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Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview

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1. Introduction

The residual dyes from different sources (e.g., textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft bleaching industries, etc.) are considered a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems.

One of the main sources with severe pollution problems worldwide is the textile industry and its dye-containing wastewaters (i.e. 10,000 different textile dyes with an estimated annual production of $7 \cdot 10^5$ metric tonnes are commercially available worldwide; 30% of these dyes are used in excess of 1,000 tonnes per annum, and 90% of the textile products are used at the level of 100 tonnes per annum or less) (Baban et al., 2010; Robinson et al., 2001; Soloman et al., 2009). 10-25% of textile dyes are lost during the dyeing process, and 2-20% are directly discharged as aqueous effluents in different environmental components.

In particular, the discharge of dye-containing effluents into the water environment is undesirable, not only because of their colour, but also because many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens, such as benzidine, naphthalene and other aromatic compounds (Suteu et al., 2009; Zaharia et al., 2009). Without adequate treatment these dyes can remain in the environment for a long period of time. For instance, the half-life of hydrolysed Reactive Blue 19 is about 46 years at pH 7 and 25°C (Hao et al., 2000).

In addition to the aforementioned problems, the textile industry consumes large amounts of potable and industrial water (Tables 1, 2 and Fig. 1) as processing water (90-94%) and a relatively low percentage as cooling water (6-10%) (in comparison with the chemical industry where only 20% is used as process water and the rest for cooling). The recycling of treated wastewater has been recommended due to the high levels of contamination in dyeing and finishing processes (i.e. dyes and their breakdown products, pigments, dye intermediates, auxiliary chemicals and heavy metals, etc.) (Tables 3, 4 and 5) (adapted from Bertea A. and Bertea A.P., 2008; Bisschops and Spanjers, 2003; Correia et al., 1994; Orhon et al., 2001).

Type of finishing process	**Water consumption, 10^{-3} m^3/kg textile product**		
	Minimum	**Medium**	**Maximum**
Raw wool washing	4.2	11.7	77.6
Wool finishing	110.9	283.6	657.2
Fabric finishing			
- Short process	12.5	78.4	275.2
- Complex processing	10.8	86.7	276.9
Cloth finishing			
- Simplified processing	8.3	135.9	392.8
- Complex process	20	83.4	377.8
- Panty processing	5.8	69.2	289.4
Carpet finishing	8.3	46.7	162.6
Fibre finishing	3.3	100.1	557.1
Non-fabrics finishing	2.5	40	82.6
Yarn finishing	33.4	212.7	930.7

Table 1. Specific water consumption in textile finishing processes (adapted from Bertea A. & Bertea A.P., 2008)

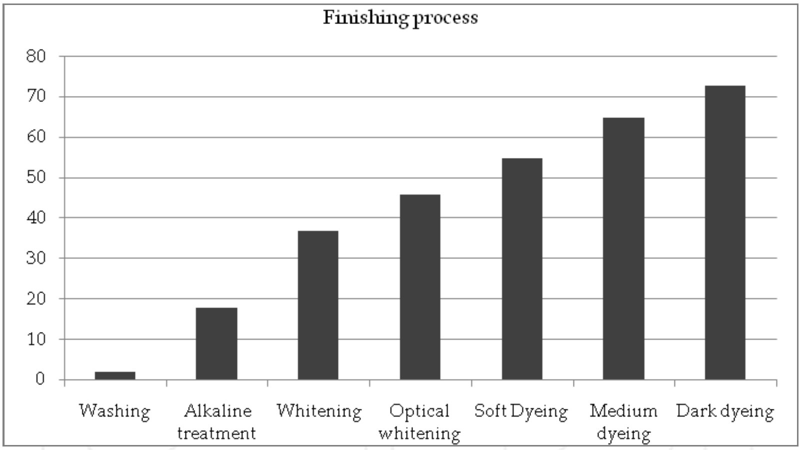


Fig. 1. Specific water consumption in different operations of textile finishing (EPA, 1997)

Operation/Process	**Water consumption** (% from total consumption of the textile plant)			**Organic load** (% from total organic load of the textile plant)		
	Minimum	**Medium**	**Maximum**	**Minimum**	**Medium**	**Maximum**
General facilities	6	14	33	0.1	2	8
Preparation	16	36	54	45	61	77
Dyeing	4	29	53	4	23	47
Printing	42	55	38	42	59	75
Wetting	0.3	0.4	0.6	0	0.1	0.1
Fabrics washing	3	28	52	1	13	25
Finishing	0.3	2	4	0.1	3	7

Table 2. Water consumption and organic load in different textile finishing steps (EWA, 2005)

The most common textile processing technology consists of desizing, scouring, bleaching, mercerizing and dyeing processes (EPA, 1997):

- *Sizing* is the first preparation step, in which sizing agents such as starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose are added to provide strength to the fibres and minimize breakage.
- *Desizing* is used to remove sizing materials prior to weaving.
- *Scouring* removes impurities from the fibres by using alkali solution (commonly sodium hydroxide) to breakdown natural oils, fats, waxes and surfactants, as well as to emulsify and suspend impurities in the scouring bath.
- *Bleaching* is the step used to remove unwanted colour from the fibers by using chemicals such as sodium hypochlorite and hydrogen peroxide.
- *Mercerising* is a continuous chemical process used to increase dye-ability, lustre and fibre appearance. In this step a concentrated alkaline solution is applied and an acid solution washes the fibres before the dyeing step.
- *Dyeing* is the process of adding colour to the fibres, which normally requires large volumes of water not only in the dye bath, but also during the *rinsing step*. Depending on the dyeing process, many chemicals like metals, salts, surfactants, organic processing aids, sulphide and formaldehyde, may be added to improve dye adsorption onto the fibres.

In general, the textile industry uses a large quantity of chemicals such as:

- *Detergents and caustic*, which are used to remove dirt, grit, oils, and waxes. Bleaching is used to improve whiteness and brightness.
- *Sizing agents*, which are added to improve weaving.
- *Oils*, which are added to improve spinning and knitting.
- *Latex and glues*, which are used as binders.
- *Dyes, fixing agents, and many in-organics*, which are used to provide the brilliant array of colours the market demands.
- *A wide variety of special chemicals*, which are used such as softeners, stain release agents, and wetting agents.

Many of these chemicals become part of the final product whereas the rest are removed from the fabric, and are purged in the textile effluent.

Type of finished textile product	**Dyes, g/kg textile product**	**Auxiliaries, g/kg textile product**	**Basic chemical compounds, g/kg textile product**
Polyester fibres	18	129	126
Fabrics from synthetic fibres	52	113	280
Fabrics from cotton	18	100	570
Dyed fabrics from cellulose fibres	11	183	200
Printed fabrics from cellulose fibres	88	180	807

Table 3. Principal pollutants of textile wastewaters (EWA, 2005)

The annual estimated load with pollutants of a textile wastewater is of: 200,000-250,000 t salts; 50,000-100,000 t impurities of natural fibres (including biocids) and associated materials (lignin, sericine, etc.); 80,000-100,000 t blinding agents (especially starch and its derivatives, but also polyacrylates, polyvinyl alcohol, carboxymethyl cellulose); 25,000-

30,000 t preparation agents (in principal, mineral oils); 20,000-25,000 t tensides (dispersing agents, emulsifiers, detergents and wetting agents); 15,000-20,000 tonnes carboxylic acids (especially acetic acid); 10,000-15,000 t binders; 5,000-10,000 t urea; 5,000-10,000 t ligands, and < 5,000 t auxiliaries (EWA, 2005). The environmental authorities have begun to target the textile industry to clean up the wastewater that is discharged. The principal quality indicators that regulators are looking for polluting effect or toxicity are the high salt content, high Total Solids (TS), high Total Dissolved Solids (TDS), high Total Suspended Solids (TSS), Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), heavy metals, colour of the textile effluent (ADMI color value - American Dye Manufacturer Institute color value), and other potential hazardous or dangerous organic compounds included into each textile processing technological steps (Tables 4 and 5).

Process	**Textile effluent**
Singering, Desizing	High BOD, high TS, neutral pH
Scouring	High BOD, high TS, high alkalinity, high temperature
Bleaching, Mercerizing	High BOD, high TS, alkaline wastewater
Heat-setting	Low BOD, low solids, alkaline wastewater
Dyeing, Printing & Finishing	Wasted dyes, high BOD, COD, solids, neutral to alkaline wastewater

Table 4. Wet processes producing textile wastewater (adapted from Naveed S. et al., 2006)

Process	**COD, g O_2/L**	**BOD, g O_2/L**	**TS, g/L**	**TDS, g/L**	**pH**	**Colour (ADMI)**	**Water usage, L/kg product**
Desizing	4.6-5.9	1.7-5.2	16.0-32.0	-	-	-	3-9
Scouring	8.0	0.1-2.9	7.6-17.4	-	10-13	694	26-43
Bleaching	6.7-13.5	0.1-1.7	2.3-14.4	4.8-19.5	8.5-9.6	153	3-124
Mercerising	1.6	0.05-0.1	0.6-1.9	4.3-4.6	5.5-9.5	-	232-308
Dyeing	1.1-4.6	0.01-1.8	0.5-14.1	0.05	5-10	1450-4750	8-300

Table 5. Principal characteristics of a cotton wet processing wastewater (Cooper, 1995)

The wastewater composition is depending on the different organic-based compounds, inorganic chemicals and dyes used in the industrial dry and wet-processing steps. Textile effluents from the dyeing and rinsing steps represent the most coloured fraction of textile wastewaters, and are characterized by extreme fluctuations in many quality indicators such as COD, BOD, pH, colour, salinity and temperature.

The colour of textile wastewater is mainly due to the presence of textile dyes, pigments and other coloured compounds. A single dyeing operation can use a number of dyes from different chemical classes resulting in a complex wastewater (Correia et al., 1994). Moreover, the textile dyes have complex structures, synthetic origin and recalcitrant nature, which makes them obligatory to remove from industrial effluents before being disposed into hydrological systems (Anjaneyulu et al, 2005).

The dye removal from textile effluent is always connected with the decolourization treatment applied for textile wastewater in terms of respectation the local environmental quality requirements and standards (Table 6) (i.e. removal values of COD, BOD, TS, TSS, TDS, colour, total nitrogen, and total phosphorus from textile wastewater higher than 70-

85% or concentration values of the specific quality indicators under the imposed or standard limits) (Zaharia, 2008).

The decolorization treatments applied for different textile effluents include current and also advanced non-biological (i.e. specific mechano-physical, chemical, electrochemical processes, etc.) and also biological processes (Suteu et al., 2009; Zaharia, 2006; Zaharia et al, 2011).

Quality indicator	**M.A.C.***, mg/L		
	Discharge directly in water bodies	*Discharge in urban WW sewerage network*	*Water bodies quality, class I -natural non-polluted state*
pH	6.5-8.5	6.5-8.5	6.5-8.5
BOD_5	25	300	3
COD	125	500	10
TSS	35	350	-
TDS	2000	250	< 500
Total N	10	15	1.5
Total P	1	5	0.1
Sulphates, SO_4^{2-}	600	600	80
Chlorides, Cl^-	500	500	<100
Sulphides (S^{2-}) + H_2S	0.5	1.0	<0.5
Synthetic detergents	0.5	25	<0.5
Others (Oil & grease)	20	30	<0.1
* M.A.C. – Maximum Admissible Concentration			

Table 6. Romanian national wastewater and water quality standard adapted to European and international standards (adapted from Zaharia, 2008)

Studies on the behavior of textile organic dyes in water and wastewater treatment processes refer predominantly to laboratory tests or investigations of semi-technical plants, sometimes under conditions related to waterworks practice. In addition, textile operators, water supply companies, local environmental authorities have collected a lot of data on the behavior of textile dyes during textile wastewater treatment, but have seldom published their results.

However, information on the behavior of textile organic dyes is needed, because the limited number of reports available that are based on realistic operating conditions or which reproduce practical conditions that are already several years old.

2. Textile organic dyes – Classification and characteristics

The dyes are natural and synthetic compounds that make the world more beautiful through coloured products. The textile dyes represent a category of organic compounds, generally considered as pollutants, presented into wastewaters resulting mainly from processes of chemical textile finishing (Suteu et al., 2011a; Zaharia et al., 2009).

The textile coloration industry is characterised by a very large number of dispersed dyehouses of small and medium size that use a very wide range of textile dyes.

2.1 Textile organic dye classification

The nature and origin are firstly considered as criteria for the general classification in natural and synthetic textile dyes.

The natural textile dyes were mainly used in textile processing until 1856, beginning in 2600 BC when was mentioned the use of dyestuff in China, based on dyes extracted from vegetable and animal resources. It is also known that Phoenicians were used Tyrian purple produced from certain species of crushed sea snails in the 15th century BC, and indigo dye produced from the well-known indigo plant since 3000 BC. The dyes from madder plants were used for wrapping and dyeing of Egyptian mummies clothes and also of Incas fine textures in South America.

The synthetic dyes were firstly discovered in 1856, beginning with ‚mauve‘ dye (aniline), a brilliant fuchsia colour synthesed by W.H. Perkin (UK), and some azo dyes synthesed by diazotisation reaction discovered in 1958 by P. Gries (Germany) (Welham, 2000). These dyes are aromatic compounds produced by chemical synthesis, and having into their structure aromatic rings that contain delocated electrons and also different functional groups. Their color is due to the chromogene-chromophore structure (acceptor of electrons), and the dyeing capacity is due to auxochrome groups (donor of electrons). The chromogene is constituted from an aromatic structure normally based on rings of benzene, naphthaline or antracene, from which are binding chromofores that contain double conjugated links with delocated electrons. The chromofore configurations are represented by the azo group (-N=N-), ethylene group (=C=C=), methine group (-CH=), carbonyl group (=C=O), carbon-nitrogen (=C=NH; -CH=N-), carbon-sulphur (=C=S; ≡C-S-S-C≡), nitro ($-NO_2$; -NO-OH), nitrozo (-N=O; =N-OH) or chinoid groups. The auxochrome groups are ionizable groups, that confer to the dyes the binding capacity onto the textile material. The usual auxochrome groups are: $-NH_2$ (amino), -COOH (carboxyl), $-SO_3H$ (sulphonate) and -OH (hydroxyl) (Suteu et al, 2011; Welham, 2000). Five examples of textile dyes are presented in Fig. 2.

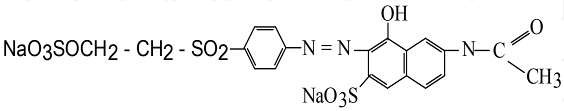
The textile dyes are mainly classified in two different ways: (1) based on its application characteristics (i.e. CI Generic Name such as acid, basic, direct, disperse, mordant, reactive, sulphur dye, pigment, vat, azo insoluble), and (2) based on its chemical structure respectively (i.e. CI Constitution Number such as nitro, azo, carotenoid, diphenylmethane, xanthene, acridine, quinoline, indamine, sulphur, amino- and hydroxy ketone, anthraquinone, indigoid, phthalocyanine, inorganic pigment, etc.) (Tables 7 and 8).

Excepting the colorant precursors such as azoic component, oxidation bases and sulphur dyes, almost two-third of all organic dyes are azo dyes (R_1-N=N-R_2) used in a number of different industrial processes such as textile dyeing and printing, colour photography, finishing processing of leather, pharmaceutical, cosmetics, etc. The starting material or intermediates for dye production are aniline, chloroanilines, naphthylamines, methylanilines, benzidines, phenylenediamines, and others.

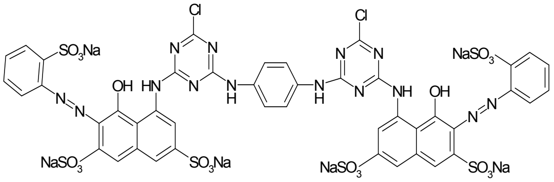
Considering only the general structure, the textile dyes are also classified in anionic, nonionic and cationic dyes. The major anionic dyes are the direct, acid and reactive dyes (Robinson et al., 2001), and the most problematic ones are the brightly coloured, water soluble reactive and acid dyes (they can not be removed through conventional treatment systems).

The major nonionic dyes are disperse dyes that does not ionised in the aqueous environment, and the major cationic dyes are the azo basic, anthraquinone disperse and reactive dyes, etc. The most problematic dyes are those which are made from known carcinogens such as benzidine and other aromatic compounds (i.e. anthroquinone-based dyes are resistant to degradation due to their fused aromatic ring structure). Some disperse dyes have good ability to bioaccumulation, and the azo and nitro compounds are reduced in sediments, other dye-accumulating substrates to toxic amines (e.g. $R_1\text{-}N{=}N\text{-}R_2 + 4H^+ + 4e^- \rightarrow R_1\text{-}NH_2 + R_2\text{-}NH_2$).

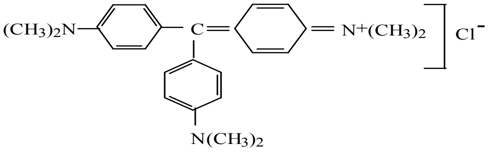
The organic dyes used in the textile dyeing process must have a high chemical and photolytic stability, and the conventional textile effluent treatment in aerobic conditions does not degrade these textile dyes, and are presented in high quantities into the natural water resources in absence of some tertiary treatments.



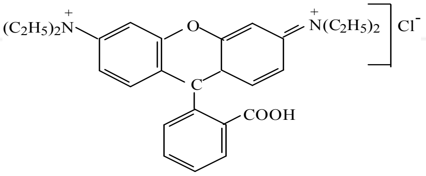
Reactive Orange 16
C.I. 18097
Anionic monoazo reactive dye;
MW = 617.54 g/mol;
λ_{max} = 495 nm



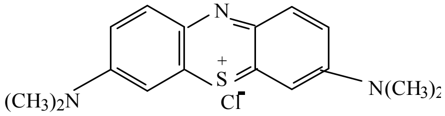
Brilliant Red HE-3B
(Reactive Red 120)
C.I. 25810
Anionic, bifunctional
azo reactive dye;
MW = 1463 g/mol;
λ_{max} = 530 nm



Crystal Violet
(Basic Violet 3)
C.I. 42555
Cationic triphenylmethane dye;
MW = 407.99 g/mol;
λ_{max} = 590 nm



Rhodamine B
(Basic Violet 10)
C.I. 45170
Cationic, Xantenic dye;
MW =479.2 g/mol;
λ_{max} = 550 nm



Methylene Blue
(Basic Blue 9)
C.I. 52015
Cationic, phenothiazine dye;
MW =319.85 g/mol;
λ_{max}= 660 nm

Fig. 2. Chemical structure and principal characteristics of different textile dyes (Suteu et al., 2011a)

Chemical class	**C.I. Constitution numbers**	**Chemical class**	**C.I. Constitution numbers**
Nitroso	10000-10299	Indamine	49400-49699
Nitro	10300-10099	Indophenol	49700-49999
Monoazo	11000-19999	Azine	50000-50999
Disazo	20000-29999	Oxazine	51000-51999
Triazo	30000-34999	Thiazine	52000-52999
Polyazo	35000-36999	Sulphur	53000-54999
Azoic	37000-39999	Lactone	55000-56999
Stilbene	40000-40799	Aminoketone	56000-56999
Carotenoid	40800-40999	Hydroxyketone	57000-57999
Diphethylmethane	41000-41999	Anthraquinone	58000-72999
Triarylmethane	42000-44999	Indigoid	73000-73999
Xanthene	45000-45999	Phthalocyanine	74000-74999
Acridine	46000-46999	Natural	75000-75999
Quinoline	47000-47999	Oxidation base	76000-76999
Methine	48000-48999	Inorganic pigment	77000-77999
Thiazole	49000-49399		

Table 7. Colour index classification of dye chemical constituents (Cooper, 1995)

Chemical class	**Distribution between application ranges, %**								
	Acid	Basic	Direct	Disperse	Mordant	Pigment	Reactive	Solvent	Vat
Unmetallised azo	20	5	30	12	12	6	10	5	-
Metal complex	65	-	10	-	-	-	12	13	-
Thiazole	-	5	95	-	-	-	-	-	-
Stilbene	-	2	98	-	-	-	-	-	-
Anthraquinone	15	2	-	25	3	4	6	9	36
Indigoid	2	-	-	-	-	17	-	-	81
Quinophthalene	30	20	-	40	-	-	10	-	-
Aminoketone	11	-	-	40	8	-	3	8	20
Phtalocyanine	14	4	8	-	4	9	43	15	3
Formazan	70	-	-	-	-	-	30	-	-
Methine	-	71	-	23	-	1	-	5	-
Nitro, nitroso	31	2	-	48	2	5	-	12	-
Triarylmethane	35	22	1	1	24	5	-	12	-
Xanthene	33	16	-	-	9	2	2	38	-
Acridine	-	92	-	4	-	-	-	4	-
Azine	39	39	-	-	-	3	-	19	-
Oxazine	-	22	17	2	40	9	10	-	-
Thiazine	-	55	-	-	10	-	-	10	25

Table 8. Distribution of each chemical class between major application ranges (adapted from Cooper, 1995)

The major textile dyes can be included in the two high classes: azo or anthraquinone (65-75% from total textile dyes). The azo dyes are characterised by reactive groups that form covalent bonds with HO-, HN-, or HS^- groups in fibres (cotton, wool, silk, nylon). Azo dyes are mostly used for yellow, orange and red colours. Anthraquinone dyes constitute the second most important class of textile dyes, after azo dyes, and have a wide range of colours in almost the whole visible spectrum, but they are most commonly used for violet, blue and green colours (Fontenot et al., 2003). Considering the nature of textile fibres that are dyeing, the textile dyes can be classified as into Table 9.

Class	**Subclass**	**PES**	**CA**	**PAN**	**PA**	**Silk**	**Wool**	**Cotton**
Disperse		+++	+++	++	++	-	-	-
Cationic		-	~	+++	++	-	-	-
Acid	Standard	-	-	~	+++	+++	+++	-
	1 : 1	-	-	-	P	+	+++	-
	1 : 2	-	-	-	++	+	+++	-
Reactive		-	-	-	~	++	++	+++
Direct		-	-	-	++	++	P	+++
Stuff		~	-	~	~	~	–	+++
Indigoid		-	-	–	~	~	~	P
Sulphur		-	+	–	–	–	–	+++
Insoluble azo		+++	-	~	~	~	–	+++
Legend: +++ very frequent; ++ frequent; + sometimes; ~ possible; P especially printing								

Table 9. Dye classes and dyeing textile substrates (adapted from Bertea A. & Bertea A.P., 2008)

The textile dyeing process is due to physico-chemical interactions developed at contacting of textile material with dye solution or dispersion, which contains a large variety of chemicals (salts, acids) and dyeing auxiliaries (tensides, dispersing agents, etc.).

2.2 Textile dye characterisation

The identification of individual unknown dyes in a coloured effluent or watercourse is difficult to be done and implies advanced analytical methods (i.e. individual and/or coupled spectrophotometry, G/L chromatography and mass spectrometry procedures), and also the colour determination and appreciation in different operating situations.

The characterisation and identification data of the textile dyes as main chemicals in dyeing process must consist of:

- dye identity data (i.e. name, C.I. or CAS number, molecular and structural formula; composition, degree of purity, spectral data; methods of detection and determination) (e.g., some examples illustrated in Fig. 2),
- dye production information (i.e. production process, proposed uses, form, concentration in commercially available preparations, estimated production, recommended methods and precautions concerning handling, storage, transport, fire and other dangers, emergency measures, etc.) (e.g. some indications in Table 3),
- dye physico-chemical properties (i.e. boiling point (b.p.), relative density, water solubility, partition coefficient, vapour pressure, self-ignition, oxidising properties, granulometry, particle size distribution, etc.) (e.g., for the first synthetic discovered dye: Aniline – 184 (b.p.), k_H= 2.05E-01, C_{sat}^{w}= 3.6E+04, pK_a= 4.6, log K_{ow}= 0.90; for 4,4’-

Methylenedianiline - 398 (b.p.), k_H= 5.67E-06, C_{sat}^w= 1000, pK_a= n.s., log K_{ow}= 1.59; for 4-Aminodiphenylamine - 354 (b.p.), k_H= 3.76E-01, C_{sat}^w= 1450, pK_a= 5.2, log K_{ow}= 1.82; where, k_H - the Henry's constant at 1013 hPa and 25°C (Pa·m^3/mol), C_{sat}^w - the water solubility (mg/L) at 25°C, pK_a – dissociation constant of the protonated azo dye at 25°C, K_{ow} – n-octanol/water partition coefficient, n.s. – not specified)

- toxicological studies (i.e. acute toxicity-oral, inhalation, dermal, skin or eyes irritation, skin sensitisation, repeated dose toxicity-28 days, mutagenicity, toxicity to reproduction, toxicokinetic behaviour),
- ecotoxicological studies (i.e. acute toxicity to fish, daphnia, growth inhibition on algae, bacteriological inhibition, degradation: ready biodegradability, abiotic degradation-hydrolysis as a function of pH, BOD, COD, BOD/COD ratio).

These characteristics and indentification data are given obligatory by the dye producers or distributors of textile products on the free market of homologated colorants, and also exist in the library data of some operating programs of advanced analysis apparatus.

The textile azo dyes are characterized by relatively high polarity (log K_{ow} up to 3) and high recalcitrance. Recalcitrance is difficult to evaluate because of the dependence of degradation on highly variable boundary conditions (e.g., redox milieu or pH). For example, aniline (the first synthetic discovered dye) is known to be easily degradable, but under specific anoxic conditions it has been proven to be easily stable (Börnick and Schmidt, 2006). Furthermore, the azo dyes are relevant in terms of eco- and human toxicity, industrially produced in high quantities, and known to occur in hydrosphere.

The azo dyes can accept protons because of the free electron pair of the nitrogen, and the free electron pair of nitrogen interacts with the delocalized π-orbital system.

Acceptor substituients at the aromatic ring such as –Cl or –NO_2 cause an additional decrease in the basic character of aminic groups. Donor groups such as –CH_3 or –OR (in metha and para position) lead to an increase in the basicity of aromatic aminic groups. However, donor substituients in the ortho position can sterically impede the protonation and consequently decrease the basicity of aminic groups. The azo dyes are characterized by amphoteric properties when molecules contain additional acidic groups such as hydroxyl, carboxyl or sulfoxyl substituents.

Depending on pH value, the azo dyes can be anionic (deprotonation at the acidic group), cationic (protonated at the amino group) or non-ionic. Accordingly, knowledge of the acidity constants is indispensable for the characterization of the behavior of azo dyes. Environmental partitioning is influenced by substituents as well as the number of carbon atoms and aromatic structure of the carbon skeleton. The presence of an amino group causes a higher boiling point, a higher water solubility, a lower Henry's law constant, and a higher mobility in comparison with hydrocarbons (the amino group can also reduce the mobility by specific interactions with solids via covalent bonding to carbonyl moieties or cation exchange) (Börnick and Schmidt, 2006). The volatility of azo dyes in aqueous solution is in most cases very low. Some colour characteristics from different studies, tests and literature data are presented in Table 10, especially for reactive dyes.

The chromophore distribution in reactive dyes indicated that the great majority of unmetallised azo dyes are yellow, orange and red. Contrarily, the blue, green, black and brown contain a much more proportion of metal-complex azo, anthraquinone, triphenyldioxazine or copper phthalocyanine chromophores (Table 10).

Chemical class	**Yellow**	**Orange**	**Red**	**Violet**	**Blue**	**Green**	**Brown**	**Black**	**Proportion of all reactive dyes**
Unmetallised azo	97	90	90	63	20	16	57	42	66
Metal complex azo	2	10	9	32	17	5	43	55	15
Anthraquinone	-	-	-	5	34	37	-	3	10
Phthalocyanine	-	-	-	-	27	42	-	-	8
Miscellanous	1	-	1	-	2	-	-	-	1

Table 10. Distribution of chemical classes in reactive dye range (adapted from Cooper, 1995)

In general, colour in wastewater is classified in terms of true/real colour (i.e. colour of turbidity-free water sample), or apparent colour (i.e. colour of non-treated water sample). The most common methods to measure the colour of dye solution or dispersion, and/or wastewater are visual comparison and spectrophotometry, although there is still a lack of an universal method to classify coloured wastewater discharges. By *visual comparison*, colour is quantified by comparing the colour of sample with either known concentrations of coloured standards (normally a platinum-cobalt solution), or properly calibrated colour disks, and is less applicable for highly coloured industrial wastewaters. In the *spectrophotometric method*, colour-measuring protocols differ between the methodologies, of which the most commonly used are Tristimulus Filter Method, American Dye Manufacturer Institute (ADMI) Tristimulus Filter Method, and Spectra record (Table 11).

Spectrophotometric method	**Description**
Tristimulus	Three tristimulus light filters combined with a specific light source (i.e. tungsten lamp) and a photoelectric cell inside a filter photometer. The output transmittance is converted to trichromatic coefficient and colour characteristic value.
ADMI Tristimulus	The ADMI colour value provides a true watercolour measure, which can be differentiated in 3 (WL) ADMI (i.e. the transmittance is recorded at 590, 540 and 438 nm) or 31 (WL) ADMI (i.e. the transmittance is determined each 10 nm in the range of 400-700 nm).
Spectra record	The complete spectrum is recorded, and the entire spectrum, or a part of it, is used for comparison. A modified method has been suggested in which areas beneath an extinction curve represent the colour intensity, being expressed as space units.

Table 11. Spectrophotometric methods for colour determination in dye solution or dispersion, water and wastewater (adapted from Dos Santos et al., 2004).

2.3 Dye fixation on textile fibres

In general, textile fibres can catched dyes in their structures as a result of van der Waals forces, hydrogen bonds and hydrophobic interactions (physical adsorption). The uptake of the dye in fibres depends on the dye nature and its chemical constituents. But the strongest dye-fibre attachment is a result of a covalent bond with an additional electrostatic interaction where the dye ion and fibre have opposite charges (chemisorption).

In alkaline conditions (i.e. pH 9-12), at high temperatures (30-70ºC), and salt concentration from 40-100 g/L, reactive dyes form a reactive vinyl sulfone ($-SO_3-CH=CH_2$) group, which creates a bond with the fibres. However, the vinyl sulfone group undergoes hydrolysis (i.e. a spontaneous reaction that occurs in the presence of water), and because the products do not have any affinity with the fibres, they do not form a covalent bond (Dos Santos et al., 2004). Therefore, a high amount of dye constituents are discharged in the wastewater.

The fixation efficiency varies with the class of azo dye used, which is around 98% for basic dyes and 50% for reactive dyes (Table 12) (Bertea A. & Bertea A.P., 2008; O'Neill et al., 1999). Large amounts of salts such as sodium nitrate, sodium sulphate and sodium chloride are used in the dyebath, as well as sodium hydroxide that is widely applied to increase the pH to the alkaline range. It is estimated that during the mercerising process the weight of these salts can make up 20% of the fibre weight (EPA, 1997).

Dye class	**Fibre type**	**Fixation degree, %**	**Loss in effluent, %**
Acid	Polyamide	80-95	5-20
Basic	Acrilic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal complex	Wool	90-98	2-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Dye-stuff	Cellulose	80-95	5-20

Table 12. Fixation degree of different dye classes on textile support (EWA, 2005).

The problem of high coloured effluent or dye-containing effluent has become identified particularly with the dyeing of cellulose fibres (cotton – 50% of the total consumed fibres in the textile industry worldwide), and in particular with the use of reactive dyes (10-50% loss in effluent), direct dyes (5-30% loss in effluent), vat dyes (5-20% loss in effluent), and sulphur dyes (10-40% loss in effluent).

The research for dynamic response and improved dyeing productivity has served to focus the attention of the textile coloration industry on right-first-time production techniques that minimise wastes, make important contribution to reduce colour loads in the effluent by optimisation of processes, minimising of dye wastage, and control automatically the dyeing and printing operation.

After the textile dyeing and finishing processes, a *predicted environmental concentration* of a dye in the receiving water can be estimated based on the following factors: (*i*) daily dye usage; (*ii*) dye fixation degree on the substrate (i.e. textile fibres or fabrics); (*iii*) dye removal degree into the effluent treatment process, and (*iv*) dilution factor in the receiving water.

Some scenario analyses were mentioned the values of dye concentration in some receiving rivers of 5-10 mg/L (average value, 50 days each year) or 1300-1555 mg/L (the worst case, 2 days each year) for batchwise dyeing of cotton with reactive dyes, and of 1.2-3 mg/L (average value, 25 days each year) or 300-364 mg/L (the worst case, 2 days each year) for batchwise dyeing of wool yarn with acid dyes (adapted from Cooper Ed., 1995).

Limits on dye-containing organic loads will become more restrictive in the future, which makes cleaning exhausts an environmental necessity.

3. Textile organic dyes – Environmental problems and polluting effects

The environmental issues associated with residual dye content or residual colour in treated textile effluents are always a concern for each textile operator that directly discharges, both sewage treatment works and commercial textile operations, in terms of respecting the colour and residual dye requirements placed on treated effluent discharge (Zaharia et al., 2011).

Dye concentrations in watercourses higher of 1 mg/L caused by the direct discharges of textile effluents, treated or not, can give rise to public compliant. High concentrations of textile dyes in water bodies stop the reoxygenation capacity of the receiving water and cut-off sunlight, thereby upsetting biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae (Zaharia et al., 2009).

The colour in watercourses is accepted as an aesthetic problem rather than an eco-toxic hazard. Therefore, the public seems to accept blue, green or brown colour of rivers but the ‘non-natural’ colour as red and purple usually cause most concern.

The polluting effects of dyes against aquatic environment can be also the result of toxic effects due to their long time presence in environment (i.e. half-life time of several years), accumulation in sediments but especially in fishes or other aquatic life forms, decomposition of pollutants in carcinogenic or mutagenic compounds but also low aerobic biodegradability. Due to their synthetic nature and structure mainly aromatic, the most of dyes are non-biodegradable, having carcinogenic action or causing allergies, dermatitis, skin irritation or different tissular changes. Moreover, various azo dyes, mainly aromatic compounds, show both acute and chronic toxicity. High potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs, and also formation of hemoglobin adducts and disturbance of blood formation. LD_{50} values reported for aromatic azo dyes range between 100 and 2000 mg/kg body weight (Börnick & Schmidt, 2006).

Several azo dyes cause damage of DNA that can lead to the genesis of malignant tumors. Electron-donating substituents in ortho and para position can increase the carcinogenic potential. The toxicity diminished essentially with the protonation of aminic groups. Some of the best known azo dyes (e.g. Direct Black 38 azo dye, precursor for benzidine; azodisalicylate, precursor for 4-phenylenediamine) and their breakdown derivatives inducing cancer in humans and animals are benzidine and its derivatives, and also a large number of anilines (e.g. 2-nitroaniline, 4-chloroaniline, 4,4′-dimethylendianiline, 4-phenylenediamine, etc.), nitrosamines, dimethylamines, etc.

The main pollution characteristics and category (pollution risk) of the principal products used in processing of textile materials are summarized in Table 13 (EWA, 2005).

In different toxicological studies are indicated that 98% of dyes has a lethal concentration value (LC_{50}) for fishes higher than 1 mg/L, and 59% have an LC_{50} value higher than 100 mg/L (i.e. 31% of 100-500 mg/L and 28% higher than 500 mg/L).

Other ecotoxicological studies indicated that over 18% of 200 dyes tested in England showed significant inhibition of the respiration rate of the biomass (i.e. wastewater bacteria) from sewage, and these were all basic dyes (adapted from Cooper, 1995).

The bioaccumulation potential of dyes in fish was also an important measure estimating the bioconcentration factor (dye concentration in fish/dye concentration in water). No bioaccumulation is expected for dyes with solubility in water higher than 2000 mg/L.

Dyes are not biodegradable in aerobic wastewater treatment processes and some of them may be intactly adsorbed by the sludge at wastewater biological treatment (i.e. bioelimination by adsorptive removal of dyes).

Products used in textile industry	**Pollution characteristics**	**Pollution category**
Alkali, mineral acids, salts, oxidants	Inorganic pollutants, relatively inofensive	1
Sizing agents based on starch, natural oils, fats, waxes, biodegradable surfactants, organic acids, reducing agents	Easy biodegradables; with a moderate - high BOD_5	2
Colorants and optic whitening agents, fibres and impurities of polymeric nature, synthetic polymeric resins, silicones	Difficult to be biodegraded	3
Polyvinyl alcohols, mineral oils, tensides resistant to biodegradation, anionic or non-ionic emolients	Difficult to be biodegraded; moderate BOD_5	4
Formaldehyde or N-methylolic reagents, coloured compounds or accelerators, retarders and cationic emolients, complexants, salts of heavy metals	Can not be removed by conventional biological treatment, low BOD_5	5

Table 13. Characterization of products used in textile industry vs. their polluting effect

Some investigations of adsorption degree onto sludge of some azo dyes indicated typically high levels of adsorption for basic or direct dyes, and high to medium range for disperse dyes, all the others having very low adsorption, which appears to depend on the sulphonation degree or ease of hydrolysis. These tested azo dyes are presented in Table 14.

Group 1		**Group 2**	**Group 3**
Dyes unaffected by biological treatment		*Dyes eliminated by adsorption on sludge*	*Dyes with high biodegradability*
CI Acid Yellow 17	CI Acid Red	CI Acid Red 151	CI Acid Orange 7
CI Acid Yellow 23	CI Acid Red 14	CI Acid Blue 113	CI Acid Orange 8
CI Acid Yellow 49	CI Acid Red 18	CI Direct Yellow 28	CI Acid Red 88
CI Acid Yellow 151	CI Acid Red 337	CI Direct Violet 9	
CI Acid Orange 10	CI Acid Black 1		
CI Direct Yellow 4			

Table 14. Fate of water-soluble azo dyes in the activated sludge treatment (Cooper, 1995)

The high degree of sulphonation of azo dyes in Group 1 enhanced their water solubility and limited their ability to be adsorbed on the biomass. The dyes in Group 2 were also highly sulphonated but permitted a relatively good adsorption performance on sludge.

Other information in bioelimination of different reactive dyes mentioned that monoazo dyes are particularly poorly adsorbed, and disazos, anthraquinones, triphendioxazines and phthalocyanines are generally much better adsorbed than monoazos.

It is important to underline that toxic compounds (e.g. toxic aromatic amines, benzidine and its derivatives) can be formed in the environment via transformation of textile dye-precursors (e.g., reduction or hydrolysis of textile azo dyes). The textile dye-precursors are introduced in water environment due to industrial production of dyes and industrial production of textile fibres, fabrics and clothes via wastewater, sludge, or solid deposits.

The quality problem of dye content and/or colour in the dyehouse effluent discharged in watercourses can be solved by using of a range of advanced decolourisation technologies investigated by the major dye suppliers, textile operators and customers who are under pressure to reduce colour and residual dye levels in their effluents.

4. Textile organic dyes – Separation and elimination procedures from water environment (especially industrial wastewater)

The textile organic dyes must be separated and eliminated (if necessary) from water but especially from industrial wastewaters by effective and viable treatments at sewage treatment works or on site following two different treatment concepts as: (*1*) separation of organic pollutants from water environment, or (*2*) the partial or complete mineralization or decomposition of organic pollutants. Separation processes are based on fluid mechanics (sedimentation, centrifugation, filtration and flotation) or on synthetic membranes (micro-, ultra- and nanofiltration, reverse osmosis). Additionally, physico-chemical processes (i.e. adsorption, chemical precipitation, coagulation-flocculation, and ionic exchange) can be used to separate dissolved, emulsified and solid-separating compounds from water environment (Anjaneyulu et al., 2005; Babu et al., 2007; Robinson et al., 2001; Suteu et al., 2009a; Suteu et al., 2011a; Zaharia, 2006; Zaharia et al., 2009; Zaharia et al., 2011).

The partial and complete mineralization or decomposition of pollutants can be achieved by biological and chemical processes (biological processes in connection with the activated sludge processes and membrane bioreactors, advanced oxidation with ozone, H_2O_2, UV) (Dos Santos et al., 2004 ; Oztekin et al., 2010 ; Wiesmann et al., 2007 ; Zaharia et al., 2009).

A textile operator will decide on options available to plan forward strategy that will ensure compliance with the environmental regulators' requirements on a progressive basis focused on some options and applied solutions of different separation processes (sedimentation, filtration, membrane separation), and some physico-chemical treatment steps (i.e. adsorption; coagulation-flocculation with inorganic coagulants and organic polymers; chemical oxidation; ozonation; electrochemical process, etc.) integrated into a specific order in the technological process of wastewater treatment for decolourization or large-scale colour and dye removal processes of textile effluents.

To introduce a logical order in the description of treatment methods for textile dye and colour removal, the relationship between pollutant and respective typical treatment technology is taken as reference. The first treatment step for textile wastewater and also rainwater is the separation of suspended solids and immiscible liquids from the main textile effluents by gravity separation (e.g., grit separation, sedimentation including coagulation/flocculation), filtration, membrane filtration (MF, UF), air flotation, and/or other oil/water separation operations.

The following treatment steps are applied to soluble pollutants, when these are transferred into solids (e.g., chemical precipitation, coagulation/flocculation, etc.) or gaseous and soluble compounds with low or high dangerous/toxic effect (e.g., chemical oxidation, ozonation, wet air oxidation, adsorption, ion exchange, stripping, nanofiltration/reverse osmosis). Solid-free wastewater can either be segregated into a biodegradable and a non-biodegradable part, or the contaminants responsible for the non-biodegradable wastewater part that can be decomposed based on physical and/or chemical processes. After an adequate treatment, the treated wastewater (WW) can either be discharged into a receiving water body, into a subsequent central biological wastewater treatment plant (BWWTP) or a municipal wastewater treatment plant (MWWTP).

Some selected treatment processes for dyes and colour removal of industrial wastewater applied over the time into different textile units are summarized in Table 15. Some of these methods will be further detail and some of authors' results summarized.

Treatment methodology	**Treatment stage**	**Advantages**	**Limitations**
		Physico-chemical treatments	
Precipitation, coagulation-flocculation	Pre/main treatment	Short detention time and low capital costs. Relatively good removal efficiencies.	Agglomerates separation and treatment. Selected operating condition.
Electrokinetic coagulation	Pre/main treatment	Economically feasible	High sludge production
Fenton process	Pre/main treatment	Effective for both soluble and insoluble coloured contaminants. No alternation in volume.	Sludge generation; problem with sludge disposal. Prohibitively expensive.
Ozonation	Main treatment	Effective for azo dye removal. Applied in gaseous state: no alteration of volume	Not suitable for dispersed dyes. Releases aromatic dyes. Short half-life of ozone (20 min)
Oxidation with NaOCl	Post treatment	Low temperature requirement. Initiates and accelerates azo-bond cleavage	Cost intensive process. Release of aromatic amines
Adsorption with solid adsorbents such as:			
Activated carbon	Pre/post treatment	Economically attractive. Good removal efficiency of wide variety of dyes.	Very expensive; cost intensive regeneration process
Peat	Pre treatment	Effective adsorbent due to cellular structure. No activation required.	Surface area is lower than activated carbon
Coal ashes	Pre treatment	Economically attractive. Good removal efficiency.	Larger contact times and huge quantities are required. Specific surface area for adsorption are lower than activated carbon
Wood chips/ Wood sawdust	Pre treatment	Effective adsorbent due to cellular structure. Economically attractive. Good adsorption capacity for acid dyes	Long retention times and huge quantities are required.

Silica gels	Pre treatment	Effective for basic dyes	Side reactions prevent commercial application
Irradiation	Post treatment	Effective oxidation at lab scale	Requires a lot of dissolved oxygen (O_2)
Photochemical process	Post treatment	No sludge production	Formation of by-products
Electrochemical oxidation	Pre treatment	No additional chemicals required and the end products are non-dangerous/hazardous.	Cost intensive process; mainly high cost of electricity
Ion exchange	Main treatment	Regeneration with low loss of adsorbents	Specific application; not effective for all dyes
Biological treatments			
Aerobic process	Post treatment	Partial or complete decolourization for all classes of dyes	Expensive treatment
Anaerobic process	Main treatment	Resistant to wide variety of complex coloured compounds. Bio gas produced is used for stream generation.	Longer acclimatization phase
Single cell (Fungal, Algal & Bacterial)	Post treatment	Good removal efficiency for low volumes and concentrations. Very effective for specific colour removal.	Culture maintenance is cost intensive. Cannot cope up with large volumes of WW.
Emerging treatments			
Other advanced oxidation process	Main treatment	Complete mineralization ensured. Growing number of commercial applications. Effective pre-treatment methodology in integrated systems and enhances biodegradability.	Cost intensive process
Membrane filtration	Main treatment	Removes all dye types; recovery and reuse of chemicals and water.	High running cost. Concentrated sludge production. Dissolved solids are not separated in this process
Photocatalysis	Post treatment	Process carried out at ambient conditions. Inputs are no toxic and inexpensive. Complete mineralization with shorter detention times.	Effective for small amount of coloured compounds. Expensive process.
Sonication	Pre treatment	Simplicity in use. Very effective in integrated systems.	Relatively new method and awaiting full scale application.
Enzymatic treatment	Post treatment	Effective for specifically selected compounds.	Enzyme isolation and purification is tedious.

		Unaffected by shock loadings and shorter contact times required.	Efficiency curtailed due to the presence of interferences.
Redox mediators	Pre/ supportive treatment	Easily available and enhances the process by increasing electron transfer efficiency	Concentration of redox mediator may give antagonistic effect. Also depends on biological activity of the system.
Engineered wetland systems	Pre/post treatment	Cost effective technology and can be operated with huge volumes of wastewater	High initial installation cost. Requires expertise and managing during monsoon becomes difficult

Table 15. Various current and emerging dye separation and elimination treatments applied for textile effluents with their principal advantages and limitations (adapted from Anjaneyulu et al., 2005; Babu et al., 2007; Robinson et al., 2001)

4.1 Physical treatments

4.1.1 Adsorption

One of the most effective and proven treatment with potential application in textile wastewater treatment is adsorption. This process consists in the transfer of soluble organic dyes (solutes) from wastewater to the surface of solid, highly porous, particles (the adsorbent). The adsorbent has a finite capacity for each compound to be removed, and when is 'spent' must be replaced by fresh material (the 'spent' adsorbent must be either regenerated or incinerated).

Adsorption is an economically feasible process for dyes removal and/or decolourization of textile effluents being the result of two mechanisms: adsorption and ion exchange. The principal influencing factors in dye adsorption are: dye/adsorbent interaction, adsorbent surface area, particle size, temperature, pH, and contact time. Adsorbents which contain amino nitrogen tend to have a significantly larger adsorption capacity in acid dyes.

The most used adsorbent is activated carbon, and also other commercial inorganic adsorbents. Some 'low cost' adsorbents of industrial or agricultural wastes (i.e. peat, coal ashes, refused derived coal fuel, clay, bentonite and modified bentonite, red soil, bauxite, ebark, rice husk, tree barks, neem leaf powder, wood chips, ground nut shell powder, rice hulls, bagasse pith, wood sawdust, grounded sunflower seed shells, other ligno-cellulosic wastes, etc.) are also used for removal of dye and organic coloured matter from textile effluents (i.e. a removal of 40-90% basic dyes and 40% direct dyes, with maximum adsorption capacities for basic dyes of 338 mg/g) (Anjaneyulu et al., 2005; Bhattacharyya & Sarma, 2003; Gupta et al., 1992; Nigam et al., 2000; Ozcan et al., 2004; Robinson et al., 2001; Suteu & Zaharia, 2008; Suteu et al., 2009b; Suteu et al., 2011a,b; Zaharia et al., 2011). The use of these materials is advantageous mainly due to their widespread availability and cheapness. Sometimes the regeneration is not necessary and the 'spent' material is conventionally burnt although there is potential for solid state fermentation (SSF) for protein enrichment. The use of 'low cost' adsorbents for textile dye removal is profitable but requires huge quantity of adsorbents, being lower efficient than activated carbon. Some authors' results for dye adsorption are summarized in Table 16.

Adsorptive material	**Operating conditions / Optimal doses** (Adsorption + Sedimentation/Filtration)	**Adsorption efficiency for some tested textile dyes, %**
Peat	pH= 2 (BRed); 5.7 (MB, RhB); C_{dye}= (20-300) mg/L BRed; (19-134) mg/L MB; (28-155) mg/L RhB; $C_{adsorbant}$= 12 g/L	(67.50 – 85.60) BRed (65.70– 89.30) MB (98.30– 99.00 RhB
Wood sawdust	pH= 2 (BRed); 5,7 (MB; CV; RhB); 1 (RO); C_{dye}= (20-150) mg/L BRed; (6-40) mg/L MB; (8-50) mg/L CV; (9-58) mg/L RhB; (24-160) mg/L (RO); $C_{adsorbant}$= 20 g/L (BRed); 4 g/L (MB, CV, RhB); 8 g/L (RO)	(63.90– 83.00) BRed (69.40 – 91.80) MB (66.00 – 80.00) CV (52.20 – 72.00) RhB (38.30 – 50.80) RO
Sunflower seed shell	pH= 1 (RO); 6 (MB); C_{dye}= (25–160) mg/L RO; (25–280) mg/L MB; $C_{adsorbant}$= 8 g/L (RO), 4 g/L (MB)	(80.60 – 82.60) RO (84.40 – 93.00) MB
Corn cobs	pH= 1 (RO) or 6 (MB); C_{dye}= (24-160) mg/L RO; (25-280) mg/L MB; $C_{adsorbant}$= 8 g/L (RO), 4 g/L (MB)	(83.00 – 86.20) RO (87.20 – 98.10) MB
Lignine	pH= 1.5 (BRed); 1 (RO); 6 (MB); C_{dye}= (50-300) mg/L BRed; (25.60-280) mg/L MB; (30-150) mg/L RO; $C_{adsorbant}$= 14 g/L (BRed); 4 g/L (MB); 12 g/L (RO)	(49.50-59.50) BRed (43.50-60.70) RO (55.30-64.30) MB
Cellolignine	pH=6; C_{dye}= (25.6-281.6) mg/L MB; $C_{adsorbant}$= 4 g/L	(96.60 – 98.40) MB
Abbreviations: BRed - Brilliant Red HE-3B (Reactive Red 120)/CI 25810; RO - Reactive Orange 16/CI 17757; MB - Methylene Blue (Basic Blue 9)/CI 52015; RhB - Rhodamine B (Basic Violet 10)/CI 45170; CV - Crystal Violet (Basic Violet 3)/CI 42555		

Table 16. Dye adsorption performance onto some natural adsorptive materials (adapted from Suteu et al., 2009b; Suteu et al., 2011a,b).

Adsorption with activated carbon. Activated carbon have been engineered for optimal adsorption of the contaminants found in dyehouse effluents: large, negatively charged or polar molecules of dyes. Powdered or granular activated carbon (specific surface area of 500-1500 m^2/g; pore volume of 0.3-1 cm^3/g; bulk density of 300-550 g/L) has a reasonably good colour removal capacity when is introduced in a separate filtration step. The activated carbon is used as granulate (GAC) in columns or as powder (PAC) in batchwise treatment into a specific treatment tank or basin. High removal rates are obtained for cationic mordant and acid dyes (Anjaneyulu et al., 2005), and a slightly lesser extent (moderate) for dispersed, direct, vat, pigment and reactive dyes (Cooper, 1995; Nigam et al., 2000) with consumable doses of 0.5-1.0 kg adsorbent/m^3 wastewater (i.e. dye removal of 60-90%).

Most recent studies mentioned that an effective irreversible adsorption of dye molecules onto the adsorbent particles takes place via a combination of physical adsorption of dye onto adsorbent surfaces within the microporous structure of the particles, enhanced by an ion-exchange process wherein the interlayer anions of the adsorbent are displaced by the dye molecules, and also inter-particle diffusion processes. Removal of pollutants can take place at any pH between 2 and 11, and at any temperature between 0 and 100°C (effluent temperature as received, generally 30-40°C).

The adsorption on activated carbon without pretreatment is imposible because the suspended solids rapidly clog the filter, and may be feasible in combination with flocculation-sedimentation treatment or a biological treatment (Masui et al., 2005; Ramesh Babu et al., 2007). The main important disadvantage of this process is attributed to the high cost of activated carbon. Performance is dependent on the type of activated carbon used and wastewater characteristics, and can be well suited for one particular wastewater system and ineffective in another. The activated carbon has to be reactivated otherwise disposal of the concentrates has to be considered (reactivation results in 10-15% loss of the adsorbent).

4.1.2 Irradiation

The irradiation treatment is a simple and efficient procedure for eliminating a wide variety of organic contaminants, and as well disinfecting harmful microorganism using gamma rays or electron beams (e.g., source for irradiation can be a monochromatic UV lamps working under 253.7 nm). A high quantity of dissolved oxygen is required for an organic dye to be effectively broken down by irradiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. Irradiation treatment of a secondary effluent from sewage treatment plant reduced COD, TOC and colour up to 64%, 34% and 88% respectively, at a dose of 15 K Gy gamma-rays (Borrely et al., 1998). The efficiency of irradiation treatment increases when is used catalyst as titanium dioxide (Krapfenbauer et al., 1999). A lot of data are reported with the practical results obtained at the simple exposure of different dye solutions or dispersions and dye-containing textile wastewaters to sunlight for a period of a half, one or two months (direct photolysis with natural sunlight into open basins). All these reports indicated high removals of colour (>84%), dye destruction by photooxidation following first order kinetics at treatment of some vat dye effluents. But the direct photolysis of textile organic dye in the natural aquatic environment has proven difficult due to strong dependence of the decay rates on dye reactivity and photosensitivity. Most of all commercial dyes are usually designed to be light resistant. Therefore, the recent researches have been directed towards investigation of organic dye photodegradation by sensitizers or catalysts in aqueous/dispersion systems by UV irradiation. Moreover, there are reported high removal of indigo-colour when is initiated a laser fading process for indigo coloured denim textile mainly based on basic interaction of laser beam with indigo-coloured textile (Dascalu et al., 2000).

4.1.3 Membrane processes

The increasing of water cost and necessity of reduction of water consumption implies treatment process which is integrated with in-plant water circuits rather than subsequent treatment (Baban et al., 2010; Machenbach, 1998). From this point of view, membrane filtration offers potential application in combination with other textile effluent treatments.

Membrane processes for wastewater treatment are pressure-driven processes, capable to clarify, concentrate, and most important, separate dye discontinuously from effluent (Xu & Lebran, 1991). These are new technologies, which can restrict organic contaminants and microorganisms presented in wastewater (i.e. color removal, BOD reduction, salt reduction, Polyvinyl Acetate (PVA) recovery, and latex recovery). The common membrane filtration types are: Micro-Filtration (MF), Ultra-Filtration (UF), Nano-Filtration (NF), and Reverse Osmosis (RO). The choice of the membrane process must be guided by the required quality of the final effluent.

Micro-filtration is mainly used for treatment of dye baths containing pigment dyes as well as for subsequent rinsing baths (Ramesh Babu et al., 2007). Chemicals that can not be filtrated by microfiltration will remain in the dye bath. Microfiltration can be used as a pretreatment for nanofiltration or reverse osmosis (Ghayeni et al., 1998), and also to separate suspended solids, colloids from effluents or macromolecules with pores of 0.1 to 1 micron.

MF performance is typically of >90% for turbidity or silt density index. Microfiltration membranes are made of specific polymers such as Poly (Ether Sulfone), Poly (Vinylidiene Fluoride), Poly (Sulfone), Poly (Vinylidene Difluoride), Polycarbonate, Polypropylene, Poly Tetrafluoroethylene (PTFE), etc. Ceramic, glass, carbon, zirconia coated carbon, alumina and sintered metal membranes have been employed where extraordinary chemical resistance or where high temperature operation is necessary. MF and UF operate at 20 to 100 psi transmembrane pressures (Ptm) (low pressure membrane procees) and velocities of 20 to 100 cm/s (Naveed et al., 2006).

Ultra-filtration is used to separate macromolecules and particles, but the elimination of polluting substances such as dyes is never complete (only 31-76% dye removal). The quality of treated wastewater does not permit its reuse for sensitive processes, such as textile dyeing (Ramesh Babu et al., 2007) but permit recycling of 40% treated wastewater in stages in which salinity is not a problem, such as rinsing, washing, etc. Ultrafiltration can only be used as a pretreatment for reverse osmosis (Ciardelli & Ranieri, 2001) or in combination with a biological reactor (Mignani et al., 1999) or to remove metal hydroxides (reducing the heavy metal content to 1 ppm or less) (Naveed et al., 2006). UF membranes are made of polymeric materials (i.e. polysulfone, polypropylene, nylon-6, polytetrafluoroethylene (PTFE), polyvinyl chlorides (PVC), acrylic copolymer etc.

Nano-Filtration was used for the treatment of coloured effluents from the textile industry, mainly in a combination of adsorption (for decreasing of concentration polarization during the filtration process) and nanofiltration (NF modules are extremely sensitive to fouling by colloidal material and macromolecules). NF membranes are generally made of cellulose acetate and aromatic polyamides, and retain low-molecular weight organic compounds, divalent ions, large monovalent ions, hydrolized reactive dyes, and dyeing auxiliaries. Inorganic materials, such as ceramics, carbon based membranes, zirconia, are also used in manufacturing NF and RO membranes. Typical NF flux rates are 5 to 30 GFD (Gross Flow per Day) (Naveed et al., 2006). A performance of above 70% colour removal for a NF plant was reported working at 8 bar/18°C, with four polyethersulphonate membranes with molecular weight cut offs of 40, 10, 5 and 3 kda for three different effluents coming from dyeing cycle of textile industry (Alves & Pinho, 2000). Values of colour removal higher than 90% were reported for single NF process, and also combination MF and NF, in the case of different effluents from textile fabrics processing. Harmful effects of high concentrations of dye and salts in the dye house effluents were frequently reported (i.e. concentration of dye > 1.5 g/L, and of mineral salts >20 g/L) (Tang & Chen, 2002). An important problem is the acculumation of dissolved solids, which makes discharge of treated effluents in watercourses almost impossible. NF treatment can be an alternative fairly satisfactory for textile effluent decolourization.

Reverse Osmosis is used to remove in a single step most types of ionic compounds, hydrolized reactive dyes, chemical auxiliaries, and produce a high quality of permeate (Ramesh Babu et al., 2007). Like NF, RO is very sensitive to fouling and the influent must be carefully pretreated. RO membranes are generally made of cellulose acetate and aromatic polyamides but also of inorganic materials. The Ptm in RO is typically 500 to 1000 psi, with cross flows of 20 to 100 cm/s. The range of typical RO fluxes is 5 to 15 GFD (Naveed et al., 2006). In combination with physio-chemical treatment, the membrane processes has advantages over the other conventional treatments, such as the ability to recover materials with valuable recyclable water, reducting fresh water consumption and wastewater treatment costs, small disposal volumes which minimizes waste disposal costs, reduction of regulatory pressure and fine improved heat recovery systems. Membrane processes have many cost-effective applications in textile industry.

4.2 Chemical treatment

4.2.1 Oxidative processes

Chemical oxidation represents the conversion or transformation of pollutants by chemical oxidation agents other than oxygen/air or bacteria to similar but less harmful or hazardous compounds and/or to short-chained and easily biodegradable organic components (aromatic rings cleavage of dye molecules).

The modern textile dyes are resistant to mild oxidation conditions such those existing in biological treatment systems. Therefore, efficient dye and colour removal must be accomplished by more powerful oxidising agents such as chlorines, ozone, Fenton reagents, UV/peroxide, UV/ozone, or other oxidising procedures or combinations.

Oxidative processes with hydrogen peroxide. The oxidation processes with hydrogen peroxide (H_2O_2) (oxidation potential, E°= 1.80 V at pH 0, and E°= 0.87 V at pH 14) can be explored as wastewater treatment alternatives in two systems: (1) homogenous systems based on the use of visible or ultraviolet light, soluble catalysts (Fenton reagents) and other chemical activators (e.g. ozone, peroxidase etc.) and (2) heterogenous systems based on the use of semiconductors, zeolites, clays with or without ultraviolet light, such as TiO_2, stable modified zeolites with iron and aluminium (i.e. FeY_5, $FeY_{11.5}$ etc.) (difficulty encountered in the separation of the solid photocatalysts at the end of the process) (Neamtu et al., 2004; Zaharia et al., 2009).

Fenton reagent is usually hydrogen peroxide (H_2O_2) that is activated by some iron salts (i.e. Fe^{2+} salts) (without UV irradiation) to form hydroxyl radicals ($HO\cdot$) which are strong oxidants (oxidation potential, E°= 3.06 V) than H_2O_2 and ozone. The Fenton oxidation reactions are detailed in other chapters of this book, and the treatment efficiency depends mainly of effluent characteristics, and operating parameters (e.g., colour removal of 31.10 or 56.20%, at a pH of 4.00, for Fenton oxidation of textile Remazol Arancio 3R, Remazol Rose RB dye-containing effluents working with 0.18-0.35 M H_2O_2 and 1.45 mM Fe^{2+}, after 30 or 120 min) (Zaharia et al., 2011).

Heterogenous catalytic oxidation with 20 mM H_2O_2 and $FeY_{11.5}$ (1 g/L) of Procion Marine H-EXL dye-containing effluents lead to colour removal of 53-83%, COD removal of 68-76% and TOC removal of 32-37% at pH=3-5, after 10 min of oxidation (Neamtu et al., 2004). Working with FeY_5 (1 g/L) and 20 mM H_2O_2, at pH=3 and 5, for the same textile effluent the treatment *efficiency*, was of 95 and 35% for colour and COD removal after 10 min of oxidation, and 97% for colour after 60 min of oxidation; COD removal (60 min) of 64.20% (Zaharia, 2006).

When small quantities of wastewater are involved or when there is no biotreatment available at the textile site, chemical oxidation might be recommendable treatment option instead of installing a central biological WWT plant. Advantages of this oxidative treatment include reduction of effluent COD, colour and toxicity, and also the possibility to be used to remove both soluble and insoluble dyes (i.e. disperse dyes). Complete decolourization was obtained after the complete Fenton reagent stage (generally 24 hours).

Ozonation process. Ozone is a powerful oxidising agent (oxidation potential, E°= 2.07 V) capable of cleavage the aromatic rings of some textile dyes and descomposition of other organic pollutants from industrial effluents. The ozone decomposes the organic dyes with conjugated double bonds forming smaller molecules with increased carcinogenic or toxic properties, and so ozonation may be used alongside a physical method to prevent this (i.e. irradiation, membrane separation, adsorption, etc). Ozone can react directly or indirectly with dye molecules. In the direct pathway, the ozone molecule is itself the electron acceptor, and hydroxide ions (i.e. pH > 7-8) catalyze the auto decomposition of ozone to hydroxyl radicals (·OH) in aqueous effluents (very strong and non-selective oxidants) which react with organic and inorganic chemicals. At low pH ozone efficiently reacts with unsaturated chromophoric bonds of a dye molecule via direct reactions (Adams & Gorg, 2002).

The main advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. A disadvantage of ozonation is its short half-life, tipically being 20 min, the destabilisation by the presence of salts, pH, and temperature, and the additional costs for the installation of ozonation plant. The improvement of ozonation preformance is obtained in combination with irradiation (Surpateanu & Zaharia, 2004a; Zaharia et al., 2009) or with a membrane filtration technique (Lopez et al., 1999). Treatment of dye-containing wastewater with ozone followed by chemical coagulation using $Ca(OH)_2$ indicated 62% colour removal after ozonation (Sarasa et al., 1998).

Oxidation process with sodium hypochlorite. This treatment implies the attack at the amino group of the dye molecule by Cl^+, initiating and accelerating azo-bond cleavage. The increasing of chlorine concentration favors the dye removal and decolourization process, and also the decreasing of pH. The dye containing amino or substituted amino groups on the naphthalene ring (i.e. dyes derived from amino-naphtol- and naphtylamino-sulphonic acids) are most susceptible for chlorine decolourization (Omura, 1994). This treatment is unsuitable for disperse dyes, and is becoming less frequent due to the negative effects at releasing into watercourses of aromatic amines or otherwise toxic molecules. Moreover, althought about 40% of the pigments used worldwise contain chlorine this corresponds to only less than 0.02% of the total chlorine production (Slokar & Le Marechal, 1997).

Photochemical oxidation process. The UV treatment in the presence of H_2O_2 can descomposed dye molecules to low weight organic molecules, or even to CO_2, H_2O, other inorganic oxides, hydrides, etc. There can be also produced additional by-products such as halides, metals, inorganic acids, organic aldehydes and organic acids depending on initial materials and the extent of decolourisation treatment (Yang et al., 1998). The dye decomposition is initiated by the generated hydroxyl radicals ($H_2O_2 + h\upsilon \rightarrow 2HO\cdot$) and hydroperoxide radicals ($H_2O_2 + HO\cdot \rightarrow HO_2\cdot + H_2O$).

The treatment may be set-up in a batch or continuous column unit, and is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition (Slokar & Le Marechal, 1997). The performance of photooxidation treatment in the presence of hydrogen peroxide are high (i.e. >60-90% for colour removal, working with 400-500 mg/L H_2O_2 at pH 3-7, for Red M5B, H-acid and Blue MR dye-containing effluents) (Anjaneyulu et al., 2005) or 81-94% dye removal after 60 min, working with 88 mM H_2O_2 at pH of 4-6, for Acid Red G dye-containing effluent (Surpateanu & Zaharia, 2004b; Zaharia et al., 2009).

Electrochemical oxidation process. As an advanced process, the electrochemical treatment of dye-containing effluents is a potentially powerful method of pollution control, offering high removal efficiencies (Anjaneyulu et al., 2005) especially for acid dyes as well as disperse and metal complex dyes. The main advantages of this treatment are considered the requirement of simple equipment and operation, low temperature in comparison with other non-electrochemical treatments, no requirement of any additional chemicals, easy control but crucial for pH, the electrochemical reactors (with electrolytic cells) are compact, and prevent the production of unwated by-products. The principal oxidising agent in electrochemical process is hypochlorite ion or hypochlorous acid produced from naturally occuring chloride ions. Hydroxyl radical and other reactive species also participate in electrochemical oxidation of organics (Kim et al., 2002) that can be achieved directly or indirectly at the anode. The breakdown compounds are generally not hazardous being discharged into watercourses without important environmental and health risks.

The electrochemical oxidation is considered an efficient and economic treatment of recycling textile wastewater for the dyeing stage. The environmental advantage mainly achieved is the minimization of all emissions: emission of gases, solid waste, and liquid effluent. Other important advantage is its capacity of adaptation to different volumes and pollution loads. The main disadvantage is the generation of metallic hydroxide sludge (from the metallic electrodes in the cell), that limits its use (Ramesh Babu et al., 2007).

Some studies reported colour removals of about 100% for dyeing wastewater within only 6 min of electrolysis (Vlyssides et al., 2000) (e.g., complete decolourization of textile effluent containing blue-26 anthraquinone dye by electrochemical oxidation with lead dioxide coated anode - Titanium Substract Insoluble Anode (TSIA), at neutral pH, in the presence of sodium chloride, current density of 4.5 A/dm^2, electrolysis time of 220 min, or maximum 95.2% colour and 72.5% COD removal of textile azo dye-containing effluent in a flow reactor working at rate of 5 mL/min and current density of 29.9 mA/cm^2) (Anjaneyulu et al., 2005).

4.2.2 Coagulation-flocculation and precipitation

It is clearly known that the coloured colloid particles from textile effluents cannot be separated by simple gravitational means, and some chemicals (e.g., ferrous sulphate, ferric sulphate, ferric chloride, lime, polyaluminium chloride, polyaluminium sulphate, cationic organic polymers, etc.) are added to cause the solids to settle. These chemicals cause destabilisation of colloidal and small suspended particles (e.g. dyes, clay, heavy metals, organic solids, oil in wastewater) and emulsions entrapping solids (coagulation) and/or the agglomeration of these particles to flocs large enough to settle (flocculation) or highly improve further filtration (Zaharia et al., 2006; Zaharia et al., 2007). In the case of flocculation, anionic and non-ionic polymers are also used.

The mechanism by which synthetic organic polymer removes dissolved residual dyes from effluents is best described in terms of the electrostatic attraction between the oppositely charged soluble dye and polymer molecules. Many of the most problematic dye types, such as reactive dyes, carry a residual negative charge in their hydrolysed dissolved form, and so positively charged groups on the polymers provide the neccesary counter for the interaction and subsequent precipitation to occur. The immediate result of this coprecipitation is the almost instantaneous production of very small coloured particles, having little strength and breaking down at any significant disturbances. The agglomeration of the coloured precipitates by using appropriate high polyelectrolyte flocculants produces stable flocs (Zaharia et al., 2007, 2011). The main disadvantages of this treatment are the process control that is a little difficult, the potential affection of precipitation rate and floc size by impurities such as non-ionic detergents remaining in the effluent, and the sludge production which has to be settled, dewatered and pressed into a cake for subsequent landfilling tipping.

There are reported very effective chemical coagulation-flocculation (C-F) and precipitation of textile wastewater which reduced the load on the biological treatment, working with polyaluminium chloride along with an organic polymer (Lin & Chen, 1997) or ferrous/ferric chloride and a commercial organic coagulant aid at pH of 6.7-8.3 (colour removal > 80%) (Venkat Mohan et al., 1999) or alum at pH=8.2 (54-81% colour removal) with addition of bentonite (3 g/L) for Remazol Violet dye-containing effluent (Sanghi et al., 2001). Other efficient textile treatments mentioned by different textile operators consist in coagulation-flocculation followed by membrane technology (especially for recycling textile effluents).

Some of authors' results in different (C-F) treatments are summarized in Table 17.

Process	**Coagulant/ Flocculant**	**Wastewater characteristics or dye type / Results**
Coagulation-flocculation/ sedimentation/ filtration	Ferrous sulphate (5 mg/L) + Ponilit GT-2 anionic polyelectrolyte (15 mg/L) + bentonite (3 g/L)	*Wastewater characteristics*: pH=6.5-7; TSS=250-1000 mg/L; colour=650 UH; COD_{Cr}=152.7-272 mg O_2/L *Process efficiency*: turbidity removal=70.31-91.34%; colour removal=70.20-90.50% and COD_{Cr} removal=34.90-45.20%
Precipitation/ flocculation/ flotation with dissolved air	NaOH + Na_2CO_3 + $Ca(OH)_2$, Ponilit GT-2 anionic polyelectrolyte	*Wastewater characteristics*: pH=7.0-9.5; total metallic ions= 48.30 mg/L; extractable substances in organic solvents= 980 mg/L *Process efficiency*: Metallic ions removal=78.67-92.33%
Coagulation-flocculation/ sedimentation/ filtration	Ferric sulfate (2-5 mg/L) +Prodefloc CRC 301 (0.25-1.5 mg/L) cationic polyelectrolyte	*Wastewater characteristics*: pH=6.98; T=20°C, Turbidity=556 FTU; COD_{Cr}=152.60 mg O_2/L; colour=1320 UH *Process efficiency*: maximal turbidity removal=95.87% and colour removal= 93.90-98.10%

Table 17. Some applications of coagulation- flocculation in wastewater treatment (adapted from Zaharia, 2006; Zaharia et al., 2006, 2007).

4.2.3 Electrocoagulation

An advanced electrochemical treatment for dye and colour removal is electrocoagulation (EC) that has as main goal to form flocs of metal hydroxides within the effluent to be cleaned by electro-dissolution of soluble anodes. EC involves important processes as electrolytic reactions at electrodes, formation of coagulants in aqueous effluent and adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation and flotation. This treatment is efficient even at high pH for colour and COD removals being strongly influenced by the current density and duration of reaction. The EC treatment was applied with high efficiency for textile Orange II and Acid red 14 dye-containing effluents (i.e. > 98% colour removal) (Daneshvar et al., 2003) or Yellow 86 dye-containing wastewater (i.e. turbidity, COD, extractible substances, and dye removal of 87.20%, 49.89%, 94.67%, and 74.20%, after 30 min of operation, current intensity of 1 A, with monopolar electrodes) (Zaharia et al, 2005) when iron is used as sacrificial anode. In general, decolorization performance in EC treatment is between 90-95%, and COD removal between 30-36% under optimal conditions (Ramesh Babu et al., 2007).

4.2.4 Ionic exchange

The ion exchange process has not be widely used for treatment of dye-containing effluents, mainly because of the general opinion that ion exchangers cannot accomodate a wide range of dyes (Slokar & Le Marechal, 1997).

The ionic exchange occurs mainly based on the interaction of ionic species from wastewater with an adsorptive solid material, being distinguished from the conventional adsorption by nature and morphology of adsorptive material or the inorganic structure containing functional groups capable of ionic exchange (Macoveanu et al., 2002). The mechanisms of ionic exchange process are well known, and two principal aspects must be mentioned: (1) ionic exchange can be modeling as well as adsorption onto activated coal; (2) the ion exchangers can be regenerated without modifying the equilibrium condition (e.g., by passing of a salt solution containing original active groups under ion exchanger layer). In the case of wastewater treatment, the effluent is passed over the ion exchanger resin until the available exchange sites are saturated (both cationic and anionic dyes are removed).

The ionic exchange is a reversible process, and the regenerated ion exchanger can be reused. The essential characteristic of ionic exchange that makes distinction of adsorption is the fact that the replace of ions takes place in stoechiometric proportion (Macoveanu et al., 2002).

The effluent treatment by ionic exchange process contributes to the diminishing of energetic consumption and recovery of valuable components under diverse forms, simultaneously with the wastewater treatment. In practice, the ion exchangers are used in combination with other wastewater treatments. The main advantages of ion exchange are removal of soluble dyes, no loss of adsorbent at regeneration, and reclamation of solvent after use. The important disadvantages of this process is the cost, organic solvents are expensive, and ion exchange treatment is not efficient for disperse dyes (Robinson et al., 2001). Our results in batchwise treatment of Brilliant Red HE-3B dye-containing effluents (0.05 – 0.3 mg/mL) using anionic Purolite A-400 and Purolite A-500 indicated dye removal of 48-89% working in the optimal conditions, or dye removal of 56-78% for Crystal Violet (Basic Violet 3) using Purolite C-100 or dye removal between 78-89% for Reactive Blue M-EB using ion exchange celluloses (Suteu et al., 2002).

4.3 Biological treatments

Biological treatments are considered reproduction, artificially or otherwise, of self-purification phenomena existing in natural environment. There are different biological treatments, performed in aerobic or anaerobic or combined anaerobic/aerobic conditions. The processing, quality, adaptability of microorganisms, and the reactor type are decisive parameters for removal efficiency (Börnick & Schmidt, 2006).

Biological treatment process for decolorization of industrial effluents is ambiguous, different and divergent (Anjaneyulu et al., 2005). Previous subchapters indicate that dyes themselves are not biologically degradable since microorganisms do not use the coloured constituents as a source of food. The most currently used biodegradation involve aerobic micro-organisms, which utilize molecular oxygen as reducing equivalent acceptor during the respiration process. But biodegradation in anaerobic environment conditions (anoxic and hypoxic environments) also occurs, and survival of microorganisms is possible by using sulphates, nitrates and carbon dioxide as electron acceptors (Birch et al., 1989).

Research data indicates that certain dyes are susceptible to anoxic/anaerobic decolourization, and also that an anaerobic step followed by an aerobic step may represent a significant advancement in biological decolourization treatment in future (Ong et al., 2005). The treatment plant that receives dye-containing effluents has high potential to form toxic biodegradation products such as toxic amines, benzidine and its derivates, etc. To avoid that risk, anaerobic/aerobic sequential reactor systems seem to be an efficient procedure (i.e. efficient colour removal takes place during the anaerobic treatment, and high reduction of aromatic amines and other organic compounds occurs during the subsequent aerobic treatment). Under aerobic conditions, most of the azo dye metabolites are quickly degraded by oxidation of the substituents or of the side branches. However, some of them are still rather recalcitrant. Successful removal of poorly degradable amines was often achieved by adaptation of microorganisms (i.e. acclimatization of biological sludge to nitroaniline-containing wastewaters; after gradual adaptation, the microorganisms are able to eliminate 3- and 4-nitroaniline simultaneously) (Börnick & Schmidt, 2006). Difficult to be biodegraded are also the aromatic amines containing sulfo substituents in metha position (e.g., 3-aminobenzenesulfonate) that can be treated with good efficiencies with flow-through bioreactors within 28 days. Contrarily, some experimental results found anaerobic mineralization to be efficient for aromatic amines.

The main advantage of biological treatment in comparison with certain physico-chemical treatments is that over 70% of organic matter expressed by COD_{Cr} may be converted to biosolids (Anjaneyulu et al., 2005).

4.3.1 Aerobic biological treatment

Biological treatment with 'activated sludge' was the most used in large scale textile effluent treatment, and the trickling filter or biological aerated filter (BAF) is an alternative, permitting a 34-44% dye-colour removal for different high dyeing loads of industrial effluents. The main microorganisms contributing to biodegradation of organic compounds are bacteria (e.g. *Bacillus subtilis*, *Aeromonas Hydrophilia*, *Bacillus cetreus*, *Klebsiella pneunomoniae*, *Acetobacter liquefaciens*, *Pseudomonas* species, *Pagmentiphaga kullae*, *Sphingomonas*, etc.), fungi (e.g., white-rot fungi: *Phanerochaete chrysosporium*, *Hirschioporus larincinus*, *Inonotus hispidus*, *Phlebia tremellosa*, *Coriolus versicolor*, etc.), algae (e.g. *Chlorella* and *oscillotoria* species) etc. Moreover, some bacteria, white-rot fungi, mixed microbial cultures from a wide variety of habitats are found to be able to degrade dyes using enzimes, such as lignin peroxidases (LiP), manganese dependent peroxidases (MnP), H_2O_2-producing enzime such as glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenoloxidase. Biological aerated filters involve the growth of an organism on inert media that are held stationary during normal operation and exposed to aeration. In aerobic conditions, the mono- and dioxygenase enzymes catalyse the incorporation of dissolved oxygen into the aromatic ring of organic compounds prior to ring fission. Although azo dyes are aromatic compounds, their nitro and sulfonic groups are quite recalcitrant to aerobic bacterial degradation (Dos Santos et al., 2004). However, in the presence of specific oxygen-catalysed enzymes called azo reductases, some aerobic bacteria are able to reduce azo compounds and produce aromatic amines (Stolz, 2001). The batch experiments with aerobic activated sludge confirmed the biodegradability of sulphonated azo dyes. Only aerobic degradation of the azo dyes is possible by azo reduction (i.e. high colour removal (>90%) of Red RBN azo dye-containing effluents (3000 mg/L) working with *Aeromonas hydrophilla* in the specific optimal conditions of pH (5.5-10), temperature (20°-38°C), and time (8 days)), and mineralization does not occur. The subsequential anaerobic and aerobic bioreactor was able to completely remove the sulphonated azo dye (i.e. MY10) at a maximum loading rate of 210 mg/L per day (Tan et al., 2000). The degradation of azo dyes (i.e. Acid Red 151; Basic Blue 41; Basic Red 46, 16; Basic Yellow 28, 19) in an aerobic biofilm system indicated 80% colour removal (Anjaneyulu et al., 2005). The improvement of dye biodegradation performance (i.e. >90% colour removal) are made by adding activated carbon (PAC) or bentonite in aeration tank.

4.3.2 Anaerobic biological treatment

Anaerobic biodegradation of azo and other water-soluble dyes is mainly reported as an oxidation-reduction reaction with hydrogen, and formation of methane, hydrogen sulphide, carbon dioxide, other gaseous compounds, and releasing electrons. The electrons react with the dye reducing the azo bonds, causing the effluent decolourization. Azo dye is considered an oxidising agent for the reduced flavin nucleotides of the microbial electron chain, and is reduced and decolourized concurrently with reoxidation of the reduced flavin nucleotides (Robinson et al., 2001). An additional carbon organic source is necessary, such as glucose which is a limiting factor in scale set-up technology application. The azo and nitro-components are reduced in anoxic sediments and in the intestinal environment, with regeneration of toxic amines (Banat et al., 1996). A major advantage of anaerobic system along with effluent decolourization is the production of biogas, reusable for heat and power generation that will reduce energy costs. Since textile industry wastewaters are generally discharged at high temperatures (40–70°C), thermophilic anaerobic treatment could serve as an interesting option, especially when closing process water cycles is considered. Anaerobic decolourization of textile effluents (e.g., colour removal of >99% for a Orange II, Black 2HN under anaerobic condition, more than 72 h) is not yet well established although successful pilot-scale and full-scale plants are very well operating (Tan et al., 2000). Among the different studied reactors, anaerobic filter and UASB thermophilic anaerobic reactor gave good colour removals, using or not redox mediator (e.g., antraquinone-2,6, disulphonic acid) as catalyst capable of acceleration the colour removal of azo dye-containing wastewaters.

5. Conclusions

The dyes are natural and synthetic compounds that make the world more beautiful through coloured products but are also considered as pollutants of some water resources.

The textile sector will continue to be vitally important in the area of water conservation due to its high consumption of water resources, and its individual or combined effluents' treatments for no environmental pollution generation (i.e. polluting colourants).

The satisfaction of both discharge criteria for sewerage systems, watercourses and textile reuse standards within economically viable limits implies critical analyses of industrial effluents (total wastewater and raw reusable stream characterisation) and removal of all pollutants from final effluents. The special category of organic pollutants - textile organic dyes - must respect the strict limits in final effluents discharged or not in natural water resources. This fact imposes the colour and/or dye removal from final effluents (especially industrial effluents).

Dye removal from textile effluents in controlled conditions and strict reproductibility is an environmental issue achievable by application of adequate mechano-physico-chemical and also biological treatment procedures.

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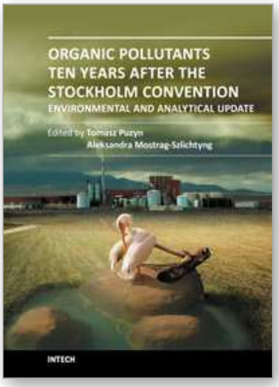

Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update

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Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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