



Review article

Textile finishing dyes and their impact on aquatic environs



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ABSTRACT

In the present review, we have been able to describe the different families of dyes and pigments used in textile finishing processes (Yarns, fabrics, nonwovens, knits and rugs) such as dyeing and printing. These dyes are reactive, direct, dispersed, indigo, sulphur and vats. Such that their presence in the liquid effluents resulting from the textile washing constitutes a serious risk, in the absence of their purification, for the quality of receiving aquatic environments. Indeed, the presence of these dyes and pigments can cause a significant alteration in the ecological conditions of the aquatic fauna and flora, because of the lack of their biodegradability. This has a negative impact on the equilibrium of the aquatic environment by causing serious dangers, namely the obvious dangers (Eutrophication, under-oxygenation, color, turbidity and odor), the long-term dangers (Persistence, bioaccumulation of carcinogenic aromatic products and formation of by-products of chlorination), mutagenicity and carcinogenicity.

1. Introduction

The textile finishing industries are chemical industries in which dyes and pigments are used in very large quantities with such a large volume of water [1, 2, 3, 4]. The dyes and pigments of textile finishing used in the dyeing and printing of natural, synthetic, man-made and mixed textile materials such as wool, silk, nylon, polyester, acrylic, polyacetate and polyurethane are numerous and can reach 100,000 types on the market of which world annual production is about 700,000 tonnes [5, 6, 7]. The washing of tinted or printed textile articles/fabrics produces a large volume of liquid effluents laden with these dyes and pigments with a variable proportion (10–60 %) cause a waste of 280,000 tons of dyes per year, and chemical products and auxiliaries such as phosphates, nitrates who are direct effects not inconsiderable on aquatic fauna, flora and human health [8, 9, 10, 11, 12, 13]. Because, these textile effluents are characterized by high values in terms of several physicochemical and biological parameters, indicating the degree of pollution, including coloring, temperature, salinity, pH, biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total

nitrogen (TN), total phosphorus (TP) and non-biodegradable organic compounds, on the other hand, these effluents also contain heavy metals, metalliferous and phthalocyanine dyes, such as chromium (Cr), arsenic (Ar), copper (Cu) and zinc (Zn) [14, 15, 16]. The objective of this review is to describe the different families of textile dyes (Chemical and dye classification) and pigments, and their impact on the aquatic environment.

2. Main text

2.1. Textile finishing dyes

The textile finishing dyes are organic compounds capable of absorbing the light radiation in the visible range of the spectrum and of reflecting or diffusing complementary radiation on the one hand, and dyeing a substance in a sustainable manner on the other hand [17]. They consist of chromophoric groups, auxochromes and conjugated aromatic structures. These groups have specific independent properties, i.e., the color and the ability to be fixed on such a textile support, during dyeing

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and/or printing [18]. Chromophoric groups are unsaturated groups consisting of atoms or groups of atoms, in which the arrangement of successive single and double bonds resonates with the unstable mesomeric form thus allowing the absorption of light rays [17]. Table 1 gathers the mainchromophoric and auxochromic groups classified by the increasing intensity [17, 18, 19].

The classification of the dyes of textile finishing is based either on their chemical structure or on their method of application to different substrates such as textile fibers, paper, leathers and plastics [17, 19, 20]. Thus, there are two types of classifications such as chemical and dye classification's, in the following.

2.2. Chemical classification

It is based on the chemical structure of the dyes and more particularly on the nature of their chromophore grouping, such that dyeing plants will be able to predict the chemical reactions between the dye and the reducing agents, the oxidants and the other compounds [19].

2.2.1. Azo dyes

They constitute the largest family, including 70% of the world's annual production of synthetic dyes [17, 18, 19]. They are characterized by the presence of one or more azo groups (-N=N-) linked to the -OH or -NH₂ type auxochrome groups, namely the monoazo, the diazo and the triazo dyes whose grouped examples are in Table 2 [21, 22].

2.2.2. Anthraquinone dyes

They are the most important class after azo dyes. Their general formulas derived from anthracene show that the chromophore group is a quinone nucleus to which hydroxyl or amino groups can be attached [23]. This group gives the dye molecule good light resistance. Table 3 lists some examples of anthraquinone dyes [24, 25].

Table 1
Chromophoric and auxochromic groups of textile dyes.

Groups chromophoric	Groups auxochromic
Azo	(-N=N-)
Nitroso	(-NO or -N-OH)
Carbonyl	(>C=O)
Ethylenic	(>C=C<)
Nitro	(-NO ₂ or = NO-OH)
Sulphide	(>C=S)
Ketone-imine	(>C=NH)
Polymethine	(=HC-HC = CH-CH =)
Anthraquinone	
Phtalocyanine	
Triphenylmethane	

2.2.3. Indigo dyes

Indigo dyes are derivatives of indigo. Thus, the selenium, sulfur and oxygen homologues of indigo blue cause significant hypochromic effects with colors ranging from orange to turquoise, some examples of which are summarized in Table 4 [26, 27].

2.2.4. Xanthene dyes

They are endowed with an intense fluorescence of which the best known compound is fluorescein. These dyes are little used in dyeing but they are used in the marking technique as markers in maritime accidents or tracers in underground rivers [28]. Table 5 groups together chemical structures of some xanthene dyes [29, 30].

2.2.5. Phthalocyanine dyes

The phthalocyanine dyes are a family of dyes that are obtained by the reaction of dicyanobenzene in the presence of a metal type of Cu, Ni, Co, Pt. The phthalocyanine nucleus gives the molecule a good fastness to light. The most widely used dye in this family is copper phthalocyanine, because of its high chemical stability [31]. Table 6 summarizes the chemical structures of some phthalocyanine dyes molecules [32, 33, 34].

2.2.6. Nitrated and nitrosated dyes

Nitrated and nitrosated are class of dyes very limited in number and relatively old. They are still in use because of their very moderate price linked to the simplicity of their molecular structure characterized by the presence of a nitro group (-NO₂) at ortho position relative to an electron-donor group (hydroxyl or amino groups) [17]. Table 7 groups the chemical structures of some nitro and nitrosated coloring molecules [35, 36].

2.2.7. Diphenylmethane and triphenylmethane dyes

Diphenylmethane and triphenylmethane dyes represent the least important category, diphenyl methane is derivatives of auramine and triphenylmethanes are the origin of the oldest synthetic dyes such as fuchsin and malachite green [37]. The sulfonation of triphenylmethane gives acid dyes. While OH-auxochromes, neighboring carboxyl groups, form metallizable dyes. Table 8 below lists some chemical structures of diphenylmethane and triphenylmethane dyes [38, 39].

2.2.8. Polymethinic dyes

Also, called cyanines, they are constituted by a polymethine chain carrying at the ends of various heterocyclic whose examples are grouped in Table 9 [40, 41].

2.3. Dyes classification

Dyes classification is defined by the grouping auxochromes which is of interest for the dyer who prefers a classification by fields of application. This classification is informed about the dye solubility in the dye bath, its affinity for the various fibers and the nature of the fixation [42, 43]. In this classification, there are two families of dyes, soluble and water-insoluble dyes [44, 45].

2.3.1. Water-soluble dyes

2.3.1.1. Acid or anionic dyes. They are also called anionic dyes used for the dyeing of fibers which contain an amino group (NH₂) such as wool, polyamide, silk and mod acrylic which should be fixed on the NH₄⁺ cations of these fibers in acid medium. They consist of a chromophore group and one or more sulphonates groups allowing their solubilization in water [46]. Most of these dyes are azo, anthraquinone or triarylmethanes [26, 47]. Table 10 lists the chemical structures and maximum wave lengths λ_{\max} of some examples of acid dyes [48, 49, 50].

2.3.1.2. Basic dyes or cationic dyes. They are also called cationic dyes

Table 2Chemical structures and maximum wave lengths (λ_{\max}) of some azo dyes.

Dyes	Chemical structures	λ_{\max} (nm)	Groupings
Yellow reactive 4 (YR4)		385	monoazo
Black reactive 5 (BR5)		590	disazo
Direct blue 71 (DB71)		575	triazo

Table 3Chemical structures and λ_{\max} of some anthraquinone dyes.

Dyes	Reactive blue 19 (RB19)	Acid blue 62 (AB62)
Chemical structures		
λ_{\max} (nm)	592	635

Table 4Chemical structures and λ_{\max} of some indigo dyes.

Dyes	Indigo blue	Blue acid 74 (BA74)
Chemical structures		

which are salts of organic bases capable of directly dyeing the fibers bearing anionic sites and the cost only after treatment with metal salts. They are composed of diarylmethane, triarylmethane, anthraquinone and/or azo structures [51, 52]. Table 11 groups together some chemical structures and maximum wave lengths λ_{\max} of basic dyes [53, 54].

2.3.1.3. Metalliferous dyes. In order to facilitate the dyer work by avoiding the etching operation, the idea has been to incorporate the metal into the dye itself by forming the metalliferous complex

beforehand instead of precipitating it into the fiber in a subsequent manner [55]. Thus, metalliferous dyes are molecules derived from acid dyes with a metal atom (Cr, Cu, Ni and Co) incorporated into their chemical structures [55]. These dyes can be categorized in two complex forms: A metalliferous complex 1/1, in which the metal atom can be associated with a single molecule of the dye and a metalliferous complex 1/2, in which the metal atom can be associated with two molecules of dyes. Metalliferous dyes are often azo and phthalocyanine structures of which some examples are given in previous Table 6 [32, 33, 34].

Table 5
Chemical structure and λ_{\max} of some xanthene dyes.

Dyes	Chemical structure	λ_{\max} (nm)
Fluorescein: R ₁ = R ₂ = H		480–500
Dibromofluorescein: R ₁ = H, R ₂ = Br		490–510
Eosin Y: R ₁ = R ₂ = Br		510–530
Erythrosine B: R ₁ = R ₂ = I		520–540

2.3.1.4. Reactive dyes. Reactive dyes contain chromophore groups mainly derived from azo, anthraquinone and phthalocyanine families [43]. Their name is linked to the presence of a reactive chemical function, of the triazine or vinylsulfone type, ensuring the formation of a strong covalent bond with the fibers [17]. They are more soluble in water and in the dyeing of cotton and possibly in that of wool and polyamides. Table 12 lists some examples of reactive dyes [56, 57].

2.3.1.5. Direct or substantive dyes. Direct or substantive dyes are large molecules capable of forming positive or negative charges

electrostatically attracted by fiber charges. They are distinguished by their affinity for cellulosic fibers without mordant application that is related to the plane structure of their molecule [17]. They are used for dyeing cellulosic fibers. These dyes are applied directly to the bath containing the salt (sodium chloride or sodium sulfate) and auxiliary products that facilitate the wettability of the fiber and the dispersion effect. The mixtures of nonionic and anionic surfactants are used for this purpose. The main advantages of these dyes are the wide variety of colors, their ease of application and their low price. On the other hand, their main disadvantage is their low wet strength. Table 13 below gives some examples of direct dyes [58, 59].

2.3.2. Insoluble dyes in water

2.3.2.1. Vat dyes. The vat dyes are water-insoluble dyes when they are fixed on the fibers, but they become soluble and substantive by the reduction in very alkaline medium (in vat) in leuco-derivatives soluble in water [44, 60, 61]. They are then re-solubilized by oxidation in air or with the aid of an oxidizing agent and are generated within the fiber, on the other hand [62]. They are known for their good resistance to degradation agents (washing and solar rays) and their affinity for certain fibers such as cotton, linen, wool, silk, rayon and other cellulosic fibers such as indigo for dyeing jeans (or denim). Among the vat dyes used, there is indigo (vat blue 1) which is already mentioned in Table 4 [27].

Table 6
Chemical structures and λ_{\max} of some phthalocyanine dyes.

Dyes	Chemical structures	λ_{\max} (nm)
Pigment blue 15/3		785–793
Nickel (II) tetrasulfonic acid		620–626
Iron (III) phthalocyanine chloride		650–658

Table 7Chemical structures and λ_{\max} of some nitro and nitrosated dyes.

Dyes	Picric acid (2, 4, 6-trinitrophenol)	2-nitrophenol	2-amino-4-nitrophenol
Chemical structures			

Table 8Chemical structures and λ_{\max} of diphenylmethane and triphenylmethane dyes.

Dyes	p-dimethylamino-phenylethynyl	Light green
Chemical structures		
λ_{\max} (nm)	727	660
Type of dyes	diphenylmethane	triphenylmethane

Table 9Chemical structures and λ_{\max} of some polymethine dyes.

Dyes	Basic yellow 28	Polymethine dye 2630
Chemical structures		
λ_{\max} (nm)	439	700

Also, there is the blue indanthrene RS (vat blue 4) and vat green 1 which are collated in [Table 14](#) [61, 62, 63, 64].

2.3.2.2. Sulfur dyes. Sulfur dyes are quite similar to vat dyes by the method of use, but they represent sulfur-containing molecules and have different chemical structures with high molecular weight [65]. They are insoluble in water but applied as a soluble derivative after reduction in an alkaline medium by sodium sulphide. They are then reoxidized to their insoluble state in the fiber. Sulfur dyes are typically applied to cotton to produce cost-effective dark shades with a medium to good wash and light fastness [17]. [Table 15](#) lists some examples of sulfur dyes [26, 27, 65].

2.3.2.3. Disperse or dispersible dyes. They are also called plastosolubles, examples of which are shown in [Table 16](#), which are very insoluble in water and applied as a fine powder dispersed in the dye bath [57, 66]. They are stable during at high temperature dyeing, to diffuse in the synthetic fibers and then to fix it. Disperse dyes are widely used in the dyeing of most manufactured fibers, especially polyester and polyamide in the presence of a dispersing agent that is always added to the solution [17].

2.3.2.4. Pigments. The pigments are colored compounds that are insoluble in water, in the solvent (basic and acidic) and do not contain any group that can react with the textile fiber by means of a binder. They are commonly used in printing processes (pigment printing) [67, 68]. Organic pigments are largely benzoic derivatives and inorganic pigments (minerals) are derivatives of metals such as titanium, zinc, barium, lead, iron, molybdenum, antimony, zirconium, calcium, aluminum, magnesium, cadmium and chromium [69]. They must be very finely divided so that they can be kept in suspension thanks to dispersants, such as the film formed by the heat treatment (drying), is flexible and transparent and leaves the pigments all their vivacity and their solidarity to the light with good resistance to mechanical tests.

2.3.2.5. Fixing different dye classes. During the various stages of dyeing and printing process, a greater or lesser quantity of dyes and pigments is lost, despite the use of fixing agents, due to affinity for the surfaces [70, 71]. Indeed, the dyes are fixed on the textile fibers by Van der Waals type interaction, hydrogen and hydrophobic interaction, the fixing of the dye depends on its nature, its chemical composition and the type of fiber on which it is applied [17]. When the dye and the fiber have opposite

Table 10Chemical structures and λ_{\max} of some acid dyes.

Chemical structures	Dyes	λ_{\max} (nm)	Groupings
	Acid Blue 74	612	indigoid
	Acid Blue 90	580	triphenylmethane
	Red acid 27 (AR27)	521	azo

charges, a very strong bond between the dye and the fiber within the complex is enhanced by additional electrostatic interaction [18, 43]. Table 17 presents a relative estimate of the rates of fixation and rejection of different dyes tuffs according to the nature of the textile fibers to be dyed [17, 72]. Besides, it appears that a fairly large percentage of the dyes are discharged with the effluents which are, in most of the time, discharged directly into the streams without any prior treatment. This has a negative influence on the aquatic environment.

According to this table, it turns out that larger amounts of dyes are lost due to the lack of affinity for the textile surfaces to be dyed or colored. This requires a more appropriate regeneration technique (or treatment).

2.4. Impact of dyes textile finishing on aquatic environment

The presence of textile dyes in wastewater discharged by textile industries in aquatic environments such as wadis, rivers, seas, oceans... and the lack of their biodegradability, under normal ecological conditions can destroy the vital conditions of these different environments, while preventing the penetration of light to the depths of aquatic environments

[73, 74, 75, 76]. As a result, there are serious ecological consequences such as changing the nature of aquatic environments and reducing photosynthesis compared to aquatic flora [8, 77, 78, 79].

In addition, these waste waters can produce several dangerous problems, namely aesthetic and health problems such as changes in the quality (color and odor) of water and make it toxic, as they can cause allergies, dermatitis, skin irritations, cancers and mutations in humans [77, 80, 81, 82, 83]. Furthermore, between 60 and 70% of azo dyes are toxic, carcinogenic and are refractory to conventional physicochemical processes because of their resistance to conventional physicochemical destruction and the absence of their biodegradability [84]. This interrupted the phenomenon of photosynthesis in marine plants by triggering the phenomenon of eutrophication, under the effect of the release of mineral elements such as nitrates, nitrites and phosphates in an uncontrolled manner, and produced the long-term hazards of persistence, bioaccumulation, by products of chlorination, mutagenicity and carcinogenicity [84, 85, 86].

In addition, the existence of dyes and textile pigments in wastewaters makes them very characterized by a high degree of coloration, a very fluctuating pH and high levels in terms of biochemical oxygen demand

Table 11Chemical structures and λ_{\max} of some basic dyes.

Dyes	Basic blue 9 (BB9)	Basic yellow 37 (BY37)	Blue nile (BN)
Chemical structures			
λ_{\max} (nm) Groupings	665 phthalocyanine	440 ketone imine	638 sulphonates

Table 12Chemical structures and λ_{\max} of some reactive dyes.

Chemical structures	Dyes	λ_{\max} (nm)	Groupings
	Reactive red 198 (RR 198)	515	carbonyl
	Red cibacrom 3 (RC3)	540	azo

Table 13Chemical structures and λ_{\max} of some direct dyes.

Chemical structures	Dyes	λ_{\max} (nm)	Groupings
	Direct blue 1 (BD-1)	594	azo
	Direct blue 86 (BD-86)	594	phthalocyanine

Table 14
Chemical structures and λ_{\max} of some vat dyes.

Dyes	Blue indanthrene RS	Vat green 1
Chemical structures		
λ_{\max} (nm) Groupings	631 anthraquinonique	630 anthraquinonique

Table 15
Chemical structures and λ_{\max} of some sulfur dyes.

Dyes	Sulfur black (SB)	Sulfur blue 15 (SB15)
Chemical structures		
λ_{\max} (nm)	597	593

(BOD), chemical oxygen demand (COD), total organic carbon (TOC) and suspended solids (TSS) [3, 87, 88, 89, 90]. The uncontrolled increase in these pollution indicators can cause an imbalance in biological treatment plants because of the high toxicity of the metal elements contained in these dyes (metalliferous and pigments) [91]. As well as, the presence of mineral elements with very high levels in water and lack of their consumption by aquatic plants (algae, bryophytes, pteridophytes, spermatophytes and vascular plants) accelerates their uncontrolled proliferation in an uncontrolled manner and consequently leads to the

oxygen depletion by inhibition of photosynthesis in the strata, deeper watercourses and stagnant waters [17, 77, 78, 79, 80]. This can affect the life of aquatic fauna and flora, modify the quality of drinking water production [81].

In case of disposal of organic matter including dyes and pigments to the receiving media via textile finishing effluents, the natural processes of regulation can no longer compensate the bacterial oxygen consumption [47, 92]. This may lead to under-oxygenation of stagnant aquatic environments, such that the degradation of 7–8 mg of organic matter by

Table 16
Chemical structures and λ_{\max} of some disperses dyes.

Dyes	Red disperse60 (RD60)	Blue disperse 7 (BD7)
Chemical structures		
λ_{\max} (nm) Groupings	536 anthraquinonique	570 anthraquinonique

Table 17

Rate of fixation and rejection of dyes in relation to the textile fibers used.

Dyes	Textile fibers	Fixation rate (%)	Discharge rate (%)
Acid	wool and nylon	80–93	7–20
Azo	cellulose	90–95	5–10
Basic	acrylic	97–98	2–3
Vat	cellulose	80–95	5–20
Direct	cellulose	70–95	5–30
Dispersed	synthetic	80–92	2–20
Reagents	cellulose	50–80	20–50
Sulfur	cellulose	60–70	30–40

microorganisms is sufficient to consume the amount of oxygen in one liter of water [17, 93].

The agglomeration of organic matter (dyes, pigments, etc.) in wa-tercourses induces the appearance of bad taste, bacterial proliferation, pestilential odors and abnormal colorations [68, 71, 85, 86]. In such a way that coloration could be perceived with the naked eye from a mass concentration of dyes equal to 5 µg/L [17, 94]. Apart from the unsightly appearance, the coloring agents have the ability to interfere with the transmission of light in the water, thus blocking the photosynthesis of aquatic plants.

Synthetic organic dyes are compounds that cannot be purified (persistent) by the processes of natural biological degradation [95]. This persistence is closely related to their chemical reactivity, so that the unsaturated compounds are less persistent than the saturated compounds. The persistence of aromatic compounds increases with the number of substituents and the halogen substituents increase the persistence of the dyes having the alkyl groups [17].

Given the widespread use of dyes, these contaminants can be found in the environment and accumulate biologically throughout the food chain in organisms (fish, algae...) of freshwater [70].

Species at the high end of the food web, including humans, are exposed to toxic concentrations up to a thousand times higher than initial concentrations in water [17, 64]. Such as the analysis of the data recorded by the Ecological and Toxicological Association of Dyes and synthetic organic pigments (ETAD) concerning their toxicity towards fish, showed that 98% of these dyes have a limited concentration CL₅₀ above 1 mg/L, and 59% have a CL₅₀ greater than 100 mg/L [96].

During the elimination of pathogenic micro-organisms by chlorine, the latter reacts with the organic matter to form trihalomethanes (THM) chlorination by-products [17, 41]. The prolonged exposure to these substances causes' health problems in humans, including carcinogenic effects (bladder, colon, colorectal etc.), health effects, including the immune and reproductive system with genotoxic and carcinogenic properties [70, 97, 98].

In terms of toxicity, the most toxic synthetic organic dyes are azo dyes and more particularly diazo and cationic dyes [81, 99, 100]. These types of dyes have carcinogenic effects on humans and animals primarily, as the electron-withdrawing character of azo groups generates electronic deficiencies. This makes azo compounds uncomfortable with oxidative catabolism under aerobic environmental conditions [101, 102, 103].

3. Conclusion

In the light of this review, we can conclude that synthetic dyes and pigments applied to textile finishing processes are numerous and diverse in terms of chromophore groups (Azo groups, anthraquinone groups, indigoids, xanthenes, phthalocyanines, nitrosed, triphenylmethanes and polymethines) and application techniques (Water-soluble dyes (Acidic, basic, metalliferous, reactive and direct dyes) and water-insoluble dyes (Vat dyes, sulfur dyes and dispersible)). The majority of these dyes are azo (60–70 %) characterized by high chemical stability with respect to chemicals and products due to the combination of azo groups with aromatic rings. The presence of these dyes and its residues in the effluents discharged into aquatic environments, as well as their relative

biodegradability, have a negative impact on the environment and more particularly on aquatic ecosystems because of their toxic and carcinogenic effects as they occur. Accumulate throughout the food chain of aquatic fauna, on the one hand and dysfunctional physiological processes of aquatic flora (Plants, diatoms and algae) by disrupting their photosynthesis mechanisms by the lack of circulation of the oxygen and absorption of light in aquatic environments, on the other hand. Besides, these textile dyes must eliminate according to processes, which will be the interest of a future review, of biological, chemical, physical and physicochemical treatment before their evacuation in aquatic environments.

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