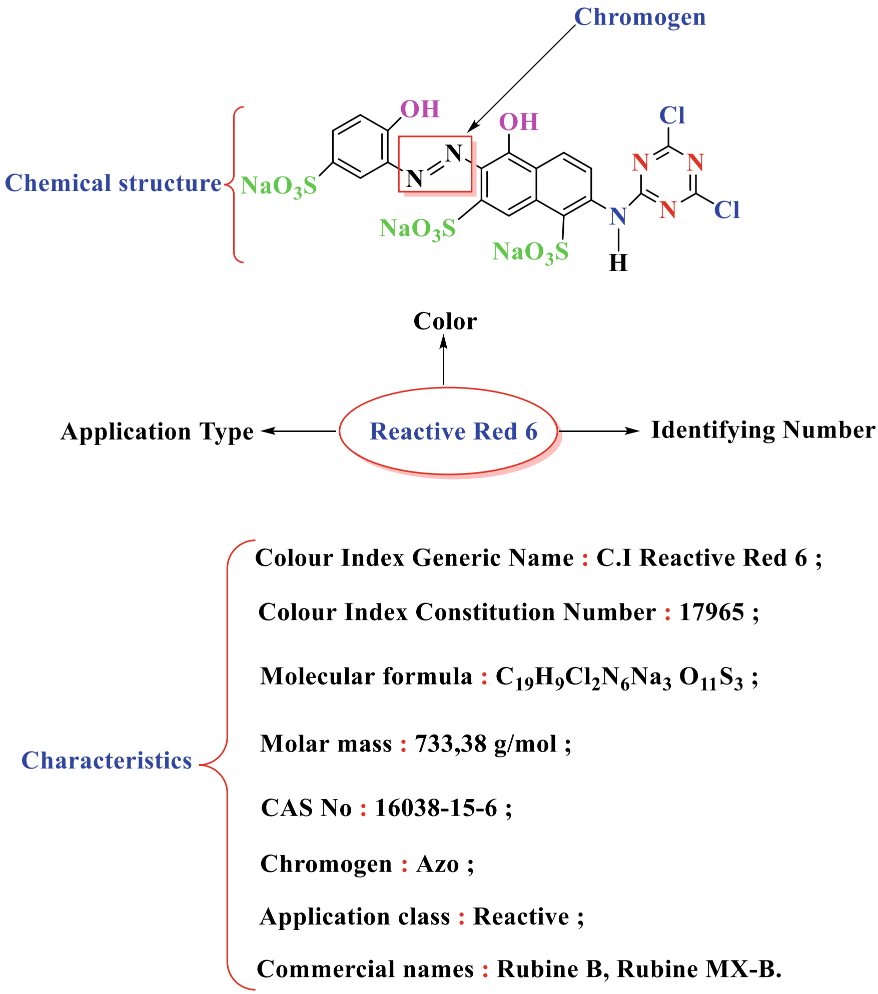


Fig. 32 Description example for the color index classification (S. Benkhaya)

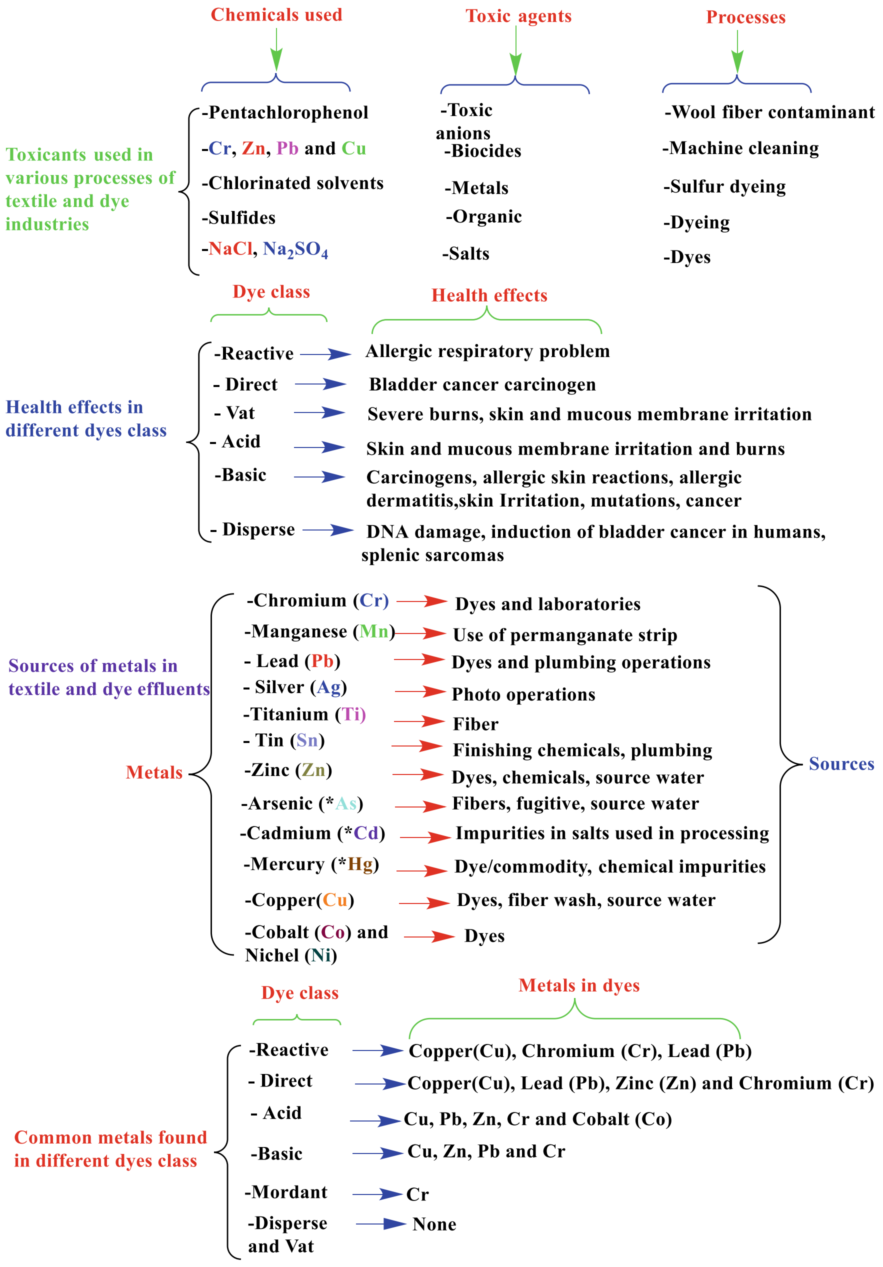


Fig. 33 Toxics from the textile and dyeing industries and their effects on human health (S. Benkhaya)

6 Conclusion

In the light of this review about textiles dyes, it is clear that many chemical classes of synthetic dyes are frequently employed on an industrial scale; anthraquinones dyes, triarylmethanes, indigoids, phenothiazine, xanthenes, and azos are among the most widespread. Some of the synthetic dyes are toxic to aquatic ecosystems. They can pose a threat to the balance of the ecosystem due to their high toxicity across different food chains. Thus, the presence of these dyes in the environment with particular regard to the aquatic environment must be monitored.

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