

Production, Characterization and Treatment of Textile Effluents: A Critical Review

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Abstract

Textile industry is one of the major industries in the world that provide employment with no required special skills and play a major role in the economy of many countries. There are three different types of fibres used in the manufacture of various textile products: cellulose fibres, protein fibres and synthetic fibres. Each type of fibre is dyed with different types of dyes. Cellulose fibres are dyed using reactive dyes, direct dyes, naphthol dyes and indigo dyes. Protein fibres are dyed using acid dyes and lanaset dyes. Synthetic fibres are dyed using disperse dyes, basic dyes and direct dyes. The textile industry utilizes various chemicals and large amount of water during the production process. About 200 L of water are used to produce 1 kg of textile. The water is mainly used for application of chemicals onto the fibres and rinsing of the final products. The waste water produced during this process contains large amount of dyes and chemicals containing trace metals such as Cr, As, Cu and Zn which are capable of harming the environment and human health. The textile waste water can cause haemorrhage, ulceration of skin, nausea, skin irritation and dermatitis. The chemicals present in the water block the sunlight and increase the biological oxygen demand thereby inhibiting photosynthesis and reoxygenation process. The effluent water discharged from the textile industries undergoes various physio-chemical processes such as flocculation, coagulation and ozonation followed by biological treatments for the removal of nitrogen, organics, phosphorous and metal. The whole treatment process involves three steps: primary treatment, secondary treatment and tertiary treatment. The primary treatment involves removal of suspended solids, most of the oil and grease and gritty materials. The secondary treatment is carried out using microorganisms under aerobic or anaerobic conditions and involves the reduction of BOD, phenol and remaining oil in the water and control of color. The tertiary treatment involves the use of electro dialysis, reverse osmosis and ion exchange to remove the final contaminants in the wastewater. The major disadvantages of using the biological process are that the presence of toxic metals in the effluent prevents efficient growth of microorganisms and the process requires a long retention time. The advanced oxidation processes is gaining attention in the recent days due to the ability to treat almost all the solid components in the textile effluents. The photo oxidation of the effluents is carried out using H_2O_2 , combination of H_2O_2 and UV and Combination of TiO_2 and UV. Advanced oxidation process generates low waste and uses hydroxyl radicals (OH^*) as their main oxidative power. The hydroxyl radicals (OH^*) are produced by chemical, electrical, mechanical or radiation energy and therefore advanced oxidation processes are classified under chemical, photochemical, catalytic, photocatalytic, mechanical and electrical processes. The effluents treated with advanced oxidation process were found to reduce 70-80% of COD when compared to 30-45% reduction by biological treatment.

Keywords: Textiles; Dyes; Textile Wastewaters; Primary Treatment; Secondary Treatment; Tertiary Treatment; Advanced Oxidation; UV; TiO_2 ; H_2O_2 ; Exposure Time; COD.

Introduction

Textile and Clothing (T&C) is one of the largest and oldest industries present globally [1]. The T&C industry provides jobs with no required special skills, which in turn plays a major role in providing employment in poor countries like Bangladesh, Vietnam, Sri Lanka and Mauritius. Therefore, it plays a vital role in the increase of Gross Domestic Product (GDP) value of these countries [2].

The textile industry is classified into three main categories: cellulose fibres (cotton, rayon, linen, ramie, hemp and lyocell), protein fibres (wool, angora, mohair, cashmere and silk) and synthetic fibres (polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene). The type of dyes and chemicals used in the textile industry are found to differ depending on the fabrics manufactured. Reactive dyes (remazol, procion MX and cibacron F), direct dyes (congo red, direct yellow 50 and direct brown 116), naphthol dyes (fast yellow GC, fast scarlet R and fast blue B) and indigo dyes (indigo white, tyrian purple and indigo carmine) are some of the dyes used to dye cellulose fibres [3-5]. Protein fibres are dyed using acid dyes (azo dyes, triarylmethane dyes and anthraquinone dyes) and lanaset dyes (Blue 5G and Bordeaux B) [5-7]. Other dyes, like dispersed dyes (Disperse yellow 218 and disperse

navy 35), basic dyes (basic orange 37 and basic red 1) and direct dyes, are used to dye synthetic fibres [8,4].

Reactive dyes are the most commonly used cellulose fibre dye. Cotton, one of the most widely used fibres is dyed mainly using reactive dyes. The world use of reactive dyes increased from 60,000 tonnes in 1988 to 178,000 tonnes in 2004 [9]. Cotton could also be dyed using direct dyes, indigo dyes and naphthol dyes. The export and import world market for direct dyes and their preparations increased from 53,848 tonnes in 1992 to 181,998 tonnes in 2011 [10]. The annual world production of indigo dye is 80,000 tonnes [11], while the global import and export market for naphthol dye was about 112, 000 tonnes per year

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Received December 04, 2013; Accepted December 30, 2013; Published January 03, 2014

Citation: Ghaly AE, Ananthashankar R, Alhattab M, Ramakrishnan VV (2014) Production, Characterization and Treatment of Textile Effluents: A Critical Review. J Chem Eng Process Technol 5: 182. doi: [10.4172/2157-7048.1000182](https://doi.org/10.4172/2157-7048.1000182)

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[10]. Rayon, linen, ramie, hemp and lyocell could be dyed using both reactive dyes and direct dyes [4].

High pH is found to denature proteins; hence acid dyes are the most commonly used protein fibres. The chemical reactions between the acid dye and the fibres are found to form an insoluble dye molecule on the fibre [12]. Acid dyes are found to contain azo groups (-N=N-) in the center. It is estimated that the global import and export market for acid dye was 680,000 tonnes in 2011 [10]. Lanaset dyes are one popular group of dyes which are classified under both reactive and acid dyes that are used to dye protein fibres. Reactive dyes are commonly used to dye protein fibres. Wool, angora, mohair, cashmere and silk could be dyed using acid dyes or reactive dyes. Silk could also be dyed using naphthol dyes [13,14].

Dispersed dyes are the most commonly used synthetic fabrics dye used to dye polyester, nylon or acetates. The global import and export market for dispersed dyes and their preparations was increased from 150,000 tonnes in 1998 to 570 000 metric tonnes in 2011 [10]. Nylon fibres are found to be effective when dyed with direct dyes [4]. Basic dyes are found to be a powerful colouring agent when used on acrylic fibres [15].

Textile industries produce large amounts of liquid wastes that contain organic and inorganic compounds [16]. During the dyeing processes, not all dyes that are applied to the fabrics are fixed on them and there is always a portion of these dyes that remains unfixed to the fabrics and gets washed out. These unfixed dyes are found to be in high concentrations in textile effluents [17]. The amount of water consumed and released also varies depending on the type of fabrics produced. About 0.08-0.15 m³ of water is used to produce 1 kg of fabrics [18]. Pagga and Brown [19] and Kdasi et al. [20] estimated that about 1,000-3,000 m³ of water is let out after processing about 12-20 tonnes of textiles per day. These effluents are rich in dyes and chemicals, some of which are non-biodegradable and carcinogenic and pose a major threat to health and the environment if not properly treated.

Several primary, secondary and tertiary treatment processes have been used to treat these effluents. These included flocculation, chemical coagulation, simple sedimentation, aerated lagoons, aerobic activated sludge, trickling filters, reverse osmosis and electrodialysis. However, these treatments are not found effective against the removal of all dyes and chemicals used in the industry [20,21]. These effluents do not only contain high concentration of dyes, but also contain the chemicals used in the various processing stages. Some trace metals such as Cr, As, Cu and Zn are present in these effluent and are capable of causing several

health problems including haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis [22]. Textile effluents are also found to contain other organic and microbial impurities [23].

Advanced oxidation processes (AOPs) were developed to generate hydroxyl free radicals using different oxidants under different combinations. These radicals were found to destroy components that are not destroyed under conventional oxidation processes [24,20]. AOP using ozone, ultra violet, TiO₂, fenton, photo-phenton and hydrogen peroxide can be used to treat textile dyes. The main advantage of AOPs over the other treatment processes is its pronounced destructive nature and mineralization of organic contaminants present in wastewater [20]. AOPs are considered as a low or non-waste generation technologies that destroy complex structures using short lived chemical species with a high oxidation power. The hydroxyl radical (OH[•]) is the main oxidative power of AOPs [24,25]. The OH[•] radicals can be generated by chemical, electrical, mechanical or radiation energy. Therefore, AOPs are classified under chemical, photochemical, catalytic, photocatalytic, mechanical and electrical processes.

Types of Textiles and Textile Industries

The word textile means to weave which was adopted from the Latin word 'texere'. Textiles can be woven by both hand and machines. The raw materials for textiles are natural and synthetic fibers [16]. The sources of natural fibers are minerals, animals and plants. With the advancement of technology, fibers can now be extracted from chemicals. However, plant sources yield a large amount of fibers than those obtained from animal and mineral sources. Most of the textiles produced are as a result of spinning of fibers from the yarns [26,27].

The textile industries are classified on the basis of the types of textile fiber they use. These are cellulose fibers, protein fibers and synthetic fibers. Cellulose fibers are obtained from plant sources such as cotton, rayon, linen, ramie, hemp and lyocell [28]. Protein fibers are obtained from animals and include wool, angora, mohair, cashmere and silk. Artificially synthesized fibres include polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene. However, the majority of textiles are produced from cotton liners, petrochemicals and wood pulp. China is the biggest exporter of almost all the textiles followed by European Union, India, USA and Korea as shown in Table 1 [29]. The world production of different textiles during the past century (1900-2011) is shown in Figure 1 [30]. The quality of a textile depends on the type of raw material used and characteristics of the yarn spun.

Various manufacturing processes are carried out for different types of textiles. The major exporters of clothing are shown in Table 2 [29]. The production process of textiles can be broadly divided into two categories: the spinning process (the dry process) and the wet process (involves the usage of dyes). Production of cotton textiles involves the separation of cotton fibres from the cotton seeds which are then spun into cotton yarns [31]. These yarns are weaved successfully into cloths. The cloths then undergo various wet processes including singeing and scouring. This process uses a large amount of water. Dyeing is one of the most important steps in the wet process which involves changing the colour of the textile spun using dyes. Finishing is the final step in manufacturing and uses chemicals like HS-ULTRAPHIL, ECODESIZE-PS-10 and Amino silicone fluid to treat the cloths for obtaining a better quality [32]. An overall textile processing is shown in Figure 2. The major producers of cotton, wool, cocoons, jute and nylon are shown in Tables 3-7.

The first step in the production of leather products involves the

Country	Value (\$Billion)	Share (%)
China	94.4	32.1
EU27	76.6	26.1
India	15.0	5.1
United States of America	13.8	4.7
Korea Republic	12.4	4.2
Turkey	10.8	3.7
Pakistan	9.1	3.1
Indonesia	4.8	1.6
Vietnam	3.8	1.3
Bangladesh	1.6	0.5
Rest of the World	51.7	17.5
Total	294	99.9

*EU = European Union

Table 1: Major exporters of textiles [29]

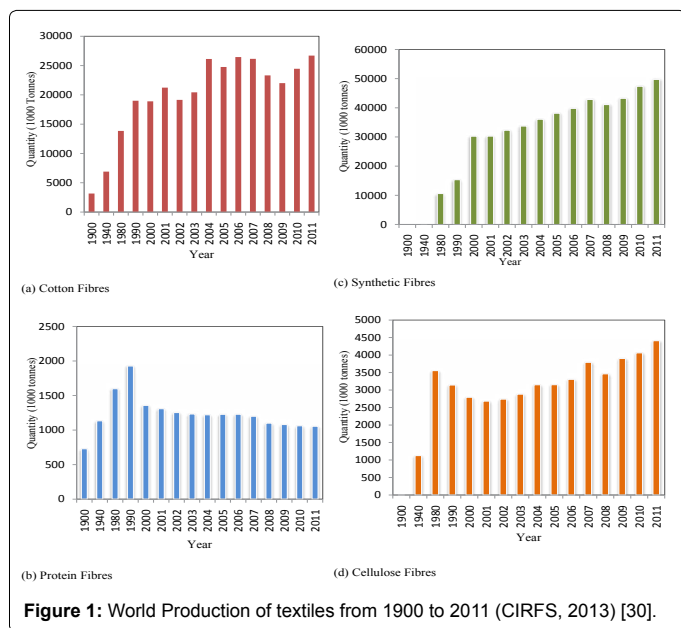


Figure 1: World Production of textiles from 1900 to 2011 (CIRFS, 2013) [30].

Country	Value (\$Billion)	Share (%)
China	153.8	35.6
EU27	116.4	27.1
Bangladesh	19.9	4.6
India	14.4	3.3
Turkey	13.9	3.2
Vietnam	13.2	3.1
Indonesia	8.0	1.8
United States of America	5.2	1.2
Pakistan	4.6	1.1
Korea Republic	1.8	0.4
Rest of the World	79.8	18.5
Total	431	99.9

*EU = European Union

Table 2: Major exporters of clothing [29]

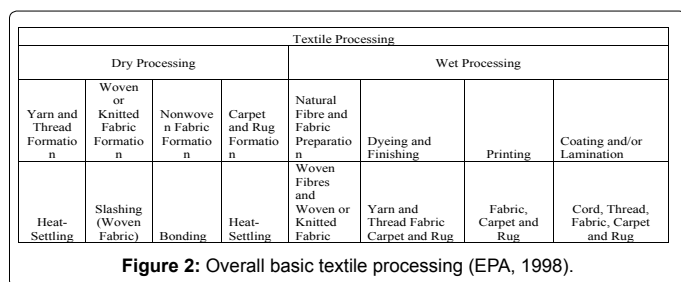


Figure 2: Overall basic textile processing (EPA, 1998).

removal of hair, inter-fibrillary protein and epidermis using physical and mechanical methods. The leather is first treated with digestive enzymes to remove the non-fibrous proteins and then soaked in sulphuric acid to lower the pH. Then, it undergoes tanning using various types of tanning process: mineral/chrome tanning, vegetable tanning and oil tanning. Finally, the leather undergoes dyeing and finishing processes [33].

The production of silks involves the extraction of silk threads from the cocoons. The threads have a glutinous substance which is removed by washing and bleaching. The threads are then weaved and undergo

the dyeing process which gives the silks a different shade. After the dyeing process, the threads undergo the finishing process [34].

Dyes Used In the Textile Manufacturing Process

Different types of textiles are dyed using different types of dyes. The distribution of world consumption of dyes is shown in Figure 3. Dyes can be classified into different types depending on their chemical compositions and properties. Therefore, the usage of dyes varies from industry to industry depending on the fabrics they manufacture.

Dyes for cellulose fibres

Cellulose is made up of repeating glucose units. The most commonly used dye for cellulose textiles is reactive dyes. The other types of dyes

Countries	Amount (Millions bales)
China	34.0
India	28.0
United States	13.5
Pakistan	9.5
Brazil	7.0
Australia	4.5
Uzbekistan	4.5
Turkey	2.3
Turkmenistan	1.5
Burkina	1.1
Other Countries	12.1
Total	118.0

Table 3: Top ten cotton producing countries in 2013 [120,10].

Country	Wool Produced (Tonnes)
China	393,072
Australia	368,330
New Zealand	165,800
United Kingdom	67,000
Iran	60,000
Morocco	55,300
Sudan	55,000
Argentina	54,000
Russian Federation	52,575
India	43,000
Rest of the world	682,315
Total world annual production	2,438,061

Table 4: Top ten wool producing countries in 2011[121].

Countries	Production (Tonnes)
China	370,002
India	151,000
Uzbekistan	25,500
Thailand	4,600
Iran	3,300
Brazil	3,219
Vietnam	2,500
Korea Republic	900
Romania	790
Afghanistan	690
Other countries	1,008
Total world annual production	563,509

Table 5: Top ten cocoons producing countries in 2011 [121].

Countries	Production (Tonnes)
India	1,960,380
Bangladesh	1,523,315
China	43,500
Uzbekistan	18,930
Nepal	14,418
Vietnam	8,304
Sudan	3,200
Myanmar	2,508
Zimbabwe	2,298
Thailand	2,184
Rest of the World	4198
Total	3,583,235

Table 6: Top ten jute producing countries in 2011 [121].

Countries	Share (%)
Asia	43
North America	30
Western Europe	13
Middle East	3
Rest of the world	11
Total	100

Table 7: World production of nylon fiber [122].

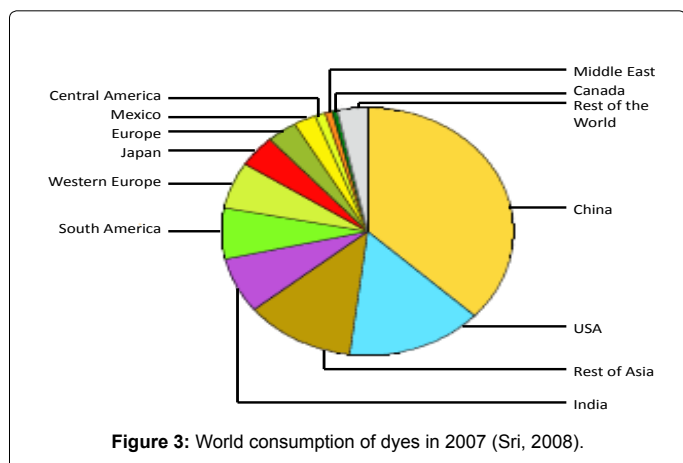


Figure 3: World consumption of dyes in 2007 (Sri, 2008).

used are direct dyes, vat dyes, sulphur dyes, indigo dyes and naphthol dyes. The structures of these dyes are presented in Table 8.

Reactive dyes: The reactive dyes are sometimes called as fibre reactive dyes. They are most important dyeing class for cellulosic fibres and are also used to dye protein fibres such as wool and silk. Reactive dyes are capable of forming covalent bonds with the fibre molecule and are considered to be the most effective and permanent dyes used. They are found to work well on any cellulose fibre under different temperatures [3, 35].

Reactive dyes are of two types: homobifunctional and heterobifunctional. The homobifunctional reactive dyes contain two monochlorotriazine groups and the heterobifunctional reactive dyes contain one monochlorotriazine and one vinyl sulphone group. Under alkaline conditions around 50-70% of the dye is fixed onto the fibre using the dyes containing one reactive group and around 80-95% of the dye is fixed onto the fibre using the dyes containing two reactive groups. The important reactive dye systems are shown in Table 9 [36].

United Nations Statistics Division [10] reported that the total world import and export market for reactive dyes and preparations based thereon, increased from 125,000 tonnes in 1988 to 350,000 tonnes in 2011 (~3 fold increase in 23 years). The individual production statistics for the reactive dyes were not found in the literature.

Procion MX: Procion MX is a cold water reactive dye that could be used at normal room temperature. These fibre reactive dyes are found to produce colour inside the fibre rather than on its surface, hence have light fastness and wash fastness. They are found to be excellent for direct applications, printing, spatter-painting and immersions dyeing methods. However, they are most commonly used in tie dyeing [37]. Procion dyes are found to be inactive when not exposed to alkaline conditions. The mixed procion dye solution after losing its alkaline condition is found to be inactive on fabrics. Apart from cellulose

Dyes	Structure
Procion MX	
Cibacron F	
Sabracron F	
Drimarene K	
Remazol	
Direct Dyes (Direct red 81)	
Indigo Dyes (Dark blue)	
Naphthol Dyes (Naphthol AS)	

Table 8: Structures of reactive dyes [4].

System	Typical Brand Name
Monofunctional	
Dichlorotriazine	Procion MX (BASF)
Aminochlorotriazine	Procion H (BASF)
Aminofluorotriazine	Cibacron F (Ciba)
Trichloropyrimidine	Drimarene X (Clariant)
Chlorodifluoropyrimidine	Drimarene K (Clariant)
Dichloroquinoxaline	Levafix E (DyStar)
Sulphatoethylsulphone	Remazol (DyStar)
Sulphatoethylsulphonamide	Remazol D (DyStar)
Bifunctional	
Bis(aminochlorotriazine)	Procion H-E (BASF)
Bis(aminonicotinotriazine)	Kayacelon React (Nippon Kayaku)
Aminochlorotriazine-sulphatoethylsulphone	Sumifix Supra (Sumitomo)
Aminofluorotriazine-sulphatoethylsulfone	Cibacron C (Ciba)

Table 9: Important reactive dye systems [36]

fibres, they are also known to dye wood paper, wool, silk and basketry materials [13,38].

Cibcron F: Cibcron F is another commonly used reactive dyes. Unlike procion MX dyes, these dyes could only work in a slightly warmer temperature (40-48°C), remain active and could be stored and used later. Cibcron F dyes are also known to provide an easy wash fastness. One of the drawbacks of the cibcron F dyes, over procion MX dyes, is that they do not have a wide colour range. These dyes are found to be effective on cellulose fibres, wool and silk [14].

Sabracron F: Sabracron F dyes are found to work completely similar to Procion MX dyes but could only be used in a slightly warmer temperature of (40-48 °C). Sabracron F dyes are found to be a little less reactive than Procion MX but they provide an excellent wash fastness property. The colour ranges from delicate pastels to vibrant. These dyes are also found to dye cellulose fibres, wool and silk [39].

Drimarene K: Drimarene K dyes are fibre reactive dyes that are stable in both liquid and powder form. They could be used under a wide range of temperature (30-50°C), both cold and warm temperature dyeing [40]. They are suitable for printing and dye bath. Drimarene K dyes are suitable for dyeing all cellulose fibres and silk but were found to be not suitable for synthetic fabrics. Their advantage over procion MX dyes is that excess drimarene K dyes could be easily washed away. These dyes do not get inactive after a few hours and can be stored and used later [4].

Remazol: Remazol dyes are fibre reactive dyes that are used most commonly in painting silk. They can also be used to dye cellulose fibres and wool. Remazol dyes are a group of dyes that are found to be less reactable compared to the other reactive dyes such as procion MX, which makes them more stable in water than procion MX. Remazol dyes are found to have a masking group which prevents them from reacting with water thereby making it more lasting in water. This condition could be removed by increasing the pH or by heating the dye solution [4].

Direct Dyes: Direct dyes are applied under an aqueous bath containing electrolytes and ionic salts. These dyes do not form strong bonds and are loosely associated with the fibre molecules. Thus, they lack the property of drying up quickly after they are applied on fabrics. These dyes are applied under temperatures of 79.4 - 93.3 °C [3,4]. Textiles dyed with direct dyes should only be cold washed along with similar colours since they lack the fixative property. Direct dyes are used for dyeing rayon, linen and cellulosic fibres, they could also be

used to dye wool and silk by using chemical fixative agents. One of the advantages of these dyes is that they are the cheapest among all other dyes. Phillips [9] reported that the usage of direct dyes increased from 53,848 tonnes in 1992 to 181,998 tonnes in 2011 (237.98%) [10].

Indigo: Indigo is a dark blue crystalline powder that is insoluble in water. Reducing agents like sodium hydrosulfite make it soluble in water. Normally, indigo dyes do not have an affinity towards cotton, but in a reduced state they tend to enter the space in the cotton fibres. The dye molecules inside the fibre are then exposed to air, which makes it insoluble again and easily trapped inside the fibre [41,4]. These dyes are the primary colour of blue jeans. The dye comes under the classification of vat dyes [5]. Around 80,000 tonnes of indigo dyes were produced in the year 2010 [11].

Naphthol: Naphthol dyes are made with a combination of two different chemicals: the diazo salts and the naphthol. This combination determines the colour of the dye. This dye is treated as a cold water dye. The temperature of cold water used with other groups of dyes may range from 35 to 41°C but this type of dye can be used even with ice water [4]. Rayon, cotton or other cellulosic fibres as well as silk could be dyed using naphthol dyes. A major disadvantage of this group of dyes is that they are found to contain more hazardous chemicals than other reactive dyes, which makes them less appropriate for home use [42]. The global import and export market for naphthol and their salts is about 112, 000 tonnes per year [10].

Dyes for protein fibres

All fibres obtained from animals (such as wool and silk) are considered as protein fibres. Proteins are made up of twenty essential amino acids. They are more complex than cellulose which is made of repeated sugar units. High pH denatures proteins and acid dyes are, therefore, used to dye wool, angora, cashmere and silk. These dyes are applied to the fabrics along with acid solutions. The chemical reaction between the dye and the fibre results in the formation of an insoluble dye molecule on the fibre [12]. The three most important acid dyes are azo dyes, triarylmethane dyes and anthraquinone (Table 10).

Azo dyes: Azo dyes account for 60-70% of all the dye groups and are found to give out bright and high intensity colours compared to the other classes of dyes [43]. The colour of a dye is due to the electronic transition between various molecular orbital, the probability of which determines the intensity of the colour of the dye. These dyes are found to contain two groups: the chromophore (N=N, C=C, C=O) and the auxochrome (-OH, -NH₂, -NR₂) [44]. Cotton in general, is not found to bind well with picric acid or other anionic or cationic dyes due to the presence of hydroxylic groups in its structure. Hence, simple azo dyes are found to be not that effective in dyeing cotton [45].

Azo dyes in general can be defined as ones which have: (a) a chromophoric azo group (-N=N-) attached to an aromatic or heterocyclic nucleus at one end and (b) an unsaturated molecule of carbocyclic, heterocyclic or aliphatic type at the other end. These dyes are found to be the largest classification of dyes with the Colour Index (CI) of more than 10,000 [46]. CI is the systematic arrangement of colours based on their hue, brightness and saturation. Azo dyes are classified into groups (mono, di, tri, tetra etc.)

Based on the number of azo groups attached to its center. A mono azo dye has one N=N bond while di and tri azo groups have two and three N=N bonds, respectively. To avoid confusions, the dyes with three or more azo groups are often considered as poly azo dyes [5]. The various classifications of azo dyes are listed in Table 11. The azo groups

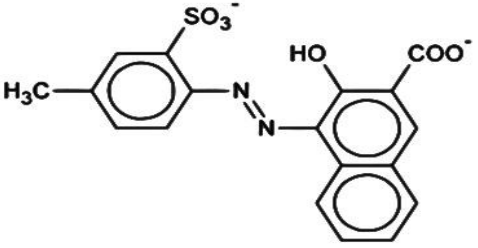
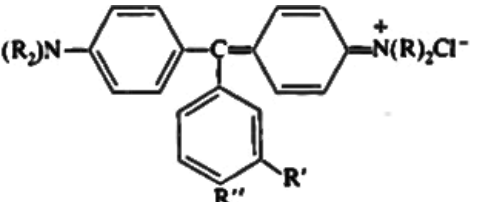
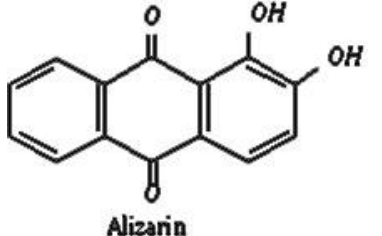
Dye	Structure
Azo Dyes	
Triarylmethane Dyes	
Anthraquinone Dyes	 Alizarin

Table 10: Structures of acid dyes.

are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups. The side groups attached imparts the colour to the dye. The colour index of a dye is found to vary depending on the number of azo groups attached as shown in Table 12 [47]. The chromogen: chromophore structure is responsible for solubility and adherence of the dye to the fibre. The bonding affinity groups are amines, hydroxyl, carboxyl and sulfonic radicals or their derivatives. The aromatic ring structure of the dye coupled with a side chain is usually required for resonance and in turn imparts colour by causing displacement or appearance of absorption bands in the visible spectrum [48,20].

Triarylmethane dyes: Triarylmethane dyes are derivatives of the hydrocarbon triarylmethane a hydrocarbon. Acidic triarylmethane dyes containing atleast two SO_3H group are used to dye wool and silk fibres. Dyes containing only one SO_3H group are used as indicators (e.g. phenolphthalein). Basic triarylmethane dyes are used extensively in the manufacture of stamping inks, writing and printing [49].

Anthraquinone dyes: Anthraquinone dyes have a sulfonic acid group which make them soluble in water. They are used to dye wool and silk due to their affinity towards auxiliary binding agents. A subclass of acid dye called food colouring dyes are used to dye protein fibres and some nylon fibres under high temperature [5,6].

Another subclass of the anthraquinone dyes is called the fibre reactive dye which is used to dye protein fibres. The most important and distinguishing characteristics of these dyes are the property of forming covalent bonds during the application process with the substrates that is to be coloured [50]. Unlike other dye groups, these dyes consist of a known chromophore system which contains various reactive groups. Based on these reactive groups, they are classified into (a) mono anchor dyes, (b) double anchor dyes and (c) multiple anchor dyes [51].

Dyes for synthetic fibres

The commonly used dyes for synthetic fibres are dispersed dyes. These dyes are mainly used in the Printing of polyesters, nylon and acetates. Some dispersed dyes are also used as printing ink in industries. Dispersed dyes are categorised into three types based on their energy. The E type is low energy and is used in thermosol dyeing. The S type is high energy and is used in High temperature/high pressure dyeing. The other SE type is suitable for all dyeing methods [52]. These dyes

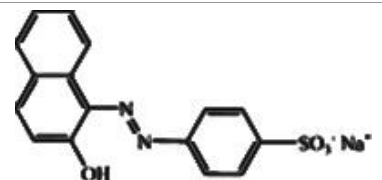
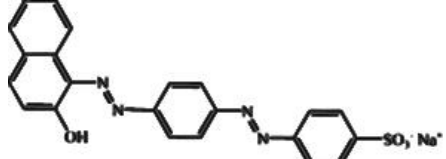
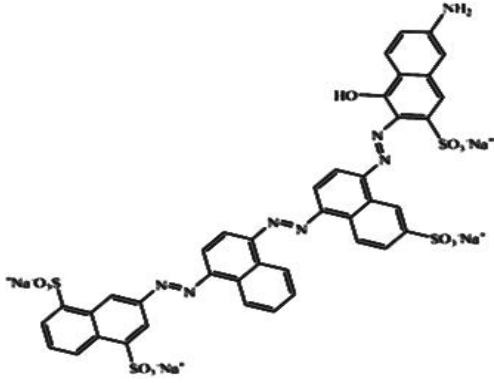
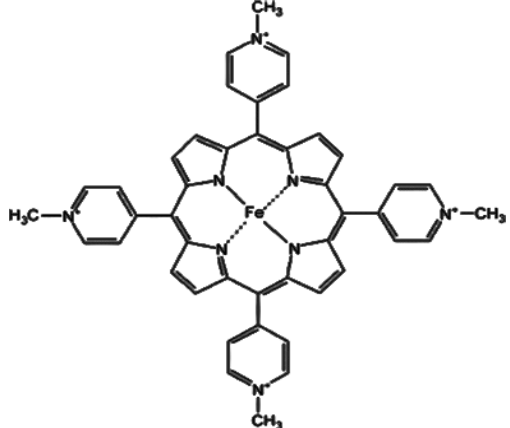
Classifications	Structure
Mono azo	
Diazo	
Triazo	
Tetrakis	

Table 11: Classifications of azo dyes

Chemical Class	Colour Index
Monoazo	11,000-19,999
Disazo	20,000-29,999
Trisazo	30,000-34,999
Polyazo	35,000-36,999

Table 12: Azo dyes [47].

Process	Emission	Wastewater	Solid Wastes
Fibre preparation	Little or none	Little or none	Fibre waste and packaging waste
Yarn spinning	Little or none	Little or none	Packaging wastes, sized yarn, fibre waste, cleaning and processing waste
Slashing/sizing	VOCs	BOD, COD, metals, cleaning waste, size	Fibre lint, yarn waste, packaging waste, unused starch-based sizes
Weaving	Little or none	Little or none	Packaging waste yarn and fabric scraps, off-spec fabric, used oil
Knitting	Little or none	Little or none	Packaging waste, yarn, fabric scraps.
Tufting	Little or none	Little or none	Packaging waste, yarn, fabric scraps, off-spec fabric
Desizing	VOCs from glycol esters	BOD from sizes lubricants, biocides, anti-static compounds	Packaging waste, fibre lint, yarn waste, cleaning and maintenance materials
Scouring	VOCs from glycol ester and scouring solvents	Disinfectants, insecticide residues, NaOH, detergents oils, knitting lubricants, spin finishes, spent solvents	Little or none
Bleaching	Little or none	H ₂ O ₂ , stabilizers, high pH	Little or none
Singeing	Small amount of exhaust gases from the burners exhausted with components	Little or none	Little or none
Mercerising	Little or none	High pH, NaOH	Little or none
Heat setting	Volatilisation of spin finish agents-synthetic fibre manufacture	Little or none	Little or none
Dyeing	VOCs	Metals, salt, surfactants, organic processing assistants, cationic materials, colour, BOD, COD, sulphide, acidity/alkalinity, spent solvents	Little or none
Printing	Solvents, acetic acid- drying and curing oven emission combustion gases	Suspended solids, urea, solvents, colour, metals, heat, BOD, foam	Little or none
Finishing	VOCs, contaminants in purchased chemicals, formaldehyde vapours, combustion gases	COD, suspended solids, toxic materials, spent solvents	Fabric scraps and trimmings, packaging waste

Table 13: Types of textile wastes produced [18].

Processing Subcategory	Water Consumption (m ³ / ton fibre material)		
	Minimum	Median	Maximum
Wool	111	285	659
Woven	5	114	508
Knit	2	84	377
Carpet	8.3	47	163
Stock/yarn	3.3	100	558
Nonwoven	2.5	40	83
Felted fabric finishing	33	213	933

Table 14: Average water consumption for various fabrics [18].

are present in a colloidal state with a low water solubility property and are applied under a dye bath condition under the required temperature which depends on the thickness of the fibre to be dyed [8].

Direct dyes which are used extensively to dye protein fibres can also be used to dye synthetic fibres like nylon and rayon. These dyes are applied under an aqueous bath containing electrolytes and ionic salts. Direct dyes lack the property of getting dried-up fast after they are applied on fabrics [4].

Basic dyes are also considered as cationic dyes. They form a coloured cationic salt when dissolved in water. These cationic salts are found to react with the anionic surface of the substrate. These dyes are found to be powerful colouring agents for acrylic fibres [53].

Water Use and Textile Wastes Produced

The textile industry is considered to be one of the biggest threats to the environment. The various processes carried out in the textile industries produce large amounts of gas, liquid and solid wastes. Some of the most commonly generated wastes are listed in Table 13.

The textile industry uses a variety of chemicals and a large amount

of water for all of its manufacturing steps. About 200 L of water are used to produce 1 kg of textile. Water is mainly used for: (a) the application of chemical onto textiles and (b) rinsing the manufactured textiles [54]. The amount of water consumed by various types of fabrics is listed in Table 14. However, the exact quantity of water required varies from industry to industry depending on the dyeing process and the type of fabrics produced. The percentages of water used during the wet processes are shown in Table 15. Wet processes usually use a lot of chemicals and water. About 80-150 m³ of water are used to produce 1 kg of fabrics. It is estimated that about 1,000-3,000 m³ of waste water is reproduced after processing about 12-20 tonnes of textiles per day [55]. The amount of water consumed by cotton and synthetic textile producing industries are shown in Tables 16 and 17.

The water let out after the production of textiles contains a large amount of dyes and other chemicals which are harmful to the environment? The amounts of chemicals used in wet processes are shown in the Tables 18 and 19. The level of toxicity or harmfulness of the textile effluents varies among industries [56]. In the textile dyeing process, there is always a portion of unfixed dye which gets washed away along with water. The textile wastewater is found to be high in the

Process	Water Consumed (%)
Bleaching	38
Dyeing	16
Printing	8
Boiler	14
Other uses	24

Table 15: Total water consumed during wet process [54].

Process	Water Consumption (L/1000 kg of products)
Sizing	500-8200
Desizing	2500-21000
Scouring	20000-45000
Bleaching	2500-25000
Mercerizing	17000-32000
Dyeing	10000-300000
Printing	8000-16000

Table 16: Water required by cotton textile industry for the wet process [54]

Process	Water Requirements (L/1000 kg of products)				
	Rayon	Acetate	Nylon	Acrylic/Modacrylic	Polyester
Scouring	17000-34000	25000-84000	50000-67000	50000-67000	25000-42000
Salt bath	4000-12000	-	-	-	-
Bleaching	-	33000-50000	-	-	-
Dyeing	17000-34000	34000-50000	17000-34000	17000-34000	17000-34000
Special finishing	4000-12000	24000-40000	32000-48000	40000-56000	8000-12000

Table 17: Water required by synthetic textile industry for its wet process [54].

Chemical	Utilization (kg/100kg of cloth)	
	Soft Flow Machine	Winch
Wetting agent	0.5	0.5
Caustic soda	2.5	4.0
Peroxide	3.0	4.0
Lubricants	0.2	0.3
Stabilizers	0.2	0.3
Peroxide killer (oxidizing agent)	1.0	1.0
Acetic acid	2.0	2.0

Table 18: Chemicals used in bleaching [21].

concentration of these unfixed dyes are as shown in Table 20. Most of the solid wastes originate from the dry process while the wet process yields only a small amount of solid wastes. The majority of solid wastes are made of pieces of fabrics and packaging materials. The dried out sludge from the textile production is also a major source of solid waste. Solid wastes are not found to be hazardous in general. However, the emptied chemical containers may contain traces of harmful substances [57,58]. Sources and types of solid wastes produced in mechanical operations and dyeing and finishing operations are listed below in Table 21.

The majority of the processes being carried out in textile industries produce gaseous emissions. Boilers, ovens and storage tanks are the three most important sources of air pollution in the textile industry. The boilers generate sulphur oxides and nitrogen. The high temperature textile drying process emits hydrocarbons. Pollutants are also emitted from residues of fibre preparation during the heat settling process. Gases can also be emitted from chemicals during the dyeing process [58]. Some of the major gaseous pollutants are listed in Table 22.

Environmental Impacts of Textile Effluent

The characteristics of textile effluents vary and depend on the type of textile manufactured and the chemicals used. The textile wastewater effluent contains high amounts of agents causing damage to the environment and human health including suspended and dissolved solids, biological oxygen demand (BOD), chemical oxygen demand (COD), chemicals, odour and colour. Most of the BOD/COD ratios are found to be around 1:4, indicating the presence of non-biodegradable substances [45]. Typical characteristics of textile effluent are shown in Table 23. The possible pollutant and the nature of effluents released from each step of the wet process are listed in Table 24.

The textile effluents contain trace metals like Cr, As, Cu and Zn, which are capable of harming the environment [21]. Dyes in water give out a bad colour and can cause diseases like haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis [22]. They can block the penetration of sunlight from water surface preventing photosynthesis [23]. Dyes also increase the biochemical oxygen demand of the receiving water and in turn reduce the reoxygenation process and hence hamper the growth of photoautotrophic organisms [22]. The suspended solid concentrations in the effluents play an important role in affecting the environment as they combine with oily scum and interfere with oxygen transfer mechanism in the air-water interface [23].

Chemicals	Utilization (kg/100 kg of cloth)	
	Soft Flow	Winch
Lubricants (kg)	0.3	0.4
Sequestering agent (kg)	0.6	1.0
Dye stuff (kg)		
Light Shade	0.150	0.150
Medium Shade	1.5	1.5
Dark Shade	10.0	10.0
Soda ash (g/L)		
Light Shade	6.0	6.0
Medium Shade	11.0	11.0
Dark Shade	20.0	20.0
Sodium chloride (g/L)		
Light Shade	15.0	15.0
Medium Shade	45.0	45.0
Dark Shade	90.0	90.0
Acetic acid (kg)	2.5	3.0
Soap (kg)	1.0	1.0
Fixing (kg)	1.0	1.0
Softener (kg)	2.0	2.0

Table 19: Chemicals used in dyeing [21].

Fibre	Dye Type	Unfixed Dye (%)
Wool and nylon	Acid dyes/ reactive dyes for wool	7-20
	Pre-metallised dyes	2-7
Cotton and viscose	Azoic dyes	5-10
	Reactive dyes	20-50
	Direct dyes	5-20
	Pigment	1
	Vatdyes	5-20
	Sulphur dyes	30-40
Polyester	Disperse	8-20
Acrylic	Modified basic	2-3

Table 20: Unfixed dyes [17]

Source	Type of Solid Waste
Mechanical operations of cotton and synthetics	
Yarn preparation	Fibres and yarns
Knitting	Fibres and yarns
Weaving	Fibres, yarns and cloth scraps
Dyeing and finishing of woven fabrics	
Sizing, desizing, mercerizing, beaching, washing and chemical finishing	Cloth scraps
Mechanical finishing	Flock
Dyeing/printing	Dye containers
Dyeing/printing (applied finish)	Chemical containers
Dyeing and finishing of knitted fabrics	Cloth scraps, dye and chemical containers
Dyeing and finishing of carpets	
Tufting	Yarns and sweepings
Selvage trim	Selvage
Fluff and shear	Flock
Dyeing, printing and finishing	Dye and chemical containers

Table 21: Types and sources of solid wastes in textile manufacturing [18]

Process	Source	Pollutants
Energy production	Emission from boiler	Particulates, nitrous oxides (Nox), sulphur dioxide (SO ₂)
Coating, drying and curing	Emission from high temperature ovens	Volatile organic components (VOCs)
Cotton handling activities	Emission from preparation, carding, combing and fabrics manufacturing	Particulates
Sizing	Emission from using sizing compound (gums, PVA)	Nitrogen oxides, sulphur oxide, carbon monoxide
Bleaching	Emission from using chlorine compound	Chlorine, chlorine dioxide
Dyeing	Disperse dyeing using carriers sulphur dyeing Aniline dyeing	Carriers H ₂ S Aniline vapours
Printing	Emission	Hydrocarbons, ammonia
Finishing	Resin finishing heat setting of synthetic fabrics	Formaldehydes Carriers – low molecular weight Polymers- lubricating oils
Chemical storage	Emission from storage tanks for commodity and chemicals	Volatile organic components (VOCs)
Waste water treatment	Emission from treatment tanks and vessels	Volatile organic components, toxic emissions

Table 22: Types and sources of gaseous emissions in textile manufacturing [18]

Inorganic substances in the textile effluents make the water unsuitable for use due to the presence of excess concentration of soluble salts. These substances even in a lower quantity are found to be toxic to aquatic life [59]. Some of the inorganic chemicals like hydrochloric acid, sodium hypochlorite, sodium hydroxide, sodium sulphide and reactive dyes are poisonous to marine life [59,60]. The organic components are found to undergo chemical and biological changes that result in the removal of oxygen from water [59]. The seriousness of water pollution depends on the quantity of water and chemicals used in the wet process [23]. The dye concentration in a dye house range from 0.01g/L to 0.25 g/L depending on the type of the dye and the process carried out [61-63]. Vat dyes are used at a concentration in the range of 0.05-0.1 g/L [61,63,64], while indigo dyes are used at a

concentration of 0.02 g/L [63]. Textile dyestuffs are found to contain a large amount of organic substances which are difficult to degrade and are resistant to aerobic degradation. They are also found to be reduced into carcinogenic agents under anaerobic conditions [65]. Some of the carcinogenic compounds produced due to the degradation of azo dyes are as shown in Table 25. Table 26 shows the pollution loads from wet

Parameter	Range
pH	6-10
Temperature (°C)	35-45
Total dissolved solids (mg/L)	8,000-12,000
BOD (mg/L)	80-6,000
COD (mg/L)	150-12,000
Total suspended solids (mg/L)	15-8,000
Total Dissolved Solids (mg/L)	2,900-3,100
Chlorine (mg/L)	1,000-6,000
Free chlorine (mg/L)	<10
Sodium (mg/L)	70%
Trace elements (mg/L)	
Fe	<10
Zn	<10
Cu	<10
As	<10
Ni	<10
B	<10
F	<10
Mn	<10
V	<10
Hg	<10
PO ₄	<10
Cn	<10
Oil & grease (mg/L)	10-30
TNK (mg/L)	10-30
NO ₃ -N (mg/L)	<5
Free ammonia (mg/L)	<10
SO ₄ (mg/L)	600-1000
Silica (mg/L)	<15
Total Kjeldahl Nitrogen (mg/L)	70-80
Color (Pt-Co)	50-2,500

Table 23: Characteristics of typical untreated textile wastewater [21]

Process	Possible Pollutants	Nature of Effluent
Desizing	Starch, glucose, PVA, resins, fats and waxes do not exert a high BOD.	Very small volume, high BOD (30-50% of total), PVA.
Kiering	Caustic soda, waxes, soda ash, sodium silicate and fragments of cloth.	Very small, strongly alkaline, dark colour, high BOD values (30% of total)
Bleaching	Hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids.	Small volume, strongly alkaline, low BOD (5% of total)
Mercerizing	Caustic soda	Small volume, strongly alkaline, low BOD (Less than 1% of total)
Dyeing	Dye stuff, mordant and reducing agents like sulphides, acetic acids and soap	Large volume, strongly coloured, fairly high BOD (6% of total)
Printing	Dye, starch, gum oil, china clay, mordants, acids and metallic salts	Very small volume, oily appearances, fairly high BOD.
Finishing	Traces of starch, tallow, salts, special finishes, etc.	Very small volume, less alkaline, low BOD.

PVA – Poly Vinyl Alcohol
 BOD – Biological Oxygen Demand
 COD – Chemical Oxygen Demand

Table 24: Sources of water Pollution at various stages of processing [23]

Aromatic Amine Group	Human Carcinogenic Evidences
1-Naphthylamine	Slight/Mixed
2-Naphthylamine	Good
2,5-Diaminotoluene	Slight
3,3'-Dichlorobenzidine	Slight/Mixed
3,3'-Dimethoxybenzidine	Slight/Mixed
3,3'-Dimethylbenzidine	Slight
4-Biphenylamine	Good
4-Nitrophenyl	Slight/Mixed
4,4'-Methylenebis (2-chloroaniline)	Slight
Auramine	Slight
Benzidine	Good
Magenta	Slight
N-Phenyl-2-naphthylamine	Slight
N,N-Bis(2-chloroethyl)-naphthylamine	Good

Table 25: Toxic aromatic amines derivatives from azo dyes [65]

Source of effluent generation	Parameters		
	pH	COD (mg/L)	BOD (mg/L)
Process Effluent			
Desizing	5.83-6.50	10000-15000	1700-5200
Scouring	10-13	1200-3300	260-400
Bleaching	8.5-9.6	150-500	50-100
Mercerizing	8-10	100-200	20-50
Dyeing	7-10	1000-3000	400-1200
Wash Effluent			
After beaching	8-9	50-100	10-20
After acid rinsing	6.5-7.6	120-250	25-50
After dyeing (hot wash)	7.5-8.5	300-500	100-200
After dyeing (acid & soap wash)	7.5-8.64	50-100	25-50
After dyeing (final wash)	7-7.8	25-50	
Printing washing	8-9	250-450	115-150
Blanket washing of rotary printer	7-8	100-150	25-50

Table 26: Characteristics of the effluent from various wet textile processing operations [123]

processing plants. The pollution loads after processing various textiles are as shown in Tables 27-30.

Human exposure to textile dyes have resulted in lung and skin irritations, headaches, congenital malformations and nausea [66]. Lima et al. [67] detected benzidine, a known carcinogen in a textile effluent which contained disperse orange 37, disperse blue 373 and disperse violet 93 dyes. Mathur et al. [68], tested a total of seven dyes (cremazoles blue S1, cremazoles brown GR, cremazoles orange 3R, direct bordeaux, direct royal blue, direct congo red and direct violet) using AMES tests and witnessed the presence of mutagenic agents. It was noted that direct violet was the only dye with a mutagenicity ratio less than 2:0. They observed that the cremazoles dyes were so toxic to microorganisms. Morikawa et al. [68], reported evidence of kidney, liver and urinary bladder cancers on workers after prolonged exposure to textile dyes. It was found that dermatitis, asthma, nasal problems and rhinitis were acquired by workers after prolonged exposure to reactive dyes [69].

Textile Wastewater Disposal Standards

Several environment protection agencies worldwide have imposed rules entrusted with the protection of human health and guarding the environment from pollution caused by the textile industry. These agencies imposed certain limits on the disposal of effluents into the

environment. Some of the regulations imposed by several countries are presented in Table 31. The disposal limits are found to differ from country to country. However, a constant check is to be kept on these discharge limits every now and then to maintain a safe and a healthy environment [70].

Conventional Treatments of Textile Effluents

Effluents discharged from the textile industries undergo various physico-chemical treatments such as flocculation, coagulation and ozonation and biological treatment for the removal of nitrogen, organics, phosphorus and metal removal [71]. The disadvantages of the physico-chemical treatment process are: (a) the formation and disposal of sludge and (b) the required space [72]. The disadvantage of biological treatment processes are: (a) the presence of toxic heavy metals in the effluent which affects the growth of microorganism (b) most of the dyes used are a non-biodegradable in nature and (c) the long time required for treating the effluent [21]. Treatment of textile effluents involves three treatment processes: primary, secondary and tertiary treatments.

Primary treatment

The first step in textile wastewater treatment is the removal of suspended solids, excessive quantities of oil and grease and gritty materials [21]. The effluent is first screened for coarse suspended materials such as yarns, lint, pieces of fabrics, fibres and rags using bar and fine screens [72]. The screened effluent then undergoes settling for the removal of the suspended particles. The floating particles are

Process	pH	SEV (l/kg)	BOD	COD	TSS	TDS	Oil&Gas	pH
kg per 1000 kg of product								
Desizing								
Enzyme starch	6-8	2.5-9	45.5	91	89	5	5	6-8
Acid starch	6-8		45.5	91	89.5	7.5	5	6-8
Polyvinyl alcohol (PVA)	6-8		2.5	5	5	48	2.5	6-8
Carboxymethyl cellulose (CMC)	6-8		4	8	5	45	9.5	6-8
Scouring								
Unmercerised greige fabric	12.5	2.5-43	21.5	64.5	5	50	40	12.5
Mercerised greige fabric	12.5		16.5	49.5	5	50	30	12.5
Mercerising								
Greige fabric	12	231-306	13	39	5	148	10	12
Scoured fabric	12		4	12	5	148	-	12
Bleached fabric	12		2	6	5	148	-	12
Bleaching								
Hydrogen peroxide	9-12	2.5-124	0.5	2	4	22	-	9-12
Sodium hypochlorite	9-12		1	4	4	5	-	9-12
Dyeing								
Fibre reactive HE dyes (woven)	12		6	24	-	180		12
Basic	6-7.5	149-300						6-7.5
Direct	6.5-7.6	14-53						6.5-7.6
Vats	5-10	8.3-166						5-10
Sulphur	8-10	24-212						8-10

SEV - Specific Effluent Volume

Table 27: Typical pollution loads from the processing of 100% cotton [124]

Source	Effluent (l/kg)	pH	COD	BOD	TS	SS	TDS
kg per 1000 kg of product							
Desizing							
Starch	12.5	6-8		38.5	97	77	20
PVA	12.5	6-8		2.5	55.4	5	50.4
CMC	12.5	6-8		3.93	59.5	5	54.5
Mixture	4.2		74		78		
Scouring							
Unmercerised	25	12		10.8	14.8	5	9.8
Mercerised	25	12		8.34	14.7	5	9.7
Bleaching							
Peroxide	16.7			1.3	24	4	20
Oxidative-desize-bleach	5.1		23		184		
Mercerising							
Poly/cotton	16.7			3.2	82	5	77
Dyeing							
Disperse-vat	42	12	68	22.8	122		122
Vat	100				150		
Disperse	80				20		
Direct-disperse		6-8	32	10.7			114
Sulphur-disperse		11	68	22.8			69.7
Reactive-disperse		12	41	13.8			192
Printing							
Pigment (woven)		6-8	5	1.26		0.13	2.5
Pigment (knit)		6-8	5	1.26		0.13	2.5
Vat (woven)		10	86	21.5		25	34
Vat (knit)		10	86	21.5		25	35
Machine wash	100						
Screen wash	7						
Hose vessels	30						
Pigment wash	12.5			1	3	0	3
Finishing							
Resin finishing		6-8					22
Resin finishing flat curling		6-8		25	6.32		17.3

Table 28: Pollution load from the processing of 50/50 cotton-polyester blend [124]

Process	pH	BOD	TS
Scouring	9-10.4	30,000-40,000	1,129-64,448
Dyeing	4.8-8	380-3,000	2,000-10,000
Washing	7.3-10.3	4,000-11,455	4,830-19,267
Neutralising	1.9-9	28	1,241-4,830
Bleaching	6	390	908

Table 29: Pollution load from the processing of wool [124]

Fabric	BOD	COD	SS	TDS
Kg per 1000 kg product				
Rayon	30	52	55	100
Acetate	45	78	40	100
Nylon	45	78	30	100
Acrylic	125	216	87	100
Polyester	185	320	95	150

Table 30: Pollution load from the processing of synthetic fibres [124]

removed by mechanical scraping systems. Neutralization is done to reduce the acidic contents of the effluents. Sulphuric acid and boiler flue gas are the most commonly used chemicals to alter the pH. A pH value of 5-9 is considered ideal for the treatment process [74,21]. Figure 4 shows the components of a primary treatment process. The reductions in pollution parameter of the primary treatment process are shown in Table 32.

The first step of screening (coarse screening), the effluent is carried out to prevent damages from plastics, metals paper and rags. Coarse screens have an opening of 6 mm or larger. Coarse screening is followed by fine screening (1.5-6 mm opening) and very fine screening (0.2-1.5mm opening). Fine screening helps in the reduction of suspended solids in the effluent [75]. Screening is followed by sedimentation which makes use of gravity to settle the suspended particles such as clay or silts present in the effluent. According to Das [73], simple sedimentation was not found to be effective because it does not remove colloidal particles in the effluents. Another disadvantage of the process is the large space it occupies. Therefore, settling could be carried out by coagulation. Colloidal particles in the effluent carry charges on their surfaces and addition of chemicals to the effluent changes the surface property of the colloids hence causing them to clump together and settle. Ferrrous sulphate, lime, alum, ferric sulphate and ferric chloride are some of the most commonly used chemicals in the coagulation step [76]. The settled particles are collected as sludge. Disposal of sludge is one of the biggest challenges of treatment plants.

Mechanical flocculation is a physical process which involves slow mixing of the effluent with paddles bringing the small particles together to form heavier particles that can be settled and removed as sludge [77,78]. Some of the disadvantages with flocculation system are: (a) they are in a risk of getting short-circuited and (b) the floc formation in the system is difficult to control. Care should be taken that the sludge disposed from the bottom of the system would not suspend the solids into the system again [79].

Secondary treatment

The Secondary treatment process (Figure 5) is mainly carried out to reduce the BOD, phenol and oil contents in the wastewater and to control its colour. This can be biologically done with the help of microorganisms under aerobic or anaerobic conditions. Aerobic Bacteria use organic matter as a source of energy and nutrients. They oxidize dissolved organic matter to CO₂ and water and degrade nitrogenous organic matter into ammonia. Aerated lagoons, trickling filter and activated sludge systems are among the aerobic system used in the secondary treatment. Anaerobic treatment is mainly used to stabilize the generated sludge [73].

Aerated lagoons are one of the commonly used biological treatment processes. This consists of a large holding tank lined with rubber or polythene and the effluent from the primary treatment is aerated for about 2-6 days and the formed sludge is removed. The BOD removal efficiency is up to 99% and the phosphorous removal is 15-25% [73]. The nitrification of ammonia is also found to occur in aerated lagoons. Additional TSS removal can be achieved by the presence of algae in the lagoon [80]. The major disadvantage of this technique is the large amount of space it occupies and the risk of bacterial contamination in the lagoons [73,81].

Trickling filters are another common method of secondary treatment that mostly operates under aerobic conditions. The effluent for the primary treatment is trickled or sprayed over the filter. The filter usually consists of a rectangular or circular bed of coal, gravel, Poly Vinyl Chloride (PVC), broken stones or synthetic resins [82]. A gelatinous film, made up of microorganisms, is formed on the surface of the filter medium. These organisms help in the oxidation of organic matter in the effluent to carbon dioxide and water [83]. Trickling filters do not require a huge space, hence making them advantageous compared to aerated lagoons. However, their disadvantage is the high capital cost and odour emission [82].

Parameter	CCME	China	BIS	Hong Kong	FEPA	Mexico	Thailand	Philippines	Indonesia	Bangladesh	SL
pH	6.5-8.5	6-9	5.5-9	6-10	6-9	6-8.5	5-9	6-9	6-9	6.5-9	6-8.5
Temperature (°C)	30	-	50	43	40	-	-	40	-	40-45	40
Colour (Pt-Co)	100	80	None	1(Lovibond)	7(Lovibond)	-	-	100-200	-	-	30
TDS mg/L	2000	-	2100	-	2000	-	2000-5000	1200	-	2100	2100
TSS mg/L	40	150	100	800	30	-	30-150	90	60	100	500
Sulphide µg/L	200	1000	2000	1000	200	-	-	-	-	1000	2000
Free Chlorine µg/L	1000	-	1000	-	1000	-	-	1000	-	-	-
COD mg/L	80	200	250	2000	80	< 125	120-400	200-300	250	200	600
BOD ₅ mg/L	50	60	30	800	50	< 30	20-60	30-200	85	150	200
Oil & Grease mg/L	-	-	10	20	10	-	300	5-15	5	10	30
Dissolved Oxygen µg/L	6000	-	-	≥ 4000	-	-	-	1000-2000	-	4500-8000	-
Nitrate µg/L	13000	-	10000	-	20000	10000	-	-	-	10000	45000
Ammonia µg/L	0.1	-	-	500	0.2	-	-	-	-	5000	60
Phosphate µg/L	<4000	1000	5000	5000	5000	-	-	-	2000	-	2000
Calcium µg/L	-	-	-	-	200000	-	-	200000	-	-	240000
Magnesium µg/L	200000	-	-	-	200000	-	-	-	-	-	150000
Chromium µg/L	1	-	100	100	<100	50	500	50-500	500	2000	50
Aluminium µg/L	5	-	-	-	<1000	5000	-	-	-	-	-
Copper µg/L	<1000	1000	3000	1000	<1000	1000	1000	1000	2000	500	3000
Manganese µg/L	5	2000	2000	500	5.0	200	5000	1000-5000	-	5000	500
Iron µg/L	300	-	3000	1500	20000	1000	-	1000-20000	5000	2000	1000
Zinc µg/L	30	5000	5000	600	<10000	10000	-	5000-10000	5000	5000	10000
Mercury µg/L	0.026	-	0.01	1	0.05	-	5	5	-	10	1

CCME - Canadian Council of Ministers of the Environment
 BIS - Bureau of Indian Standards
 FEPA - Federal Environmental Protection Agency (United States)
 SL - Sri Lanka

Table 31: Discharge limits of various countries [70, 123-133]

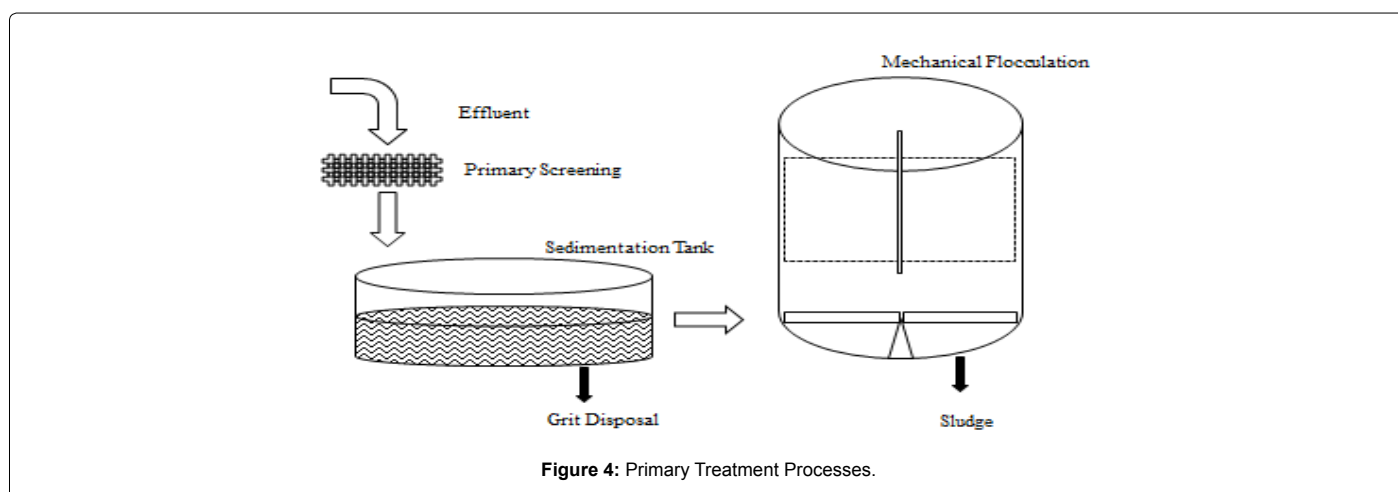


Figure 4: Primary Treatment Processes.

Aerobic activated sludge processes are commonly used. It involves a regular aeration of the effluent inside a tank allowing the aerobic bacteria to metabolize the soluble and suspended organic matters. A part of the organic matter is oxidized into CO₂ and the rest are synthesized into new microbial cells [84]. The effluent and the sludge generated from this process are separated using sedimentation; some of the sludge is returned to the tank as a source of microbes. A BOD removal efficiency of 90-95% can be achieved from this process, but is time consuming [85].

Sludge's formed as a result of primary and secondary treatment processes pose a major disposal problem. They cause environmental problems when released untreated as they consist of microbes and organic substances [86]. Treatment of sludge is carried out both, aerobically and anaerobically by bacteria. Aerobic treatment involves the presence of air and aerobic bacteria which convert the sludge into carbon dioxide biomass and water. Anaerobic treatment involves the absence of air and the presence of anaerobic bacteria, which degrade the sludge into biomass, methane and carbon dioxide [87].

Properties	(%) Percentage of Reduction
Total suspended solids	80-90
BOD	40-70
COD	30-60
Bacteria	80-90
Total suspended matter	50-70
Organic matter	30-40

Table 32: Reduction in pollution parameters after primary treatment processes [73].

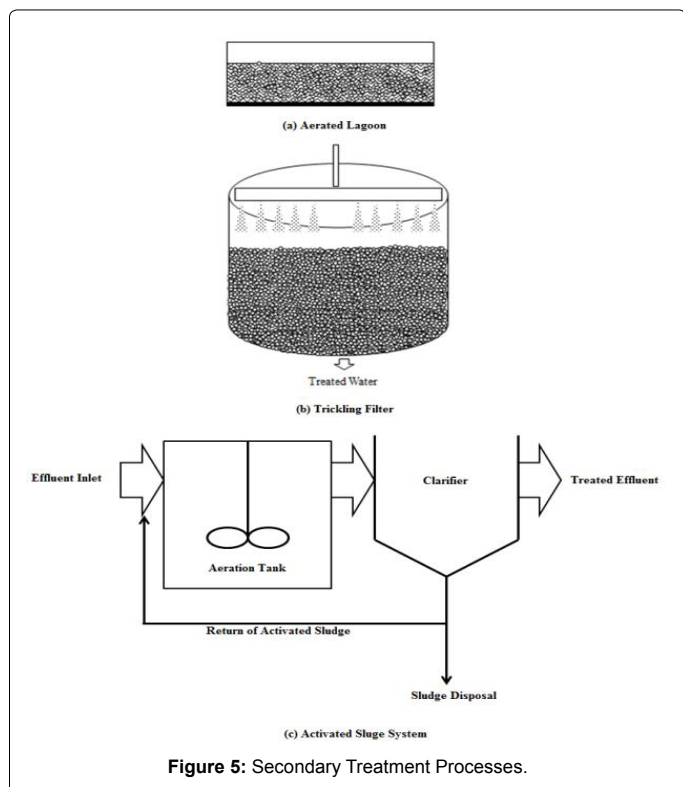


Figure 5: Secondary Treatment Processes.

Tertiary treatment

There are several technologies used in tertiary treatments including electro dialysis, reverse osmosis and ion exchange as shown in Figure 6. Electrolytic precipitation of textile effluents is the process of passing electric current through the textile effluent using electrodes. As a result of electro chemical reactions, the dissolved metal ions combine with finely dispersed particles in the solution, forming heavier metal ions that precipitate and can be removed later [88]. One of the disadvantages is that a high contact time is required between the cathode and the effluent [73].

Reverse osmosis is a well-known technique which makes use of membranes that have the ability to remove total dissolved solid contents along with ions and larger species from the effluents. A high efficiency of >90% has been reported [74]. Cotton dyeing processes use electrolytes such as NaCl in high concentrations. These high concentrations of salts can be treated using reverse osmosis membrane [89].

Electrodialysis is another process which uses membranes, that has the ability to separate dissolved salts. The electricity used in electro dialysis influences the ions to get transported through a semi permeable membrane by passing an electrical potential across water

[90]. The membranes used are charge specific and anion-selective which allows negatively charged particles to pass through and traps positively charged particles and vice versa. Placing numerous membranes throughout the system hinders the flow of effluent and the effluent would reach a point at which the ions are trapped or settled down and the remaining ions are neutral in charge [91]. Membrane fouling (the process where solutes or other particles get attached to the membrane or into the membrane pore) has to be prevented by removing suspended solids, colloids and turbidity prior to electro dialysis [92].

Ion exchange method is a commonly used tertiary method which involves the passage of effluents through the beds of ion exchange resins. These ion exchange resins are either cationic or anionic charged. Effluent passing through a cationic resin would have its cations removed by the resin and replaced with hydrogen ions making it acidic. When the acid solution is passed through anion resin, the anions would be substituted with hydroxyl ions [93,94].

Photocatalytic degradation is another method by which a wide range of dyes can be decolorized depending on their molecular structures [95]. Adsorption is also found to be effective in the removal of colours. Thermal evaporation using sodium persulfate is also found to have a good oxidizing potential. This process is found to be eco-friendly because they do not have the property to form sludge and also do not emit toxic chlorine fumes during evaporation [73].

Advanced Oxidation Processes

Mechanism of photo oxidation

Advanced oxidation processes have gained attention due to their

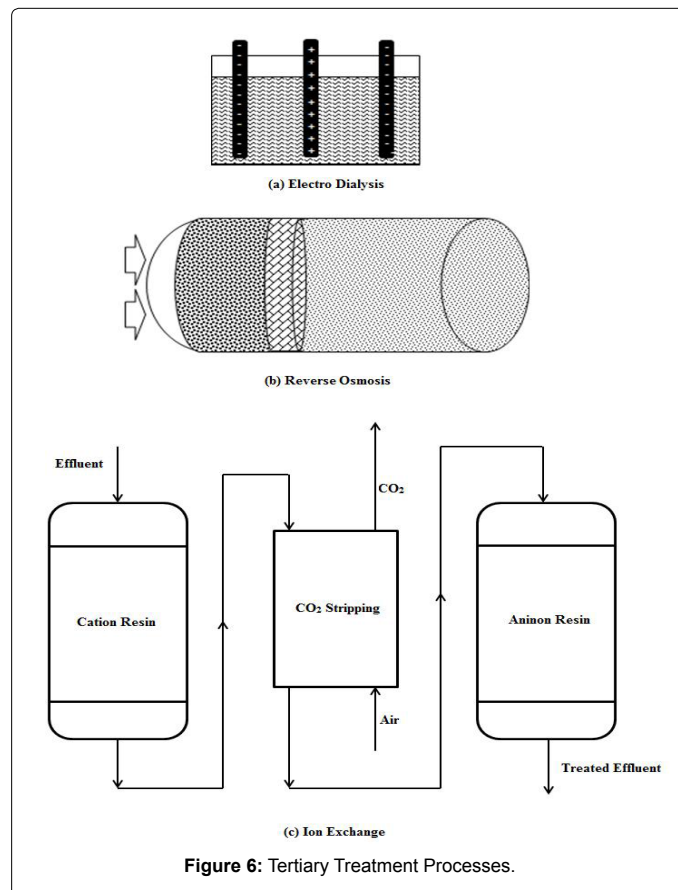


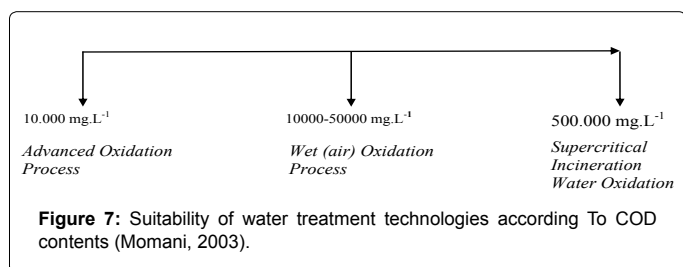
Figure 6: Tertiary Treatment Processes.

Oxidation Species	Oxidation Power
Hydroxyl radical	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.31
Permanganate	1.24
Chlorine	1.00

Table 33: Relative oxidizing power of some oxidizing species (Voglpohl and Kim, 2003) [134].

Group	Compounds
Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, <i>tert</i> -butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine, n-propylamine
Esters	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

Table 34: Oxidizable compounds by hydroxyl radicals (Momani, 2003) [102].



efficiency and ability to treat almost all solid components in textile effluents. The effluents treated with advanced oxidation processes were found to obtain 79% COD removal while, effluents treated biologically with *Fusarium oxysporum*, *Pleurotus ostreatus* and *Trichiderma viridae* were found to obtain 42%, 39% and 33% COD removal, respectively [96,97].

Photo-oxidation can take place at any temperature and pressure and does not produce any secondary components [21]. The basic mechanism of advanced oxidation processes is the production of OH[•] radicals which are capable of destroying components that are hard to be oxidised [20,98,99]. Generation of OH[•] radicals are generally accelerated by the combinations of H₂O₂, UV, O₃, TiO₂, Fe²⁺, electron beam irradiation and ultra sound [20]. The oxidizing potential of commonly used oxidants is presented in Table 33. The components that can be oxidized by hydroxyl groups are shown in Table 34.

OH[•] radicals are considered as reactive electrophiles due to their preference to electrons and hence they react rapidly towards electron rich organic compounds [100]. The radicals are found to have an oxidation potential of 2.33 V and are hence found to oxidize substances more quickly than conventional oxidants [100,101]. The organic substances are first attacked by the generated hydroxyl radicals, followed by hydrogen abstraction and then the electron transfer as follows [100].



Where: R Reacting organic compound

The oxidation rate depends on three main factors: (a) the concentration of the target pollutant, (b) the concentration of the radical and (c) the concentration of oxygen present in the surrounding. The maintenance of sufficient radical concentration depends on the temperature, pH, presence of ions in the solution, presence and concentration of radical scavengers and type of pollutant targeted [101]. The oxidizing reaction is a first order kinetics and has a rate constant of 10⁸-10¹⁰ M⁻¹s⁻¹ with a hydroxyl concentration of 10⁻¹²-10⁻¹⁰ M [102]. The type of treatment process that is suitable is found to differ according to the amount of COD present in the effluent as shown in Figure 7. The combination of oxidant which gives the maximum amount of OH radicals must be chosen. Some of the different combinations of oxidants and their uses are as listed in Table 35.

Photooxidation treatments

Treatment with H₂O₂: H₂O₂ is one of the most powerful oxidant known and is completely harmless because H₂O₂ is found to be amongst the natural metabolites of many organisms which have the ability to convert H₂O₂ into oxygen and water. Hydrogen peroxide as a single compound does not have the ability to split itself into hydroxyl radicals and hence is usually used in combination with ferrous salts. The reaction with ferrous salts results in the production of OH[•] which helps in the propagation of the reaction [103].



Where: RH Organics

Equation (4) shows the initiation processes, which involves the reaction between the ferrous ions and hydrogen peroxide and the formation of HO₂[•]. Equations (5) and (6) show the chain propagation reactions with the organics present in the effluents. Equation (7) shows that OH[•] radicals are also capable of decomposing H₂O₂ resulting in the production of HO₂[•] radicals. Equations (8), (9) and (10) show that the chain propagation can be terminated by the reaction of OH radical with the intermediates produced R and hence resulting in the formation of H₂O₂[•] and O₂[•], thus terminating the reaction. Equations (11) and (12) show that the chain termination can also take place by the reactions taking place between the radicals R[•] and RO₂[•] [103].

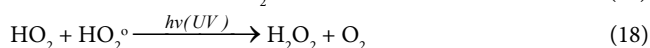
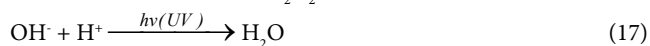
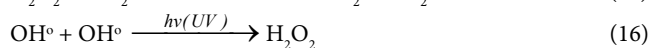
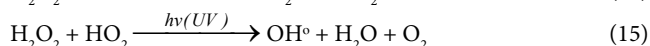
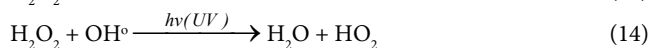
Goi [104], stated that hydrogen peroxide when used individually is not found to be so effective as compared to it being used under a combination of different oxidants. Alaton et al. [105], recorded that when H₂O₂ was used with UV-C, it completely decolourized the effluent containing a mixture of procion blue HERD, procion crimson HEXL, procion yellow HE4R, procion navy HEXL and procion yellow HEXL in just 10 minutes and was found to be better than O₃ when

Oxidants +	Use
H ₂ O ₂ / Fe ²⁺	Fenton
H ₂ O ₂ / UV/ Fe ²⁺	Photo assisted Fenton
O ₃ / UV	Also applicable in gas phase
O ₃ / H ₂ O ₂	Advance Oxidation
O ₃ /UV/H ₂ O ₂	Advance Oxidation
O ₃ /TiO ₂ /Electron beam irradiation	Advance Oxidation
O ₃ /TiO ₂ /H ₂ O ₂	Advance Oxidation
O ₃ + Electron beam irradiation	Advance Oxidation
O ₃ /Ultrasonic	Advance Oxidation
H ₂ O ₂ /UV	Advance Oxidation

Table 35: Advanced oxidation processes (Kdasi, et al., 2004) [20].

used alone. A 99% decolourization in 30 min for reactive yellow 15 dye was noted when H₂O₂ was used alongside fenton's reagent, the dye's initial absorbance value being 2430 at 415nm [106]. Arslan et al. [107] stated that UV catalyzed by H₂O₂ is more efficient than ozone when used alone, while H₂O₂/O₃ was found to be the quickest in removing colour from a dye bath which includes a mixture of seven dyes and has an absorbance of 0.47 in 40 folds at 600 nm.

Treatment with H₂O₂ and UV: Oxidation of textile effluent using H₂O₂ alone as known was not found to be effective on both acids and alkalis, but the combination of H₂O₂/UV was found to be very effective in the degradation of organic compounds [20]. Wang et al. [32], recorded that H₂O₂/UV treatment is capable of destroying the chromophore structure of azo dyes and that UV irradiation in the presence of H₂O₂ resulted in the complete decolourization of sulphonated azo and anthraquinone dyes. The production of OH° radicals in the H₂O₂/UV processes is as follows [108].



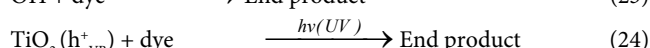
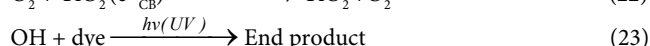
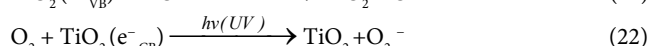
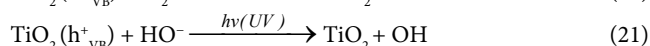
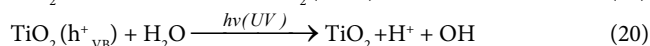
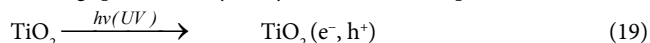
Equation (13) shows the chain initiation processes as the hydrogen peroxide present in the effluent is split into two OH° radicals. Equations (14) and (15) show the reaction between the OH° radicals formed and the hydrogen peroxide present in the system which results in chain propagation. Equations (16), (17) and (18) show the chain termination mechanism [108].

The decolourization efficiencies of the H₂O₂/UV combination were found to increase as the concentration of H₂O₂ was increased in the effluent [109]. Kdasi et al. [20] found that 99.9% decolourization of remazol brilliant blue dye was obtained when a H₂O₂ concentration of 12.5 mL L⁻¹ was used and temperature did not play any significant role in the removal of colour. Mahmoud et al. [98] stated that excess concentration of H₂O₂ added to the effluent was not found to cause problems due to their property to react with the OH° radicals resulting in the formation of H₂O and O₂.

Some of the advantages of UV/H₂O₂ combination are: (a) it lacks the property of developing any chemical sludge, (b) it is effective in the removal of phenolic compounds [100], chlorinated compounds and chlorophenols [110], from effluents, (c) UV acts as a disinfectant and (d) it is effective in removal of TOC, 80-82% removal efficiency after

1-2 hours of exposure [20,105,109].

Treatment with TiO₂ and UV: First step of Photocatalytic degradation of the aromatic compounds results in the formation of hydroxyl derivatives, which in turn modifies the product distribution in the solution. Photocatalytic degradation is carried out by two types of oxidizing species: the hydroxyl radicals and the positive holes [111].



Where:

TiO₂(h⁺_{VB}) - Valence-band holes

TiO₂(e⁻_{CB}) - Conduction-band Electrons

Upon irradiation by UV, the electrons on the surface of the semiconductor gets excited to the conduction band forming positive holes in the valance band (Equation 19). The valance band holes thus formed are good oxidizers; they have the potential to oxidise water or OH ions into OH radicals as shown in Equations 20 and 21. The conduction band electrons on the other hand act as reducers (Equation 22). Chain termination would occur as shown in Equations 23 and 24.

Oxidation of TiO₂/UV is suggested to have a larger advantage over H₂O₂/UV, this is because titanium dioxide is found to absorb light up to 385 nm which is greater than that absorbed by H₂O₂ [112].

Halmann et al. [111], reported that the dye Acid Orange 5 which is normally found in effluents in concentrations of 10⁻⁴ to 10⁻⁶ M can be completely degraded using black-light mercury lamp as a UV radiation source. Koprivanac et al. [113] reported a 71% reduction in colour when the effluent was treated at a pH of 3 under UV/TiO₂. Liu et al. [114], stated that a highest of 70.6% reduction and a lowest of 44.3% reduction of acid yellow 17 was achieved when the effluent was treated under UV/TiO₂.

Toxicity Measurement Parameters: The by-product produced may be more harmful than the original organic compound [115]. Hydroxyl functional groups and aldehydes are found to be the usual by-product after destruction of azo dyes [116]. Therefore, it is important to analyse the intermediates produced before letting the effluent into the environment [117]. By-products of dyes with simple structure could be identified by simple procedures. For dyes with extremely complex structures, identification can be carried out using chromatographic technologies, HPLC, GC techniques [115]. Further tests due to degradation such as Chemical Oxygen Demand (COD) analysis could be done on the treated effluents to note down the amount of chemicals present in the effluent.

Lidia et al. [118], reported a COD removal of 10% when dispersed dyes were treated with 0.5g dm⁻³ of ozone at a pH 8. AO₃/UV treatment of textile effluents was found to be far more effective than O₃ treatment. A COD reduction of 50 mg/L from 400 mg/L was achieved in 30 minutes [119]. Arslan and Balcioglu [25], noted down 67.58% COD reduction in Turquoise Blue G133 and 80.36% reduction in Remazol Black B dye when treated with UV/TiO₂.

Summary and Conclusion

Textile industry is one of the major industries in the world that provide employment with no required special skills and play a major role in the economy of many countries. There are three different types of fibers used in the manufacture of various textile products: cellulose fibers, protein fibers and synthetic fibers. Each type of fiber is dyed with different types of dyes. Cellulose fibers are dyed using reactive dyes, direct dyes, naphthol dyes and indigo dyes. Protein fibers are dyed using acid dyes and lanaset dyes. Synthetic fibers are dyed using disperse dyes, basic dyes and direct dyes.

The textile industry utilizes various chemicals and large amount of water during the production process. About 200 L of water are used to produce 1 kg of textile. The water is mainly used for application of chemicals onto the fibers and rinsing of the final products. The waste water produced during this process contains large amount of dyes and chemicals containing trace metals such as Cr, As, Cu and Zn which are capable of harming the environment and human health. The textile waste water can cause hemorrhage, ulceration of skin, nausea, skin irritation and dermatitis. The chemicals present in the water block the sunlight and increase the biological oxygen demand thereby inhibiting photosynthesis and reoxygenation process.

The effluent water discharged from the textile industries undergoes various physio-chemical processes such as flocculation, coagulation and ozonation followed by biological treatments for the removal of nitrogen, organics, phosphorous and metal. The whole treatment process involves three steps: primary treatment, secondary treatment and tertiary treatment. The primary treatment involves removal of suspended solids, most of the oil and grease and gritty materials. The secondary treatment is carried out using microorganisms under aerobic or anaerobic conditions and involves the reduction of BOD, phenol and remaining oil in the water and control of color. The tertiary treatment involves the use of electro dialysis, reverse osmosis and ion exchange to remove the final contaminants in the wastewater. The major disadvantages of using the biological process are that the presence of toxic metals in the effluent prevents efficient growth of microorganisms and the process requires a long retention time.

The advanced oxidation processes is gaining attention in the recent days due to the ability to treat almost all the solid components in the textile effluents. The photo-oxidation of the effluents is carried out using H_2O_2 , combination of H_2O_2 and UV and Combination of TiO_2 and UV. Advanced oxidation process generates low waste and uses hydroxyl radicals (OH^\bullet) as their main oxidative power. The hydroxyl radicals (OH^\bullet) are produced by chemical, electrical, mechanical or radiation energy and therefore advanced oxidation processes are classified under chemical, photochemical, catalytic, photocatalytic, mechanical and electrical processes. The effluents treated with advanced oxidation process were found to reduce 70-80% COD when compared to 30-45% reduction in biological treatment.

Acknowledgement

The research was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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