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Chapter 1

A Review of State-of-the-Art Technologies in Dye-Containing Wastewater Treatment – The Textile Industry Case

Serkan Arslan, Murat Eyvaz, Ercan Gürbulak and Ebubekir Yüksel

Additional information is available at the end of the chapter

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Abstract

Recently, new single or hybrid/combined processes have attracted much attention for treatment of textile and dyeing wastewaters. These processes which may be termed as "state of the art technologies" are membrane separation processes, ultrasonic, photochemical and electrochemical processes. Although the conventional methods still have been tried with some new materials such as, new adsorbents or coagulants, employing the new generation methods such as, electrocagulation-electrooxidation, sonooxidation or photo oxidation are gaining in popularity when the treatment of textile wastewaters is discussed. The purpose of the book chapter is to bring an overview on the new treatment methods for textile wastewaters, one of the most important source of environmental pollution. Despite the fact that there is no uniform standard currently, many countries have legalized some strict discharging standards and scientists and researchers face new technologies including electrical, sonic, magnetic, optical and thermal methods. Although many researches on treatment of synthetic or real wastewaters with various methods are available, very few researches have been carried out on the cutting-edge technologies. Moreover, there are a lot of review article or book chapters on textile wastewater treatment processes individually based on each conventional process such as coagulation, adsorption, chemical oxidation, and biological decolorization. Therefore, in this part of the book, following major and minor titles are stated truly on the aforementioned new technologies. Besides, these parts are not only about cutting-edge technologies, but also related with conventional methods and their new applications in colored wastewater treatment area briefly.

Keywords: Textile wastewater treatment, decolorization, membrane processes, ultrasonic treatment processes, electrochemical treatment processes, photochemical treatment processes, hybrid processes

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1. Introduction

Textile wastewaters are one of the most polluted wastewaters due to their characteristics, such as high chemical oxygen demand (COD) concentration, strong color, high pH and temperature, and low biodegradability [1–3]. These effluents can exhibit serious environmental problems and public health concerns if improperly disposed. These highly colored components, when discharged with wastewater into the water bodies, stop the reoxygenation capacity of the receiving water and cut-off sunlight, thereby upset biological activity in aquatic life [4]. Since diversity of textile products increases, different dyestuffs with highly varying chemical characteristics are used in this sector, which complicates further the treatment of textile wastewaters [1]. Several conventional methods have been applied for this purpose, such as adsorption, biological treatment, oxidation, coagulation, and flocculation [5–8]. Although these methods have been widely applied, they have some disadvantages. For example, adsorbents are usually difficult to regenerate [9]. Chemical coagulation causes extra pollution due to the undesired reactions in treated water and produces large amounts of sludge [3]. Biological methods are not suitable for most textile wastewaters due to the harmful effects of some commercial dyes on the organisms used in the process. Furthermore, these conventional methods are also usually expensive, and treatment efficiency is inadequate because of the large variability of the composition of textile wastewaters [10].

The main problem that environmental engineers have to deal with is the elimination of the wastewater's color, which is due to the remaining dyes. However, color removal has been a great challenge over the past decades, and up to now there is no single and economically attractive treatment that can effectively decolorize dyes, and new technologies for wastewater decolorization are especially needed [11–13]. Recently, new single or hybrid/combined processes have attracted much attention for the treatment of textile and dyeing wastewaters. These processes which may be termed as "state of the art technologies" are membrane separation, ultrasonic, photochemical, and electrochemical processes. Although the conventional methods still have been tried with some new materials such as new adsorbents or coagulants, employing the new generation methods such as electrocoagulation-electrooxidation, sono-oxidation, or photo-oxidation are gaining in popularity when the treatment of textile wastewaters is discussed.

The purpose of this chapter is to bring an overview on the new treatment methods for textile wastewaters, one of the most important sources of environmental pollution. Despite the fact that there is no uniform standard currently, many countries have legalized some strict discharging standards, and scientists and researchers face new technologies, including electrical, sonic, magnetic, optical, and thermal methods. Although many researches on treatment of synthetic or real wastewaters with various methods are available, very few researches have been carried out on the cutting-edge technologies. Moreover, there are a lot of review article or book chapters on textile wastewater treatment processes individually based on each conventional processes, such as coagulation, adsorption, chemical oxidation, and biological decolorization. Therefore, in this part of the book, the following major and minor titles are stated truly on the aforementioned new technologies. Besides, these parts are not only about cutting-edge technologies but also related to conventional methods and their new applications in colored wastewater treatment area briefly.

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2. Processes in textile industry

2.1. General process description

The textile industry is a global industry in all around the world, which provides a huge income and employment for several countries. Besides, textile manufacturing includes several sequencing processes that are characterized as whole by consumption of resources, such as water, electricity, and fuel, and usage of several types of chemicals. Another important load of textile production on environment is the production of wastewater, which consists of many impurities such as dyes and pigments, heavy metals, and surfactants with high concentrations. These wastewaters should be treated before discharging into the surface water sources; otherwise, they can threaten the quality of water source and wildlife. It must not also be underestimated that a big amount of energy consumption is necessary for the treatment of wastewaters containing dye. After the treatment of wastewater, sludge remains, which includes high percentage of chemicals, and needs to be disposed with methods used for hazardous waste.

All these have totally enormous impact on environment, which makes it necessary to increase the efficiency and sustainability of processes to decrease the load on environment in long term. The content of dye of textile wastewater comes mainly from the dyeing and printing processes, including washing process; but before these processes, pretreatment steps should be applied for the quality of dyeing/printing. The process stages by textile industry can be summarized as follows:

- **Singeing:** The process of burning off protruding fibers from yarn or fabric.
- **Sizing:** The process of giving a protective coating on the warp yarn to minimize yarn breakage during the weaving.
- **Desizing:** The process of removing sizing agent from woven fabric prior to subsequent processes, such as bleaching, dyeing, and finishing.
- **Scouring:** The process of removing impurities.
- **Bleaching:** The process of removing or lightening colored materials.
- **Mercerization:** The process of improving lustre, dyeability, and strength of cellulosic material.
- **Dyeing:** The process of coloring fibers, yarns, or fabrics.
- **Printing:** The application of colorants in definite, repeated patterns to fabric, yarn, or sliver by any one of a number of methods other than dyeing.
- **Finishing:** The final process given to a textile material to give good appearance, functional properties, such as water-repellent, shrink-resistant, and wrinkle-resistant.

Washing and drying processes are also applied after different process stages, such as desizing, bleaching, and mercerizing, and especially after dyeing process to remove the dyestuff, which is not fixed on the textile [14–16].

2.2. Types and chemistry of dyestuffs

To color the final products of textile industry such as fabric, different dyestuffs are used after pretreatment steps of fabric. The textile dyes is an important part of not only the dyes but also the chemicals of the world business. The most used dyes in textile industry are on synthetic basis. They are produced mainly from coal tar and petroleum-based products. The dyes are sold in market as powders, granules, pastes, or liquid dispersions. The properties of textile materials such as fabric have been continually changed according to the new developments in textile industry. The dyes should also meet the demands of these new fabricated materials of textile industry. These can cause to increase the percent of the active materials in dyes, which causes more pollution in environmental systems. According to their chemical properties, the dyes can be classified as follows [17].

- Reactive dyes
- Acid dyes
- Basic dyes
- Disperse dyes
- Vat dyes
- Sulfur dyes
- Mordant dyes
- Direct dyes
- Ingrain dyes (Naphthol dyes)
- Solvent dyes (Lysochromes)
- Pigment dyes (Organic pigments)
- Other dye classes such as food dyes and natural dyes

Not 100% of the dyes are fixed to the fiber during the dyeing process. For example, reactive dyes show the minimum fixing range with 20–50% to cotton and viscose. A big part of the colored wastewater coming from textile dyeing processes is caused dyeing process such as cotton dyeing with reactive dyes with the poorest fixation property. Therefore, the fixation ratio of dye on textile product is also very important to minimize the dye consumption and production of colored wastewater from the industry [18].

2.3. Environmental effects of textile industry wastewaters

The most important load on environment caused by the textile industry can be summarized as follows:

- Consumption of natural and energy sources, such as water, fuel, and electricity.
- Usage of chemicals especially dyes by dyeing and printing processes.

- Production of wastewater with many impurities such as color, which has to be treated before discharging into the canalization or surface water [19].

During the treatment processes for the textile wastewater, a big amount of energy should be used and besides after the treatment process, sludge remains, which is evaluated as hazardous waste, and needs special disposal processes such as incineration which consumes also energy.

As seen, water consumption and pollution belong to the most important environmental issues regarding the textile industry. Therefore, the production organizations in textile sector should develop more efficient and environment friendly technologies to consume less water and to reduce discharged effluent increasing the quality of discharged wastewater at the same time to meet the discharge limitations [20].

During the production of textile products, big amounts of water are consumed especially by dyeing and printing processes. A textile facility with a daily production capacity of 8000 kg has a daily water consumption of nearly 1.6 million liters [21]. Nearly 25% of water of whole consumption is required for dyeing and printing processes. According to the US EPA [22], 40 liters of water is required averagely for dyeing 1 kg of cloth, changing according to the textile material and dyeing process. Water is also required for other processes such as washing of dyed textile material. Table 1 shows the consumption of water, chemicals, and energy for production of 1 kg of colored fabric.

System unit	Input	Conventional process
Pre-treatment	Water	20 l
	Solvent	120 kg
	Gas	—
	Energy	0.13 kwh
Dyeing	Water	20 l
	Solvent	20.98 g
	Dyestuff	10 g
	Auxiliary	25 g
	Energy	3.82 kwh
Washing	Water	10 l
	Washing agents	5 g
	Energy	0.16 kwh
Drying	Energy	0.04 kwh
	Gas	0.27 kwh

Table 1. Global inventory for the dyeing process (functional unit: 1 kg of colored fabric) [23]

There have been several efforts to decrease this enormous effect on environment caused by textile industry. Especially, the trends to decrease environmental load of textile products on environment at the design phase is a very important aspect, which affect the later stages of

supply chain. Low impact dyes and processes managed by green technology, which require less water, is more effective than the efforts taken after production or during the production. Also the need for the more effective measurement of the textile processing systems is an important point. The processes should be traced and measured effectively to determine the load on environment of each used materials and processes [23].

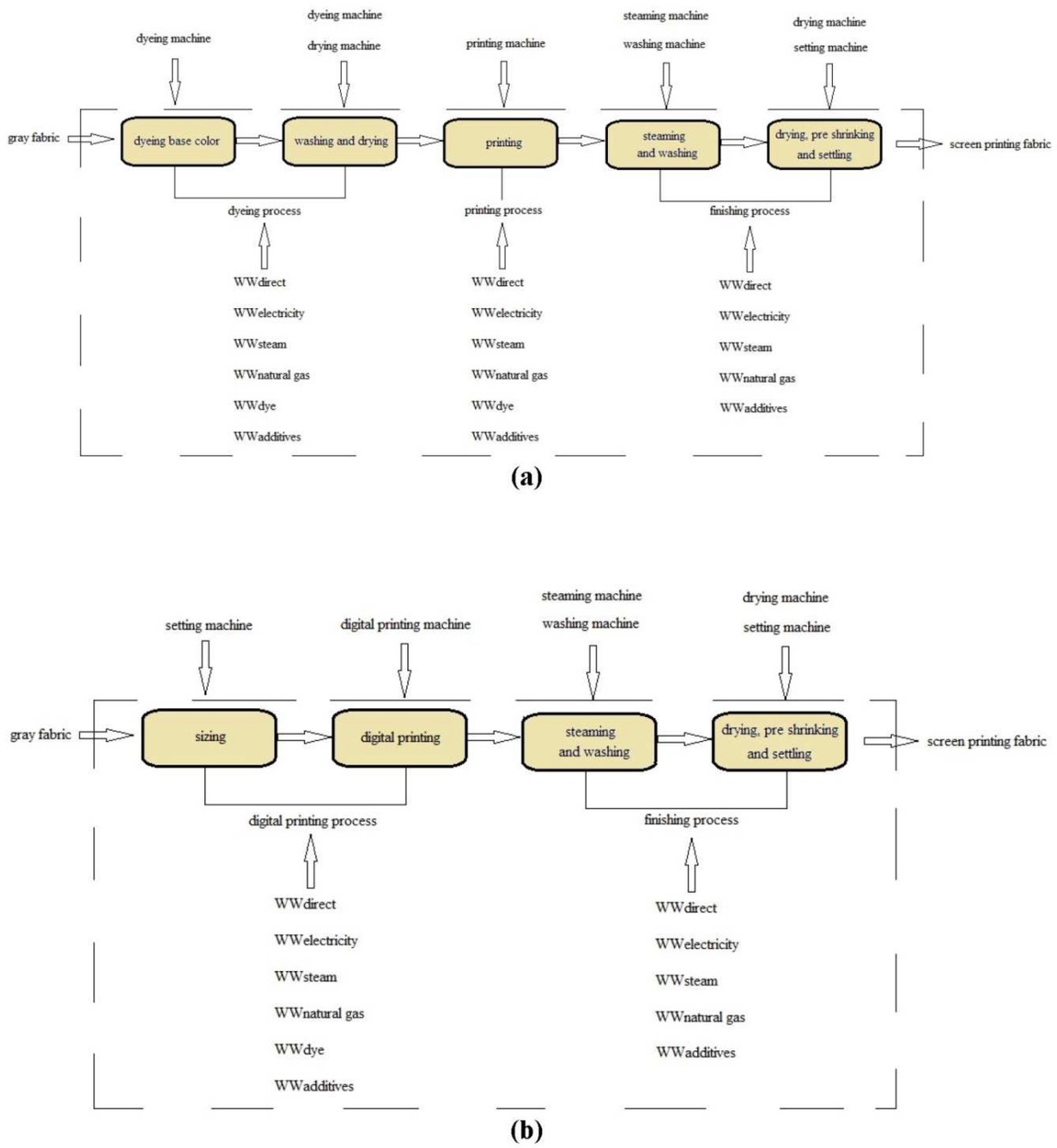


Figure 1. System boundary of the evaluation and production of screen printing (a) and digital printing (b) fabrics [20]. Water withdrawal (WW) is the volume of water taken from a catchment for production process.

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Figure 1 is a good example to show the effect of using more technological processes to decrease the water consumption. The system boundaries of two production systems: one of which includes a screen printing and the other digital printing as printing process. The main water withdrawal is coming from both systems by the printing process. There is also indirect water withdrawal from other processes such as vapor production and water used for additives. It can be seen from Figure 3 also that digital printing system has a more compact system, which realizes the process without dissolving the dye in the water and reduces water use and pollution at the dyeing and printing processes. These kinds of technological developments by dyeing and printing processes are very important besides the increasing of the treatment efficiency and reuse of treated wastewater in textile industry [20].

In this context, new projects are supported by governmental and regional institutions. One of them is called BISCOL project co-founded by European commission. The aim of the project is to develop new technologies in dyeing processes, which make available to convert the raw material into the eco-viable final products. For this purpose, innovative technologies such as enzymatic synthesis of dyes or textile pre-treatment based on plasma technology have been used. The results which compare the environmental loads on environment of both conventional textile processes and processes supported by BISCOL project are shown in Figure 2. As shown in Figure 2, the BISCOL processes provide incredible benefits in terms of environmental pollution and consumption of natural resources [24].

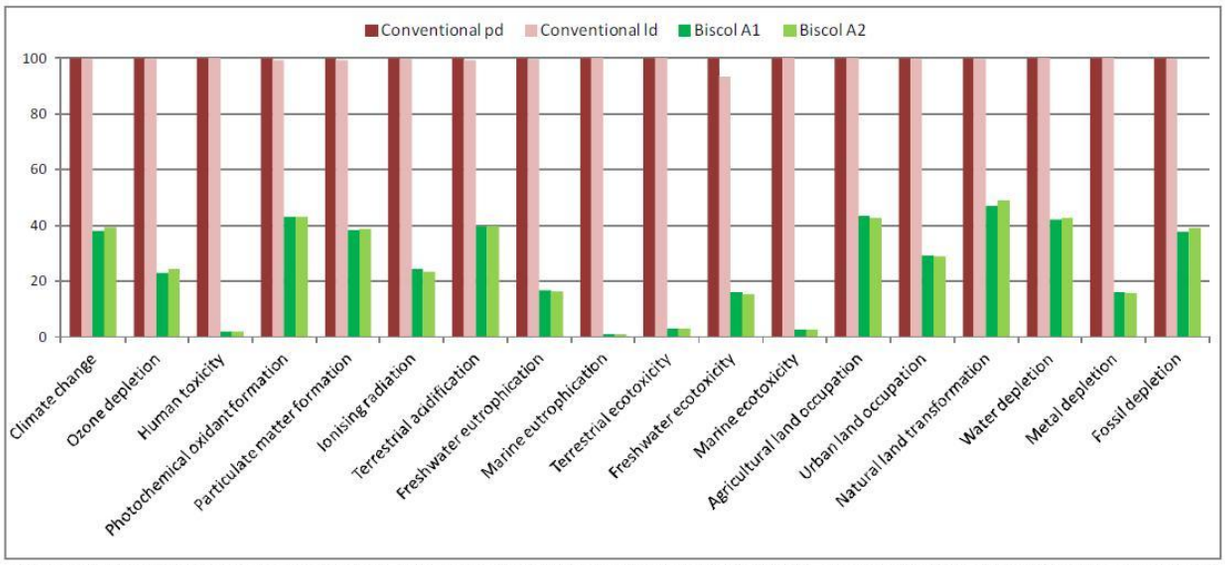


Figure 2. Comparison of dyeing processes for 1 kg woolen fabric production with BISCOL process (auxillary 1 and 2) and conventional ones (liquid and powder dye) [24].

2.4. Environmental standards for the discharging of textile industry effluents in the world

Typical textile wastewater characteristics in five different containers appearing in a study are shown in Table 2 [25]. Because of the strong characteristics of the textile wastewaters, there are

strict limits for discharging of textile wastewater into the canalization or receiving environment in many countries. Textile facilities are not allowed to discharge their wastewater into aquatic environment or canalization requiring establishing wastewater treatment plants of which the outlet water has to meet the discharge limits according to receiving system. Also, polycyclic aromatic hydrocarbons (PAHs) are included in textile dyeing sludge as components of synthetic dyes, which are known to be potent carcinogens and given high priority for environmental pollution regulation and in risk assessment of industrial discharges [25, 26]. In Table 3, the discharge standards of water pollutants for dyeing and finishing of textile industry in a country are shown. The direct discharge limits show the limits to be obeyed when discharging directly into the aquatic environment. The indirect discharge limits show the limits to be obeyed when discharging into the canalization system. If the Tables 2 and 3 are considered together, it is seen that essential removal rate of pollutants in textile wastewater described by parameters such as COD, biological oxygen demand (BOD5), or TSS (total suspended solids) at least over 90% which makes necessary to establish well-designed wastewater treatment plants in the textile mills [27].

Parameters	**C_1**	**C_2**	**C_3**	**C_4**	**C_5**	**C_6**
pH	10.95	12.48	12.60	12.34	11.78	11.26
EC (mS/cm)	5.12	8.32	13.22	11.76	6.41	8.26
COD (mg/l)	3089	1916	1838	1463	2220	1871
BOD_5 (mg/l)	300	900	600	900	1375	1250
BOD/COD	0.1	0.47	0.33	0.62	0.62	0.67
TOC (mg/l)	898	686	563	614	439	629
TSS (g/l)	0.46	1.07	0.22	1.21	0.67	0.21
VSS (g/l)	0.26	0.61	0.12	0.71	0.01	0.11
Ions (mg/l)						
Calcium (Ca)	6.94	1.34	9.33	10.88	11.9	7.64
Potassium (K)	1.13	8.13	68.84	90.84	110.8	17.13
Sodium (Na)	100.4	162.4	142.4	226.0	118.0	142.4
Magnesium (mg)	10.39	40.39	40.13	34.13	40.13	8.39
Heavy metals (mg/l)						
Copper (Cu)	0.003	0.001	—	0.011	—	—
Zinc (Zn)	0.092	0.018	0.106	0.104	0.179	0.012
Nickel (Ni)	—	—	0.027	—	—	—
Chrome (Cr)	—	—	—	—	—	—
Cadmium (Cd)	0.008	0.008	—	—	—	—
C: Container						

Table 2. Characteristics of real textile wastewater [28]

Parameters	Limit value (max)		Monitoring Location
	Direct discharge	Indirect discharge	
pH	6–9	6–9	Wastewater total outfall from factory
COD	100 mg/l	200mg/l	
BOD_5	25 mg/l	50mg/l	
TSS	60 mg/l	100 mg/l	
Color (dilution) ratio)	70	80	
Ammonia nitrogen	12 mg/l	20 mg/l	
N total	20 mg/l 35 mg/l (batik industry)	30 mg/l 50 mg/l (batik industry)	
P total	1.0 mg/l	1.5 mg/l	
Chlorine dioxide	0.5 mg/l	0.5 mg/l	
AOX	15 mg/l	15 mg/l	
Sulfide	1.0 mg/l	1.0 mg/l	
Anilines	1.0 mg/l	1.0 mg/l	
Antimony total	0.10 mg/l	0.10 mg/l	
Chromium VI	0.5 mg/l		wastewater outfall from factory workshop of production facility

Table 3. Discharge limits of typical contaminants for textile factory effluents [27]

3. Treatment processes of textile industry wastewaters

3.1. Conventional physochemical processes

The dyes could be used in higher amounts than needed actually for the dyeing or printing processes. As a result of insufficient bounding of dye molecules to the textile, unbounded dye molecules are released as the waste product. This causes 10% of dyes to be produced yearly out of the total usage as waste. The dyes have carcinogenic, mutagenic, allergic, and toxic nature on one hand, and on the other hand, they cause environmental pollution. High concentrations of BOD, COD, color, pH, and the presence of metals make the textile wastewater difficult to be treated. Because of these reasons, the combination of different treatment processes, such as conventional and/or advanced physical, chemical, and biological, is needed to be combined to treat these wastewaters [17]. Figure 3 shows the major pollutants discharged from various stages of a textile manufacturing industry.

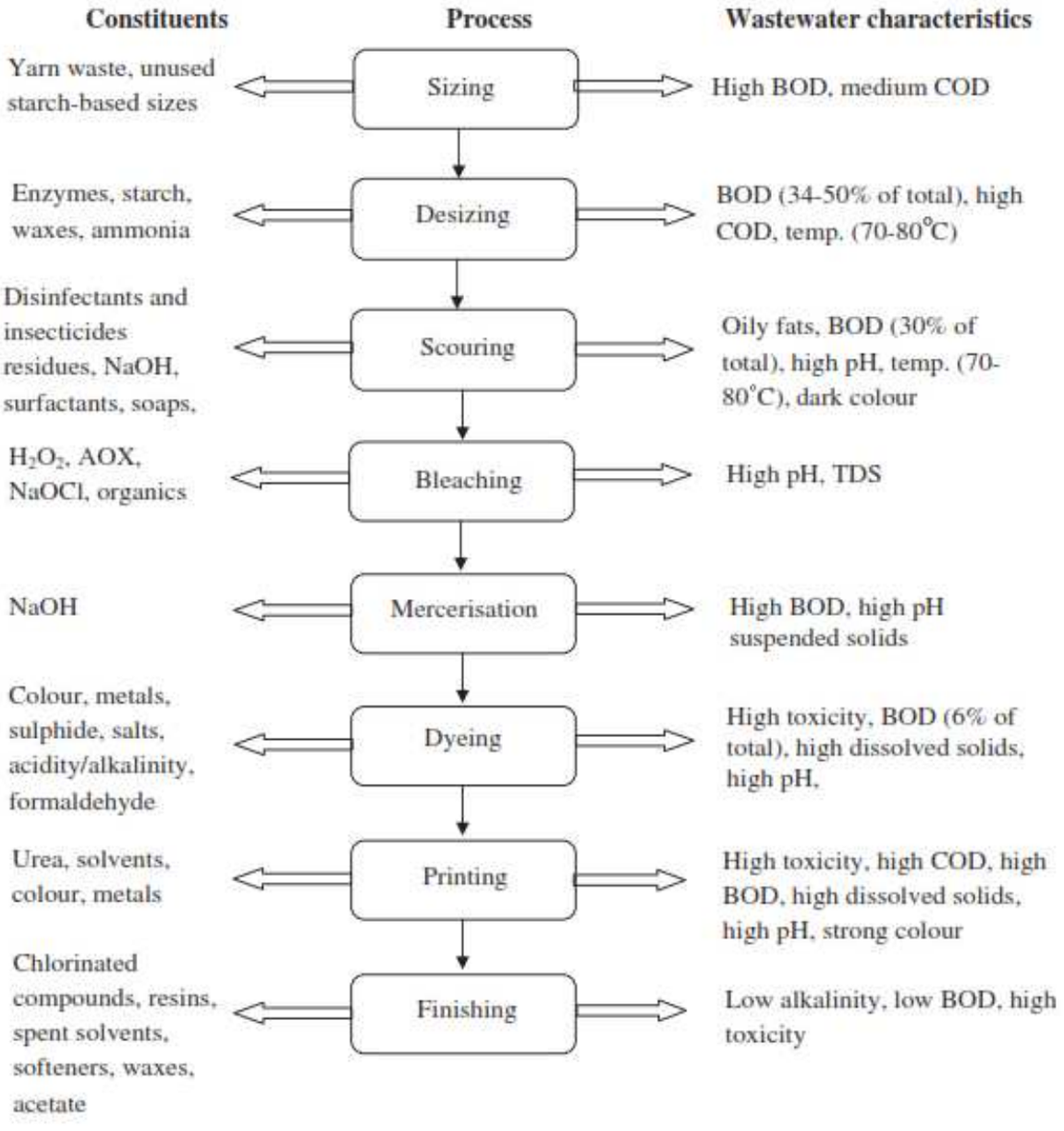


Figure 3. The component of major pollutants involved at various stages of a textile manufacturing industry [29].

By the treatment of industrial wastewater, mostly different physical, physicochemical, and biological treatment processes are used together depending on the pollutants to remove and discharge quality. These combinations are also used for textile wastewater, which constitutes an important part of the industrial wastewater.

The conventional physicochemical processes can be considered as follows:

- Coagulation/flocculation
- Adsorption
- Ion exchange

- Membrane separations
- Oxidation
- Cavitation [30].

According to the wastewater character and discharge limits, more than one process can be used together and also combined effectively with biological processes for the treatment of textile wastewater.

Coagulation and flocculation processes (C/F) are used in the treatment of industrial wastewater effectively. The aim of the process is to destabilize colloidal material using coagulants agents and after destabilizing to form aggregation of small particles with synthetic or natural polymers. Herewith, the bigger aggregates can be removed by separation processes like sedimentation easily [28]. C/F process is also used effectively by treatment of textile wastewater. Mostly, inorganic coagulants, such as aluminum sulfate ($Al_2(SO_4)_3$), aluminum chloride ($Al_2(Cl)_3$), and ferric sulfate ($Fe_2(SO_4)_3$), are used in the process. However, using inorganic coagulants has some disadvantages like high residual aluminum concentration, which can cause development of Alzheimer's disease and senile dementia [31].

Adsorption is one of the most efficient processes in the physical treatment of wastewater because of its efficient ability to separate dissolved/undissolved chemical compounds and easy operation [30]. The adsorption process is based on a surface phenomenon by which organic and inorganic pollutants are removed by adsorption on the surface of the adsorbent. The adsorbent materials like active carbon have a very large specific surface area, and if the absorbable solute comes into contact with the surface structure, they are concentrated on the solid surface because of the attraction forces between molecules. This process can be used effectively to remove the dissolved organic content of the textile wastewater [32].

The ion exchange process is also applied in the area of textile wastewater treatment effectively. Ion exchange is the reversible interchange of ions between a solid (ion exchange material) and a liquid in which there is no permanent change in the structure of the solid. In industrial wastewater treatment, the wastewater is the ion-containing solution from which the unwanted ions should be removed. Mostly, complex ion exchangers like ion exchange resins (functionalized porous or gel polymer) are used by industrial wastewater including textile wastewater for the ion source, which is to be exchanged with ions that are to be removed from aqueous matrix. Cation ion exchangers like weak acid cation exchange resins exchange the positively charged ions (cations), and the anion exchangers like weak base resins exchange negatively charged ions. In Figure 4, a cationic ion exchange resin is schematically shown by which the hydrogen ions are weakly bound to the negatively charged matrix. By the treatment of industrial wastewater, the hydrogen ions are given to the aqueous matrix and from the aqueous matrix; the unwanted ions like calcium (Ca^{2+}) are received and bound to the resin [33].

By textile wastewater treatment, the ion exchange process can be applied with the combination of other main processes, such as biological treatment or electrochemical techniques. After the biological treatment process, the residual dissolved organic carbon (DOM) consists of dissolved dye and auxiliaries, which are not biodegradable and can still exhibit acute and chronic

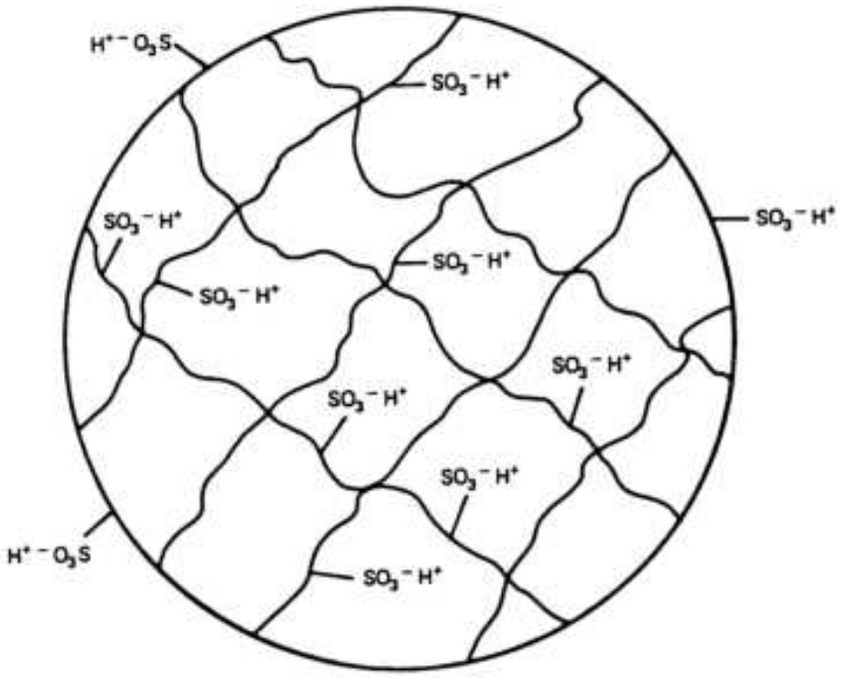


Figure 4. Cation exchange resin schematic showing negatively charged matrix and exchangeable positive ions [33].

toxicities. Dyes used by the textile industry are made up of chromophores and auxochromes, which are defined as typical anionic groups. Therefore, commercially available anion exchange resins can be employed in dye wastewater treatment for the removal of DOM [28]. However, ion exchange processes, which are mostly used by industrial wastewater treatments, are applied in fixed beds, which are expensive and exhibit flux restriction. Fan et al. investigated the removal of dissolved organic carbon after biological treatment process using magnetic anion exchange resin to find a more economical way to remove the nonbiodegradable DOM, which is toxic to aquatic environment. As a result, they found that magnetic anion exchange resin, which has remarkable regeneration behavior, could be used to remove DOM in actual biological treatment process effluent of textile wastewater [34–36].

3.2. Biological processes

Almost all kinds of commercial and industrial wastewaters have biological degradable constituents. Although the textile wastewater is a strong polluted industrial wastewater, an important part of the organic content is the biodegradable (See the Table 2). Therefore, the aerobic, anoxic, and anaerobic biological processes and their combinations have been applied effectively by the treatment of textile wastewaters. Except the biological degradation, the processes of adsorption and complexation with microorganism play an important role by treatment processes for the removal of pollutants like heavy metals [37].

Textile wastewaters contain many refractory compounds, which are biologically hard or nondegradable and mostly toxic for environmental systems. The biodegradation can also

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occur for these compounds that have organic structure, but in comparison with easy biodegradable organics, they can need slow processes like anaerobic digestion and specific microorganisms [37].

Biological treatment systems can be divided into different categories such as aerobic, anaerobic, and anoxic systems or according to growth system of microorganism suspended growth and attached growth. Figure 5 shows the biological treatment methods, which are applied also for the treatment of industrial wastewaters including textile wastewater.

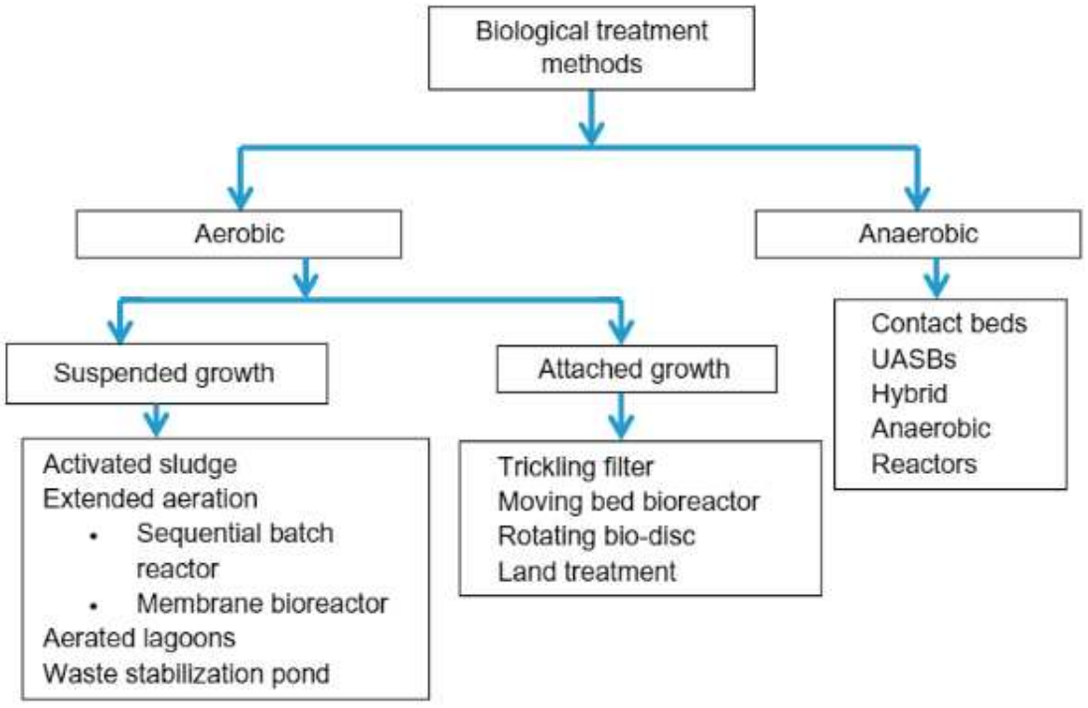


Figure 5. Biological wastewater treatment methods [38].

The systems are categorized according to the existence of the air in the treatment system. In the aerobic systems, oxygen is present in biological systems as the electron acceptor. On the other hand, oxygen is absent in the anaerobic system and the electron acceptor is the organic material. Figure 6 shows the principles of two biological treatment processes. The oxygen is used as oxidation element of organic material and carbon dioxide, water, and new cells are produced as final products in aerobic system. However, no air (thus molecular free oxygen) should be absence in the anaerobic medium and methane, carbon dioxide and new cells is produced at the end of the digestion process.

Recently, both aerobic and anaerobic processes have been applied for the treatments of textile wastewater successfully. According to the physicochemical and oxidation methods, the biological treatment methods of textile wastewater have significant advantages. They are firstly more environmental friendly because no chemical usage is needed mostly and the produced sludge as the result of the cell production has a low chemical content and amounts.

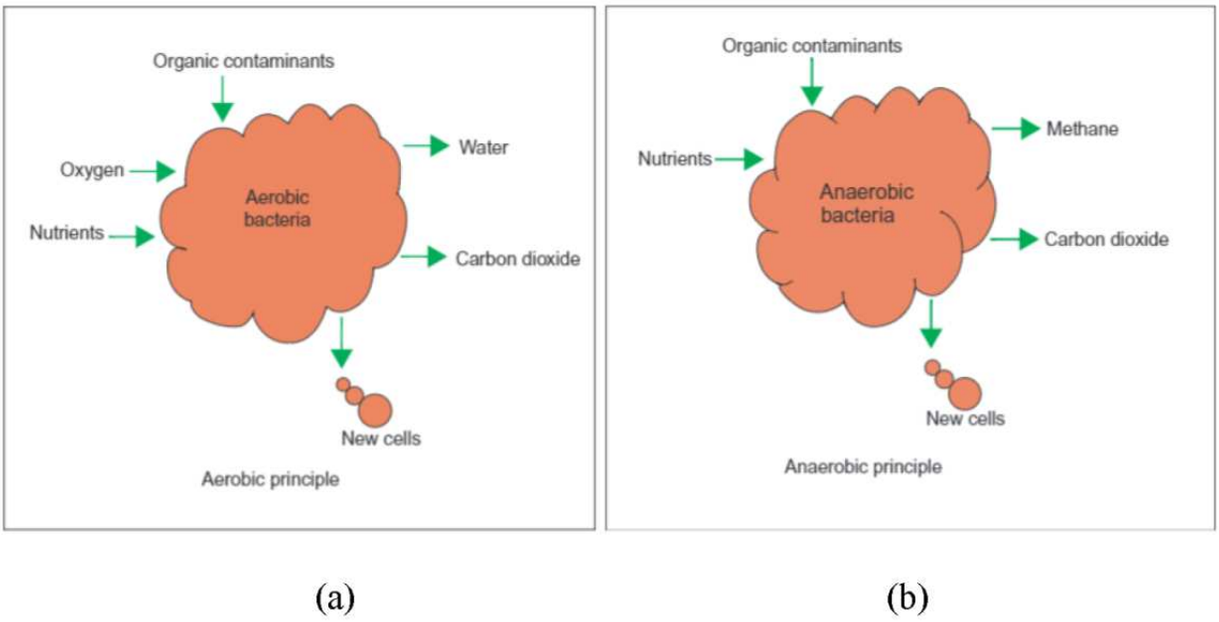


Figure 6. Aerobic (a) and anaerobic (b) degradation principles [38].

They are more cost-competitive because of the less or no usage of chemicals. The yielding end products are nontoxic or have complete mineralization, and they require less water consumption compared to physicochemical methods [39, 40].

Conventionally, the biological treatment of textile wastewater occurs under anaerobic, facultative anaerobic, and aerobic conditions by different groups of bacteria. By the treatment process, pure cultures of microorganism or composed of mixed microbial populations can be used. The mixed microbial cultures can be more effective because of their synergistic metabolic activities compared with the pure cultures by the treatment process of textile wastewater [41]. The dye molecules can be attacked by different individual strains at different positions of bonds and the co-existing strains may help for the further decomposition processes. This is very important for the total mineralization of organic content of textile wastewater, because by not complete degradation of organic content, toxic organic compounds can be present in the discharge water already [42].

The membrane processes are also used effectively with combination of biological processes by the treatment of the industrial wastewaters. The system is called as membrane bioreactor and has many advantages compared with the conventional biological system using final sedimentation tank. By the biological treatment systems, the microorganisms consume the organic matter and as a result new cells are produced. The exceeded sludge that contains the old microorganisms should be removed from the system for the stability of the system. This separation process of sludge from mixed liquor can be achieved mainly in two ways. The conventional system, which has been used at many treatment plants, is the sedimentation process. By the sedimentation process, the sludge flocks are precipitated in the sedimentation tanks and removed from the bottom of the tank. Sometimes chemicals like flocculants can be

used to accelerate the sedimentation process. Recently, membrane separation processes have been applied effectively as an alternative separation process to the conventional sedimentation. By the membrane process, the separation of sludge from the mixed liquor occurs with the help of a membrane with a significant pore wide. The biological membrane processes have many advantages compared to the sedimentation processes like high quality of discharge water, high sludge age, less excess sludge production, less area need, and more effective biological degradation. Because of these advantages, membrane bioreactors are also used effectively by the treatment of textile wastewaters.

4. State of the art processes

4.1. Membrane processes

Membrane process is the transport of substances between two fractions with the help of membranes, which are permeable or nonpermeable for specific substances to be removed from the matrix or to be concentrated. For different separation purposes, different membrane processes are applied, which are classified according to membrane art, size of the particles to separate, and separation mechanism. Table 4 gives an overview about the membranes operated under pressure. The transitions between the single membrane processes are flexible [43].

Membrane process	Pore width [nm]	Pressure interval ΔP [bar]	Permeability [L/m².h.bar]	Membrane type	Application
Microfiltration	50–5000	0.1–2	>50	Porous membrane	Separation of suspended solids
Ultrafiltration	2–200	1–5	10-50	Porous membrane	Concentration, fractioning and treatment of macromolecules in fluid systems
Nanofiltration	1–2	5–20	1,4-12	Nonporous membrane	Fractioning of dissolved materials in fluid systems
Reverse osmosis		10–100	0,05-1,4	Solution-diffusion membrane	Concentration of dissolved materials in fluid systems

Table 4. Under pressure operated membranes [43]

The membranes are applied by the treatment of textile wastewater as a separated process or in combination of other processes especially with biological processes. The membrane bioreactors are the combination of the membrane and biological processes and have a very wide application area in industrial wastewater treatment. The separated application of membranes for the treatment of textile wastewater has also been applied effectively for this

purpose. The main advantage of membrane processes compared with the chemical treatment of textile wastewater is no usage of the chemicals. On the other hand, membrane processes also have disadvantages, mainly fouling. Fouling occurs in time during the operation with the clogging of the pores of the membranes, which results in the decrease of the flux and increase of the head loss. The quality of the discharge water from the membranes also decreases therefore the total performance of membrane process decreases because of the fouling [44].

Imer investigated the treatment performance of the polysulfone (PS) ultrafiltration membranes by the treatment of textile wastewater. The membranes were produced with phase inversion method under different temperatures. By the study, real textile wastewater is used with the following properties—conductivity: 5370 μS/cm, COD: 3094 mg/l, color: 1.47 (abs @530 nm), pH: 9.0, and suspended solids: 33 mg/l. The phase inversion production was conducted under four different temperatures from 25 to 65°C. The highest removal efficiency was achieved with the membrane produced under 65°C with 99% COD and 99% color removal [45].

In another study, hollow fiber nanofiltration membranes were investigated for the treatment of textile wastewater at laboratory and pilot scale. The operation was conducted under different conditions, such as temperature, conductivity of textile wastewater, and pH values. As a result, the recovery potential of the salts included in the textile wastewater was determined for the reuse of the salts at the next stage of the dyeing process. Because the textile wastewaters have high salt concentration, salt accumulation of the membranes in the membrane (internal concentration polarization) and on the membrane surface (external concentration polarization) can decline the flux. This can be prevented with the periodical washing of the membrane with the antiscaling solution The rejection of dye was over 98% in the study, which indicates that the membrane technologies are not only a treatment process but also a method to recover the dye and salt from textile wastewater [46].

4.2. MBR processes

Membrane bioreactor (MBR) is the combination of a membrane process (like ultrafiltration or microfiltration) with a suspended growth bioreactor. The MBR processes have significant advantages compared to the conventional biological treatment systems. High quality of discharge water, less production of exceeded sludge, and high concentration of mixed liquid suspended solids are the main advantages of MBRs. Except these, they need smaller area than the conventional systems because the membranes can be operated and installed in the biological reactor. The nitrogen and phosphorus removal also occurs at higher efficiency in MBRs. By two steps, membrane configuration nanofiltration or reverse osmosis steps can be used to meet the discharge limits or salt removal from the outlet of the MBR system. The recently conducted studies show that the membrane techniques can also exhibit high performances by the treatment of textile wastewater in the meaning of the high quality of discharge water and reuse possibilities of the auxiliary chemicals used for dyeing process.

In the study of Yurtsever et al., aerobic and anaerobic bioreactors were compared with regard to treatment efficiency of textile wastewater including azo dyes. No important change by the effluent concentration of azo dyes was observed with increasing azo dye concentration by the influent. This can be explained with the cleavage of the azo dye at low redox potentials [47].

Friha et al. investigated the treatment efficiency of the aerobic submerged MBR using textile wastewater as influent. In the system, a flat sheet membrane module was used with operating transmembrane pressure (TMP) ranging between 70 and 350 mbar. The system was operated during 6 months, and stable treatment results were gained at the end of the operation. Except the high removal efficiency for pollution parameter color, COD, BOD_5, and SS (color, 100%; COD, 98%; biochemical oxygen demand (BOD_5), 96%; suspended solids (SS), 100%), an important decrease by toxicity of wastewater was achieved, which indicates that the membrane processes can be operated effectively by the treatment of textile wastewater [28].

4.3. Ultrasonic oxidation processes

The energy given by the ultrasonic source to the wastewater results in the cavitation, which is the nucleation and behavior of the bubbles in the wastewater. Cavitation is the formation of cavities which also grow and collapse with each other. Cavities provide the condition of strong oxidizing to occur by way of production of hydroxyl radicals and also hydrogen peroxide. In the wastewater treatment, the cavitation bubbles act as a microreactor in which the volatile organic compounds are oxidized [47, 48]. The reaction chain of consisting of radicals through the ultrasonic cavitation is shown as follows [44]:

ultrasound

$$H_2O \rightarrow H^{\bullet} + HO^{\bullet} \quad (1)$$

ultrasound

$$O_2 \rightarrow 2O \quad (2)$$

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \quad (3)$$

$$O + H_2O \rightarrow 2HO^{\bullet} \quad (4)$$

The ultrasonic catalysis (sonocatalysis) processes are among the advanced oxidation processes, which are also applied with combination of the other advanced oxidation processes like photo catalysis. The process is based on the production of radical molecules like hydroxyl radicals ($HO^{\bullet}$) with the help of an energy source. This source can be acoustic, photolytic, or hydrodynamic energy for the treatment of textile wastewater. The sonocatalysis reactions can be applied in combination with other source such as photolytic energy. This can increase the interaction between radical and dye molecules and therefore the efficiency of the treatment of the textile wastewaters [48].

4.4. Photochemical oxidation processes

The photochemical oxidation processes are also among the advanced oxidation processes, which are applied effectively as alternative method to the conventional processes. The photochemical oxidation processes are also based on the production of highly reactive radical, such as hydroxyl radicals, which can degrade the recalcitrant organic materials included in the textile wastewater. The use of photochemical oxidation processes can be applied under solar radiation, which enhances the production of hydroxyl radicals ($OH^{\cdot}$) and provides to realize the treatment processes at lower costs [49, 50].

4.5. Electrochemical processes

Electrocoagulation also offers an alternative method for the removal of color by textile wastewater to the chemical coagulation by which metal salts or polymers and polyelectrolytes are used to break the stable emulsions and suspensions. By electrocoagulation, metal plates such as iron or aluminum are used as electrodes to produce highly charged polymeric metal hydroxide species continuously in the water. These ions with opposite charges destabilize the colloids, allowing them to coagulate [19]. Because no chemical is applied during the process, electrochemical processes have been used advantageous as an alternative technology to chemical coagulation for treatment of industrial wastewaters particularly textile and dyeing wastewaters [51–56]. Electrochemical process can also be used for the production of ferrous iron and/or hydrogen peroxide, thereby allowing the generation of hydroxyl radicals. This process is a similar process with electrocoagulation. The difference between two processes is adding of H_2O_2 with in various concentrations before the electrolysis [57, 58].

In a most recent study, four different iron-based processes were applied for the decolorization of textile wastewater; electrocoagulation, electrochemical fenton, electro-fenton, and peroxi-coagulation for decolorization of real textile wastewater. The fenton process is an important process to degrade the refractory chemicals through chemical oxidation by hydroxyl radicals (OH). The important point of the Fenton process is the production of ferrous iron and/or hydrogen peroxide for the oxidation of organic materials and other refractory chemicals. At pH value of 3, they achieved decolorization efficiency by 94.4 %, which indicates the better oxidation performance of produced hydroxyl radicals at low pH values. The removal efficiency of color increase by biodegradability and energy consumption for four processes were compared. In the study, the most important parameters that affect electrocoagulation efficiency are determined as pH value and the electrical current. The highest removal efficiency for color was achieved at the pH value of 6.5 and by an electrical current of 300 Ma. They also determined the optimum electrical current for both the highest energy efficiency and removal efficiency as 200 Ma [52]. In the study, the biodegradability of textile wastewaters was also investigated after iron-based electrochemical treatment processes. The biodegradability is an important parameter for industrial wastewater pointing out how the organic content of discharged wastewater can be degraded by the microorganisms in aquatic environment. The ratio of BOD_5/COD is the main parameter to determine the biodegradability of wastewater. If the ratio is high, it shows that the biodegradable part of the organic matrix is high and the organic constituents in the discharged wastewater can be eliminated more easily at aquatic

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environment. Figure 7 shows that all iron-based electrochemical treatment methods provide an increase by biodegradability of raw textile wastewater. The highest increase was seen by Fenton process supported by electrochemical methods, because hydroxyl radicals ($OH^{\cdot}$) can oxidize the resistant organic material to smaller ones, which can be degraded by microorganisms easier [57].

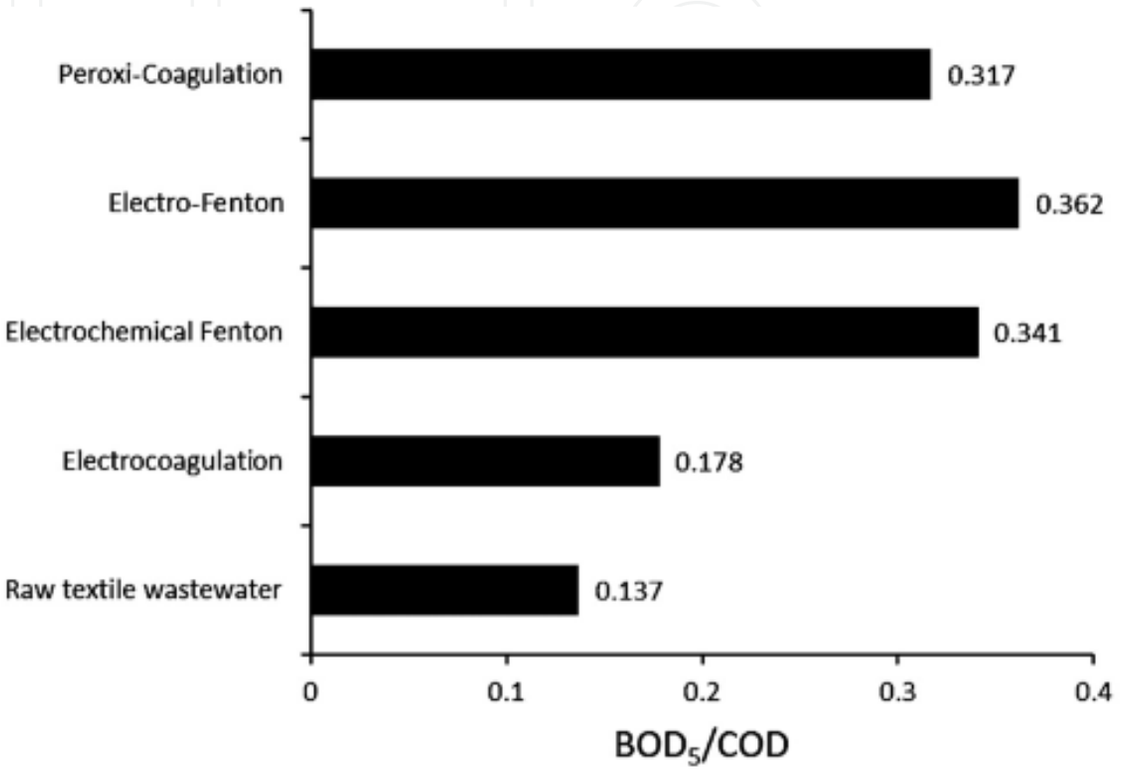


Figure 7. BOD5/COD ratio after iron-based electrochemical processes treatment [57].

4.6. Novel materials (coagulants, adsorbents)

In textile wastewaters, chemicals and other materials are used to realize the treatment processes, such as coagulants and flocculants, for coagulation-flocculation process and adsorbents for adsorption process. New materials are continually tried for a more efficient and cost-effective processes to develop.

By the coagulation process, mainly the chemical materials such as aluminum sulfate ($Al_2(SO_4)_3$), aluminum chloride ($Al_2(Cl)_3$), and ferric sulfate ($Fe_2(SO_4)_3$) are used. New coagulant agents, such as natural coagulants, have been used successfully by C/F process using the treatment of textile wastewater instead of inorganic coagulants. Natural coagulants have many advantages over chemical agents by treatment textile wastewater like particularly biodegradability, low toxicity, low residual sludge production, and low cost [31]. Renault et al. [59] also reported that using natural polymers reduces the required inorganic coagulant dosage, which results to produce less sludge, because more compact flakes by C/F process are produced. In the study of Freitas et al., okra mucilage is used (*abelmoschus esculentus*) as natural coagulant

aid dissolved in distillated water and their efficiency was compared to chloride ferric (chemical agent) in C/F process of textile wastewater treatment. They determined an important increase by the removal of pollution parameters, such as color, COD, and turbidity. The amount of Fe^{3+} was also decreased up to 72.5% using a small amount of okra mucilage [31].

Activated carbon is used for the treatment of textile wastewater, but this process is very expensive; therefore, the cost analysis should be done carefully before the establishment of the process [60]. There are also cheaper products, which have been recently used by the adsorption process. Hydroxyapatites ($Ca_5(PO_4)_3(OH)$) belong to these materials, which are abundant in the nature, and can be applied effectively by the treatment of textile wastewater. Lemlikchi et al. investigated the adsorption kinetic of textile dyes on synthetic hydroxyapatite in aqueous solution. After adsorption process, during the adsorption process, the precipitation is also applied for the separation of hydroxyapatite saturated with pollutants in the wastewater. The co-precipitation was carried out at pH = 8 at batch mode, and settling time for the three textile dyes Hydron Blue (HB), Solophenyl Blue (SB), and Solophenyl Turquoise (ST) was almost 1 day. After settling, the supernatant was filtered and analyzed by UV-vis. By scanning electron microscope (SEM) analysis, it was seen that HAP grains are strongly bonded for the HB and for the SB. Lemlikchi et al. explained this adsorption process with the strong interaction between phenol, sulfonate, and amine groups in the dyes molecule and calcium ions. This study shows that the textile wastewater can be treated effectively with adsorbent material different from active carbon with lower costs [60].

4.7. Hybrid processes

Because the textile wastewaters contain many pollutants including hard or nonbiodegradable compounds, hybrid systems can be applied more effectively to use the advantages of each process. The physical, chemical, and biological process has advantages and disadvantages. For example, the chemical usage and production of sludge with high chemical content are the most important disadvantages of the coagulation-flocculation process. On the other hand, some nonbiodegradable compounds included in the textile wastewater can be precipitated and removed wastewater by C/F process. Therefore, the most efficient and cost-effective system combination has to be investigated according to the structure of the wastewater to be treated.

In the study of Sun et al., the removal of organic compounds and nitrogen in an anaerobic–anoxic–aerobic membrane bioreactor process (A^2O-MBR) for the treatment of textile wastewater was investigated. The two different membranes were used and submerged in the aerobic reactor symmetrically to observe the biofouling behavior of two membranes observed through the TMP. One of them was hollow fiber membrane made of polyvinylidene fluoride (PVDF) with a nominal pore size of 0.1 μm, and the other one was flat-sheet membrane. As a result, the organic matters and nitrogen were removed from the textile wastewater efficiently. For many organic matters, high removal ratios were achieved. On the other hand, very low removal efficiencies were seen for some hard biodegradable organic matters such as styrene with 2%. Also, combinations of acids and oxidizing agents were offered as a good solution for chemical washing to minimize the biofouling. The schematic diagram of the pilot-scale AO-MBR system was showed in Figure 8.

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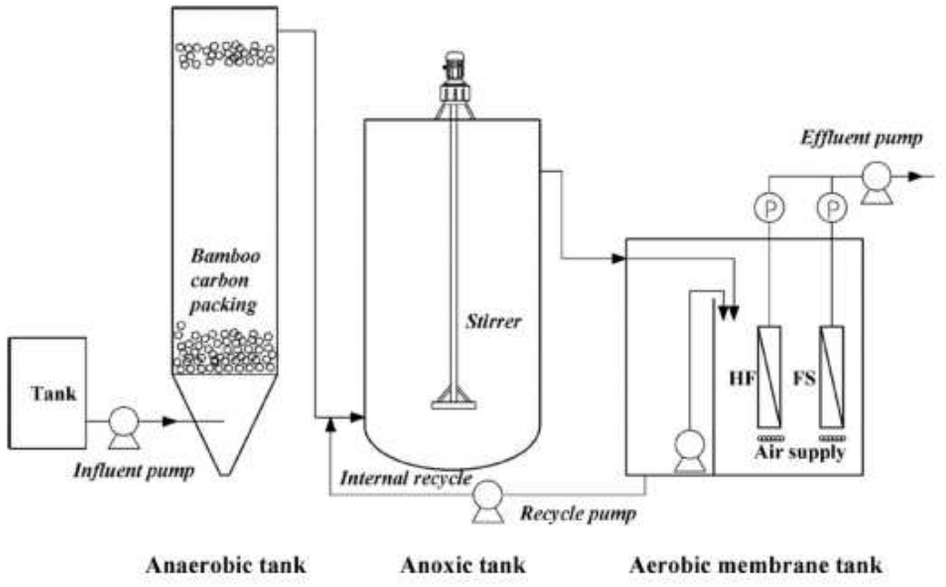


Figure 8. Schematic diagram of the pilot-scale AO-MBR system [61].

Some specific hard biodegradable pollutants can be degraded with the help of advanced oxidation processes [62]. Lee et al. [62] investigated the elimination of 1,4-dioxane contained in the textile wastewater by membrane photoreactor. UV lamps was used as photon source and TiO_2 was used as catalyst.As a result, they determined that the depredation in bioreactor with the support of photocatalytic reactions can satisfy the drinking water guidelines. The dosage concentration of TiO_2 should have been applied in high levels because of the low adsorption of 1,4-dioxane onto TiO_2 particles. The chemical precipitation methods can be applied before the biological processes to enhance the BOD_5/COD ratio. Figure 9 shows the schematic diagram of a treatment plant for textile wastewater located in Jiangmen of Guangdong Province-China.

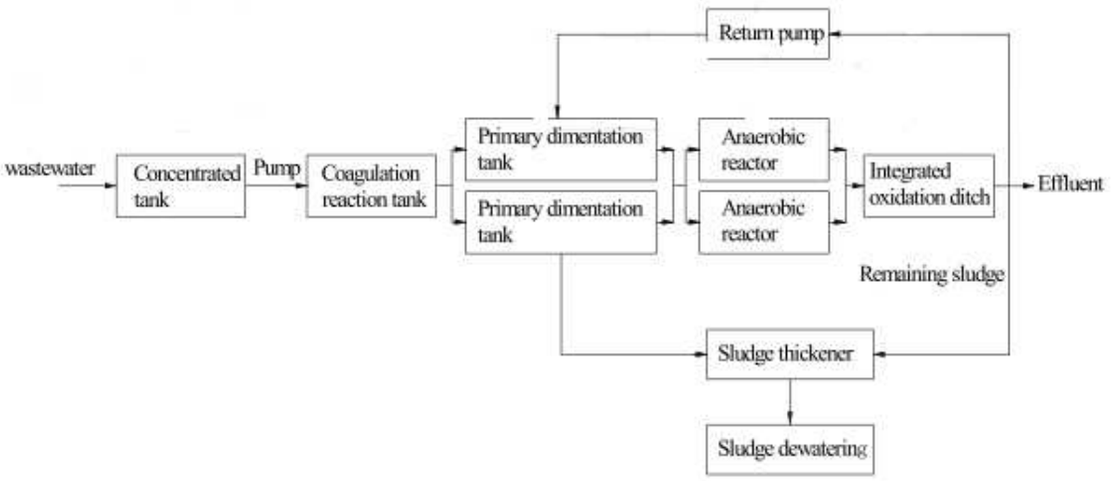


Figure 9. Schematic diagram of a textile wastewater treatment plant located in China [63].

The textile wastewater has the properties of high alkaline, color and organic matter content, and low biodegradability with 0.25 BOD_5/COD ratio. To increase the BOD_5/COD ratio before the biological processes, coagulation with $FeSO_4$ and following precipitation is applied. After chemical treatment, the two staged anaerobic-aerobic biological treatment processes are applied. The discharge limits are met according to local regulations.

The biological treatment is not sufficient for the removal and degradation of recalcitrant compounds in textile wastewaters. Therefore, chemical oxidation methods are applied before or after the biological processes for increasing biodegradability of wastewater or degradation of nonbiodegradable compounds. Punzi et al. [64] investigated the degradation of recalcitrant compounds and the removal of toxicity of textile wastewater by applying ozonation after anaerobic treatment. In that study, 99% of the color and 85–90% of COD were removed from a synthetic textile wastewater containing 100–1000 mg/l of the azo dye.

5. Conclusions and recommendations

The purpose of the book chapter is to bring an overview on the new treatment methods for textile wastewaters, one of the most important sources of environmental pollution. Despite the fact that there is no uniform standard currently, many countries have legalized some strict discharging standards, and scientists and researchers face new technologies including electrical, sonic, magnetic, optical, and thermal methods. Although many researches on treatment of synthetic or real wastewaters with various methods are available, very few researches have been carried out on the cutting-edge technologies. Moreover, there are a lot of review article or book chapters on textile wastewater treatment processes individually based on each conventional processes, such as coagulation, adsorption, chemical oxidation, and biological decolorization. Therefore, in this part of the book, following major and minor titles are stated truly on the aforementioned new technologies.

Textile effluents are highly polluted wastewaters with high concentration of chemical and biochemical oxygen demand, suspended and colloidal solids, salts, heavy metals, and other hard or nonbiodegradable organic matters, which is an important threat for environment when discharge criteria are not carefully considered. These wastewaters have complex structure and large emissions, which make them very hard to handle. Because mostly only one treatment process could not be sufficient to remove the pollutants effectively, the biological, physical, and chemical processes are used separately or in one process to support each other in a combined treatment plant. Among these processes, for example, membrane systems are very effective separation systems to be applied in the treatment of various impurities from textile wastewater. Membrane bioreactors have higher investment and operational costs compared with conventional biological processes, but they have very high quality of discharge water and reuse chances of valuable materials included in textile wastewater are high.

The adsorption process is also an important process, which can be combined with membrane processes like nanofiltration. But the adsorption materials such as active carbons are expensive materials; therefore, cheaper materials like different natural polymers are preferred. Electro-

oxidation or sonophotocatalysis process can be applied before the biological process to cleavage the bounds of the dye compounds and make them biodegradable. If the wastewater is desired to be used in the process again, an ion exchange process could be needed at the end of the process. As seen, the process combination can differ according to the structure of textile wastewater and discharge purposes. But it must not be forgotten that the green technology methods by the production of dye are more efficient and cost-effective methods to prevent the pollution and increase the reuse chances of materials contained in wastewater. Therefore, the use of natural eco-friendly materials has been investigated recently widely in the world, which is degraded in the biological treatment systems and environment more easily.

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