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Review

A Review of Treatment Technologies for Textile Industry Effluents

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Abstract

The textile industry utilizes a wide spectrum of chemicals and auxiliaries, which cause serious repercussions with regard to the environment. Wastewater generated and released from textile processing units is a potential cause of environmental pollution and health hazards because of the presence of toxic contaminants besides organic matter. One of these primary contaminants is color contributed by the dyes used in the dyeing process. There is a great focus on reusing the effluent water in the dyeing process. Hence, it is crucial to develop an economically viable treatment system for the treatment of wastewater that can meet the stringent effluent quality standards. This article presents various treatment technologies in detail for treating the textile industry effluents which includes the Physico-chemical treatment (Advanced oxidation process (AOP), Fenton process, Photocatalytic, Ozone based methods and Electrochemical AOP), the Biological treatment process (Microbial culture based, Mechanized treatment systems including attached and suspended growth processes) and finally the Hybrid treatment technologies (Anaerobic-Anoxic-Aerobic Membrane Bioreactor Process, Hybrid Anaerobic Sequencing Batch Reactor-Aerobic Process, Hybrid Forward Osmosis-Membrane Distillation (FO-MD) Process, AOP plus Activated Sludge Treatment and Biological followed by physicochemical processes). This review paper also presents the future research prospects and potential technologies that have been recommended for smooth and better process control.

Keywords

Textile industry wastewater, AOP, Fenton process, Photocatalytic, Ozone-based methods

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1. Introduction

Escalating industrialization is posing serious impacts on natural ecosystems and is a potential threat for the environment [1-3]. The textile industry is one of the vital sectors contributing to country's economy and has been booming since the last decade. It is, therefore, classified as one of the most water-intensive, lengthy and complex process chains in manufacturing units. Various types of raw materials and resources including cotton, woolen (non-cotton) and synthetic fibers are used worldwide in textile production [4]. Besides the variety of raw materials used, it consumes a large volume of water that results in wastewater generation and ultimately severe environmental pollution [5]. This wastewater results from various processing stages of the textile industry. Color-enriched wastewater is often generated as a result of printing and dyeing facilities consisting of residual dyes and auxiliaries. Besides this, toxicity of textile effluents intensifies the need for efficient treatment [6]. In addition to other organic materials from industrial processes, toxic contaminants such as cationic, anionic, and neutral dyes seriously contaminate water bodies by changing their chemical composition, decreasing sunlight penetration, and upsetting aquatic ecosystems. These persistent pollutants, which include heavy metals, solvents, synthetic dyes, and surfactants inhibit photosynthesis, raise chemical and biological oxygen demands, and are toxic and carcinogenic to aquatic life and humans. Pollution of water bodies due to untreated textile wastewater reduces the oxygen levels severely due to the presence of hydrosulfides and hinders the path of light through water body which is harmful for the aquatic life. It has been reported that organically bound chlorine, a renowned carcinogen, is present in approximately 40% of the dyes used worldwide [6]. Advanced techniques like adsorption, advanced oxidation systems, and biological remediation are necessary to remove these complex organic compounds before they are released into the environment because conventional treatment methods frequently fail [7].

The chief environmental encumbrance for the progression of the textile sector is highly polluted textile effluent in addition to other issues of economy and waste management. The untreated high-strength industrial wastewater discharge into receiving water bodies results in aesthetic problems, fatal pollution and associated detrimental effects to the ecosystem. It has been reported that dyeing and finishing of textile products contributes to approximately 20% of industrial wastewater, which needs to be treated to meet the effluent discharge standards [6,8].

2. The Textile Processes

A wide range of processes are involved in the production of various textile products. Textile processing involves various operations, including sizing, desizing, scouring, bleaching, mercerizing, dyeing and finishing that consequently result in environmental pollution. The whole process starts from the natural or synthetic fibers, with the next step involving the production of yarns from the natural or man-made fibers. These manufactured yarns are then used to produce the fabrics by using different technologies involving weaving (interlacement of these yarns at a right angle to each other), knitting, etc. Then the fabric goes through the "wet processing" in which the desired characteristics of strength, color fastness and luster are achieved [8]. The stages of wet processing of textiles are depicted in Figure 1.

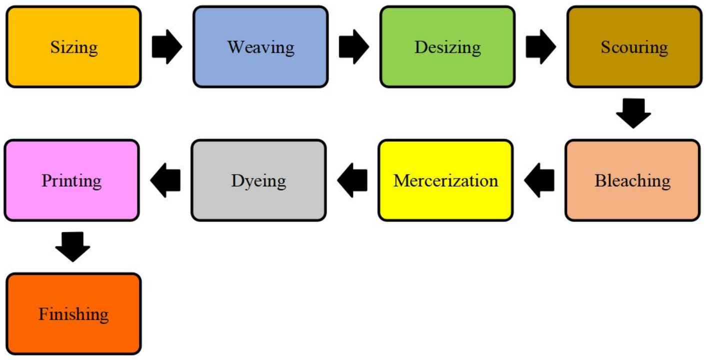

Figure 1. Processes involved in processing of fabric in a textile industry.

2.1 Sizing and De-sizing

The fibers after weaving of the yarn have to endure high strain [9] and are therefore treated to add additional strength to the fabric [10]. This is the reason that sizing agents are applied to the fabric in order to protect and increase the strength by forming a gelatinous, flexible and anti-abrasive layer. De-sizing is the first step of the wet processing carried out after singeing which is the removal of bulging fibers by heating them. The chemicals used in sizing affect the wet processes, including dyeing and printing. The dye molecule gets hindered from being diffused in the fabric due to the presence of starch and other sizing agents. Therefore, they need to be removed prior to dyeing and printing [11].

These sizes are removed by using enzymatic de-sizing agents to remove starch, an oxidative process by using persulfate to remove all types of sizes and washing to remove water-soluble sizes. This removal of sizing agents results in escalated wastewater loads. Sizing agents can contribute up to 70% of the chemical oxygen demand (COD) load in the effluent [12]. The starch is converted to simple products that are water soluble by de-sizing processes. The biochemical oxygen demand (BOD) of the wastewater generated as a result of the de-sizing process is high ranging from 300-450 mg/L [13]. The depolymerization of starch macromolecules used as sizing agents can be done by employing enzymes (amylases) which catalyze the de-sizing process. Ethanol is produced as a result of the oxidation of starch which can be used as a fuel resulting in a reduction of organic load in the effluent [14].

2.2 Scouring

Cotton fabrics are treated with hot alkali solutions (generally sodium hydroxide-NaOH), detergents and scouring chemicals to remove the natural scums like wax and non-cellulosic constituents. The process can be performed both in continuous and batch phases. The effluent is highly alkaline with a pH range of 10-11 and results in an organic load that is recalcitrant and cannot be degraded easily [15]. The scouring wastewater is also characterized by high chemical and biochemical oxygen demands with COD values up to 6000 mg/L contributed by the removal of fibers and other chemicals used in the process [15].

2.3 Bleaching

The fabric appears to be creamy due to the presence of a naturally occurring color constituent. In order to remove this color and produce additional whiteness in the fabric, the process of bleaching is carried out. Bleaching enhances the quality of dyeing and printing processes. It is done to attain extra whiteness for undyed natural constituents besides the fabrics that need to be dyed in brighter or light shades. Bleaching can be carried out continuously or in batch mode [16].

Various bleaching agents like sodium hypochlorite, sodium chlorite and hydrogen peroxide etc. are used extensively in the textile industry. Formerly, hypochlorite was generally applied as bleaching agent to the fabrics. Currently, hydrogen peroxide and peracetic acid have been replaced by hypochlorite as a bleaching agents. Peracetic acid enjoys the advantage of being more benevolent than other conventional bleaching agents. Besides it, it also produces more shine with negligible damage to the yarns [17].

2.4 Mercerization

Mercerization is a treatment of cotton fabric and its blends by using strong alkaline solutions by providing tension to the fabric. This process improves the dye uptake and absorbing capacity with increased tensile strength. Moreover, improved stability, better texture and resilient shine are achieved as a result of mercerization. Normally, cotton fabric is treated with a concentrated i.e., approximately 18%-24% by weight solution of NaOH [18]. This results in contraction of fabric longitudinally due to concentrated alkaline solution with an increase in the pH value. Thus, by providing the stress to the fabric, this shrinkage can be evaded. The fabric remains under tensile effect till the surplus caustic soda is being washed away. This washed-away caustic soda can be recovered by various techniques including membrane techniques [19].

2.5 Dyeing and Printing

Dyes are molecules with both natural and synthetic origins. They are used in the dyeing process of fabric to impart color. The atoms known as chromophores are responsible for color-imparting properties. Groups including azo having -N=N- bonds, ethylene with =C=C= bonds, nitro having $-NO_2$ bonds and quinoid groups are some of the chromophore configurations. Among them, the most challenging dyes to be treated are those manufactured from carcinogenic sources like aromatic compounds [8]. Table 1 exhibits the various categories of dyes used against major types of fabric.

Table 1. Category of dyes for different fabrics.

Fabric Type	Dye Category
Cotton	Direct, Disperse, Reactive and Vat
Wool	Acid
Silk	Acid and Direct
Polyester	Disperse and Azo
Polyester-Cotton	Vat and Disperse

The printing process is almost similar to dyeing in terms of reactions involved. The colorants (dyes) are applied in aqueous form requiring huge volumes of water. Whereas in the printing process, a blend of dyes is applied in the form of paste to prevent it from dispersing to produce multi-color designs. The wastewater is similar in characteristics to that of the dyeing effluent [9].

2.6 Finishing

Finishing is the last step in wet processing of a textile industry. Different types of treatments are applied to enhance the finished product. The processes may be mechanical, thermal or chemical. In the case of cotton fabrics, starch is mostly used to give a final touch to the fabric [20]. Figure 2 shows an overview of the finishing treatments applied.

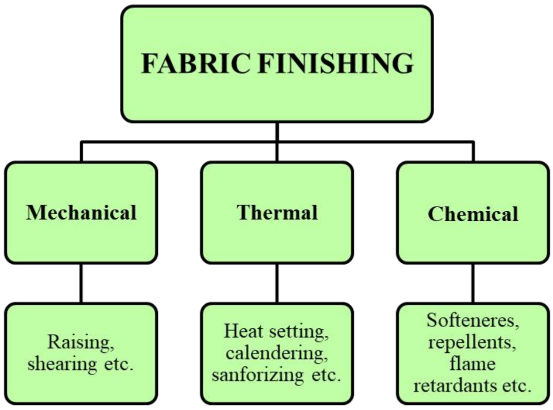

Figure 2. Finishing process and types of treatments in the finishing of fabric.

Slight amounts of the residues from the finishing process also enter the effluent. Additionally, various antimicrobial finishes are applied to produce specific characteristics in the fabric like prevention of fabric from attack by microorganisms. Similarly, flame retardants and other special finishing chemicals are applied to the textile products to protect them from fire. The compounds having aluminum and magnesium along with halogens, phosphorus and minerals are the main types of flame retardants applied to the fabrics. The toxicity and contamination as a result of the finishing process also add to the overall pollution load in textile effluent [21].

3. Textile Wastewater

The effluent generated from textile industries as a result of various processes is large in volume with escalating color, organic and other pollutant loads. This effluent is discharged as result of huge water consumption utilized in wet processing which is a high-quality water (initially treated through water softeners and reverse osmosis process). The estimated consumption of water ranges from 50 to 240 liters for each kilogram of textile product [22,23]. The yearly wastewater generation of China has reached 390 million cubic meters which comprises 51% of industrial wastewater. This is being increased at a rate of 1% each year [24].

The wastewater characteristics are different in contents but the chief contents are mainly the same. Furthermore, textile wastewater is also being characterized by high temperature and pH values. Particulate fibers or lint are also found in streams carrying the effluent which can cause clogging of pipes and malfunctioning of mechanical equipment of the treatment plant i.e., centrifugal pumps etc. [22].

The effluent generated from various operations of textile processing as shown in Figure 2 results in a cumulative wastewater known as textile wastewater. It generally consists of the sizing agents like starch, biological enzymes, polyvinyl alcohol (PVA) etc. used for the removal of sizing agents; soaps and detergents for the removal of waxes and other contaminations from the fabrics and the bleaching agents used to decolorize the fabric. The stream carrying the wastewater of the aforementioned characteristics is considered to be biodegradable in nature to a certain degree and is one of the central contributors to the organic load of textile effluents. The wastewater generated as a result of the dyeing process has a finite percentage of biodegradability. This is due to the fact that approximately 50% of the dye applied to the fabric in addition to sodium chloride and various auxiliaries, is lost into the effluent. The fabric is made in contact with aqueous heterogeneous [6] dyestuff solutions consisting of other chemicals i.e., acids, salts etc., and auxiliaries i.e., surfactants etc. All of these chemicals along with the dyes' solution enhance the binding of dyes to the fabric. The color fastness properties and the equipment in operation decide the type and amount of dyes, chemicals and dyeing auxiliaries to be used in a specific textile industry. The lowest or non-biodegradable compounds are mostly found in textile finishing effluent including oil repellents and all others that make the product ready for any intended purpose [9]. Beside these, textile wastewater contains a complex mixture of organic and inorganic pollutants resulting from various stages of textile processing. Organic pollutants include synthetic dyes like reactive, azo, disperse, and anthraquinone, as well as dye intermediates like benzidine and other aromatic amines. Surfactants, detergents, sizing agents (e.g., starch and carboxymethyl cellulose), natural impurities like pectins and waxes, and finishing chemicals like formaldehyde-based resins and softeners all contribute to the organic content. In addition, solvents and auxiliary chemicals such as urea, glycols, phenols, and phthalates are present. Inorganic pollutants are primarily composed of heavy metals such as chromium, copper, zinc, lead, cadmium, nickel, mercury, cobalt, arsenic, and antimony, which are introduced through dyes and metal-containing auxiliaries. Inorganic contamination in textile effluents is characterized by high concentrations of salts such as sodium chloride, sodium sulfate, and sodium carbonate, as well as acids such as hydrochloric and sulfuric acid, and oxidizing or reducing agents such as hydrogen peroxide and sodium hydrosulfite. Photocatalysis, Bioremediation and Ozone treatment can effectively break down and remove various organic and inorganic pollutants, including volatile organic compounds (VOCs), pesticides, dyes, and heavy metals from textile wastewater [9].

The wastewater generated as a result of textile processing results in intensified pressure on the environment when released untreated. The authorities responsible for environmental solidity have now started to regulate the industries by compelling them to treat their generated wastewater for a better and sustainable future. Major wastewater quality parameters that are considered to be the indicating parameters for pollution measurement are salt content, Total Solids (TS) including Total Dissolved Solids (TDS) and Total Suspended Solids (TSS), soluble and particulate COD and BOD along with heavy metals and color. Furthermore, 11 groups of chemicals enlisted in the manufacturing restricted substance list (MRSL) are the top priority to be eliminated due to their toxic effects and bioaccumulative nature [6]. Various textile operations and associated effluent characteristics are shown in Table 2.

Table 2. Textile wastewater characteristics produced by various processes.

Process	Effluent Characteristics
Singeing, De-sizing	BOD (high), TS (high), pH (neutral)
Scouring	BOD (high), TS (high), Alkalinity (high), Temperature (high)
Bleaching, Mercerizing	BOD (high), TS (high), Wastewater (Alkaline)
Dyeing, Printing & Finishing	Wasted dyes, BOD (high), COD, Solids, Wastewater (neutral to alkaline)

4. Environmental and Health Impacts of Textile Effluents

The presence of dyes, pigments and other color-releasing compounds contributes to colored appearance of textile effluents [8]. A significant mass of dyes is used in single-stage dyeing process causing an intense color concentration in the effluent. Furthermore, the complicated structure, synthetic production and refractory properties of dyes obligate the industries to treat them up to a safe discharge limit prior to their ultimate disposal into receiving water bodies [6].

The textile industry's finishing and dyeing units use a large amount of water as well as complex chemicals. Typically, a textile industry utilizes huge volumes of fresh and/or potable water. Out of the total consumption, 90%-94% of water is used in the processing and the remaining 6%-10% in the cooling processes [9]. About 200 liters of water are needed to produce one kilogram of textiles [25]. With ever-increasing demand for textile merchandise, textile industries and their discharged effluents have been escalating proportionately resulting in a major issue of water contamination. Pollution of water bodies due to untreated textile wastewater is considered one of the foremost environmental problems as it reduces the oxygen levels severely due to the presence of hydrosulfides and hinders the path of light through the water body which is harmful for the aquatic life. Various chemicals and the auxiliaries used in textile sector are causative agents of several ecological and health problems. It has been reported that organically bound chlorine, a renowned carcinogen, is present in approximately 40% of the dyes used worldwide [6].

The synthetic dyes were first discovered in 1856 and since their discovery more than ten thousand textile dyes have been produced exceeding 700,000 tons of yearly production. The degree of fixation of dyes on the fabric is the critical factor in their discharge to the environment. During the process of dyeing, approximately 25% of the dyes are lost out of the process and up to 20% of the dyes are released directly to the environment [6,8,9]. Figure 3 exhibits the world's total consumption of synthetic dyes.

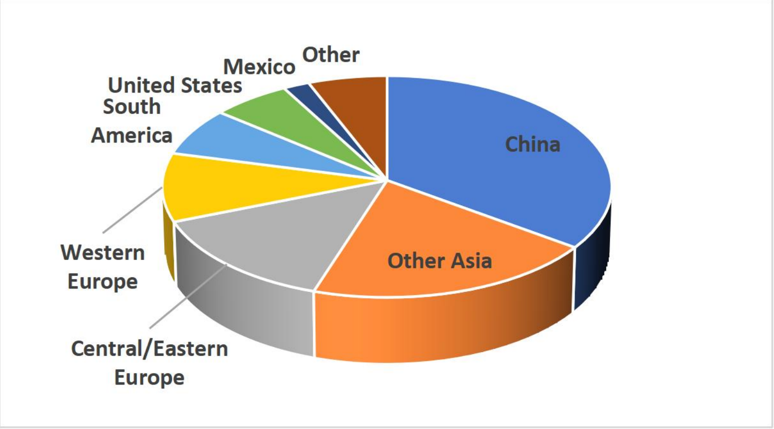

Figure 3. World Consumption of Synthetic Dyes-2017.

For the last 30 years, the production of dyes has reached nearer to the point of consumption. The major textile goods producer is China contributing approximately 55% of the world's total fiber utilization and 40% to 45% of global dye consumption [26]. The treatment of discharged dyes is carried out either by wastewater treatment plants or they become part of nature directly. The dyes are utilized during dyeing of the fabrics along with other auxiliaries. A few of the dyes are biologically degradable and they get accumulated into the microbial consortium while significant portion escapes the biodegradability. The dyes being recalcitrant in nature and hindering biological stabilization are among the most renowned class of dyes classified as azo dyes. Globally 70% of the dyes consumed in the processing of textiles are azo dyes [27]. Because of mutagenic and toxic nature of many dyes and their intermediate metabolites, the direct or untreated discharge of dyes into the environment is highly objectionable [28,29]. Moreover, the color of dyes imparted to the discharged wastewater is also undesirable as the photosynthesis in plants is affected. This highly colored untreated effluent affects the aquatic ecosystem because of light scarcity and consumption of oxygen [30].

The World Health Organization (WHO) claims that 17%-20% of the industrial water pollution is caused by dyeing wastewater. The materials applied to a substrate to impart color through a process that modifies the colored substances' crystal structure, at least momentarily, are known as dyes in the textile industry [31]. Chemical-based textile dyes have become more and more popular in the textile industry because they are more affordable and have better stability across a range of parameters, such as light and temperature, than natural dyes. As a result, highly polluted effluents are released, seriously harming the environment. Although the toxicity and mutagenicity of several synthetic dyes, especially azo dyes, have led to a reduction in their usage worldwide, they are still most favorable in the textile industry due to their reduced cost and other desired specifications. The elimination and treatment of these azo dyes to reduce their impact on environment and human life is still a challenging task due to the presence of recalcitrant bonds and compounds [31]. The foremost characteristics of pollution and related category of pollution hazard for principal goods produced in textile processing units are exhibited in Table 3.

Table 3. Chemicals used in textile industry, their characteristics and pollution hazards.

Chemicals/Auxiliaries Used in Textile Industry	Characteristics of Pollutants	Level of Pollution	Risk
Acid, Alkali, oxidants, salt	Pollutants that are inorganic in nature, comparatively harmless	1	Low
Sizing agents such as starch, natural oils, fats, waxes, biodegradable surfactants, organic acids, reducing agents	Highly biodegradable; BOD_5 ranges from moderate to a high value	2	Moderately low
Dyes and bleaching agents, fibers and impurities of polymeric nature, silicones	Not easy to degrade biologically	3	Moderate
Polyvinyl alcohols, mineral oils	Not easily biodegradable with moderate BOD_5 value	4	Moderately high
Dyes and auxiliaries, salts of heavy metals	Conventional biological (especially aerobic) treatment is ineffective; very low BOD_5 value indicating presence of low biodegradable organic matter	5	High

The non-biodegradable heavy metals present in the textile wastewater amass in crucial structures of the human body and aggravate with the passage of time. This leads to various symptoms of the diseases and causes serious illness. Moreover, disruption in natural ecosystems and endured health impacts are triggered by untreated or partially treated textile wastewater which is ultimately injurious to water and land-dwelling living beings [9].

5. Treatment Technologies for Textile Wastewater Treatment

Textile wastewater is the main source of water pollution. Several treatment technologies can be employed to treat toxic pollutants from textile industries effluent wastewaters. Because of variations in machinery, equipment, techniques, nature of fibers and types of chemicals and auxiliaries used, the composition of textile wastewater is very complex. Textile effluents are generally characterized by high pH, color and organic loads. The recalcitrant behavior of textile wastewater has led many countries and the relevant authorities to introduce stringent regulatory standards. Several treatment technologies can be employed to treat toxic pollutants from textile industries effluent wastewaters which broadly include physico-chemical. biological and hybrid treatment technologies [9]. This paper presents a detailed review about the prevailing treatment technologies used for textile wastewater treatment.

6. Physico-Chemical Treatment Technologies

Various physical methods like adsorption, coagulation and flocculation can be used along with the combination of chemical methods like oxidation, advanced oxidation and Fenton processes [32]. Some of the physico-chemical processes are (1) advanced oxidation process; (2) fenton based; (3) ozone based; (4) photocatalytic; (5) electrochemical advanced oxidation process [5].

6.1 Advanced Oxidation Process

Advanced Oxidation Process (AOP) includes ultraviolet irradiation, ozone, hydrogen peroxide and combine of some catalyst to degrade organic pollutants [33]. AOP does not form any toxic byproducts. Some famous AOP are O_3/UV, H_2O_2/O_3 ultrasound (US), H_2O_2/UV and H_2O_2/O_3/UV. AOP can also be comprised of iron catalyzed reactions, photocatalysis, microbial fuel cells and electrochemical. AOP can effectively remove TOC, BOD and COD [34,35].

AOPs are united by a single operational principle: create an abundance of hydroxyl radicals (•OH, E° ≈ 2.8 V) or other strong reactive oxygen species (ROS) that non-selectively mineralise recalcitrant organics to CO_2, H_2O and harmless inorganics. How each subclass generates those radicals and the way it is engineered differs appreciably [33].

6.2 Fenton Based

Fenton based technology is very effective in the treatment of different industrial wastewaters. At pH 3 with $FeSO_4$ of 0.2 gm/lit and H_2O_2 of 0.1 ml/lit, the Fenton process removes 98% of the color and 85% of the COD with $FeSO_4$ of 1.2 gm/lit and H_2O_2 dose of 0.6 ml/lit [36]. Advantages of Fenton based process are: (1) they can be used to treat large volumes of wastewater, and (2) efficient degradation is more remarkable under sunlight. Disadvantages of this process are: (1) need of pH regulation; (2) sludge formation; (3) production of halogenated by-products; and (4) they usually work in batch mode [37].

Mode of operation: the "classical" homogeneous Fenton is run at pH 2.8-3.5, 20-40 °C and atmospheric pressure; Fe^{2+} (0.1-1 mM) and H_2O_2 (5-50 mM) are dosed sequentially or together into a stirred tank or plug-flow loop. Heterogeneous or photo-assisted variants immobilise iron on clays, zeolites, magnetite, ZVI or add UVA/visible irradiation (photo-Fenton) to accelerate the Fe^{3+}/Fe^{2+} cycle [37].

Core reaction sequence: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + •OH$ ($k \approx 70\ M^{-1}\ s^{-1}$) initiates the chain; Fe^{3+} is regenerated via $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2•$ (Fenton-like) and, under light, $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + •OH$. Radicals attack organics ($R–H + •OH \rightarrow R• + H_2O$) until complete mineralisation; excess H_2O_2 however scavenges •OH ($H_2O_2 + •OH \rightarrow HO_2• + H_2O$) and must be controlled to keep the chain length high [37].

6.3 Ozone Based

Ozone dose, initial dye concentration, pH and UV irradiation are major factors to be considered in this technology. The ozone process is mainly used to treat the effluent wastewater color [9].

Mode of operation: ozone is produced on-site (dielectric barrier discharge, 6-10 % w/w in air) and injected through porous diffusers or venturi mixers. In peroxone, H_2O_2 is added at $O_3:H_2O_2 \approx 2:1$ (mol); in O_3/UV, low-pressure Hg lamps (λ = 254 nm) irradiate the contact chamber. Alkaline pH (8-9) accelerates ozone decay to •OH, but even acidic conditions work when H_2O_2 or UV is present [9].

Reaction sequence: $O_3 + OH^- \rightarrow HO_2^- + O_2$ (initiation); $O_3 + HO_2^- \rightarrow •OH + O_2•^- + O_2$ (chain); in peroxone $O_3 + H_2O_2 \rightarrow •OH + HO_2• + O_2$; under UV $O_3 + H_2O + h\nu \rightarrow H_2O_2 \rightarrow 2\ •OH$. Secondary radicals ($O_2•^-$, $HO_2•$) contribute, and carbonate/bicarbonate scavenge •OH, therefore alkalinity control is critical [9].

6.4 Photocatalytic

Different catalysts can be used in it like TiO_2 and ZnO in order to degrade pollutants present in textile wastewater. This technique can be used for decolorization of textile wastewater. Where decolorization increases at specific catalyst dosages and becomes constant after reaching some definite point. Mostly TiO_2 and ZnO are widely used as a photo catalyst to remove organic pollutants and dyestuff from wastewater [38]. Photo-induced reactions in Photocatalytic process increase the efficiency of process [39]. It is essential for the photo-catalyst reactions that the energy of photon should be greater than the band gap energy of catalyst [40]. Due to the ability to achieve complete mineralization, the photo-catalyst process is frequently used to degrade dyestuff from textile effluent [41-48].

Mode of operation: a slurry or thin-film reactor is irradiated with photons whose energy exceeds the semiconductor band-gap ($TiO_2 \approx 3.2$ eV, $\lambda \leq 385$ nm). Oxygen is continuously sparged; catalyst loading is 0.1-1 g L^{-1}; pH is usually natural or slightly acidic to maximise surface hydroxyls. Immobilised coatings on glass Raschig rings or fibre meshes avoid filtration [38].

Reaction sequence: photon absorption produces an electron-hole pair ($TiO_2 + h\nu \rightarrow e^-\_CB + h^+\_VB$). Valence-band holes oxidise adsorbed H_2O/OH^- to •OH ($h^+ + H_2O \rightarrow •OH + H^+$), while conduction-band electrons reduce O_2 to superoxide ($e^- + O_2 \rightarrow O_2•^-$). These ROS jointly degrade pollutants; electron-hole recombination competes and is suppressed by noble-metal doping, heterojunctions or applied anodic bias [38].

6.5 Electrochemical Advanced Oxidation Process

Integrated electrochemical processes like combination of Electrocoagulation (EC) alone and combined with Electro Fenton (EF), Anodic oxidation (AO) and Peroxi-coagulation (PC) can be used to treat textile wastewater. Among all of these combinations, EC-EF is most suitable for color and total organic removal from textile industries effluent wastewaters [49].

Mode of operation: in anodic oxidation a boron-doped diamond (BDD) or mixed-metal-oxide anode is employed; current density 10-100 mA cm^{-2}, Na_2SO_4 electrolyte, pH 3-9. For electro-Fenton, a carbon-felt or gas-diffusion cathode continuously reduces sparged O_2 to H_2O_2 ($O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$) while Fe^{2+} is added or regenerated at the cathode ($Fe^{3+} + e^- \rightarrow Fe^{2+}$), producing in-situ Fenton chemistry [33].

Reaction sequence: at the BDD surface $H_2O \rightarrow$ •OH_ads + H^+ + e^- (direct electron transfer and physisorbed •OH); in the electro-Fenton bulk Fe^{2+} + electro-generated $H_2O_2 \rightarrow Fe^{3+}$ + •OH + OH^-. Simultaneously, active chlorine (if chloride is present) and persulphate can be electro-generated, giving mixed oxidation pathways. Mass-transfer of pollutants to the anode or of •OH away from the surface governs kinetics; therefore electrodes are designed as 3-D porous beds or rotating cylinders to maximise area [33].

Tables 4,5,6 and 7 shows the AOP can be employed to produce (•OH), application of Fenton based process, application of the ozone-based process for dye removal and the comparison of different electrochemical processes along with their removal efficiencies for textile wastewater treatment respectively. Figure 4 shows the flow chart that connects all the physico-chemical treatment technologies.

Table 4. Application of AOP for textile wastewater treatment.

Dye	Catalyst/Oxidants	[Dye] (mg/L)	[Catalyst]/ [Oxidants] (mg/L)	pH/T (°C)	Color Removal %	COD/ TOC %	AOP Employed	Ref.
AO7 RR120 AB9	Fe/air	100	30	3/-	>99	96.7/- 96.7/- 85.7/-	Catalytic (Zero valent iron)	[50]
RBBR AB1	Fe/air	100	50	3/-	>99 >99	96/- 50/-	Catalytic (Zero valent iron catalyst)	[51]
Reactive Black 5	O_3 (micro-bubbles)	230	132	-/20	100	-/79.8	Ozonation	[52]
MB	UV/SiO_2/TiO_2-Ce	2.5	100	11/25	-	-	Photocatalysis	[53]
Procion blue dye	Titanium anode coated with 70TiO_2/30RuO_2/TiO_2 catalysts	100	65	3.5/-	100	89.9/-	Electro-photocatalytic	[54]
Acid Violet 7	ZnO/UV/air	$5*10^{-4}$	2000	9/-	-	94.4/-	Photocatalytic	[55]
Eosin Y	ZnO/UV	50	400	6.9/30	39	8.1/-	Photocatalytic	[42]
Methylene Blue	ZnO/UV	50	400	6.9/30	58	24/-	Photocatalytic	[42]

Table 5. Fenton process for the treatment of textile wastewater.

Dye	Anode	Cathode	Dye (mg/L)	[Catalyst]/ [Oxidant] (mM/A)	pH/T (°C)	Color Removal %	Organic (TOC) removal %	Methods	Ref.
AO7	Carbon felt	Carbon felt	10	0.1 Fe^{+3}/0.3	3-2.8/-	-	92	Electro Fenton	[56]
OG-II	Graphite cloth	Graphite cloth	50	0.2 Fe^{+2}/0.3	3/-	100	80	Photo-electro Fenton	[57]
OG-II	Graphite cloth	Graphite cloth	50	0.2 Fe^{+2}/0.3	3/-	100	63	Electro Fenton	[57]
AY36	Boron doped diamond	Carbon-PTFE air diffusion cathode	108	0.5 Fe^{+2}/3	3/35	100	71	Electro Fenton	[58]
AY36	Boron doped diamond	Carbon-PTFE air diffusion cathode	108	0.5 Fe^{+2}/3	3/35	100	95	Solar Photo-Electro Fenton	[58]

Table 6. Application of ozone-based process for dyes removal.

Dye	Catalyst/ Oxidant	Dye (mg/L)	[Catalyst]/[Oxidant] (g/L)	Frequency (kHz)	pH/T (°C)	Color Removal %	COD/TOC %	Method	Ref.
R5	O_3	363	3.36	520	7/20	-	-/76	Ozonation	[59]
RY84	O_3	500	4.5	20	4.5/25	-	-/56	Ozonation	[60]
AB & MO	O_3	100	-	500	6.5/15	-	-/80	Ozonation	[61]
4BS	O_3	100	3.2	20	8/-	100	-	Ozonation	[62]
RB19	US/O_3	500	3.8	20	8/-	100	-/65	Ozonation	[63]

Table 7. Different electrochemical treatment technologies for textile wastewater treatment.

Treatment	Removal Performance %	Ref.
Wetlands (vertical flow) along with planted Phragmites	Nitrate nitrogen (NO_3-N): 85-100	[64]
Electrochemical oxidation	COD: 98 at 60 min	[65]
Electrocoagulation phytoremediation	COD: 94; color: 97; Turbidity: 98	[66]
Electrochemical Fenton with Chemical Fenton	COD: 70.6 by electro fenton; COD: 72.9 by chemical fenton at 60 min	[67]
Electrochemical oxidation	Color: 100; Mineralization: 85 at 180 min	[68]
Electrochemical	COD: 100; color: 100 at 15 h	[69]
Combined electrochemical, microbial, and photocatalytic processes	COD: 80-95	[70]
Electrochemical process	Color: 99; COD: 97	[71]

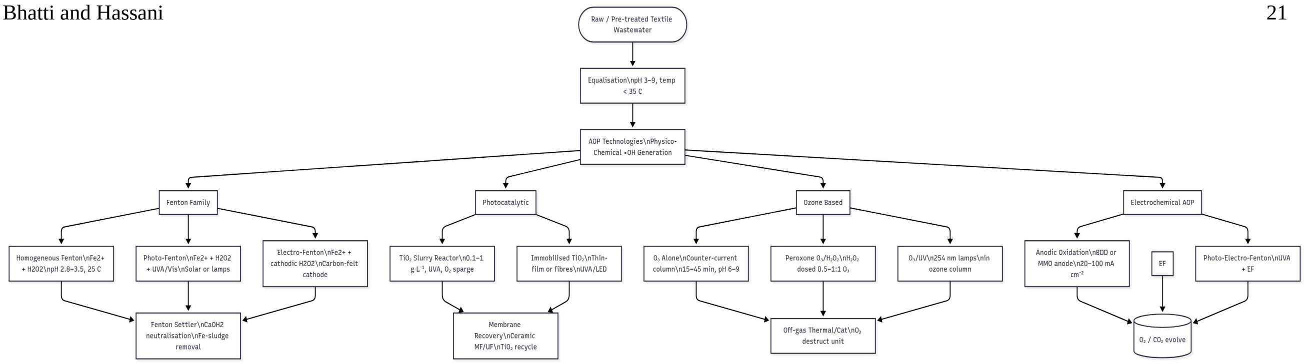

Figure 4. Flow chart that connects all the physico-chemical treatment technologies.

7. Biological Treatment Technologies

Several physical, chemical and biological processes for the treatment of textile wastewater have been developed over the years. Biological treatments are more cost effective, have an environmentally friendly approach, easy and safe operation-green chemistry concept as compared to physicochemical methods. Biological treatment transforms i.e. oxidizes, dissolves and particulates biodegradable constituents into acceptable end products and moreover it also removes nutrients such as nitrogen and phosphorous [72].

7.1 Bacterial Cultures

Numerous species of bacteria that belong to different phyla for instance Firmicutes, Bacteroidetes, Proteobacteria, Actinobacteria and Acidobacteria have been characterized and isolated [73,74] and indicated efficient synthetic dye removal [75]. Another research found that a bacterial consortium that was isolated from the inspection chamber of textile industry had enough capability to grow in impure textile wastewater and moreover had shown good efficiency in color removal and had reduced pH levels close to neutral [76].

The combination of bacterial consortium and photocatalysis has also been used to treat real textile wastewater. Photocatalytic composite used was ZnO/polypyrrole for the treatment with no pretreatment and no additional carbon sources. Direct Black 22 (DB22) azo dye was used for this study. Color removal efficiency of 95.7% and TOC removal of 99.8% were noted by combined application of both processes [77].

Removal efficiency of 85.6 % has been obtained by using Nocardiopsis sp. bacterial species for azo dye reactive orange 16 [78]. Use of Pseudomonas aeruginosa SVM16 for removal of Azo dye Reactive red 21 resulted in 97.7% removal efficiency [79]. Another research showed 91% removal efficiency of Azo dye Reactive Red 2 by using bacterial species Pseudomonas sp. SUK1 with microbial enzyme lignin peroxidase [80].

7.2 Fungal Cultures

Use of fungal cultures has been reported to be effective for treatment of textile wastewaters by different researchers in recent years. Research was conducted in which filamentous organisms were used for the development of a fungal bioactive ultrafiltration membrane. Filamentous organisms Aspergillus carbonarius M333 was used for treatment of real wastewater from textile industries. The impact of time on growth of fungus was analyzed for 3, 6 and 9 days. The bioactive fungi ultrafiltration film was put in a dead-end filtration system and was used for wastewater filtration. It was also observed during this study that the filamentous parasites Aspergillus carbonarius M333 has one-end open fiber and it acts like an empty fiber film with an external span under 10 μm. The outcomes demonstrated 91% removal of color and a 73.2% decrease in COD was also reported by fungi bioactive ultrafiltration film [81]. Color degradation of wastewater of textile industry by Coriolus versicolor fungus deactivated on polyurethane froth in an oxygen consuming bioreactor has also been studied. Color and COD reduction were reported to be 80% and 67% in 2 days, in respective order [82]. Treatment of textile wastewaters with Ganoderma lucidum fungi in a batch reactor has also been reported to give removal efficiencies of 81.4% and 91.3% for color and COD in 5 days individually [83].

Trametes versicolor fungi has also been reported efficient for color removal from wastewater of textile industry. Results showed color removal of 40%-60% in a bioreactor that worked in non-sterile conditions under 15 days. In another study, Bjerkandera adusta fungi was used in a fixed bed bioreactor for decolorization of textile wastewater. The fungus was found impactful for four cycles of decolorization and stayed dynamic for a more drawn out period (70 days) under non-sterile conditions and without nutrient addition [83].

7.3 Algal Cultures

Throughout the years, the application of microalgae at a modern scale has developed and broadened essentially. Among the microalgae applications, textile wastewater bioremediation is one of the most encouraging innovations because of the concurrent advantages: microalgae development utilizing textile wastewater as culture medium (bioremediation and CO_2 relief) followed by microalgae lipid application (production of biodiesel). The couple of researches on microalgae that are applicable to textile wastewater treatment tended to address areas like removal of carbon and nitrogen, removal of color and phytotoxicity of the treated wastewaters of textiles [21,83].

Recent studies have demonstrated that microalgae have an extremely high potential for phycoremediation. Phycoremediation is a kind of bioremediation that can be characterized from a broader perspective as the utilization of microalgae or full-scale algae growth for treatment of wastewaters. Chlorococcum vitiosum a microalgae has been utilized for treatment of textile wastewater. The outcome of this investigation indicated a decrease in pH of the textile wastewater effluent that was treated with algae. The pH decrease was fundamentally high with utilization of Chlorococcum vitiosum. Use of microalgae to the wastewater has additionally brought about a 13% change in color. Turbidity of wastewater likewise diminished by 23.23%. COD removal of 13% was accomplished utilizing microalgae [21].

7.4 Membrane Based Technologies

Various pressure-driven membranes have been explored for the treatment of textile wastewater for instance reverse osmosis (RO), microfiltration, nanofiltration and ultrafiltration. A few researchers have concluded that of reverse osmosis is defined as to the treatment and reuse of textile industry effluents. RO membranes are reasonable for eliminating particles (ions) and larger species from dyebath effluents; the permeate produced usually has no color and has low salinity. Nanofiltration was likewise studied as treatment for secondary textile effluents after microfiltration: nanofiltration (NF) saturate quality was good and worthy for water reuse. NF can be a serious option in contrast to ordinary procedures for treatment of textile effluents. The beneficial qualities of NF, as far as high dissolvable permeability, simple up-scaling, and simplicity in cleaning of chemicals, propose that membrane technology may turn into the standard treatment technology for textile effluents. By applying direct NF, the natural material can be held even more effectively because of the fact that the components are not deteriorated in the biological treatment, so dismissals are higher. Then again, the fixation is higher, and more issues with layer fouling are normal [9].

Research conducted using polyvinylidene difluoride (PVDF) ultrafiltration films for textile wastewater treatment reported 90% COD removal and 96% decolorization. This water was professed to be adequate for reuse, although some color was remaining. Film (membrane) fouling was still an issue. Membrane processes for textile wastewater treatment can be categorized into two groups i.e. integrated and stand-alone membrane processes. Former group (integrated membranes) is defined as processes in which one conventional method is combined with membrane process or a pretreatment method is combined with membrane process [19,84]. A membrane bioreactor (MBR) couples ultra-filtration (0.04 µm hollow fibres or flat sheets) directly to the aeration basin, creating a suspended-growth system that can be run at 8-15 g L^{-1} MLSS and 15-30 d sludge retention time (SRT) while producing particle-free permeate. High biomass concentration and complete solids retention enhance cometabolic biodegradation of refractory dye metabolites; soluble microbial products adsorb colour, and the physical membrane barrier removes 100 % of suspended dyes, giving 90 % COD, 85-95 % colour and 5 nephelometric turbidity unit (NTU) effluent suitable for in-plant reuse, though the concentrate requires periodic chemical cleaning to control fouling [81].

The membrane method for textile wastewater is a staged pressure-driven cascade: after equalisation and 100 µm drum screening the liquor is warmed to 30 °C, pH adjusted to 6.5-7.5, and dosed with 2 mg L^{-1} antiscalant; a low-pressure microfiltration hollow-fiber unit (0.1 bar trans-membrane pressure, TMP) removes fibres and lint, followed by an ultrafiltration spiral (0.5-1 bar TMP) that rejects macromolecular sizing agents; the UF permeate is then pushed through loose nanofiltration (8-12 bar TMP) where 90 % of salt and 98 % of dye are separated, and finally a short reverse-osmosis stroke (15-25 bar TMP) polishes the NF permeate to conductivity <200 µS cm^{-1} so that 75-85 % of the original volume can be directly reused in dye baths, while the coloured concentrates are evaporated or sent to electrochemical oxidation, creating a near-zero-liquid-discharge loop with energy demand below 2 kWh m^{-3} of product water [81].

Work has also been done on fabrication of membrane of double-layer nanofibrous SAN4-HIPS through electrospinning that is gas assisted and has been utilized for treatment of textile wastewater through direct contact membrane distillation (DCMD). The acquired outcomes demonstrated that the new layer is vigorous and capable of eliminating the contaminants, surprisingly, with practically 99.28 %, 97.93 %, and 100 % decreases for COD, BOD and color, respectively. Along with that, a flux decrease of up to 42.58 % was seen after 48 h DCMD process [19,84]. Figure 5 shows the operational flow chart of MBR technique.

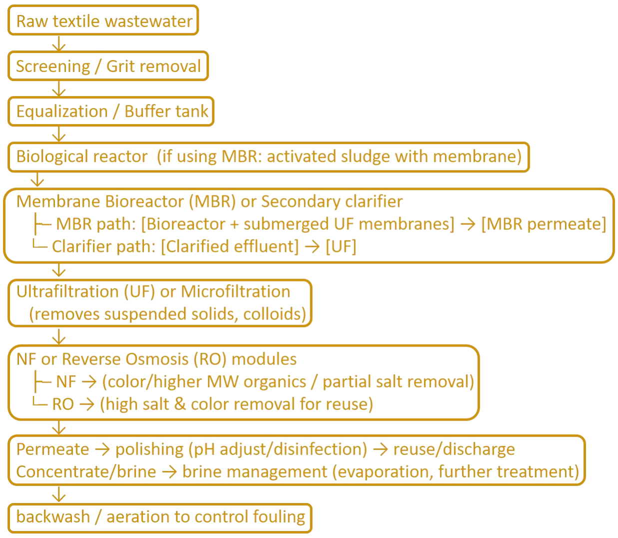

Figure 5. Operational flow chart of MBR.

7.5 Nanofiltration

Textile wastewater can be effectively treated by nanofiltration (NF), a pressure-driven membrane technology that recovers water and valuable resources while eliminating dissolved contaminants like dyes and salts [85]. NF uses charge repulsion and size exclusion to separate contaminants from water using membranes with pore sizes ranging from 1 to 10 nm [86]. Because of their increased water flux, suitability for dye/salt fractionation, and ability to be combined with other technologies like electrodialysis for resource recovery, loose nanofiltration (LNF) membranes are becoming more and more popular [87].

In a typical NF train for textile wastewater the pre-screened and UF-prefiltered liquor is pumped at 8-15 bar through spiral-wound loose-NF elements whose 0.5-2 nm pores combine size exclusion with Donnan repulsion; this allows water and monovalent ions to permeate while > 98 % of hydrolysed reactive dyes, dissolved organics and divalent salts are retained in a 5-8 % concentrate that can be returned to the dye kitchen for colour reuse or sent to a small evaporator. Operation is steady-state: pH is held at 6-8, temperature below 35 °C to limit fouling, and intermittent alkali/surfactant back-wash plus 30 s 200 mg L^{-1} NaOCl shock cleanings keep specific flux above 15 L m^{-2} h^{-1} bar^{-1} so that 80-90 % water recovery and 50 % less energy than RO are achieved in full-scale plants [87]. Figure 6 shows the operational flow chart of nanofiltration technique.

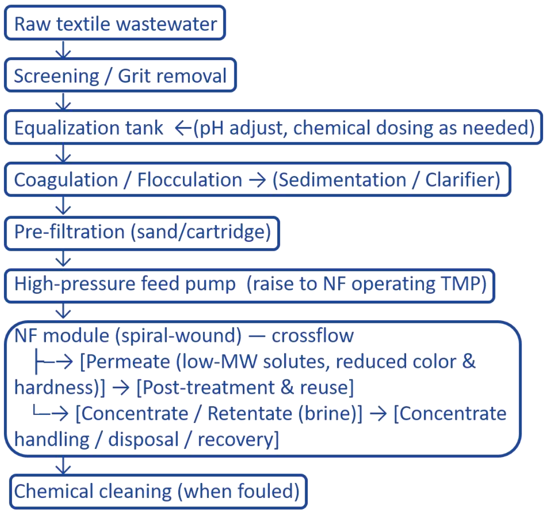

Figure 6. Operational flow chart of Nanofiltration.

7.6 Nanotechnology Via Adsorption

A potent method for treating textile wastewater is NF in via adsorption [6,9,88-90]. Adsorption is used to remove large dye molecules and contaminants, and nanofiltration is used to separate any remaining dyes and salts and recover high-quality water [84,91-94]. Sawdust and other adsorbents can pretreat wastewater, while nanofiltration membranes can recover salts for further use and retain dyes due to their specific pore sizes and characteristics. By successfully lowering COD and color, this integrated approach allows for resource recovery and water reuse from the wastewater of the highly salinized and colored textile industry [13].

Nano-adsorption uses laboratory-synthesised or commercially supplied powders, beads or membranes that carry high-surface-area (100-800 $m^2\ g^{-1}$) nanoscale phases–zero-valent iron, TiO_2, magnetic Fe_3O_4, graphene oxide, carbon nanotubes, mesoporous MCM-41 or polymer nano-composites–which are dosed at 0.1-2 g L^{-1} into stirred tanks or packed columns fed with textile effluent. Contaminants are removed by physisorption (π-π, hydrophobic, electrostatic) and chemisorption (surface complexation, redox or ligand exchange): dye molecules diffuse into 2-10 nm pores within seconds, heavy metals bind to –COOH or –OH sites, and the spent solid is separated by magnetic decantation, pressure filtration or is left embedded in a mixed-matrix membrane that is back-washed, allowing reuse for 10-50 cycles before thermal or acid regeneration [13]. Figure 7 shows the operational flow chart of nano-adsorbent technique.

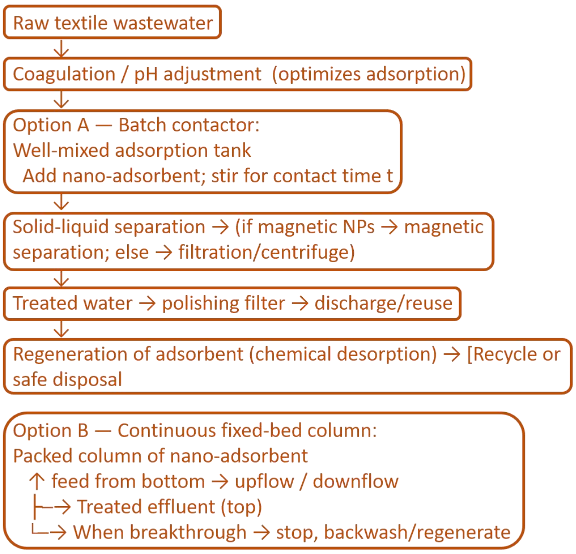

Figure 7. Operational flow chart of Nano-adsorbent.

7.7 Phytoremediation

To remove or detoxify contaminants like dyes and heavy metals from textile wastewater, phytoremediation employs plants. Phytoextraction (uptake and accumulation in plant tissues), phytodegradation (breakdown of organic pollutants), and rhizofiltration (filtering pollutants by roots) are some of the mechanisms used in this environmentally friendly, solar-driven method, which is frequently used in artificial wetlands [95-99]. Using common plants like duckweed (Lemna sp.) and water hyacinth (Eichhornia crassipes) in conjunction with microorganisms [100-102] or pretreatment techniques can increase their effectiveness [103,104].

Constructed wetlands, horizontal subsurface-flow cells or simple hydroponic raceways are planted with cattail (Typha), water hyacinth (Eichhornia), vetiver (Chrysopogon) or genetically engineered Petunia that possess intracellular azo-reductases, laccases and cytochrome P450 pathways; textile wastewater (BOD 300-800 mg L^{-1}, dye 50-200 mg L^{-1}) flows at 2-5 cm d^{-1} through 0.6 m deep gravel root zones for 4-8 d. Plants assimilate nitrate and phosphate, root exudates supply organic acids that act as electron donors for microbial azo-bond cleavage, and aerenchyma transports O_2 to rhizosphere, creating micro-aerobic sites that mineralise aromatic amines; harvested biomass containing 2-3 % N, P, K is composted into fertiliser, while effluent shows 70-90 % colour, 60-80 % COD and 95 % nutrient removal under tropical sun with almost zero energy input [103,104]. Figure 8 shows the operational flow chart of phytoremediation technique.

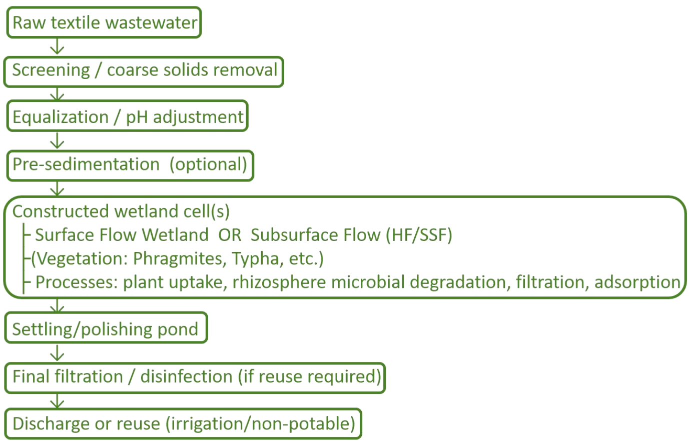

Figure 8. Operational flow chart of phytoremediation.

7.8 Activated Sludge

Degradation of colors by activated sludge process (ASP) is known as a proficient and cost-effective process. But ASP has a genuine ecological effect particularly as they produce enormous volumes of sludge containing compounds that are resistant to biodegradation [11].

Activated-sludge systems treat textile wastewater as a classic suspended-growth process: after screening, equalisation and pH correction to 7-8, the effluent is fed to a completely-mixed aeration basin where coarse- or fine-bubble diffusers maintain 2-4 mg L^{-1} dissolved oxygen; hydraulic retention is 8-24 h and solids retention 10-25 d at 3-6 g L^{-1} mixed liquor suspended solids (MLSS), while settled sludge is recycled at 50-100 % of inflow and a small waste stream controls biomass age. Hydrolysed dye auxiliaries are oxidised to CO_2 and water, azo dyes are first adsorbed on flocs and then cleaved by oxygenases to aromatic amines that feed the β-ketoadipate pathway, and long SRT ensures full nitrification to nitrate, giving 70-90 % COD, 60-80 % colour and 95 % ammonium removal [11].

A study has been performed in which textile wastewater was treated using activated sludge microorganisms. In this study, real textile wastewater (RTW) and synthetic textile wastewater (STW) were treated in 24 hr cycle time by using Sequencing Batch Reactor (SBR). Remazol Brilliant Blue R, a reactive dye, was used for study. 80.71% removal of COD was achieved for highest dye concentration of 500 mg/l with low TDS; COD removal efficiency of 59.44% was reported for 5000 mg/l TDS concentration. However, efficiency of COD elimination was reduced to 14.92% when TDS concentration increased to 10,000 mg/l and also decreases in MLSS and MLVSS (mixed liquor volatile suspended solids) concentrations were also noted. According to the reported results, COD removal efficiency was not affected by the increase in concentration of TDS up to 5000 mg/l of the activated sludge microorganisms in the treatment system [11].

7.9 Attached and Suspended Growth Systems

In a suspended-growth system, microorganisms that are responsible for treatment are maintained in a liquid suspension by appropriate mixing methods such as activated sludge process. By contrast, in attached-growth systems microorganisms that are responsible for conversion of organic material or nutrients are attached to an inert packing material [9].

7.9.1 Attached Growth Systems

In attached growth systems trickling filters have been used previously for the treatment of simulated textile wastewater (STW). STW contained reactive azo dyes with bacterial consortium under non-sterile conditions. 95% decolorization was achieved in all the trials. The involvement of microbial consortium was confirmed by the stable bacterial count of the biofilm on the trickling filter media in the treatment of textile wastewater. Results noted were 58.5%-75.1% reduction in COD, 18.9%-36.5% decrease in concentration of sulphates, and 63.6%-73.0% reduction in phosphate concentration [11].

Decrease in COD concentration and color degradation in textile wastewater has been reported in literature through RBCs (Rotating Biological Contractor). Results showed 95.3% COD removal and 90.5 % color degradation through RBCs in all four stages [11].

7.9.2 Suspended Growth Systems

A research combining the activated sludge process (suspended growth process) and microfiltration for COD and color removal. They reported more than 82% COD removal and color removal of more than 95% [6,8].

In another research study activated sludge process was combined with electrocoagulation for the treatment of textile wastewater. It was reported when activated sludge process is combined with electrocoagulation it shows better results for COD and color removal as compared to when both the processes are used individually [8,9].

Figure 9 shows the flow chart that connects all the biological treatment technologies.

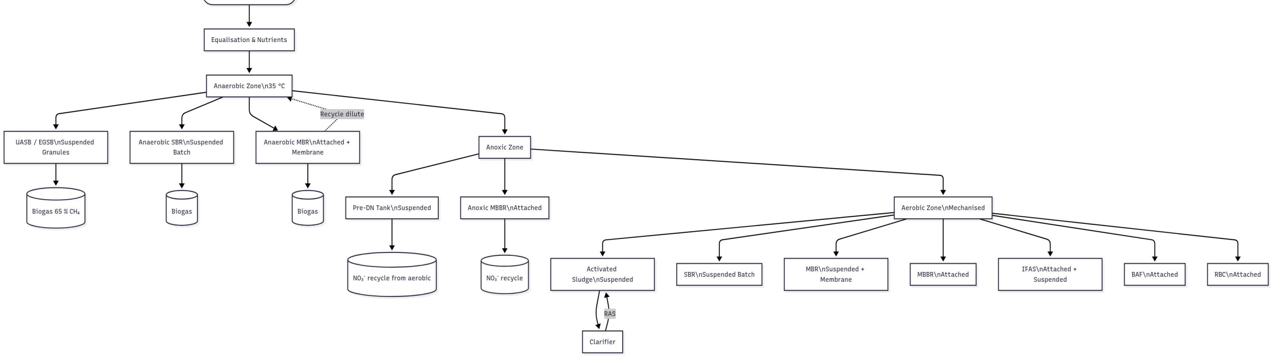

Figure 9. Flow chart that connects all the biological treatment technologies.

8. Hybrid Treatment Technologies

Since textile wastewaters contain numerous pollutants including tough or non-biodegradable compounds, the advantages of each process can be used more efficiently by using hybrid systems [85]. There are both benefits and drawbacks to the physical, chemical and biological processes. For example, the chemical use and development of highly chemical sludge is the main drawback of the coagulation-flocculation process. In comparison, the coagulation/flocculation (C/F) process can precipitate and extract wastewater from non-biodegradable compounds present in textile wastewater [9]. Therefore, according to the framework of wastewater, the most efficient and cost-effective system combination needs to be investigated.

8.1 Anaerobic-Anoxic-Aerobic Membrane Bioreactor Process (A_2O-MBR)

The disposal of organic and nitrogen compounds was studied for the treatment of textile wastewater in anaerobic-anoxic aerobic membrane bioreactor process (A_2O-MBR). The working volumes of the three reactors were 3.8 m^3, 7.5 m^3 and 5.6 m^3, respectively. Bamboo carbon was assembled in reactor A1 and produced at 600 ºC in a slow pyrolysis process of 3 to 5 mm diameter. A mechanical stirrer was mounted in reactor A_2 to shake up its contents. The O-MBR may be separated into buffer area and reaction area. The buffer area was fitted with an internal pump and mixing liquor from the bottom into the reaction zone was constantly pumped. The reaction zone was immersed and symmetrically positioned in two different types of membrane modules. One was a polylvinylidene-fluoride hollow fiber (HF) membrane assembly, nominally 0.1 µm in pores and 12.5 m^2 membranes in total [84].

The anaerobic-anoxic-aerobic membrane bioreactor (A_2O-MBR) is operated as a single recycled loop: textile wastewater is first acidified to pH 6.8-7.2, screened and fed to a completely mixed anaerobic zone (hydraulic retention time (HRT) 1.5-2 h, oxidation reduction potential ORP 250 mV) where acidogenic biofilms hydrolyse PVA sizes and azo dyes are reductively cleaved by extracellular quinone shuttles; liquor then overflows to an anoxic basin (HRT 2-3 h, ORP 100 mV) that receives nitrate-rich mixed-liquor recycle from the tail end, allowing denitrifiers to use residual dyes and fatty acids as carbon source while generating alkalinity; the stream enters a fine-bubble aerated chamber (HRT 6-8 h, dissolved oxygen (DO) 2-3 mg L^{-1}) where aerobic heterotrophs mineralise aromatic amines and nitrifiers convert ammonium to nitrate, after which the mixed liquor is ultrafiltered through 0.04 µm hollow fibres operated at 10-12 g L^{-1} MLSS and 20-25 d SRT, producing particle-free permeate with 90 % COD, 95 % colour and total-N <10 mg L^{-1} while total phosphorus is co-precipitated with ferrous sulphate dosed into the aerobic zone [84].

In order to analyze the biofouling activity of two membranes observed via the transmembrane pressure (TMP), both membranes were used and symmetrically submerged in the aerobic reactor. The organic and nitrogen compounds were thus effectively separated from the textile wastewater. High removal ratios have been achieved for many organic compounds. However, in some hard-organic contaminants, like 2% of styrene, very low removal efficiencies have been observed. In addition, combinations of acids and oxidizing agents have been proposed to reduce biofouling as a possible option for solvent cleaning [84].

8.2 Hybrid Anaerobic SBR-Aerobic Process

A research based on SBR reported that , if proper aeration is provided to the aerobic sludge in SBR, then it can enhance the development process of aerobic microorganisms, which can further improve acclimatization of sludge [84]. A hybrid anaerobic sequencing batch reactor-aerobic process treats high-strength dye-house liquor in two coupled tanks: in the first, a granular ASBR (HRT 12 h, 35 °C, ORP 300 mV) cycles through fill, anaerobic react, settle and decant, enabling syntrophic consortia to convert 70 % of COD to biogas (CH_4 65 %, CO_2 35 %) while extracellular polymeric substances adsorb and reductively decolourise 60-70 % of reactive dyes; the low-strength, partially decolourised effluent is siphoned into a subsequent continuous-flow aerobic basin (HRT 4 h, DO 2 mg L^{-1}) where suspended biomass oxidises residual aromatics and completes nitrification, giving an overall 85 % COD, 80 % colour and 95 % NH_4-N removal with 60 % less aeration energy than a stand-alone aerobic system [84].

A study was performed comparing Anaerobic MBR (AnMBR) and aerobic MBR (AeMBR). He observed that AnMBR shows better performance for decolorization as compared to AeMBR. Although anaerobic MBRs have shown better performance for treatment of textile wastewater when compared to aerobic MBRs but still most of literature studies are focused on aerobic MBRs. Less work has been done on anaerobic MBRs in context of treatment of textile wastewater [84].

In order to verify the performance capabilities for synthetic textile wastewater, the hydraulic retention duration in anaerobic SBR was set to 12, 18, 24, 42 and 48 hours. After anaerobic treatment the SBR was permeated in variable HRTs to aerobic SBR, which assessed aerobic removal efficiencies by setting the HRT reactor to 1, 2, 3, 4, 5 and 6 hours. Air supply was supplied by an air compressor to retain dissolved oxygen in the form of a coarse bubble at 8 l/min [84].

High-quality permeate was to be attained through aerobic treatment with variable HRT followed by anaerobic pretreatment. From the analysis it is clear that the treatment of both phases increases the system efficiency up to 98.0% and 99.5% respectively for synthetic and real wastewater by combining anaerobic and aerobic treatments. Therefore, the optimal HRT of the anaerobic-aerobic hybrid system is found to be 54 hours for maximum efficiency with COD removal in real textile wastewater. At the organic charge rate (OLR) 1.5 kg/m^3.d, at COD_i (i = initial) 3000 mg/L, anaerobe HRT of 48 h, the optimum performance was achieved. The MLSS can't be quickly cleaned up with hydraulic surges by SBR systems that treat industrial wastewater. The initial cycles were influenced by the high pH level of real wastewater, and thus by the organic removal rate, the F/M ratio in the hybrid system, which is restricted by the increasing concentration of more than 8000 mg/L. Literature has also shown that MLSS has a direct effect on wastewater efficiency [9,84].

VFA/alkalinity ratio was found in the whole study to be far below 0.4, while VFA/alkalinity was between 0.3 and 0.4, as this range was considered to be optimal for pH self-regulation in the anaerobic condition [86]. This is the most significant factor of aerobic process. Aerobic reactor at 6 h HRT and average COD removal concentrations were found to eliminate average total kjeldahl nitrogen (TKN). The national environmental quality standards (NEQS) was accomplished with high removal efficiencies of COD (99.5%), TKN (99.3%) and color (78.4%). Satisfactory effluents were collected [86]. Acclimated sludge has been described as having a positive effect on the performance of the system and the production of biogas [84]. The optimum removal efficiency from the hybrid system was effectively obtained compared to the individual anaerobic and aerobic systems. Adapting the hybrid anaerobic aerobic method for textile industrial wastewater treatment, therefore, is recommended for the purpose of sustainability.

8.3 Combination of Forward Osmosis and Membrane Distillation Process

The hybrid forward-osmosis-membrane-distillation (FO-MD) process is driven by osmotic pressure rather than hydraulic pressure: the warm (40 °C) textile effluent flows along the porous support side of a cellulose-triacetate FO membrane while a concentrated NaCl draw solution (1.5-2.0 M) circulates on the active layer, extracting water and leaving dyes, salts and organics behind; the diluted draw solution is then reconcentrated in a downstream air-gap membrane-distillation module heated to 55-60 °C, where water vapour passes through a hydrophobic PTFE membrane and condenses on a chilled plate, producing high-purity permeate (conductivity <50 µS cm^{-1}) that is recycled as soft process water while the retained dye concentrate is returned to the dye kitchen or sent to a small AOP polishing step, achieving 95 % water recovery and 99 % colour rejection with no high-pressure pumps [87].

Controlled the effective surface area of the membrane to 10.0 cm^2, while the cross-flow rate of 0.2 Lmin^{-1} (10.4 cm/s) on both sides is determined. As draw solution simultaneously operated as the MD process feed solution, the associated MD output was channeled to 5 different temperatures (25 ºC, 35 ºC, 45 ºC, 55 ºC and 65 ºC) [87]. During the test, the FS_{FO} temperature was held at 25 ºC. The performance was assessed in the MD unit with a 10 cm^2 efficient membrane area in direct contact membrane distillation mode (DCMD). For the feed of FS_{MD} (similar to DS_{FO}) and distillate streams respectively, cross-flow levels of solutions were set at 0.2 L min^{-1} and 0.1 L min^{-1}. Each test will take at least 30 minutes to stabilize the system before collection of accurate performance data. Importantly, the reverse salt content of the FO unit was measured by ion chromatography when a CR solution was used as FS_{FO} [84].

Three Operation Modes of FO-MD

Three different modes of operation of FO-MD are: (1) Isolated FO process, (2) Separated FO integrated with separated MD process, and (3) FO-MD hybrid process.

The water recovery ratio (WTR) is expected to remain steady at less than 30%, which is equivalent to ~ 3.3 CF. In comparison, the PTAODH-1.0 synthetic membrane has an up to 90 percent water recovery (CF of ~10) ratio which is extremely advantageous for the subsequent color recovery cycle and without much change in energy consumptive content. For feed solution, any process may achieve a high CF of ~10, while isolated FO process requires an additional drawing solution consumption in order to retain the osmotic driving force to generate a greater DS volume. The water flows were found to decrease gradually over the entire phase of separated FO integrated with separated MD process without the introduction of the drawing solution, which prolonged the treatment period greatly. In the FO_{MD} hybrid method, where the drawing solution was thinned in FO part and regenerated in the MD part at the same time, the most promising approach had been identified. The two commercial FO membranes showed no satisfactory efficiency because of the internal concentration polarization (ICP) effect owing to the difficulty in equilibrating water transfer rate (WTR). The symmetric FO membrane, on the other hand, showed superior performance in the FO_{MD} process since the FO and MD processes found almost identical WTRs, leading to much lower energy consumption. Potential developments need to be explored, including the viability of specific dyes and the possible use of other solutes, to illustrate the great potential of symmetric FO membrane for use in dye and recycling of wastewater textiles [84].

8.4 Biological and Physicochemical Process

Biological followed by physicochemical processes reverses the order to minimise chemical consumption: after equalisation and nutrient addition the wastewater undergoes high-rate anaerobic treatment (UASB or anaerobic MBR) that removes 70 % of COD and 60 % of colour through reductive dye cleavage and methanogenesis; the partially treated liquor is polished by a low-dose coagulation-flocculation step ($FeCl_3$ 80 mg L^{-1}, poly-aluminium-chloride 40 mg L^{-1}, pH 6.5) that entangles residual dye fragments and biomass fines, followed by gravity settling and a final ozonation or activated-carbon adsorption to oxidise trace organics and strip colour to <20 Pt-Co units, yielding an overall 92 %

COD, 98 % colour and 95 % total-N removal with 50 % less ozone or carbon than physicochemical treatment applied to raw wastewater [8,9].

Coagulation Process with Biological Treatment

The selection between the coagulation followed by biological or biological followed by coagulation scheme is dependent on the characteristics and the dose of coagulant, the quantity of sludge and the inhibition and non-biodegradability of the wastewater substances. Coagulation in alkaline wastewater before biological treatment may be beneficial. Ferrous sulfate cannot be used after biological treatment as the pH is near neutral. In contrast to those used in coagulation accompanied by biological treatment, the dosage of coagulants and thus the amount of the chemical sludge is less [9].

Given the prevalence of bio-resistant and harmful chemicals in textile wastewater, it seems to be a fair choice for specialized physicochemical and advanced oxidative treatment before biological treatment. However, the choice between physical and the type of wastewater determines whether oxidative pretreatment is necessary; a clever sequencing would usually enable the application of the appropriate treatment system for various streams. Conversely, in order to be effective biological pretreatment, especially segregated microorganisms are usually needed. It is necessary to eliminate these materials by means of physicochemical treatment before sufficient treatment, since a high concentration of suspended or colloidal solids can limit advanced oxidation processes. Inverse steps may allow a better physicochemical treatment after AOP, (e.g. after ozonation) or an increase in sludge settling (e.g. after electrofloatation) [8,9].

Table 8 summarizes different combinations of biological and physicochemical treatment methods for the textile wastewater [9]. Figure 10 shows the flow chart that connects all the hybrid treatment technologies.

Table 8. Combination of biological and physicochemical treatment.

Sr. #	Technology	Dye/Wastewater	Details
1	Fluidized Biofilm/Coagulation/ Electrochemical Oxidation	Textile Dyeing Wastewater	69% COD_{cr} (initial = 800-1000 mg/L) and 55% dye removal while those achieved by the complete combined method with $FeCl_3.6H_2O$ dose of 3.25 x 10^{-3} mol/L; Electrooxidation: 2.1 mA/cm^2 of current density and 0.7 L/min current flow rate, were 95% and 99% respectively.
2	Coagulation (Nabentonite)/activated sludge	Plant wastewater from tainting & natural/synthetic fibers finishing	Prior to the chemical pretreatment process (2 g/L), the potential for residual inert COD (biodegradable COD) decreased by 40%, while after biological post-treatment only 20% of the residual soluble COD was obtained leading to better discoloration.
3	Electron-beam treatment/bio	Dyeing process and polyester fiber production wastewater	Pilot plant research with a low dose of E-beam pretreatment (Flow Rates =1000 m^3/d) shows that improved biotreatment efficiency requires reduced (half) household time for the same degree of removal. In contrast to the traditional anticipation of conversion of the non-biodegradable component, the function of the electricity beam was initially biodegradable to further facilitate conversion of the biodegradable part.
4	Biological/flocculation/ O_3 +H_2O_2	Textile Wastewater	Activated flocculation and sludge treatment carried out 85%, 99.5%, 85%, DOC, BOD & COD_{cr} removal (initial values = 277, 220 or 780 mg/L) while subsequent treatment with O_3 + H_2O_2, total eradication of the BOD and over 50% removal of residual DOC, COD_{Cr} (60 min; [H_2O_2]:[DOC] = 1:1). Inversely, the elimination of COD and the rise in BOD (biodegradation) resulted in the single ozonation.
5	Biological/ O_3	Naphthalene-1,5 disulfonic acid (NADSA), a dye precursor	Combined biological fixed bed (with a 1.5 μm solid / liquid separation membrane) and semi-continuous ozonation treatment achieved approx. 80% (initial = 170-340 mg/L) DOC removal with > 50% ozone reduction (0.8 mol O_3/mol DOC) compared with ozone-only consumption.
6	Coagulation or catalytic H_2O_2/bio	Basic Dyes	Chemical precipitation with $FeCl_3$ = 400 mg/L; pH = 9.5 results in 41% COD removal from raw wastewater. After partial oxidation with H_2O_2/COD = 1; Fe^{+3} = 500 mg/L; pH = 3.5; 1 day, achieved 63% COD removal.

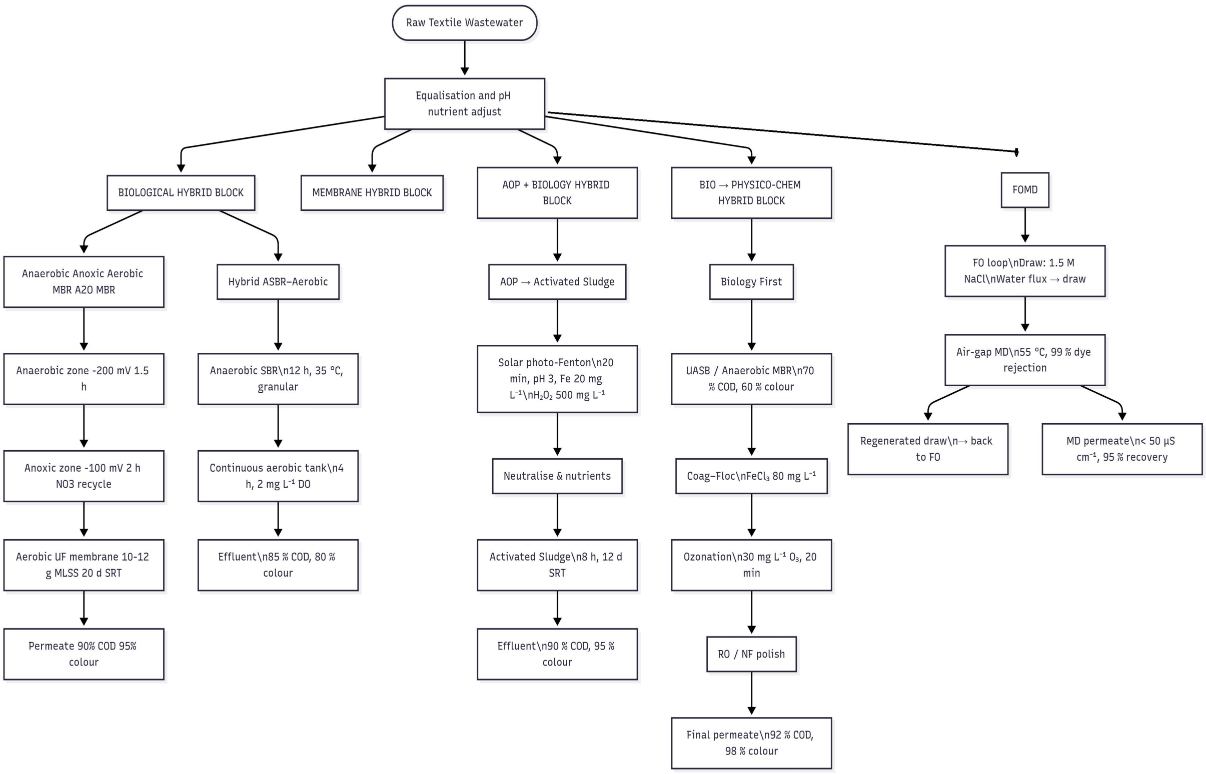

Figure 10. Flow chart that connects all the hybrid treatment technologies.

9. Comparison of Aforementioned Technologies

When the three treatment technologies (1) biological systems (suspended or attached growth), (2) physico-chemical AOPs (Fenton, photocatalytic, ozone, and electrochemical), and (3) hybrid schemes that combine biology with AOP or membrane steps—are compared to the actual drivers of a contemporary dye-house, hybrids turn out to be the best overall choice. A quick scorecard illustrates why pure biology is inexpensive and energy-efficient, but it is unable to break through stubborn chromophores, which results in troublesome sludge or brine. In contrast, hybrid trains combine the advantages of both physico-chemical and biological processes. By placing an anaerobic or short AOP stage first, they reductively cleave azo bonds or generate •OH only on a shrunken, already-partly-oxidised stream, so downstream aerobic or membrane polishing finishes the job at a fraction of the energy and reagent cost. For example, 20 min solar-photo-Fenton followed by activated sludge consumes ≈ 0.9 kWh kg^{-1} COD versus 2.5-3 kWh kg^{-1} for full-stream ozone or RO; A^2O-MBR or FO-MD hybrids deliver particle-free, low-salinity permeate (conductivity <200 µS cm^{-1}, colour <5 Pt-Co) that can be fed straight back to dye-baths [84,91-94]. The biological front-end buffers shock loads of surfactants or dark shades, protecting the expensive AOP/membrane tail, while the latter guarantees removal of non-biodegradable residues, diversifying operational risk and allowing easy retrofit of extra NF, RO or activated-carbon modules when regulations move toward zero-liquid discharge. Sludge or concentrate volumes are typically halved because the high-cost step treats only 15-25 % of the original flow, and overall COD, colour and total-N removals exceed 90%, 95% and 80% respectively. Only for very small mills, extreme salinity or emergency compliance would stand-alone options beat hybrids on life-cycle cost. Therefore, based on colour removal, COD destruction, energy use, sludge footprint, water-reuse readiness and future-proofing, hybrid treatment technologies currently offer the best solution for the majority of textile industries.

10. Future Research Prospects and Recommendations

A substantial amount of research has been carried out on various treatment technologies potentially feasible for textile wastewater treatment [6,9,88-90]. However, a single standalone treatment is not technologically and economically viable to treat recalcitrant textile effluent [84,91-94]. Therefore, a combination of various methods (physicochemical, biological and hybrid methods) is deemed to be possibly an attractive choice to cater to high values of COD, color and nutrients [95-99]. Moreover, bioaugmentation of an already operational wastewater treatment plant with textile-specific bacterial, fungal or algal cultures would not only reduce the cost of already installed plant but would also result in better process control and treatment performance [100-102]. The impact of bioaugmentation in biological treatment systems has not been completely explored which is still considered a research gap. The literature survey carried out for this article also inferred that the effect of various types of pollutants present in textile wastewater on the microbial population present in biological suspended and attached growth processes is yet to be investigated fully [103,104]. The treatment plants employing physico-chemical treatment rather than biological processes affirm better process efficiency due to complete mineralization or oxidation, but cost incurred to treat high organic loads and refractory inorganics is very high as compared to biological methods [97,105,106].

It is pertinent to propose a combination of two or more treatment technologies not only on laboratory scale but on a full scale as well. More focus should be on pilot plant treatability leading towards industrial based application of hybrid treatment systems to meet the stringent international standards of leading brands. Recently, a new paradigm shift has taken place in which modeling of different treatment methods has been examined. Hence, better optimization, operational efficiency and process control can be achieved by developing models against various parameters of selected viable technology.

11. Conclusion

The wastewater treatment plant in a textile industry aims towards maximum treatment of released effluent leading to zero liquid discharges in ultimate cases. These treatment plants have been universally accepted to reduce the pollution loads, comply with stringent effluent regulations and ensure maximum environmental safety leading towards environmental stewardship and sustainability. However, no single universally adopted treatment method is suitable to treat all types of textile effluents. Therefore, a combination of various technologies including physico-chemical, biological and integrated methods is discussed in this article so as to achieve maximum pollution reduction leading to better effluent quality. This review implies that instead of implementing various methods as standalone treatment technology, a hybrid approach would better lead to producing high effluent quality and reusable potential within the same industry.

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Conflict of Interest

The authors confirm that there are no known financial or personal conflicts of interest that could have influenced the findings or interpretations presented in this study.

Generative AI Statement

The authors declare that no Gen AI was used in the creation of this manuscript.

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