Review Article

Study of environmental concerns of dyes and recent textile effluents treatment technology: A review

ABSTRACT

The textile industry is one of the significant industries which produces large amount of wastewater effluents all year. The kind of these effluents has the features of higher rate of BOD, COD, complex structure, color, great emission and hard degradation. If being directly discharged without treatment, it will cause a potential hazard to the aquatic ecosystem and human. This paper provides the literature information about the environmental concern and their toxicity effects as well as classification of dyes. This review will present the methods for the removal of dyes from aqueous solution and wastewater effluents. The various dye removal techniques are classified into biological, chemical, physical methods, in addition to combination treatments. Biological methods include aerobic and anaerobic degradation bioremediation by bacteria & fungi and algae, while chemical methods comprise coagulation or flocculation combined through floatation and filtration, precipitation, electro floatation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents such as ozone, irradiation or electrochemical processes. Furthermore, physical technologies as adsorption, ion exchange and filtration coagulation methods etc.

Keywords: Dyes; Hazardous effects; Classification; Biological processes; Chemical processes; Physical processes.

1. INTRODUCTION

Water is a source of energy and life, although millions of people worldwide are suffering from the shortage of clean drinking and fresh water. It is well known that 70 to 80 % of all illnesses in developing countries are related to water contamination, particularly susceptible children and women [1]. The effluent discharged from textile industries is comprised mainly of residual dyes, auxiliary chemicals, surfactants, chlorinated compounds and salts [2]. Textile wastewater is a complex and highly variable mixture of many polluting substances, including dyes, which induce color coupled with organic load leading to disruption of the total ecological balance of the receiving water system [3]. In textile industries 93 % of the intake water comes out as colored wastewater due to dyes containing high concentration of organic compounds and heavy metals [4]. Wastewater treatment is becoming more critical due to diminishing water resources, increasing wastewater disposal costs and stricter discharge regulations that have lowered permissible contaminant levels in waste streams [5]. Therefore, it is necessary to remove these dyes from industrial effluents before discharging aqueous waste into the environment. This study was undertaken in order to provide comprehensive and critical review information on classification of dyes, environmental concern and their hazardous effects in addition to the application of the various removal techniques for the treatment of dye wastewater followed by the results obtained in different researches.

2. Main pollutants in textile discharge

There are three main pollutants found in textile wastewater which comprise color, toxic metals and dissolved solids.

Color*:* The existence of color in the effluentis one of the highest problems in textile industry which is easily visible to human eyes even at very low dye concentration. Most of the dyes are stable, not easily degradable and are unaffected by light [6].

Toxic metals*:* The metals may come as impurity with the chemicals (such as caustic soda, sodium carbonate and salts) used during processing or may be present in dye stuffs (like metalized mordent dyes) [7].

Metals found as integral parts of the dye chromophores (as, phthalocyanine); include mainly cobalt, copper, and chromium. But, some dyes have low-level metal impurities that are present incidentally, rather than necessity in terms of functionality and color. When mercury-based compounds are used as catalysts in dye manufacturing, there is a possibility of its presence as trace residue. Very few (e.g., only 2% commercial direct dyes) have metal as an integral part of the dye chromophore [8]. Unless textile effluent is treated properly, as a result of extensive use of dyes and pigments through out the world, toxic metals associated with the dyes and pigments inevitably reach to aquatic environments, and pose serious treats to aquatic lives and the system [9].

Dissolved solids*:* the usage of inorganic sodium salts as (Sodium Chloride, NaCl and Sodium Sulfate, Na_2SO_4) in the processes directly increase total dissolved solids (TDS) level in the wastewater which forms the main fraction of total solids (TS) and are not removable using conventional treatment.

3. Dyes - their sources, waste generation and discharge on the environment

Dyes may be defined as a coloured substance capable of imparting their characteristic colours. Both dyes and pigments appear to be coloured because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments [10].

The first synthesis dye was discovered by William Henry Perkin in 1856. There are various kinds of dyes used in textile, paper, rubber, food and paint industries for example reactive dyes, azo dyes, basic dyes, vat dyes acid dyes, disperse dyes and direct dyes [11].

Prior to displaying the effect of textile wastewater on the environment, the textile manufacturing process and the kind of toxic substances generated from this process must be known.There are main three stages of generation process involved; they are spinning, knitting or weaving and wet processing the later involves many steps like sizing, desizing, scouring, bleaching, mercerizing, dyeing, printing and finishing. Each of these operations generates huge amounts of wastewater and pollution from wet processing steps desizing is one of the largest sources of wastewater pollutants and often contributes up to 50% of the Biological Oxygen Demand (BOD) load in wastewater [12].

The scouring process also has a high BOD and also uses the highest volumes of water in the preparatory stages. The major pollution issues in the bleaching process are chemical handling, water conservation and high pH values. Also, using pentachlorophenol (PCP) during scouring, bleaching, dyeing and printing which is removed from the fabric and discharged into the wastewater. It is toxic due to its relative stability against natural degradation processes and it is also bioaccumulative [13]. But the majority of wastewater containing residual dyes is generated after dyeing and printing. Colored wastes reportedly contribute about 10-30% of the total BOD and in many cases reach 90%. Dyes also contribute about 2-5% of the Chemical Oxygen Demand (COD), while dye bath chemicals contribute about 25-35%. In addition to the high BOD and COD values of dyes, toxicity to aquatic organisms and fish toxicity have also been reported.

Dyes and pigment from printing and dyeing operation are the principal sources of colors in textile effluent. Finishing processes typically generate wastewater containing natural and synthetic polymers and a range of other potentially toxic substances [13].

There are more than 8000 chemical products associated with the dyeing process listed in the color index, it is assessed that more than 100,000 commercial dyes are known with an annual production of more than 7×10^5 tonnes per year [14]. The total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and approximately 100 tonnes per year of dyes are discharged into water streams [15]. Due to inefficiencies of industrial dyeing process, 10-15% of the dyes are lost in the effluents of textile units, rendering them highly colored [16]. It is estimated that 280.000 tons of textile dyes are discharged every year in such industrial effluents worldwide [17].

4. Importance of the textile industry and effluent discharge in Egypt

In Egypt, the textile sector consists of over 3000 companies, ranging from the very small (employing less than 8 laborers) to the very large (more than 20.000 laborers) both public and private sector companies [13].

The textiles industry is the 5th largest source of foreign currency; after oil, transactions, tourism and Suez Canal. It is the second largest manufacturing sector in Egypt after food processing and represents 25% of total industrial output (excluding petroleum products). Egypt produces 25-30% of the world's cotton, although there is strong competition from United States of America (USA), China and India. Egypt also produces some of the highest quality extra fine cotton in the world, having a 35% share of the world market. There are over 2300 private sector factories which are members of the Egyptian Textile Manufacturers Federation (ETMF). There are also many small factories and workshops which are not ETMF members, as well as informal workers who are not included in any of these groups [12]. The private sector currently dominates the market in terms of knitted fabrics and ready-made goods [13].

While textile industries are very important in Egypt, the industrial wastewater they produce is considered one of the main sources of water pollution because of their toxic chemicals and organic loading [18].

About 80 % of the whole country's annual industrial effluent is discharged untreated into the Nile, canals, wells, municipal sewerage system and the Mediterranean Sea. Egypt's 329 major factories continue to discharge as much as 2.5 million m^3 per day of untreated effluent into Egypt's water resources. The end result is that Egypt's shores and coastal fishing and tourism are being damaged, areas around industrial zones are becoming inhospitable, and water purification is becoming very costly [19].

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Cairo is the largest city in the Middle East region with continuous rapid population growth and spatial expansion. Since the city is an open environmental system, Cairo's surrounding regions are burdened with heavy wastewater discharges and increasing water demand, also the city's water resources are affected by discharges from other regions. Cairo is one of the main industrial centers in Egypt: 50-64 % of industrial activities are mainly located in the capital. Its public sector industries (75 %) consist of chemical, textile, metal (iron and steel), food, engineering and cement production operations, and they use 162 millions m^3 of fresh water per year, and discharge 129 million m^3 per year, each day they discharge 0.75 tons of heavy metals. For example, Cairo's Shoubra El-Kheima is an industrialized district north of the city, and its industries discharge to drains (which are heavily polluted) finally flowing to the Mediterranean Sea [18]. In general, water use of Egypt's chemical, iron, and steel companies (which produce the most toxic wastes) is expected to increase. Most of the discharge to the sewage collection systems is from domestic sources; also industries in Cairo discharge 56 million m^3 annually to the collection system, in many cases without pretreatment and only half of the industry had in 1992 some type of effluent treatment before discharge to the collection system. Available limited data restricts evaluation of different pollution concentrations from effluents discharge wastewater, no accurate information is available of the amount of toxic substance [18]. Therefore, government legislation is becoming more stringent in developed countries regarding the removal of dyes from industrial effluents, which is becoming an increasing problem for textile industries. Environmental protection agencies in Europe are promoting transfer prevention of pollution problems from one part of the environment to another. This means that for most textile industries, developing on site or in plant facilities to treat their own effluents before discharge is fast approaching actuality [20]. So, the Egyptian Government evaluated Law 48/1982 concerning protection of the River Nile and Egypt waterways from pollution regulating the discharge of waste to the River Nile, its branches and marine environment by a permit from the Ministry of Public Works and Irrigation after fulfilling certain criteria monitored by periodic analysis [13].

5. Classification of dyes

Dyes are natural or synthetic organic compounds used in various industries. Natural dyes (without any chemical treatment) are used to colour various materials such as leathers, fibers, papers, foods etc. Natural dyes are produced from animals, insects, plants and minerals sources.

Synthetic dyes have a high visibility even at very low concentration in water. There is no single dye that can have a complete degree of fixation to fiber during dyeing and finishing processes [21]. There are different ways for classification of dye molecules, (Fig. 1). It can be classified in terms of colour, structure or application methods [22]. Due to the complexities of the colour nomenclature from the chemical structure system, the classification in terms of application is often favourable.

Chromophores and auxochromes components play important roles in the dye's molecules for example chromophores (COOH, NR_2, NH_2, Cl, NHR and OH) are responsible for the production of colours wherever auxochromes as (NO_2, C=C,-C=O, C=N, NO, N=N) enhance the affinity of the dye toward these materials [23]. Other than that, dyes are also usually classified based on their particle charge upon dissolution in aqueous application medium such as the anionic dyes comprise reactive dyes, direct, acid and non-ionic dyes (dispersed dyes) while cationic dyes which are basic dyes [24].

<u>5.1 Classification of synthetic dyes based on their applications as following:</u>

1-Anionic dyes have negative ions due to the excess presence of the OH^- ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fibre [11].

2-Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fiber [11]. Reactive dyes contain reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, and di fluoro chloro pyrimidine that covalently bonded with the fiber during the dyeing process [25]. As the reactive dyes are highly soluble in aqueous solution and had greater negative charge density, their tendency of adsorption towards the adsorbent increases accordingly. This may be an indication that the adsorption process was related to electrical attraction between anionic dyes and positively charged surfaces of adsorbent [26].

3-Direct dyes 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 [27].

4-Basic dyes are 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 [28].

5-Disperse dyes are water-insoluble non-ionic dyes and mainly used on polyester, nylon, cellulose and acrylic fibres. It contains azo, anthraquinone, styryl, nitro and benzodifuranone groups. Which solvent dyes are used for plastics, oils, gasoline, and waxes. The chemical classes are predominantly azo and anthraquinone.

6-Sulphur dyes are used for coloring the silk, cotton, rayon, leather, paper and wood.

7-Vat dyes are water insoluble and mainly used for colouring the cellulosic fibres. The primary chemical classes are anthraquinone and indigoids.

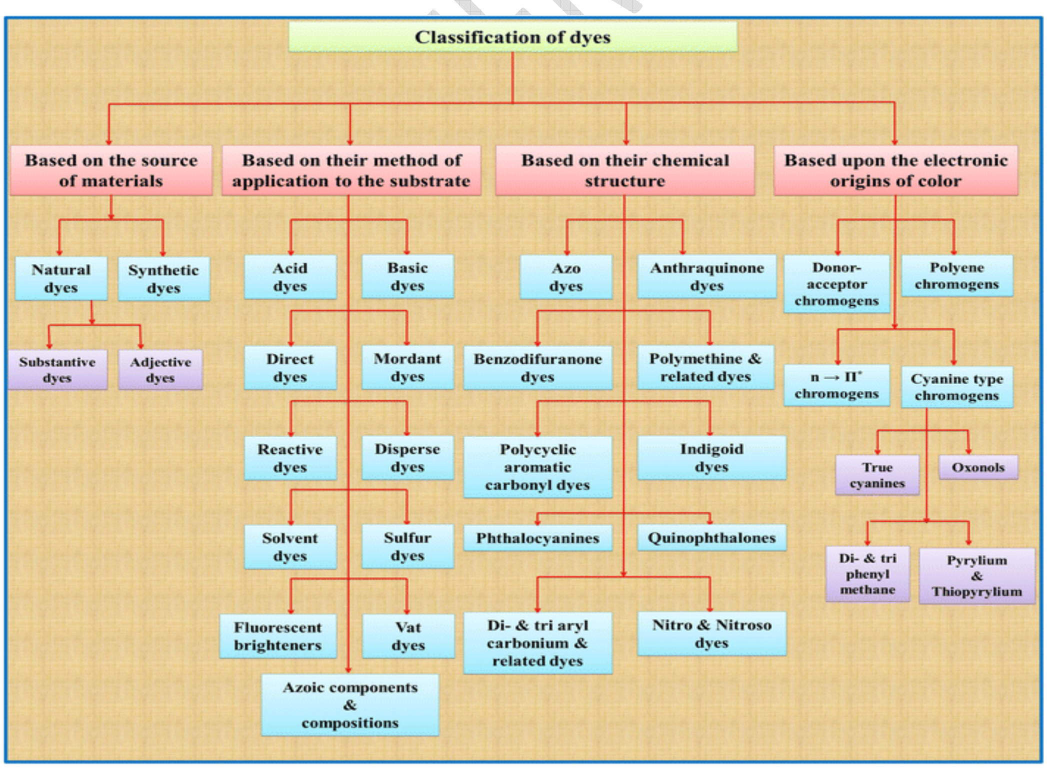

Fig.1. Classification of dyes [29]

6. Environmental concern of dyes and their hazardous effects

Many dyes are visible in water at concentrations as low as 1 mg/L.Textile-processing wastewaters, typically with dye content in the range 10-200 mg/L, are therefore usually highly coloured and discharge in open waters presents an aesthetic problem [30]. Textile industries harvest large quantities of liquid wastes which contain organic and inorganic composites [31]. Unfixed dyes are produce to be in high concentrations in textile effluents. 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. Several primary, secondary and tertiary treatment processes like flocculation, trickling filters and electrodialysis have been used to treat these effluents.

Also, as dyes designed to be chemically and photolytically stable, they are highly persistent in natural environments. The majority of dyes pose a potential health hazard to all forms of life with long-term and accidental over exposure. These dyes may cause allergic responses, skin dermatoses, eczema and may affect the liver, the lungs, the vasco-circulatory system, the immune system and the reproductive system of experimental animals as well as human systems [32]. Eren, [33] mention that basic dye are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer.

Dyes with azo bonds nitro-or amino-groups are carcinogenic, causing tumors of liver and urinary bladder in experimental animals [34]. However, reduction of azo dyes, i.e. cleavage of the dye's azo linkage (s), leads to formation of aromatic amines and several aromatic amines are known mutagens and carcinogens. In mammals, metabolic activation (reduction) of azo dyes is mainly due to bacterial activity in the anaerobic parts of the lower gastrointestinal tract. Various other organs, especially the liver and the kidneys, can, however, also reduce azo dyes [35]. The toxicity of aromatic amines depends on the nature and location of other substituents. As an example, the substitution with nitro, methyl or methoxy groups or halogen atoms may increase the toxicity; whereas substitution with carboxyl or sulphonate groups generally lower the toxicity [36]. As most soluble commercial dyestuffs contain one or more sulphonate groups, insight in the potentials danger of sulphonated aromatic amines is particularly important. Sulphonated aromatic amines, in contrast to some of their unsulphonated analogues, have generally no or very low genotoxic and tumorigenic potential [37]. Water soluble Azo dyes become dangerous when metabolized by liver enzymes. It was estimated that 130 of 3,200 azo dyes in use can form carcinogenic aromatic amines during degradation process [30].

7. Experimental methods for dyes removal from wastewater

Wastewater containing dyes are hard to treat because the organic molecules are persistent to aerobic digestion and are designed to have good resistance to light. The methods of dyes removal can be divided in three classes: biological [38], chemical and physical [39] methods, and are presented in Table 1. Owing to the complex nature of dye effluents, there is no single process that is so efficient to treat the dye wastewater. What is actually practiced is combination of different processes to achieve the desired water quality in the most economical way [40].

Table 1. Methods for dyes removal from wastewater

Biological Methods	**Chemical Methods**	**Physical Methods**
* Bleaching in the presence of fungicides; * Adsorption on microbial biomass; *Aerobic and anaerobic degradation; * Bioremediation; *Nitrification, denitrification; * Fermentation reactors; * Activated sludge tanks.	* Oxidative processes *photochemical oxidation (Fenton reactions); * Heterogeneous photo catalysis; * ozonation; * oxidation with Sodium Hypochlorite (NaOCl); * electrochemical oxidation; *Coagulation *Electrocoagulation *Ion exchange	* Irradiation * Membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmoses)

7.1 Biological Methods

Biological treatment is often the maximum economical alternative when compared with other physical and chemical techniques as showed in Table 2.

In latest years a number of studies have focused on some microorganisms that are able to absorb and degrade dyes from wastewater. A wide variety of microorganisms are able to decolorization of a wide range of dyes some of them are as bacteria: *Escherichia coli*, *Pseudomonas luteola*, *Aeromonas hydrophila* ; fungi: *Aspergillus niger*, *Phanerochaete chrysosporium, Aspergillus terricola* , *P. chrysosporium* ; algae: *Spirogyra* species , *Chlorella vulgaris* , *C. sorokiniana* , *Lemna minuscula* , *Scenedesmus obliquus, C. pyrenoidosa* and *Closterium lunula*.

These microorganisms are responsible for the biodegradation or bioaccumulation of dyes in wastewater. Based on different oxygen demand, biological treatment processes are classified into aerobic and anaerobic treatment. Anaerobic biological treatment methods use bacteria (e.g., *Bacteroides sp*., *Eubacterium sp*. and *Clostridium sp*.) to decolourise dye solutions through cleavage of the dye bond, yielding aromatic amines as products. Aerobic bacteria have been referring to oxidatively decolourise many dyes from numerous classes [41]. Besides, aerobic biological treatment is conventional biological treatment because of high efficiency and wide application. The efficiency of biological treatment systems is greatly influenced by technical constraints such as sensitivity towards seasonal variation, toxicity of some chemicals, less flexibility in design and operation and the requirement of large land areas.

To get maximum rate of dye removal, optimization of parameters of the system such as the level of aeration, temperature, pH, and redox potential, various carbon source, nitrogen source, temperature and inoculum size, are necessary.

Many researchers have investigated the use of algae, fungi and bacteria for the decolourization of dyes as reported by Crini et al. [40]; Abd-El-Rahim, [42]; Corso and Almeida [43]; Phatake et al. [44]; Khouni et al. [45] ; Wanyonyi et al. [46] and Cao et al.[47].

Lee and Chang [48] investigated the efficiency of marine algae *Chlorella marina, Isochrysis galbana, Tetarselmis* species*, Nanno chloropsis* species and *Dunaliella salina* and fresh water microalgal cells (*Chlorella* species) in dye removal from the textile effluent. Among the algal species tested, the highest colour removal was noticed in *Isochrysis galbana* (55%) followed by freshwater *Chlorella* species (43%).

Bayramoglu and Arica [49] study the adsorption of congo red dye (CRD) by native amine and carboxyl modified biomass of *Funalia trogii*, isotherms, kinetics and thermodynamics mechanisms**.** The maximum adsorption of the CRD on the native, carboxyl and amine groups modified fungal biomasses was obtained at pH 5. The amount of adsorbed dye on the adsorbent samples increased as the initial concentration of CRD in the solution increased to 200 mg/L. The adsorption capacities of native, carboxyl groups and amine modified fungal preparations were 90.4, 153.6 and 193.7 mg/g dry adsorbents, respectively.

Azza et al. [50] study the biosorption of acid orange 7, basic red 46 and basic blue 3 dyes using *Spirogyra* species. The algae showed the maximum biosorption of dyes at various biomass concentrations of 13.2, 12.2 and 6.2 mg/g respectively within 60 min.

Kumar et al. [51] studied the effect of three independent variables namely biomass dosage, dye concentration and initial solution pH for the biosorption study, of acid black 1 using *Nizamuddin zanardini, Stoepermum glaucescens* and *Stoecospermum marginatum.* The acid black 1 dye removal of 99.27%, 98.12% and 97.62%*,* respectively.

Masoud et al. [52] reported the optimized conditions used for the acid black 1 removal with brown macro algae *Stoechospermum glacescens* and *Stoechospermumm arginatum*. The dye removal capacity increased with the decrease in particle size of biosorbents and the agitation speed at 130 rpm controls the dye sorption capacity.

Omar et al. [53] removed of malachite green dye from aqueous solution by *Ulva lactuca*, *Sargassum crassifolium*, and *Gracilaria corticata* has been demonstrated in order to examine their potential use as low-cost adsorbents. The optimum pH (8), temperature (25 ℃), contact time (150 min), and biomass (2g) for removal of dye by algae are reported. The maximum removal percentage of the dye ranged between 95.6% and 98.3% by using *Sargassum crassifolium* at the optimal conditions. Adsorption of the dye by using the biomass was found to fit well with Langmuir and Freundlich isotherms.

Parvez and Devi [54] found that *Aspergillus niger* fungi has ability to adsorb colour from solution and dying industry effluent.

Al Prol et al. [55] studied bioremediation of Reactive Blue 19 and Reactive Black 5 from aqueous solution by using Fungi *Aspergillus niger. Aspergillus niger* showed maximum dye decolorization under optimum condition and found to be more efficient when added in the dye solution of pH 8 and 10 with agitation at 130 rpm and incubation time for 7 days with

25℃. The results clearly showed that additional nutrient sources are effective in increasing dye decolorization rate.

Dawood and Sen [56] studied the removal of malachite green using *Nostoc* species. The colour removal efficiency was 80% within 45min when treated with the *Nostoc.*

Roy et al. [57] study biodegradation of crystal violet dye by bacteria isolated from textile industry effluents. The decolorizing activity of the bacteria was measured using a photo electric colorimeter after aerobic incubation in different time intervals of the isolates. Complete decolorizing efficiency was observed in a mineral salt medium containing up to 150 mg/L of Crystal Violet dye by 10% (v/v) inoculums of Enterobacter sp. CV–S1 tested under 72 h of shaking incubation at temperature 35 ◦C and pH 6.5.

Zuraida et al. [58] removal of synthetic dyes from wastewater by using bacteria, *Lactobacillus delbruckii.* This study used of two commercial synthetic dyes i.e. Reactive orange 16 (RO 16) and Reactive black 5 (RB 5). The results showed that the bacteria are able to decolorize these two reactive dyes and the optimum pH, temperature and initial dye concentration were found to be 10 ppm, 6 and 37℃, respectively.

Table 2. The advantages and disadvantages of biological dye removal techniques

Organism (process)	Advantages	Disadvantages	Ref.
Bacteria (aerobic)	-decolorize both azo and anthraquinone dyes, -production of biogas	-low decolorization rates, -requires specific oxygen catalyzed enzymes, -requires additional carbon and energy sources	[59]
Bacteria (anaerobic)	-suitable for large scale application, -takes place at neutral pH for sludge treatment system, -allows obligate and facultative bacteria to reduce azo dyes	-generation of toxic substance, -requires post-treatment, -immobilization and recovery of redox mediator presents a challenge	[60]
Fungi	decolorize anthraquinone and indigo-based dyes at higher rates	decolorization rate is very low for azo dyes, -requires especial bioreactor and external carbon source, -needs acidic pH (4.5-5), -inhibition by mixture of dyes and chemical in textile effluents	[61]

7.2 Chemical Methods

Chemical techniques can be used to eliminate dyes, which contain coagulation or flocculation include floatation and filtration, precipitation, electro floatation, electro kinetic coagulation, conventional oxidation process by oxidizing agents such as ozone, irradiation and electrochemical processes. In addition to these chemical techniques are efficient for the treatment of pollutants from wastewater, they are expensive, commercially unattractive, accumulation of concentrated sludge creates a disposal problem and the possibility that a secondary contamination problem will arise due to excessive chemical use. The high electrical energy demand and the consumption of chemical reagents are common problems as presented in Table 3. Recently, other emerging methods, known as advanced oxidation techniques, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for degradation of pollutant.

Table 3. The advantages and disadvantages of chemical dyes removal techniques

Method	Advantages	Disadvantages	Ref.
Fenton's reagent	Effective decolourisation of both soluble and insoluble dyes *low cost	Sludge production; Prohibitively expensive.	[60]
Ozonation	* gases are applied * does not increase the volume of wastewater and sludge	*small half-life (20 minutes)	[61] ,
Oxidation with NaOCl	* initiates and accelerates the breaking of azo bonds	* aromatic amines release	[60]
Photochemical oxidation	* doesn't generate sludge *low cost	* by-products formation	[35]
Electrochemical destruction	* Breakdown compound are non-hazardous	* High cost of electricity and operating.	[60-61]
Coagulation–flocculation	*Simple and economically feasible. *Short detention time and low capital costs. *Good removal efficiencies	*High sludge production. *Handling and disposal problems. *High cost of chemicals for pH adjustment. *Dewatering and sludge handling problems	[62]

Chemical oxidation is very effective, however the efficiency strongly influenced by the kind of oxidant [63].

Advanced oxidation technologies (AOTs): Oxidation method is one of the conventional methods used for the elimination of inorganics/organics pollutants from wastewater. The main mechanism of AOTs is through generation of extremely reactive free radicals. The role of reactive free radicals to oxidize the complex organic components to the simpler intermediates besides end products. There are numerous ways in which degradation of organics components can occur during the oxidation process: (i) a structural change in the parent compound with same molecular formula, (ii) structural change in the parent compound to produce other composites which may be fewer or extra toxic, in addition (iii) mineralization of organic carbon in to CO2.

AOTs comprise the use of oxidants such as ozone, chloride, and Fenton reagent in addition chlorine dioxide. **Fenton's reagent** is known as hydrogen peroxide and it is more effective if applied at acidic medium. Also, iron ions such as Fe^{+2} and Fe^{+3} are the greatest common reagents which used in Fenton activation.

El Haddad et al. [63] studied use of Fenton reagent as advanced oxidative process for removing textile dyes from aqueous solutions. The optimum amounts of Fenton reagent was 25 mg/L of Fe and 250 mg/L of H_2O_2 for an initial Reactive Yellow 84 concentration at 60 mg/L. Kinetics decolorization of RY84 followed pseudo second-order reaction. The reaction characteristic of oxidative reaction for decolorization efficiency process was evaluated as thermodynamically spontaneous under natural conditions. The value of activation energy is determined and is equal to 16.78 kJ/mol, this low value may show that the oxidative reaction proceeds with low energy barrier.

Lee et al. [64] studied the degradation of Acid Red 114 using the photo-Fenton process. A complete decolourization of the dye was observed by adding the ferric ions (130 mg/L $FeCl_3.6H_2O$), hydrogen peroxide (100 mg /L H_2O_2) and the photocatalyst titanium dioxide particales (100 mg/L TiO_2) within a period of 60 to 300 minutes. The system was illuminated with the UV radiation and the pH was adjusted at 2.5 and temperature 30 ºC.

Fernandez el al. [65] investigated the bleaching and mineralization of Orange II in the presence of oxone (a mixture of potassium salts including: potassium sulfate; K_2SO_4, potassium peroxy monosulfate; $KHSO_5$ and potassium peroxodi sulfate; $KHSO_4$, and copper sulfate; $CuSO_4.5H_2O$) and a mixture of ferric nitrate ($Fe (NO_3)_3.9H_2O$) with manganese sulfate ($MnSO_4$. H_2O).

Ozonation is another type of AOTS oxidation used in the removal of synthesis dyes from wastewater effluents. It is a very effective technology in treating wastewater and is considered to be a good method in the decolourization of textile effluents as ozone (O3) attacks the nitrogen conjugated double bonds which are often associated with colours [66]. Ozonation reactions can be classified into direct reaction and indirect reaction based on the pH of the solution. The decomposition rate of ozone is affected by solution pH and initial dye concentration. At basic medium, ozone rapidly decomposes to yield the hydroxyl radical but in acidic conditions, ozone can directly react with organic substrates as an electrophile. Ozonation process does not form a sludge because of complete decomposition of dyes thus reduce the toxicity of by-products [67].

Photocatalytic oxidation on immobilized TiO_2 in presence of solar irradiation and combined with electrochlorination has been successful in decolourisation and toxicity reduction [68].

Borujeni et al. [69] study decomposition of basic blue 9 (BB-9) in aqueous solution using ozonation and catalytic ozonation system (O3/granular activated carbon [GAC]) in the bench-scale experiment. The effect of ozone dose, pH, and GAC contents in removal of BB-9 and biodegradability of effluent such as biochemical oxygen demand (BOD5); Chemical Oxygen Demand (COD), and BOD5/COD were studied. Results showed that pH of solution and ozone concentration are significant factors on removal of BB-9; COD and BOD5. The application of GAC as catalyst, in mass concentration of 2 g/l, caused 48% increase in the degradation rate of BB-9.

Photocatalyst is a method used in the removal of organics pollutants as dyes from effluents. Photon energy equal or higher than the band gap energy is essential to excite the electrons from the valence band to the conduction band in addition the movement of the electrons leave holes with posi positively charged ions (H^+) in the valence band [70]. The positively charged holes are powerful oxidants and can destroy adsorbed organic pollutants where the electrons at the conduction band react with the oxygen molecules to form strong oxidative radicals which also cause the decomposition of organic and inorganic pollutants in wastewater [71]. Photocatalyst is used in the elimination of dyes from wastewater such as Methyl Orange [72], direct green and reactive red [73]. On the other hand, some photocatalyst are degraded along the process and generate toxic products.

Electrocoagulation: In latest years, many researchers have been specially focused on the use of electrocoagulation owing to increase in environmental restrictions on wastewater effluent. Electrocoagulation is a method consisting of producing metallic hydroxide flocks inside the wastewater through electro dissolution of soluble anode made of Iron (Fe) or Aluminium (Al).

Hussein et al. [74] investigated the colour removal of reactive blue 19 from textile wastewater by electrocoagulation using iron electrodes. Effects of various factors such as pH on dye removal, current density, electrolysis time, initial dye concentration, supporting electrolyte concentration, temperature were scrutinized. The optimum operating conditions for the effective removal was at pH 11.5, applied current density of 50 mA/cm2, electrolysis time of 20 minutes, 100 mg/L dye concentration, supporting electrolyte concentration of 5g/L Nad and room temperature. Under these conditions, 99.60 % of dye effectively removed.

Electrochemical oxidation: This technique is used as an alternative treatment process for the elimination of colour in dye mixture.

El Sayed et al. [75] examined removal of indigo carmine dye from synthetic wastewater by electrochemical oxidation in a new cell with horizontally oriented electrodes. Electrochemical unit consists of anode as pb/pbO_2 and cathode as stainless steel screen. Under optimum operating conditions, complete decolourization with 88.2 % COD reduction was achieved.

Hoong and Ismai, [76] study removal of dye in wastewater by adsorption coagulation combined system with hibiscus sabdariffa as the coagulant. The results showed that the optimised process parameters for adsorption-coagulation hybrid process with hibiscus sabdariffa seeds as the coagulant and activated carbon as the adsorbent are pH 2, initial dye concentration of 385 ppm, coagulant dosage of 209 mg/L and adsorbent dosage of 150 mg/L. The dye removal reaches up to 96.67 % under optimum parameters.

Kasperchik et al. [77] study wastewater treatment for removal of dyes by coagulation and membrane processes. In this study used wastewater from direct and reactive dyeing processes, a comparative analysis has been performed of the efficiency of wastewater treatment by the following two processes: reagent coagulation with the use of aluminum hydroxychloride and anionic and cationic flocculants and ultrafiltration with the use of polyacrylonitrile, polysulfone, aromatic polyamide, and poly sulfonamide membranes and experimental membrane samples with additionally modified surfaces.

<u>7.3 Physical Methods</u>

There are different types of physical methods used in the elimination of dyes as part of water and wastewater treatments. Physical methods used usually are adsorption techniques, ion exchange, activated carbon, and membrane filtration methods (Electro dialysis, Nano filtration, Reverse osmosis) as presented in Table 4.

Table 4. Advantages and disadvantages of removal techniques for dyes from wastewater [78]

Method	Advantages	Disadvantages
Adsorption	*High adsorption capacity for all dyes. *low cost	*Need to dispose of adsorbents. *Low surface area for some adsorbents.
Activated carbon	* removes wide varieties of dyes	* very expensive, ineffective against disperse and vat dyes
Non-conventional adsorbents (agricultural and industrial byproducts)	* effective adsorbent, inexpensive, widely available, operation is easy, process design is simple	*transfer of pollutants from liquid phase to solid matrix (adsorbent) not selective
Membrane filtration	* removes all dye types, quick method and requires less space	* concentrated sludge production, membrane fouling, high cost and incapable to treat large volume
Ion exchange	* regeneration possibility * the adsorbent is not lost	* not effective for all types of dyes
Nano-filtration	* separation of low molecular weight organic compounds and of divalent	* high operation costs

	ions	
Reverse osmosis	* removal of mineral salts, dyes and chemical reagents	* high pressure needed

Adsorption, which is a well-known equilibrium separation process, is gaining much attention due to its simple design, ease of operation, flexibility and insensitivity to toxic contaminants. Adsorption method will produce great quality treated effluents. It considers an attractive alternative for the removal of contaminated water, provided that the adsorbent is low-cost and does not need much modification before its application [40].

Gezer [79], study adsorption of carob powder as the adsorbent to eliminate of organic dye from waste water. In the investigates, six inputs pH (2-8), ultrasound frequency (50-150 hz), particle size (50-150 µm), adsorption temperature (25-40 ℃), solution concentration (10-30 mg/L) and adsorption time (120-360 min) were examined using the statistical box-behnken design with parameters. As a result of the present work, it was finding that carob powder could be a strong alternative adsorbent for methylene blue elimination.

Membrane filtration is pressing the water by a very fine membrane in dead end and passed through systems. Nowadays wide ranges of various membranes are used, for example nanofiltration, microfiltration, ultrafiltration and reverse osmosis.

Rashidi et al. [80] study treatment of synthetic reactive dye wastewater by using nano-membrane filtration. In this study, application of polyamide nano-membrane to remove dyes was evaluated for five different fiber reactive dyes' wastewater, namely reactive blue 15, reactive red 194, reactive yellow 145, reactive black 5, and reactive orange 16. Dyes were tested in low concentration (16 mg/L) during a 60 min filtration process. The efficiency of filtration was calculated based on pre-process and post-process analytical experiments. The flux for all the samples ranged between 7.8 and 9.2 $ml/cm^2 s$. The permeate pH value of the samples was observed to slightly increase, within a range of 6.4–7.1.

Ion exchangers are solid materials or liquid solutions which are able to absorb negatively or positively charged ions from aqueous electrolyte mixture and at the same time release additional ions of equivalent amount into the aqueous mixture [81]. Ion exchange is a good technique to separate toxic and soluble dyes from wastewater effluents although the high capital cost associated with this process limited its use. Furthermore, ion exchange is used to eliminate toxic dyes from wastewater for example elimination of anionic dye such as orange-G [13] and cationic dye as methyl violet 2B [82].

González et al. [83] study the adsorption of textile dyes present in aqueous solution and wastewater using polyelectrolytes derived from chitosan. The results by optimizing the conditions of static adsorption, approximately 90 % of the cationic dyes present in an aqueous solution with an initial concentration of 300 mg dm^{-3} and a basic pH of around 11.5 were removed. Anionic dyes almost reach 100% adsorption on the polyampholytes. The point of zero charge (pHpzc) was determined, and it was found that both polyampholytes exhibited a basic character on their surface (pHpzc > 8.7).

7.4 Combination of Different Methods

The treatment on wastewater comprising reactive black 5 dyes by via sequencing batch reactor followed by combined aerobic membrane bioreactor and reverse osmosis was studied by You and Teng, [84]. Results indicated that in the sequencing batch reactor, reactive black 5 dyes was degraded to aromatic amine groups which would additional mineralize by aerobic membrane bioreactor/reverse osmosis to meet the criteria for reuse.

The photocatalytic and adsorption treatment of the prepared TiO_2/adsorbent nanocomposites (TNC) via a facile wet chemical method were examined by using methylene blue dyes as contaminant [85]. Synergistic effects among adsorption and photocatalysis were showed with the assistance of visible-light irradiation and all TNC succeed better methylene blue dyes elimination rates than the adsorption process alone. The joined effects of both photocatalytic oxidation and reverse osmosis membrane leads to complete elimination of the synthetic dyes wastewater with 90 % reduction of original dyes content.

The photocatalytic combined with anaerobic-photocatalytic treatment of textiles dyes was studied by Harrelkas et al. [86]. Results showed that photocatalysis was able to eliminate 90 % of color from crude in addition to autoxidized chemically reduced dye solution. The combined treatment of ozonation besides biological degradation by a biofilm to decrease the color from textile wastewater was examined by De souza et al. [87]. Results showed that ozonation of remazol black B was effective and the color decolorization could reach to 96%. The subsequent biological process was capable of decreasing the toxicity of the resulting effluents after ozonation. A number of biological besides chemical coupled treatments for removal of Cibacron Red FN-R azo dye [88].The non-biodegradable reactive dyes were removed via the catalytic effects of Fenton's reagent. Fenton's reagent can be used to combine both oxidation and coagulation techniques [89].

A comparison study on the elimination of acid green 50 from industrial wastewater by anodic oxidation besides electrocoagulation was carried out by El-Ashtoukhy and Amin [90]. Results indicated that elimination of acid green 50 is more economical through using electrocoagulation as compared to anodic oxidation owing to lower power consumption during electrocoagulation.

Table 5. Recent report on the method used for the removal of textile dyes

Type of dye	Adsorbent used	pH & Temp.	Isotherms followed	Ref.
Methyl Red	Adsorption by Guargum Powder	pH 4.2 & 34℃	Langmuir model	[91]
Amido black-10 B	Nano photo catalyst	---	--------	[92]
Synthetic dye	Adsorption by sago waste	pH 4 & 34℃	Langmuir model	[93]

Acid blue 92, Direct red 23, & Direct red 81	Polymeric Adsorbent (poly amido primary secondary amine)	pH 12	Langmuir isotherm	[94]
Reactive red 120	Nano filtration poly etherimide membrane			[95]
Acid black 210 & acid red 357	Activated carbon prepared from leather shaving wastes	pH 2	Langmuir and BET models	[96]
residual Reactive blue 49	a coagulant and a flocculant	pH 7 & 60 ℃	-----------	[97]
Reactive red	Belpatra Bark charcoal adsorbent	50℃ & pH 3	Langmuir, Freundlich and Temkin adsorption	[98]

8. Parameter affecting on removal of dyes include [6]

1. The physical and chemical characteristics of the adsorbent, i.e., surface area, pore size, chemical composition.
2. The physical and chemical characteristics of the adsorbate, i.e., molecular polarity, chemical composition.
3. The concentration of the adsorbate in the liquid phase (solution).
4. The characteristics of the liquid phase, i.e., pH and temperature.
5. The residence time of the system.
6. Some conditions which play an important role in dye decolorization in biological treatment viz. incubation time, temperature, pH, agitation rate and carbon, nitrogen, inorganic salts and phosphorus sources in growth medium [99].

9. Conclusion

Wastewater discharged by textile finishing industries has become an great environmental concern for the scientists because of the prevailing hazards in our ecosystem. This review paper provides highlights literature information about sources of dyes, its classification and toxicity. Moreover, define various technologies for removal of different dyes from industrial wastes effluent. These techniques have been discussed by various biological, chemical, physical technologies beside combination treatments. Also, Advantages and disadvantages of different techniques are discussed. Several researches have been carried out a combination of different techniques which offer many advantages such as high efficiency of dye removal, minimal amount of sludge formation, coagulant savings and economic feasibility. The author expected that the technology which is clean production, efficient, low cost and reasonable will come out soon.

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