






Review

A Comprehensive Review on the Sustainable Treatment of Textile Wastewater: Zero Liquid Discharge and Resource Recovery Perspectives

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Abstract: Clothing, one of the basic needs, demands the growth of textile industries worldwide, resulting in higher consumption and pollution of water. Consequently, it requires extensive treatment of textile effluent for environmental protection as well as reuse purposes. Primary treatment, secondary treatment, and tertiary treatment are the three major phases of textile wastewater treatment. Secondary treatment under aerobic and anaerobic circumstances is carried out to decrease BOD, COD, phenol, residual oil, and color, whereas primary treatment is utilized to remove suspended particles, oil, grease, and gritty materials. However, biological treatment is not fully capable of treating water according to discharge/reuse standards. Hence, tertiary treatment is used to remove final contaminants from the wastewater. Adsorption is regarded as one of the most feasible processes for dye and metal removal in consideration of cost and variation in the adsorbent. Though membrane filtration is an efficient process, the cost of operation limits its application. It's unfortunate that there isn't a universally applicable treatment solution for textile effluents. Therefore, the only flexible strategy is to combine several therapy modalities. Treatment of complicated, high-strength textile wastewater depending on pollutant load will be more successful if physical, chemical, and biological approaches are used in tandem. Enforcement of stringent environmental regulation policies, increasing costs and demand for freshwater, and the rising costs and difficulties associated with wastewater disposal are accelerating efforts toward achieving ZLD. Additionally, research into methods for extracting useful materials from wastewater has blossomed in recent years. As such, the purpose of this analysis is to give a holistic overview of textile wastewater treatment systems, with a focus on zero liquid discharge (ZLD) and efficient resource recovery, both of which may hasten the transition to more sustainable water management.

Keywords: zero liquid discharge; caustic recovery; dye/salt recovery; textile wastewater; dye removal techniques; membrane filtration



Citation: Jahan, N.; Tahmid, M.; Shoronika, A.Z.; Fariha, A.; Roy, H.; Pervez, M.N.; Cai, Y.; Naddeo, V.; Islam, M.S. A Comprehensive Review on the Sustainable Treatment of Textile Wastewater: Zero Liquid Discharge and Resource Recovery Perspectives. *Sustainability* **2022**, *14*, 15398. <https://doi.org/10.3390/su142215398>

Academic Editor: Agostina Chiavola

Received: 24 October 2022

Accepted: 17 November 2022

Published: 19 November 2022

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1. Introduction

One of the most pressing global concerns that affect environmental stability, ecosystem health, and long-term economic development is meeting the rising demand for water that has resulted from the worldwide expansion of industry [1–4]. The industrial sector is responsible for a significant proportion of the world's total water usage. The textile industry is well-known for producing wastewater that contains significant amounts of

wasted dyes and chemicals, which are very harmful to aquatic environments and the lives inside them [5]. In different stages of textile wet processing operations, water is consumed for sizing/de-sizing, scouring, bleaching, mercerizing, dyeing, printing, and finishing. It has been reported that around 100–200 L of water is needed in the processing of 1 kg of the textile product, depending on the type of process [6]. Inadequate treatment and subsequent release of this large amount of hazardous chemical-laden water may cause severe aquatic environment contamination, affecting aquatic ecosystems and, consequently, human health [7]. Therefore, efficient textile wastewater treatment has been prioritized by water experts and environmentalists to operate the textile industry in a sustainable way and avoid jeopardizing nature [8].

In the last few years, textile wastewater treatment has evolved significantly from its origin [9]. The first two stages of wastewater treatment, e.g., primary and secondary, were established and standardized by many water experts over the years [10]. However, the scientific community has put a lot of effort into advancing the third stage or tertiary wastewater treatment process. Earlier, the primary objective of textile wastewater treatment was the safe disposal of wastewater without the concept of reusing and resource recovery [11]. However, the wastewater treatment perspectives have now shifted towards advanced treatment and subsequent recovery, particularly in regions where water is a scarce resource [12]. The stringent regulations and legislations worldwide have mandated industries to adopt sustainable water management strategies to reduce water consumption and reclaim water to be reused to minimize environmental impact [13]. In the wet processing of textiles, there are a large number of distinct wastewater streams, each of which has its own unique properties [14,15]. These characteristics are determined by the treated materials, processing techniques, chemicals utilized, and other factors. It has been claimed that roughly 60–90% of the process water is typically utilized for rinsing and washing, which may be readily cleaned and recycled back into the process [16]. Additionally, the water that is contaminated with dyes, salts, and other chemicals may be treated using a variety of methods, which will lead to an increase in the amount of water that can be reclaimed and the number of chemicals that can be recovered. Because of this, the techniques for treating wastewater and the recovery of resources from wastewater have recently been important areas of study [17,18].

Until now, scientists have proposed different tertiary treatment techniques, e.g., adsorption, electrochemical processes, advanced oxidation, and membrane-based filtration, to achieve the highest treatment efficiency [19,20]. In different countries, the concept of zero-liquid discharge has revolutionized the wastewater treatment process. Zero-liquid discharge (ZLD) technology's ability to optimize water recycling while simultaneously lowering wastewater quantities has sparked widespread interest in its potential for reuse and resource recovery [21]. The ZLD techniques use a closed water cycle to ensure that any water that can be recycled after being properly treated is kept inside the system [22]. The clean water movement, declining groundwater levels in different countries, enforcement of stringent environmental regulation policies, increasing costs and demand for freshwater, and the rising costs and difficulties associated with wastewater disposal are accelerating efforts toward achieving ZLD [23,24].

The ZLD concept has been misunderstood by many researchers over the years in terms of its applicability and usefulness. The ZLD concept does not only deal with water reuse; the recovery of chemicals used in the total process has been an inherent goal of ZLD [25]. Thus, to achieve the ZLD goal in textile industries, comprehensive and in-depth knowledge of the overall textile wet process is required. Moreover, distinguishing different wastewater treatment techniques is also important for selecting the best treatment combination to satisfy the ZLD agenda.

In this review, we aim to provide a comprehensive overview of the sustainable treatment of textile industry wastewater, in particular ZLD-based technology, which is the first time in literature based on the author's knowledge. Firstly, different stages of the textile processing operation and effluent characteristics are discussed in order to identify

opportunities for implementing water management options. Next, different effluent treatment methods, with a particular focus on tertiary treatment methods, are outlined. This is followed by an in-depth review of the state-of-the-art resource recovery techniques that may be applied in the textile industry to reclaim and reuse valuable resources, including caustic solutions and salts. Finally, we leave some concluding remarks regarding the way forward and future research perspectives on ZLD of textile industries.

2. Stages of the Textile Processing Operation and Effluent Characteristics

There are both dry and wet processes involved in the manufacturing of fiber in textile mills. The wet processes use a significant amount of water and, as a result, discharge highly polluted effluent. The procedures of sizing, de-sizing, sourcing, bleaching, mercerizing, dyeing, printing, and finishing are included in this step of processing [26]. This section will provide a concise explanation of these steps in the wet processing of textile materials. In addition, the characteristics of the effluent are shown in Figure 1, together with the primary components of the effluent that are discharged with the wastewater at each phase. The fibers are given additional strength by the process of sizing, which comes before weaving or spinning [27]. Sizing ingredients often include things such as starch, polyvinyl alcohol, carboxymethyl cellulose, and similar compounds. A typical textile mill produces around 60,000 square meters of fabric per year, and the wastewater that is released from the mill includes roughly 750 kg of sizing material [28]. The molecules of dye have a difficult time diffusing into the yarn or fabric due to the presence of the sizing compounds. Before the cloth goes through any further processing, it must first go through a process called desizing, which involves either hydrolysis or oxidation to remove the sizing ingredients. Desizing may be accomplished with the help of enzymes, alkalines, acids, or surfactants [29]. The oxidation of starch by hydrogen peroxide results in the formation of carbon dioxide and water; enzymes, on the other hand, are responsible for the transformation of starch into ethanol. Scouring is used to remove the different impurities (natural waxes, oils, minerals, pectins, non-cellulosic components, herbicides, pesticides, etc.) that the fibers contain, which obstruct dyeing and finishing. Less scouring is needed for synthetic fibers than for cotton or wool. Generally, hot alkali, detergents, soap solutions, etc., are used as scouring solvents [30,31].

Bleaching is a process that is used to eliminate the natural color content of cloth, which results in the fabric taking on a creamier appearance. Cotton and yarn are the most common substrates for its application, but wool and synthetic fibers may also be used on occasion [32]. Bleaching agents include substances such as hypochlorite, hydrogen peroxide, and peracetic acid, among others; nevertheless, when compared to the other bleaching agents, peracetic acid is the least harmful to the environment [33,34]. Following the bleaching process comes the mercerization step, which is performed to add strength, increase luster, and enhance dye absorption. For the mercerizing process, either zinc chloride or a strong caustic soda solution of around 18–24% (which has to be neutralized by a final acid wash) is used. It is possible to recover sodium hydroxide by utilizing a membrane separation or a multiple-effect evaporator, both of which help to minimize the amount of NaOH that is used [35].

Dyeing refers to the process of imparting color to cloth by treating it with chemicals, often known as dyes and pigments. Natural dye and synthetic dye are the two kinds of dyes that are frequently used in the textile industry. In comparison to natural dyes, synthetic dye is used more often since it is simpler to produce, comes in a wider variety of colors, and does not fade as easily. There is a wide variety of poisonous dyes and compounds that result from their breakdown. In order to improve the amount of dye that is absorbed by the fibers, it is possible to add various chemicals. Some examples of these chemicals are heavy metals, salts, sulfides, surfactants, and formaldehyde. The majority of the dyeing process's byproducts, including metals, salts, and colors, may be found in wastewater from the textile industry. The dyeing process causes an increase in the electrical conductivity of the material [36]. This effect is caused by the use of sodium carbonate and salt. When

dyes with low fixing qualities are employed, the effluent from dyeing industries becomes increasingly contaminated. For instance, reactive dyes have a smaller fixing range than cotton and viscose, which may be anywhere from 20–50% [37]. In printing, dyes are added as a thick paste to a selected section of the fabric to build the design. Urea, PVC, phthalates, gums, binders, etc., are used as printing substances. Printing wastewater has a higher concentration of pollutants compared to dyeing wastewater [9].

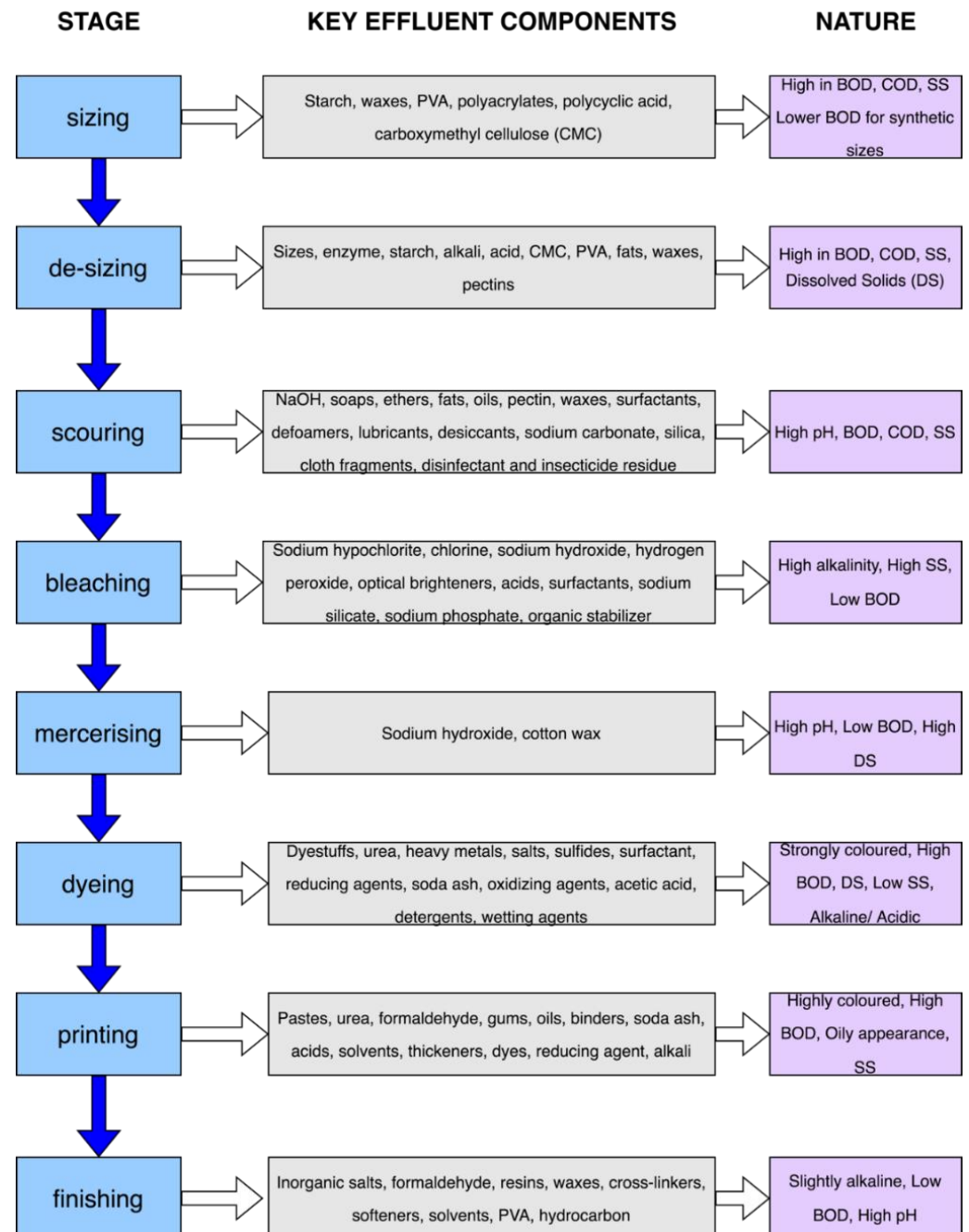


Figure 1. Wet processing stages with key effluent components and nature of the wastewater discharge from each stage.

The textile finishing process is used to develop definite properties (softening, flame-proof, anti-bacterial, mothproof, waterproofing, rotproof, UV protective, etc.) in the fabric. Wastewater from the finishing process is low in volume but can contain toxic substances such as biocides used to provide anti-microbial characteristics, pentachlorophenols,

ethylchlorophosphaes, etc. [38]. Wastewater effluent from different processes of the textile industry shows different characteristics based on fabrics processed, processing ways, chemicals used, etc. These characteristics are very important factors in selecting the treatment process, the dosage of treating chemicals, and many other factors. The effluents produced by the various steps of the textile processing stage are distinct from one another in terms of their composition and properties. In general, each section has produced some wastewater, namely a small portion from the sizing, desizing, scouring, bleaching, printing, and finishing stages. However, a relatively large amount of wastewater is produced in the dyeing stage because of dyestuffs' recalcitrant nature [39,40]. Characteristics of the effluent from each of these stages are presented in Table 1.

Table 1. Characteristics of effluent from different textile wet processing stages.

	Wet Processing Stages							Ref
	Sizing	De-Sizing	Scouring	Bleaching	Mercerizing	Dyeing	Printing	
pH	7–9.5	5.83–8	10–13	6–11.6	5.5–14	5–12.5	4–9	[27,41–45]
COD (mg/L)	-	4600–15,000	1470–8000	1149–13,500	100–2688.5	1100–4600	785–49,170	[27,41–45]
BOD (mg/L)	600–2500	4400–5060	100–2900	50–1700	20–300	10–1800	400–1800	[27,41–45]
Sulfate (mg/L)	-	-	68.5	76.3	-	224.9–758.7	-	[42]
Chloride (mg/L)	-	-	342.4	90–516	199.5	213.3–26,000	-	[27,42,43]
Copper (mg/L)	-	-	-	-	-	0.38–0.43	-	[42]
Chromium (mg/L)	-	-	-	-	-	0.39–1.23	-	[42]
TDS (mg/L)	-	8700–10,200	6323	2400–22,000	5000–12,000	35,000	2000	[27,41]
TS (mg/L)	-	76,000–32,000	7600–17,400	2300–14,400	600–1900	500–50,000	2500	[27,41,44]
TSS (mg/L)	-	400–4000	-	288.5	105.2	499.4	125–9500	[27,43]
SS (mg/L)	240–260	200–270	55	420–6500	2200	26,000	15,000–20,000	[41]
NO ₃ ⁻ (mg/L)	-	-	-	5.54	9.4	6.06	-	[41,43]
NH ₄ ⁺ (mg/L)	-	-	-	8.0	8.53	14.34	20–370	[27,43]
H ₂ S (mg/L)	-	-	-	5.44	1.31	1.62	-	[43]

3. Treatment Methods

The process of treating wastewater from textile mills typically consists of three core stages: primary, secondary, and tertiary treatment. Throughout each of these processes, various impurities are eliminated, resulting in cleaner water. In general, the primary treatments involve the removal of SS, floating, and gritty materials; the secondary treatments involve the reduction in oxygen demands, other chemicals, and the color of the pollutant; and finally, the tertiary treatments involve the removal of any final contaminants that are still present in the pollutant after the primary and secondary treatments have been completed. In this analysis, numerous techniques for treating the dye in textile wastewater and reducing the pollutant load were addressed. These techniques have the potential to be implemented. Figure 2 shows a recommended logic diagram to guide the selection of possible treatment methods. BOD₅/COD₅ test should be conducted, followed by primary

treatment, to assess the biodegradability criteria. Yukseler et al. [46] have mentioned the reuse criteria of textile wastewater for different parameters such as COD, color, pH, turbidity, TDS, TSS, etc. Moreover, Katheresan et al. [47] listed the international standard for dye effluent discharge. Depending on the analysis results, the treated stream can either be recycled as process water towards the manufacturing section or discharged into the environment.

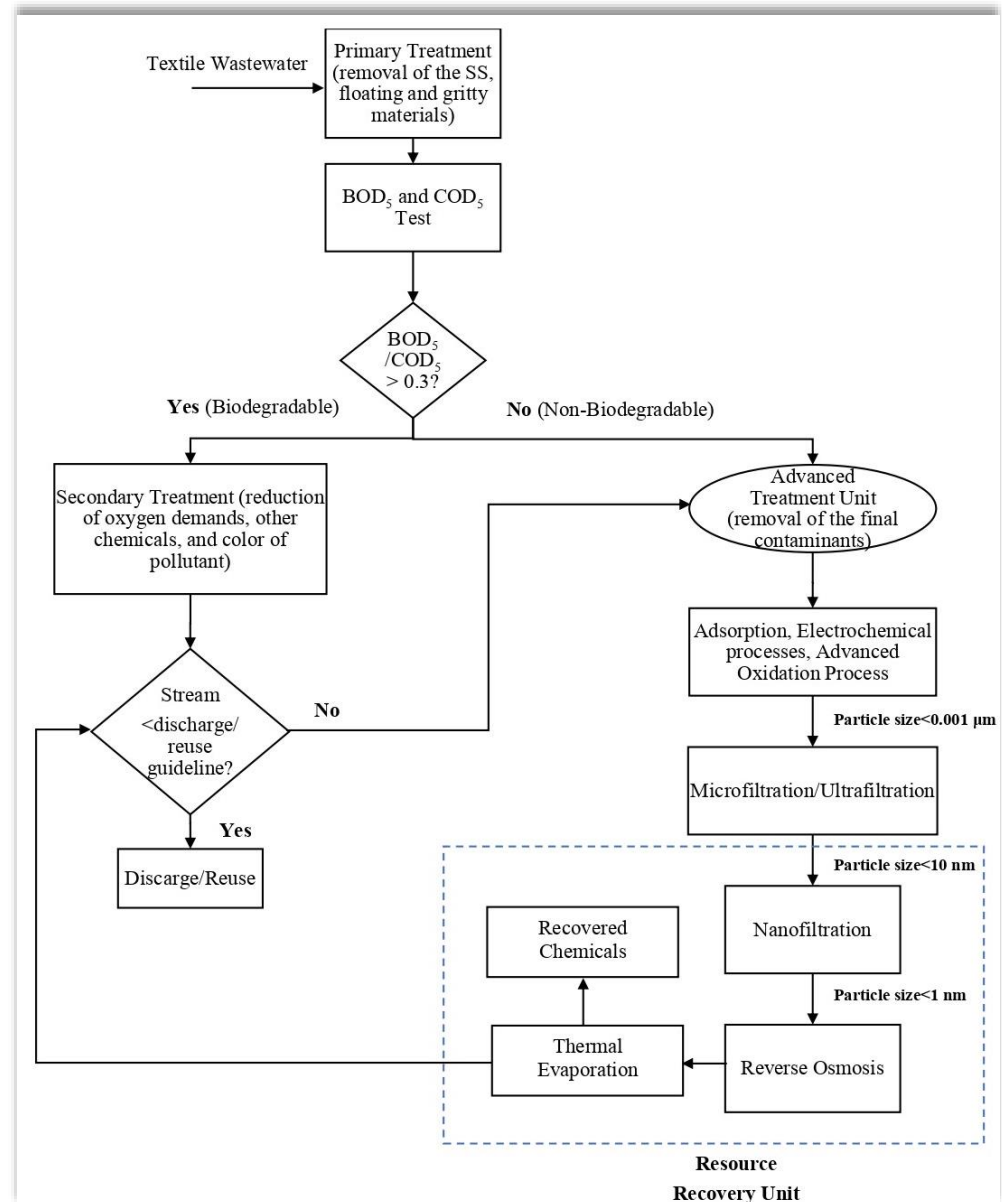


Figure 2. Logic diagram for the selection of wastewater treatment method.

3.1. Primary Treatment

Primary treatment is comprised of physical methods such as screening, sedimentation, equalization, neutralization, chemical coagulation, and mechanical flocculation [48]. Effluent from different stages generally carries coarse suspended particles, including yarns, lint, cotton, pieces of fabrics, fibers, and rags [49]. These may clog pipelines, machineries, and other treatment units if not removed. Therefore, screens of different sizes and shapes are used to remove these particles [41,50]. Next, the effluent undergoes sedimentation for the removal of fine suspended particles. When passed through slowly, suspended particles, i.e., clay or silts, gritty materials present in the effluent, settle at the bottom of sedimentation

tanks due to gravity force [51]. The settled sludge is removed using mechanical scraping from the sedimentation tanks, which can further be treated before disposal [52]. Scum, such as oil and grease floating at the top of the sedimentation tank, is removed by a skimmer.

Generally, textile effluent from various operational stages varies significantly in color, turbidity, pH, BOD, COD, TDS, and other characteristics. In this regard, equalization becomes one of the most important stages which controls the effluent flow velocity and composition to reduce shock loads [53]. By enabling the wastewater to mix and acquire a consistent quality prior to being sent at a continuous pace to the remaining treatment units, equalization boosts the efficiency of secondary and advanced wastewater treatment operations [54]. Afterward, neutralization helps in achieving a uniform pH ranging between 5 to 9 by removing excess acidity or alkalinity in wastewater [55]. Sulfuric acid and boiler flue gas are reported to be mostly used chemicals in altering pH. Other common acid reagents include concentrated (66°Be) sulfuric acid, concentrated (20 or 22°Be) hydrochloric acid, carbon dioxide, sulfur dioxide, and nitric acid. Moreover, caustic soda (NaOH), ammonia, soda ash (Na₂CO₃), hydrated chemical lime (Ca[OH]₂), and limestone (CaCO₃) are used as basic reagents [54]. Since simple sedimentation occupies a large space and is not effective in the removal of colloidal particles, chemical coagulation and mechanical flocculation are employed for the removal of these particles. Effluent colloidal particles have charges on their surfaces, and when chemicals are added to the effluent, the colloidal particles' surface properties change, causing them to coagulate and settle. Alum, poly aluminum chloride, ferrous and ferric chloro-sulfates, and ferric chloride are commonly applied coagulants [56,57]. Mechanical flocculation is a physical process that enables small particles to agglomerate and settles through mixing with paddles [58]. The process produces a considerable volume of sludge, and the disposal of sludge is one of the biggest challenges. Alum sludge combined with chitosan coagulants has been found to be an effective CEPT (chemically enhanced primary treatment) alternative to traditional coagulants in laboratory experiments [59]. This combination extensively reduced the cost of high-volume sludge disposal associated with the sole use of alum sludge.

3.2. Secondary Treatment

The primary component of the secondary treatment technique is a biological treatment, which involves the breakdown of the organic content in wastewater that may be broken down biologically by microorganisms such as algae, fungi, and bacteria in either an aerobic or anaerobic environment [60]. Biological treatment procedures are able to be categorized as either aerobic, anaerobic, anoxic, or a mix of these, depending on whether or not oxygen is present in the environment. The elimination level of BOD and COD, which is between 80 and 85%, is accomplished by the breakdown of soluble organics by bacteria [41]. Suspended and attached growth processes are two examples of typical bioprocesses that may be used for the treatment of wastewater from the textile industry [61]. The effectiveness of biological treatment is affected by a variety of parameters, including organic loading, the concentration of microorganisms, temperature, the presence of hazardous chemicals, nutrition levels, and oxygen content [5]. The structure of the dye, as well as the microbial system itself, are both factors that influence the method by which microorganisms degrade dye. Table 2 presents a variety of experimental conditions, including pH, initial dye concentration, length of incubation time, and temperature, for a variety of combinations of dye and microorganisms.

Table 2. Various microorganisms are applied for dye degradation.

Dyes	Name of Strain	Types of Microorganism Culture	Experiment Condition				Removal (%)	Ref
			IDC ** (mg/L)	pH	Temp.** (°C)	Incubation Period (h)		
Congo Red	Acinetobacter baumannii MN3	Bacteria	100	8	37	5 h	89	[62]
Azure-B	Serratia liquefaciens		100	7.6	30	48 h	>90	[63]
Reactive red 120	Bacillus cohnii RAPT1		200	8	35	4 h	~100	[64]
Acid blue 93, and basic violet 3	Pseudomonas putida MTCC 4910		50	6–7	37–45	48 h	~100	[65]
Acid blue 25	Bacillus sp1		300	8	37	48 h	74	[66]
Reactive green	Candida sp. VITJASS		100	7	30	4 days	84	[67]
Acid Red 88	Achaetomium strumarium	Fungus	10	4	40	4 days	99	[68]
Acid Red 18	Paraconiothyrium variabile		100	5	40	15 min	97	[69]
Scarlet RR	Peyronellaea prosopidis		10	6	35	5 days	90	[70]
Malachite Green	Bjerkandera adusta SWUSI4		50	5	26–30	24 h	>90	[71]
Reactive Black 5	Chlorella vulgaris	Algae	200	5	40	10 days	80	[72]
Methyl Red	Nostoc lincki		20	7	24–26	7 days	~82	[73]
Basic Red 46	Enteromorpha sp.		15	1	25	5 h	83.45	[74]
Basic Fuschin	Oscillatoria rubescens		5	7	24–26	7 days	~95	[73]
Direct Blue 71	Chlorella vulgaris		300	8	40	10 days	78	[72]

** IDC—Initial dye concentration, Temp.—Temperature.

Aerobic microorganisms use oxygen to metabolize suspended solids, organics (BOD and COD), color, and nutrients. The treatment process is environmentally friendly, cost-effective, and efficient as it turns the pollutants into different stable products [75]. Degradation rates are affected by a variety of factors, including but not limited to temperature, hydraulic retention time (HRT), nutrient availability, pH, food-to-microorganism (F/M) ratio, aeration/oxygen transfer rate, organic loading rates, and so on [60]. A rotating biological contactor (RBC) is a kind of aerobic reactor often employed in the treatment of textile wastewater. Good interaction between organics and microorganisms is facilitated by the high interfacial area offered by the revolving disk [76]. Vairavel et al. carried out a decolorization study of Congo Red dye using a rotating biological contactor (RBC) reactor, achieving maximum color removal of 90.15% at 303 k and pH 6. The experiment was conducted with 20 discs (40% submergence) rotating at 16 rpm while maintaining an air flow rate of $1.5 \text{ L} \cdot \text{min}^{-1}$ for $50 \text{ mg} \cdot \text{L}^{-1}$ inlet dye concentration. Their experimental data indicates that both biomass production and color removal increase substantially with the increase in disc number, rotation speed, and percent disc submergence in the liquid medium. Major disadvantages of this reactor include—difficulties in scale-up, a larger area requirement, susceptibility to shock loads, etc. Albahnasawi et al. investigated the performance of an aerobic sequential batch reactor with varied hydraulic retention times in treating real textile wastewater. Their proposed system resulted in 86.6% COD and 62.44% color removal for 12 h retention time. Moreover, increasing the retention time four times yielded 90% COD removal. Though this reactor occupies less space and is capable of handling fluctuations in the influent, it requires higher maintenance expertise. Another promising reactor is the membrane bioreactor which can replace three conventional treatment units (conventional activated sludge process and tertiary filtration) with a single compact unit [76]. Khouni et al. assessed the performance of an aerobic membrane bioreactor for treating dyeing effluent at a laboratory scale. Their findings show the vital role of biomass concentration in dye removal from textile effluent. Even 100% decolorization was achieved with a biomass concentration of $8 \text{ g}_{\text{MLVSS}} \cdot \text{L}^{-1}$ for $7.5 \text{ mg} \cdot \text{g}_{\text{MLVSS}}^{-1} \cdot \text{d}^{-1}$ dye concentration. Except for the membrane clogging problem and screened feed stream requirement, this reactor is a very good option for the biological treatment of wastewater which can operate with high sludge

concentration. Moreover, aerobic fluidized bed bioreactors are capable of handling a large volume of wastewater with a lesser retention time [61,76]. This reactor has found good application in treating hospital wastewater, removing nitrate from petroleum industry-produced wastewater, etc. [77,78]. However, control of bed expansion and attrition of solids may cause difficulties in its operation [76]. Balaji et al. evaluated the performance of an aerobic fluidized bed bioreactor for the decolorization of synthetic wastewater, which resembled real textile effluent characteristics. Their findings showed a maximum COD and color removal of 83.3% and 89%, respectively, for a COD concentration of 750 mg/L.

Two types of circulating fluidized bed bioreactors (CFBBR) are represented in Figure 3. The fundamental difference between the two is that Figure 3a consists of two fluidization regimes, while Figure 3b consists of only one. Moreover, the CFBBR system has liquid-solid separators at the top of each column. The riser operates in the circulating regime (high enough fluid velocity to entrain particles), and the downer operates in the conventional regime (low fluid velocity incapable of entraining particles). At the top of the riser, the gathered particles are transferred to the downer. Since the particles are more densely packed in the downer, the biofilm surrounding these particles is lost due to abrasion resulting from a collision between them. So, the downward flow of particles is enhanced in the downer due to their increased density. The solids collected at the downer's base are recycled up the system. Effluent is collected from the downer's LS separator, where the vast majority of solids are removed for sludge disposal. The leftover fluid is recycled between the downer and the riser. Both the downer and the riser function under anaerobic environments, with the former being used for biological organic oxidation [79]. Figure 3b illustrates a schematic of a CFBBR system with two columns, both of which operate in the conventional regime, as opposed to the aforementioned system. Since there is no constant siphoning between the two columns, one of them may be considered aerobic while the other is anaerobic. The shear rate is less than in the preceding system since both columns are functioning in the conventional regime. This results in a reduced rate of separation and an increased period during which solids are retained [80]. The advantages, disadvantages, and applications of some commonly used aerobic reactors are represented in Table 3.

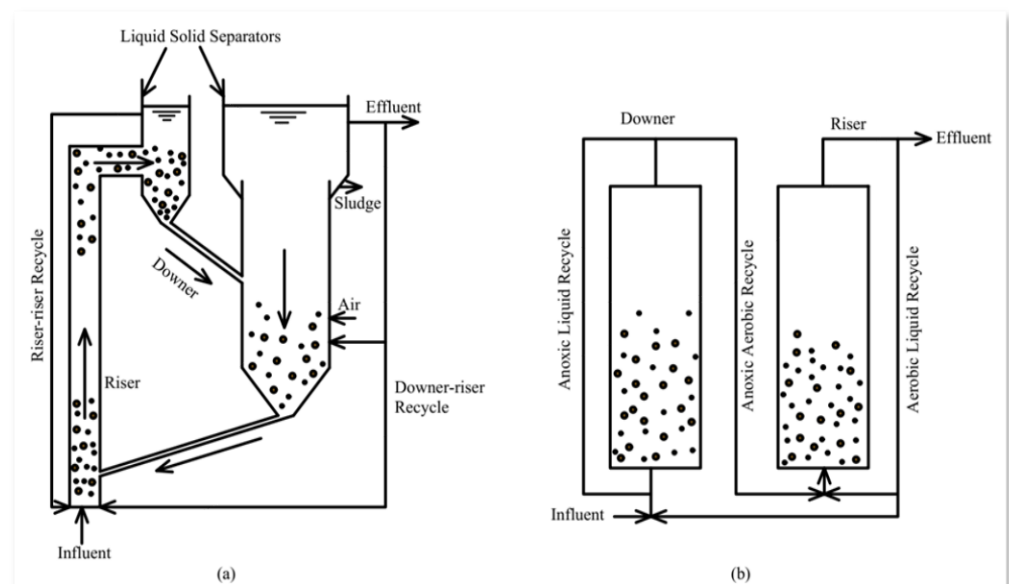


Figure 3. Schematic diagram of two types of Circulating Fluidized Bed Bioreactor containing a) two fluidization regimes, b) one fluidization regime [81].

Table 3. Advantages, disadvantages, and application of some commonly used aerobic biological reactors.

Name of the Aerobic Reactor	Rotating Biological Reactor	Sequencing Batch Reactor	Membrane Bioreactors	Fluidized-Bed Bioreactors
Description	Attached is the growth biofilm system	Suspended growth batch bioreactor	Suspended growth bioreactor	Suspended/attached growth bioreactor
Advantage	<ul style="list-style-type: none"> good contact between organics and microorganisms low maintenance and operational cost 	<ul style="list-style-type: none"> occupies less space capable of handling fluctuations in influent 	<ul style="list-style-type: none"> easy sludge separation can operate with high sludge concentration 	<ul style="list-style-type: none"> capable of handling a large volume of wastewater lower hydraulic retention time
Disadvantage	<ul style="list-style-type: none"> difficult to scale up requires large space susceptible to shock loads 	<ul style="list-style-type: none"> requires sophisticated control units and more automation requires expertise for maintenance 	<ul style="list-style-type: none"> clogging in membrane requires screened (1–3 nm) feed stream 	<ul style="list-style-type: none"> difficulties in control of bed expansion attrition of solids may occur
Application	<ul style="list-style-type: none"> high load industrial wastewater treatment pharmaceuticals and complex compound removal chemical agriculture waste bioremediation 	<ul style="list-style-type: none"> high-strength wastewater treatment domestic wastewater landfill leachate 	<ul style="list-style-type: none"> high-strength industrial wastewater treatment pharmaceutical and chemical wastewater treatment oilfield wastewater 	<ul style="list-style-type: none"> hospital wastewater treatment high organic load wastewater treatment nitrate removal from petroleum industry wastewater
References	[76,82,83]	[84–87]	[12,76,88]	[61,76–78]

Because of their chemical structure, azo dyes are resistant to aerobic breakdown and, instead are often digested anaerobically through biotic and abiotic interactions [89]. In the lack of oxygen, anaerobic microbes decompose organic contaminants. Organic pollutants with high molecular weight are broken down into smaller molecules in the anaerobic reactor, making them more manageable for the aerobic reactor. With a combination anaerobic-aerobic bioreactor, Song et al. showed that a noble biological approach is possible for treating textile effluent containing polyacrylate. They used an air-lift external circulation vortex enhancement nitrogen removal fluidized bed bioreactor (AFB) and a spiral symmetry stream anaerobic bioreactor (SSSAB) to remove 95.2% and 96% of COD and $\text{NH}_4^+\text{-N}$, respectively, from their experimental setup. This SSSAB reactor's efficiency is enhanced by its novel design, which has three separate reaction zones and centers on the anaerobic three-stage theory offered by elliptical plates. Textile dye removal is another strong suit of up-flow anaerobic sludge blanket (UASB) reactors. According to Somasiri et al., a UASB reactor can remove more than 90% of the COD and 92% of the color from genuine textile effluent. Figure 4 shows a diagram of a UASB reactor, which is a submerged anaerobic sludge bed where the substrate is pumped. The water comes in at the bottom and rises to the top in a vertical motion. The reactor has a digestive area and a settling area. High solid retention time is achieved by maintaining a high sludge concentration in the reactor throughout the digestion zone. There is little hydraulic retention time. The deep sludge bed makes excellent contact with the up-flowing substrate. Biogas bubbles are created in the sludge bed (digestion zone) and rise through the bed to combine with the sludge. Baffles help channel methane bubbles into the separators. Because there is no turbulence in the settler compartment, settlement takes place there. When solids reach the settler, they stay there for a while before slipping back into the sludge bed [90,91]. The key benefits of this reactor are its low sludge formation rate, simple design, high organic load handling capacity, and cheap operating and maintenance costs [92]. The drawbacks of this reactor include a lengthy start-up time, the release of unpleasant odors and gases, gas leaks, and corrosion-related upkeep.

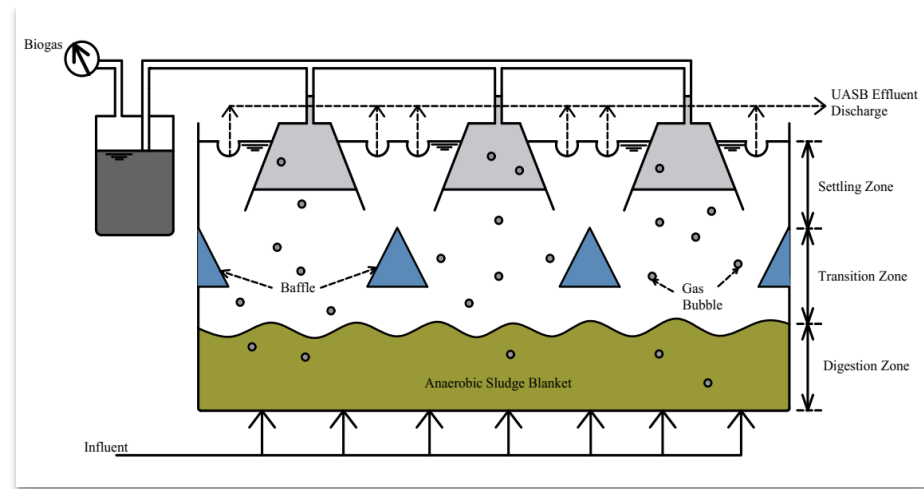


Figure 4. Schematic diagram of different components and zones of a UASB reactor [90].

Among the possible reactors, the anaerobic baffled reactor (ABR) stands out for its many benefits, such as its cheap construction cost, its ability to longitudinally split processes, its longer solid retention time, its independence from hydraulic retention time, etc. [93]. For around 400 days, Ozdemir et al. evaluated azo dye degradation in a sulfidogenic anaerobic baffled reactor (ABR) at 30 °C and 2 days of hydraulic retention time (HRT). The effective removal of COD and environmentally friendly treatment of dyeing effluents were made possible by dividing the tank into four equal compartments separated by vertical baffles. At a COD/sulfate ratio of 0.8, azo dye and COD removals were both at their maximum of 98%. Dye removal efficiency had little effect on increasing COD/sulfate ratios.

3.3. Tertiary and Advanced Treatment

Synthetic dyes are stable, non-biodegradable compounds that cannot be efficiently removed by physical, chemical, or biological means. Many years have been spent on the development of cutting-edge treatment procedures that are effective, affordable, flexible, and user-friendly. Adsorption, photocatalysis, enhanced oxidation, and electrochemical process are only a few of the cutting-edge techniques used to purge color from wastewater. Many of these methods, however, are prohibitively expensive, particularly when used to handle massive quantities of garbage.

However, due to the shown effectiveness in the removal of organic and mineral contaminants, simplicity of operation, and cheap cost, adsorption methods appear to offer the greatest promise for future usage in the treatment of industrial wastewater. It is a physical process in which soluble molecules, known as adsorbate, are removed from a solution by attaching themselves to the surface of a solid substrate, known as an adsorbent. The process by which a textile dye or heavy metal is adsorbed onto the surface of an adsorbent may be explained in one of two different ways: either via physical adsorption or through chemical adsorption. Chemical adsorption requires a reaction or the creation of a complex between the adsorbent and the adsorbate, while physical adsorption takes place as a result of interactions involving the Van der Waals forces, hydrogen bonds, and—forces. The structure and functional qualities of the surface of both the adsorbent and the adsorbate are what define the kind of interaction. It is referred to as biosorption when the process of dye adsorption takes place on either live or dead microbial cells. The physical structure of the dye does not get fractured during this process, as it does during biodegradation; rather, the dye and the pollutant become trapped inside the matrix of the microbial biomass [94]. Activated carbon, biochar, chitosan, clay, resins, zeolite, and other substances such as these are examples of common adsorbents. However, considerable investigations are being conducted in order to identify low-cost adsorbents produced from agricultural waste for the

effective removal of dye and heavy metals from wastewater [95,96]. Additionally, efforts are being undertaken to manufacture novel adsorbents for the simultaneous removal of heavy metals and organic dyes. These adsorbents will be used in this process. In addition, researchers discovered that nanoparticles demonstrate better effectiveness and quicker removal compared to traditional adsorbents owing to their huge surface area and porosity [97,98]. It has been found that the adsorption effectiveness of metal oxide composites is greater than that of single metal oxides [99]. Particle diameter, adsorbate concentration, temperature, pH, and other variables are some of the most important elements that influence adsorption. Because of its superior decolorization effectiveness for wastewater containing a wide range of colors, the procedure has garnered a substantial amount of interest in recent years. The primary disadvantage of adsorption is that it is a time-consuming process, and the sludge that is formed as a byproduct of this process may be difficult to manage. The results of the use of a number of different adsorbents, which were effective in removing a number of dyes and heavy metals from aqueous solution, are shown in Table 4.

Table 4. Different types of adsorbents are used in the process of cleaning textile effluents of dye and heavy metal.

Dye/Heavy Metal	Adsorbent	Experimental Condition						Percent Removal (%)	Mechanism Involved	Adsorption Model		Ref
		pH	Adsorbent Dose (g/L)	IDC (mg/L)	Maximum Adsorption Capacity, q_m (mg/g)	Contact Time	Temp. (°C)			Kinetic Model	Isotherm Model	
Malachite green	Potato leave powder	7	2	10	33.3	33 min	30	75	-	Pseudo-second-order	Freundlich	[100]
Acid blue 92	Carbon nanotube	3–11	0.01–0.21	10–200	86.91	75 min	60	99.4	hydrogen bonds, dipole-dipole bonds, London dispersion interactions, π - π interactions, hydrophobic effect	Pseudo-second-order	Langmuir	[101]
Methyl Orange (MO)	Polyaniline-kapok fiber nanocomposite	6	1–2	200	136.75	24 h	25	-	electrostatic interaction	Pseudo-second-order	Langmuir	[102]
Crystal violet (CV) dye	Olive leaves powder	7.5	2	50	181.1	20 min	25	99.2	electrostatic interaction	Pseudo-second-order	Langmuir	[103]
Methylene Blue	Reduced graphene oxide	7	0.1–0.25	350	2000	7 h	25	93.47	π - π interactions, hydrogen bonds, electrostatic interaction	Pseudo-second-order	Langmuir	[104]
Chromium (Cr)	Mixed waste tea	2	2	10–30	94.34	180 min	30–50	~100	-	Pseudo-second-order	Freundlich	[105]
Iron (Fe)	Activated carbon from cocoa pod	6.4	1–6	25–150	37.45	180 min	30	99.19	electrostatic interaction, van der Waal's force	Pseudo-second-order	Langmuir	[105]
Copper (Cu)	Chitosan/orange peel hydrogel composite	5	40	100	116.64	360 min	28	82.47	electrostatic interaction, sharing of electrons	Pseudo-second-order	Freundlich	[106]
Cadmium (Cd)	Rice husk	3–7	0.1–0.7	10–250	137.16	120 min	15	93.73	ion exchange and chelation	Pseudo-second-order	Langmuir	[107]
Lead (Pb)	Polyaniline-kapok fiber nanocomposite	6	1–2	200	63.60	24 h	25	-	ion exchange and electrostatic interaction	Pseudo-second-order	Langmuir	[102]

3.3.1. Electrochemical Processes

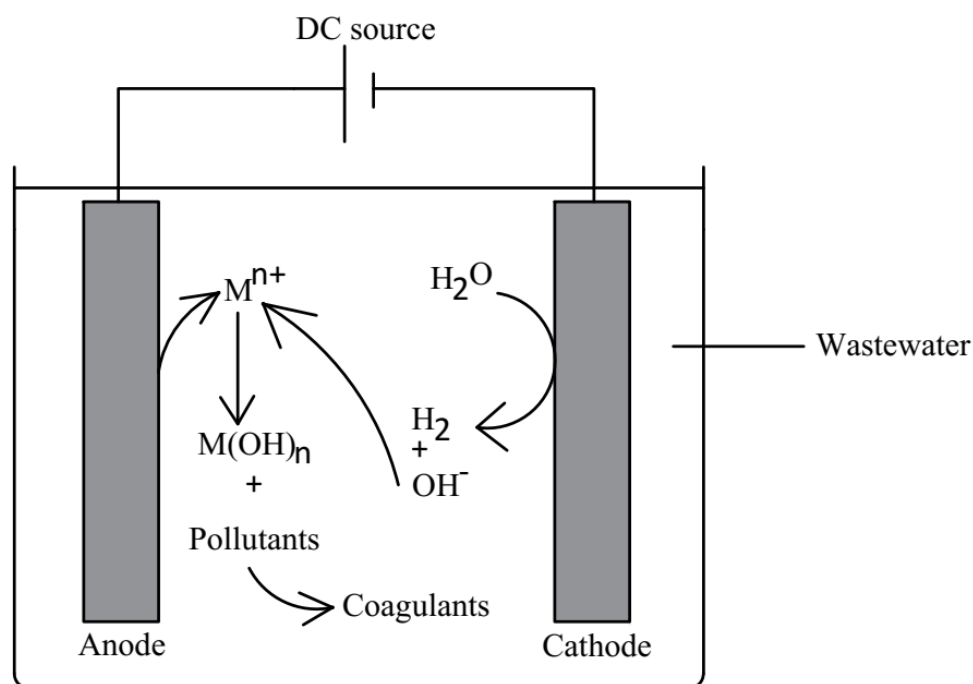
Electrochemical discoloration focuses mostly on the degradation of reactive dyes, which account for around 20–30% of the overall market owing to the robustness and radiance of their colors. In general, biological treatments are insufficient for color removal, physicochemical processes produce residue requiring additional treatment and the absorbent materials need regeneration after several uses. The main advantage of electrochemical treatments is the production of less or no sludge [108]. Dye and heavy metal removal percentages, along with the experimental conditions, have been summarized in the following Table 5.

Table 5. Textile dye and heavy metal removal using different electrochemical processes and experimental conditions.

Dye/Heavy Metal	Electrochemical Method	Electrodes	Concentration (mg/L)	Time (min)	Current Density (mA/cm ²)	pH	Percent Removal (%)	Ref
Basic Red 18	Electrocoagulation	Al-Al	50	60	-	7	97.7	[109]
Acid Red 73	Electrocoagulation	Al-SS	25	60	16	7	99	[110]
Lead (Pb)	Electrocoagulation	Fe-Fe	2	-	8	7	99.3	[111]
Copper II	Electrocoagulation	Fe-Fe	250	-	0.2–2.5	8.95	96	[112]
Congo Red	Photo-assisted electrochemical	Pt-air diffusion	181	240	100	3	~100	[113]
2-nitrophenol and orange II	Photo-assisted electrochemical	WO ₃ -EG (EG- exfoliate graphite)	20,30	180, 120	10	5.5	82, 95	[114]
Indigo blue	Electrochemical oxidation	Boron doped diamond	-	300	3.5	5.23	60.83	[115]
Reactive orange 107	Electrochemical oxidation	Graphite	-	16	34.96	9.4	98	[116]
Copper, Nickel	Electrochemical oxidation	Fe-Fe	-	60	-	4.5	80,100	[117]
Reactive red 120	Electrochemical reduction	Graphite-SS	200	30	-	-	32.38	[118]
Cr (VI)	Electrochemical reduction	Ti/TNT-Pt	100	15	-	-	97	[119]

Electrocoagulation

In the electrocoagulation treatment method, an external voltage is applied from a DC source to increase the surface charge of the pollutants to form coagulants in an electrochemical cell (Figure 5). The anode acts as a sacrificial electrode, and the metal ion formed from the anode creates metal hydroxide, which adsorbs pollutants and forms coagulants to be separated using coagulation [120].

**Figure 5.** Electrolytic reaction and formation of metal hydroxide in electrocoagulation process.

Anode half-cell reaction: $M \rightarrow M^{n+} + ne^{-}$

Cathode half-cell reaction: $2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2$

Formation of metal hydroxide: $M^{n+} + nOH^{-} \rightarrow M(OH)_n$

Electrocoagulation has been shown to have excellent pollutant removal effectiveness, in addition to having reduced capital costs, easy setup, minimal chemical consumption, and no harmful byproducts, which makes it one of the finest solutions for the treatment of wastewater [121]. An investigation was conducted into the use of electrocoagulation (EC) using iron electrodes in a continuous flow regime rather than a batch process. This was accomplished by optimizing a number of parameters, including current density, detention duration, and time of electrolysis. As a consequence of this work, 76% of the color and 95% of the COD were removed from a solution containing 300 mg/L of basic red dye 5001 B [122].

Photo-Assisted Electrochemical Method

Photoelectrochemical treatment methods involve the irradiation of a photoactive electrode and the electrolysis of water with UV or solar light [123]. A typical photoelectrochemical cell consists of a photoactive working electrode which can either be a p-type or n-type semiconductor, and a reference electrode with a suitable electrolyte. If the working electrode is made of an n-type semiconductor, the photo-generated holes travel to the electrode/electrolyte surface while the photoexcited electrons migrate through the external wire to the reference electrode. The holes combine with oxygen ions in water and form oxygen gas, and the electrons combine with hydrogen ions, forming hydrogen gas. When a p-type semiconductor is used as the working electrode, the semiconductor acts as a photocathode, which is the location where hydrogen evolution takes place. Otherwise, these cells can be formed with a photoanode, a photocathode, and no reference electrode [124].

The water-splitting reaction: $H_2O + h\nu \rightarrow \frac{1}{2} O_2 + H_2$

Two half-cell reactions: $2H^{+} + H_2O \rightarrow 2H^{+} + \frac{1}{2} O_2$; $2H^{+} + 2e^{-} \rightarrow H_2$

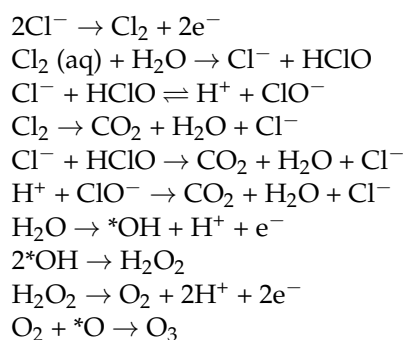
There are different types of photoelectrochemical methods, such as photoelectrocatalysis, photoelectron-Fenton, photoanodic oxidation, etc. Wastewater treatment by photoelectrochemical methods is preferred nowadays because it produces H_2 , which can be used to produce clean energy, requires comparatively cheaper energy sources, and is very efficient in removing persistent organic pollutants [125]. In a study, real textile wastewater was photoelectrochemically treated using Ti/Ru_{0.3}Ti_{0.7}O₂DSA type electrode at constant current. The effect of initial pH and electrolytes such as Na₂SO₄ or NaCl was observed. Under the working parameters used in this investigation, 72% color and up to 59% COD was removed in 120 min [126]. In another study, azo and phthalocyanine reactive dyes were treated, and surfactants were also present. The presence of surfactants impeded the dye degradation rate due to competitive surfactant degradation reactions [127].

Electrochemical Reduction Method

Electrochemical reduction treatment of textile wastewater is significantly inefficient compared to electrochemical oxidation in terms of dye removal. In electrochemical reduction processes, electrons can be directly transferred to the oxidized contaminants at the cathode/electrolyte surface or can be indirectly transferred through a mediator such as a catalyst or other adsorbed species. So, the oxidized contaminants are reduced [128]. In a recent study, electrochemical oxidation and electrochemical reduction were compared in the case of synthetic textile effluent treatment containing reactive red 120. Electrolysis time was found to be the most influential factor for an electrochemical reduction since dye removal doubled by increasing the electrolysis time by 15 min while keeping the other parameters constant. Under optimum conditions (RR120 concentration 200 mg/L, NaCl concentration 7914.29 mg/L, current intensity 0.12 A, reaction time 30 min), only 32.38% dye removal was achieved via an electro-reduction mechanism consuming 1.21 kWhm⁻³ of electrical energy. For the electro-oxidation mechanism, this percentage was 99.44%. This further proved that electrochemical reduction is inefficient compared to electrochemical oxidation.

Electrochemical Oxidation Method

The anode in electrochemical oxidation is responsible for the oxidation of pollutant species, whereas the cathode is responsible for the reduction. It is possible to classify it into two distinct subtypes, namely direct oxidation and indirect oxidation. In contrast, indirect oxidation takes place when highly oxidant species, such as active chlorine species or reactive oxygen species, are electro-generated at the surface of the anode. Direct oxidation involves direct charge transfer at the anode/electrolyte surface and requires the prior adsorption of contaminants onto the surface of the anode. Indirect oxidation can take place without the presence of contaminants. The following reactions are responsible for the formation of the high oxidant species [129,130].



In a study, textile effluent was treated by electrochemical oxidation using different cathode and anode materials with sodium chloride as the electrolyte. Copper was concluded as the best anode, and stainless steel was found to be the best cathode material. In another study, artificially treated textile wastewater containing 5.26 mg/L azo dye reactive-black 5 in a 16 L reactor from secondary treatment was investigated, and 100% color removal along with 75% COD removal within five minutes of ozonation was achieved in an ozone dose of 24.66 mg/minute in a batch system [131].

3.3.2. Advanced Oxidation Process

AOP is usually used as a pretreatment method to reduce the toxicity of organic compounds. In AOP, $\text{OH}\cdot$ and $\text{SO}_4^{\cdot-}$ radicals are produced, which are strong oxidants, non-selective, and able to destroy recalcitrant pollutants. They destroy the wastewater pollutants to a considerable level and lower their toxicity than before to make them acceptable constituents. The application of AOPs can reduce the COD of textile wastewater by up to 50% [132]. However, under some particular circumstances, AOPs produce intermediates and end products that are more toxic than their parent compound [133]. Very large treatment time can contribute as a factor to increase toxicity which was found in the experiment of Maniakova et al. [134]. As AOP can transform a chemical structurally, it can produce chemicals with another level of toxicity. When nitrobenzene quinolone, methamidophos, and N-nitroso-di-n-propylamine are treated by the AOP method in wastewater, mutagenicity is increased [135]. According to Gunten et al. [136], mutagenic N-di-nitrosodimethylamine is formed during the ozonation of dimethylsulfamide and dimethylamino-containing functional groups. Bromate (BrO_3^-) is formed while water treatment by ozonation, which can act as a carcinogenic substance for the human body [137]. Qutob et al. [138] found that a dimer of Acetaminophen (ACT) which is a very toxic chemical, can be produced while mineralizing ACT by ozonation as ozone does not possess sufficient energy for the reaction. In spite of these, the application of AOP is increasing rapidly for its' large degradation efficiency and eco-friendly nature. Another reason for the popularity of the oxidation process is the production of more stable and less amount of sludge [139]. The typical form of textile wastewater treatment through oxidation processes includes Fenton, hydrogen peroxide, ozonation, photocatalysis, etc. (Figure 6).

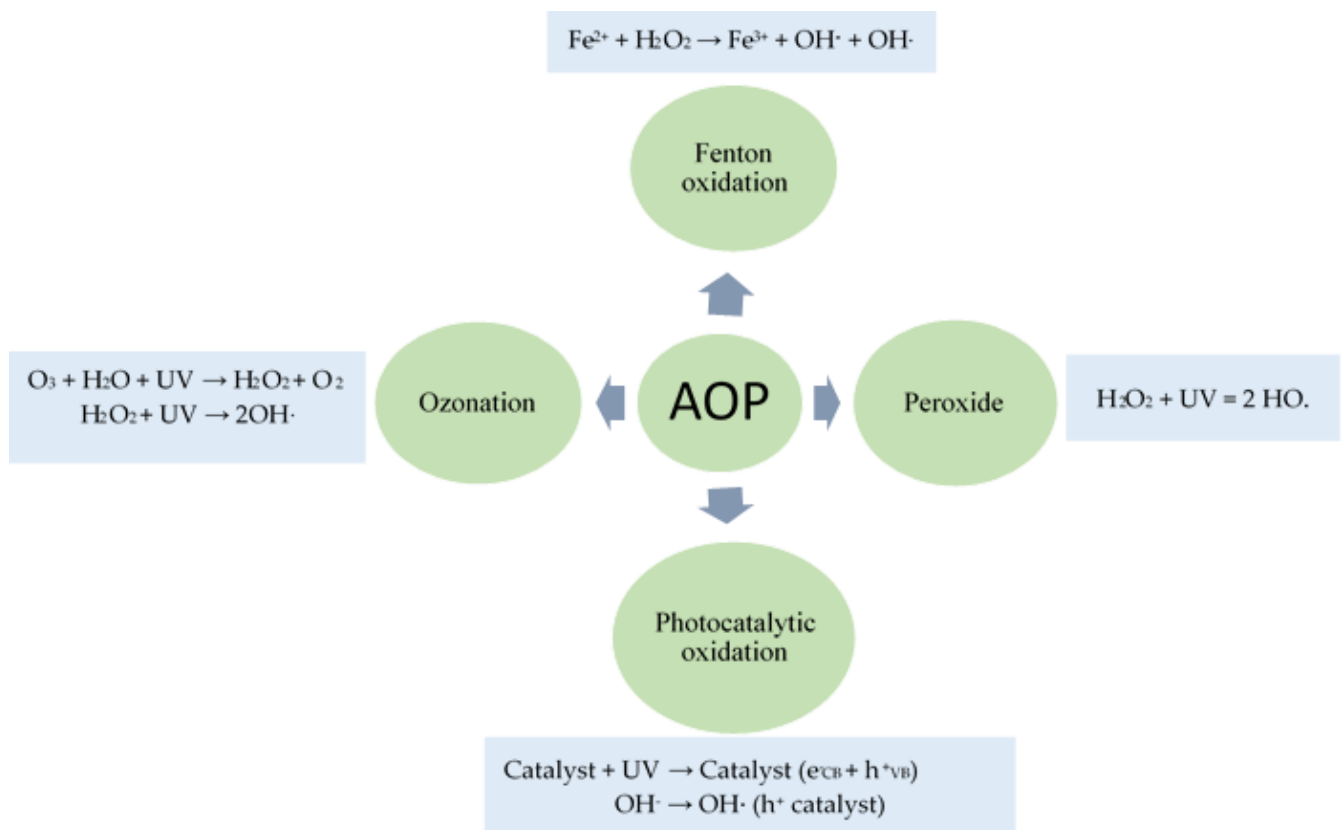
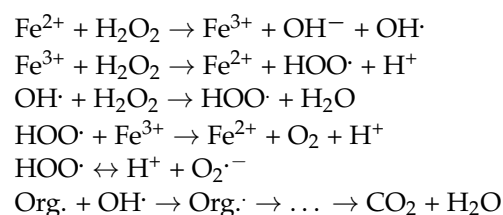


Figure 6. Different types of advanced oxidation process (AOP).

Fenton Oxidation

Among the mostly used oxidation methods of textile water, the Fenton oxidation method is a highly promising one since it does not need a lot of money and is simple to implement [140,141]. In spite of the fact that its primary function is to remove the color from the effluent, it is also capable of degrading organic contaminants. It is possible to utilize H_2O_2 as an oxidant with or without a catalyst, with examples of possible catalysts including ferrous salts, Al^{3+} , Cu^{2+} , and others [142]. By using the breakdown of hydrogen peroxide that is catalyzed by ferrous ion (Fe^{2+}), Fenton's reagent, also known as $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, is a technique that may be used to generate hydroxyl radicals (OH^\cdot). Here H_2O_2 is slowly added dropwise to the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystal while stirring. The generated OH^\cdot radical is a good oxidizer with a higher redox potential (2.81 V) than H_2O_2 (1.78 V), which decomposes even less bio-degradable portion of the textile effluent water, especially the dyestuff by oxidation. The decoloration of effluent for all dyestuffs proceeds in the fastest path with pH value 3 (range 2.5 to 4) [143]. This low value is used because OH^\cdot is produced largely in this acidic environment. When H_2O_2 and Fe^{2+} are used together at this pH, OH^\cdot is formed following a complex chain reaction [139].



If the wastewater contains any surfactant above Critical Micelle Concentration (CMC), a shield is formed against the attack of the free radicals causing the emulsification of the dyestuff followed by a significant decrease in the discoloration efficiency [132]. COD removal is sensitive to the amount of H_2O_2 and FeSO_4 , so the optimum amount of Fenton

reagent is needed to be determined carefully. Again, increasing the H_2O_2 and FeSO_4 dose beyond the optimum point decreases the color removal efficiency but increases COD removal efficiency. Application of poly aluminum chloride (PAC) and polymer at low temperatures can reduce the amount of COD to some extent.

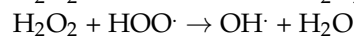
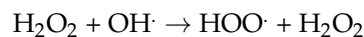
Peroxide (H_2O_2)

The extremely effective $\text{OH}\cdot$ radical, responsible for both chemical degradation and mineralization of organic compounds, is produced from another oxidant, H_2O_2 . Additionally, the production of non-hazardous halide ions and non-toxic compounds such as CO_2 and H_2O occurs during the treatment of halogenated compounds [144]. One important thing is that the single-step addition of H_2O_2 in a recirculated photoreactor is much more efficient than addition in multiple steps. As the lifetime of $\text{OH}\cdot$ is very small, it is produced in-situ in accordance with UV irradiation by the following reaction [145].

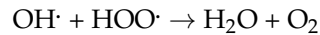
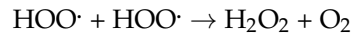
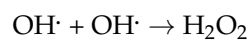


The $\text{OH}\cdot$ radical is responsible for the degradation of organic contaminants through four fundamental pathways: radical addition, hydrogen abstraction, electron transfer, and radical combination [145]. H_2O_2 -UV destroys the chromophoric structure of the dye and thus degrades it under ambient conditions, producing O_2 , which can be used for aerobic biological treatment [146].

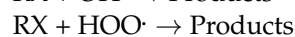
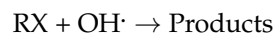
Propagation:



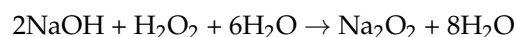
Termination:



Decomposition:



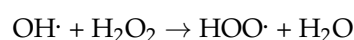
Decoloration of wastewater is more effective in an acidic environment (low pH) [147]. As a part of H_2O_2 is used to oxidize the alkali and forms dioxygen and H_2O , available H_2O_2 for $\text{OH}\cdot$ the radical formation is decreased, decreasing decoloration efficiency [146].



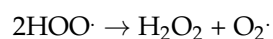
Also, H_2O_2 -UV is more sensitive to the scavenging effect of carbonate at higher pH, so $\text{OH}\cdot$ formation decreases, decreasing the treatment efficiency. The effect of temperature is not that significant here. At very low H_2O_2 concentration, enough $\text{OH}\cdot$ radical is not produced, so the oxidation rate is very low. Efficiency increases with increasing peroxide concentration. After reaching a certain critical value, H_2O_2 starts competing with dye molecules for $\text{OH}\cdot$ radical, so efficiency decreases [146]. Moreover, at high concentrations, $\text{OH}\cdot$ radicals dimerize among themselves and produce H_2O_2 reversing the reaction [148].



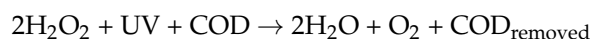
High concentration of $\text{OH}\cdot$ reacts with H_2O_2 forming $\text{HOO}\cdot$ which has a lower ability to decompose any organic matter than $\text{OH}\cdot$ radical [149].



As some of the produced $\text{OH}\cdot$ reacts with H_2O_2 , the formation of $\text{OH}\cdot$ is not proportional to H_2O_2 concentration. Moreover, $\text{HOO}\cdot$ forms H_2O_2 again, and this continues [146].



A high reaction time is needed to remove more dye molecules from effluent water. Dye removal efficiency is inversely related to initial dye concentration because of the absence of enough H_2O_2 present to remove all the dye particles. Moreover, more dye presence means more internal optical density, so UV cannot pass through the solution properly [148]. As a consequence, H_2O_2 photolysis is decreased, decreasing the efficiency. The decomposition of dye increases with the intensity of UV [140]: the stronger the UV, the faster the decomposition of H_2O_2 to $\text{OH}\cdot$ radical. Removal of COD is not as easy as color removal in this process. COD is removed by the following reaction [147]:



The presence of air bubbling decreases the COD removal efficiency since O_2 is increased in this manner, and the reaction goes in the reverse direction.

Ozonation

After fluorine and $\text{OH}\cdot$ radical, the oxidation and disinfection power of ozone is the highest as it has a high oxidation potential (2.08 V) because of its instability. Hence, it is produced on-site by high-voltage discharge from dry air or pure oxygen using conventional fine bubble contactor ozone generators because of its high ozone transfer efficiency (90%) and high performance [150]. Ozonation is an environment-friendly process of wastewater treatment as it does not produce any residues or any harmful chlorinated byproduct after oxidizing color, odor, and microorganisms. It is normally carried out at alkaline conditions ($\text{pH} > 9$) as the decomposition of ozone in water increases then. The oxidation of inorganic substances and dissolved organic substances by ozone has two mechanisms [151]:

- The direct reaction by ozone molecules is more selective, slow reaction, favorable in acidic condition
- The indirect reaction by free radicals such as $\text{OH}\cdot$, $\text{HOO}\cdot$ etc., less selective, favorable in basic condition

So in which path the reaction will occur depends on the pH of the medium and the dosage of ozone [152]. Reaction in an alkaline solution is faster than in an acidic solution as the oxidation potential of hydroxyl radical is higher than the ozone itself. However, as radicals are less selective, sometimes the removal efficiency of dye is decreased at higher pH. Dye stuff is decomposed when the chromophoric structure with a double bond is broken by selectively attacking the unsaturated bond of the chromophore through the addition mechanism, ozonide mechanism, or substitution mechanism, and thus, decoloration happens [152].

The more the ozone feed rate concentration, the more oxidation will occur, resulting in less color of the effluent, as increasing ozone concentration enhances mass [144]. Another important feature is that if the dye contains an electron-donating group at its ortho and para positions rather than an electron-withdrawing group, it becomes more reactive [146]. Although the ozonation process is hindered by the presence of salts such as NaCl or Na_2SO_4 , the presence of NaCl is more unwanted than Na_2SO_4 because the later produces sulfate or peroxysulfate radical that can assist the ozonation process to some extent [147]. Moreover, carbonate and bicarbonate are not welcomed because of their scavenging property. COD and TOC removal by ozonation is not very efficient; only decoloration and partial oxidation to improve biodegradability are significant. TOC and COD removal are favored at pH around 7 because radical type reaction becomes effective, and the scavenging effect of carbonate ion is not very prominent yet at this pH. Now about the effect of temperature, the solubility of ozone is decreased with an increase in temperature from $18\text{ }^\circ\text{C}$ to $70\text{ }^\circ\text{C}$ [148]. As a result, available ozone molecules for oxidation are decreased along with decreasing dye and COD removal. Decolorization efficiency decreases with increasing dye concentration due to the shortage of available ozone molecules to conduct oxidation and the presence of more intermediates to absorb ozone [144].

Also, in this case, the required time to oxidize all the dye molecules with the constant ozone will increase. The reasons behind this can be inferred as [143]:

- With the increase in initial dye concentration, OH^\cdot radical reaches the saturation level
- More inorganic anions are produced from a higher initial concentration of dye, so available OH^\cdot for degradation of organics is reduced

Most of the time, ozone is used in accordance with UV or H_2O_2 for higher efficiency. When ozone is used with UV, UV activates ozone molecules and makes the path of OH^\cdot formation easier by assisting in completing the oxidation process. By using only O_3 , organics sometimes are not completely converted to CO_2 and H_2O . They form intermediates that can be toxic. Here ozone molecules are activated by the UV, then an oxygen radical is formed, which then combines with water. Moreover, the intermediate reaction H_2O_2 goes under photolysis to form a hydroxyl radical that decomposes the dye molecules [153].



When H_2O_2 is used with ozone for oxidation purposes, it acts as a catalyst in order to increase OH^\cdot formation by decomposition of ozone. H_2O_2 reacts very slowly with ozone at acidic pH, but the reaction becomes very fast at higher pH [147]. In this case, HOO^\cdot is formed from H_2O_2 , which is more efficient than OH^\cdot for the decomposition purpose of ozone. The inhibitory performance of oxane on microbial growth is dependent on H_2O_2 to O_3 ratio, which varies from 0.3 to 0.6 for various kinds of dye [154]. However, other operating factors are the same as the conventional ozonation process, rate of OH^\cdot generation from the decomposition of ozone is enhanced when H_2O_2 is added to the ozone-UV process. This combination of ozone/UV/ H_2O_2 is the most efficient one among all the AOPs in terms of the decoloration of effluent [155].

Photocatalytic Oxidation

The most popular way of treatment of textile effluent water is the photocatalytic process, as it has the added advantage of optical absorption, which other AOPs do not. Photocatalytic sensitization is a process where a semiconductor acts as a catalyst in producing free radicals such as OH^\cdot to conduct the oxidation of organic compounds and completely convert them to non-toxic compounds such as CO_2 and H_2O by adsorption of photons. A schematic of the fundamental mechanism of the photocatalytic oxidation process is given in Figure 7.

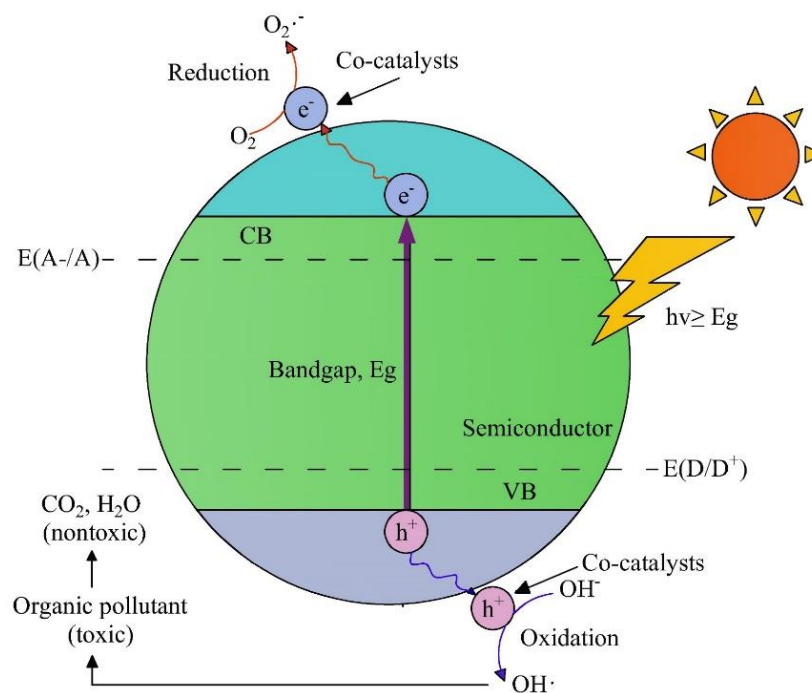
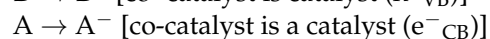
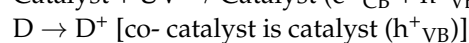
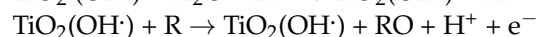
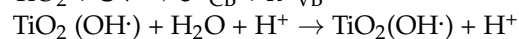
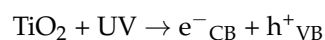


Figure 7. The fundamental mechanism of photocatalytic oxidation process [156].

The energy gap between the valance band and the conduction band is clearly visible here. This energy gap (E_g) is resolved when a photon with an energy equal to or greater than this gap is adsorbed on the surface of a catalyst. Once this gap has been overcome, the electron is excited from the valance band to the conduction band, which results in the formation of a hole in the valance band. The $h^+ - e^-$ combinations generated by light absorption release energy in the form of heat or light and transfer it to the catalyst surface. They both can participate as co-catalysts in many reactions. This hole mainly provides a site for oxidation reaction to generate hydroxyl radical that oxidizes pollutants of wastewater [157], and the surface electron contributes to the reduction in oxygen to O_2^- . This mechanism can be represented by the following reactions:



As this process is dependent on light, the reactor or the photocatalyst can be designed in such a way that the free source of energy, i.e., sunlight, can be used here to perform the reaction to minimize the cost [154]. The photocatalysts used here must be easily available, reproducible, photoactive, non-toxic, non-corrosive, biologically or chemically inert, low cost, and suitable to use in near UV or visible range of light. A great variety of semiconductors can be used as a catalyst here, but among them, TiO_2 is the most used one for its high stability and great photocatalytic activity required for the efficient degradation of toxic chemicals in wastewater. There is a slight energy gap (3.3 eV) between the valance band and the conduction band of TiO_2 . When a photon with an energy equal to or more than this energy gap is adsorbed on the surface of TiO_2 , this gap is overcome, and the electron is then excited from the valance band to the conduction band, creating a hole in the valance band. This hole mainly provides a site for a redox reaction to generate hydroxyl radical that oxidizes pollutants of wastewater. The associated mechanism can be represented by the following reactions [158].



Results of the treatment of effluent by photocatalysis can be studied by UV-Vis double beam spectrophotometer. The rate of degradation of dye depends on the formation of hydroxyl radicals, and the formation is decreased when an adsorbed dye is substituted by dye ions, $OH\cdot$ radical [158]. Dye concentration decreases with increasing irradiation time and light energy. Degradation increases with increasing the dosage of photocatalyst up to a certain level and then decreases afterward. The reason behind this is that up to this optimum mass, decolorization efficiency increases with an increasing available site on the photocatalyst [159]. Beyond the optimum value, excess catalyst particles increase the opacity of the medium, so photo energy cannot pass through as required, and light is scattered. Lastly, increasing temperature assists in increasing decoloration efficiency with time. Removal of various types of dye, dissolved organic material (DOC), and heavy metal through the photocatalytic process from wastewater, along with their efficiency and experimental conditions, are shown in Table 6.

Table 6. Textile wastewater treatment efficiency of the photocatalytic process for the removal of DOC, COD, dye, and heavy metal and experimental conditions.

Dye/ Heavy Metal	Photocatalyst	Experimental Condition	Percent Removal (%)	Ref
Phenanthrene dye	Cu ²⁺ , TiO ₂ /TiNTs	i. 200 µg/L, ii. 25 ± 0.5 °C, iii. 300 mL, iv. 4 h v. Cu ²⁺ : 20 mg/L, TiO ₂ : 0.5 g/L, vi. 5 ± 0.2	93.2%	[160]
DOC & color	Fe ²⁺ /H ₂ O ₂	ii. 25 °C, iii. 0.9 L, iv. 120 min, v. 4 ppm Fe ²⁺ , 100 ppm H ₂ O ₂ , vi. 3	98% & 100%	[161]
Methylene Blue dye & COD	TiO ₂	i. 60 mg/L, iii. 1 L(batch), 81.2 cm ³ (tubular), iv. 60 min, v. 1.2 mg/L, vi. 7	Dye: 100% (batch), 93% (tubular), COD: 42.2% (batch), 47.8% (tubular)	[162]
Acid Red 73 dye	TiO ₂ coated sackcloth fibre	i. 25 mg/L, iii. 1 L, v. H ₂ O ₂ 0.5 mg/L vi. 3	92.24%	[163]
Rhodamine B dye	OxCN ₂	i. 20 mg/L, ii. 25 °C, iv. 120 min, v. 30 mg, vi. natural	93.88%	[164]
Crystal Violet dye	MoS ₂ NFs	i. 100 mL, iv. 40 min, v. 20 mg, vi. natural	99.3%	[165]
Cadmium (Cd)	CuCo ₂ S ₄ modified Z-scheme MoSe ₂ /BiVO ₄	i. 3.14 g/L Cd ²⁺ , 4.84 g/L Fe ³⁺ , iv. 210 min, v. 0.5 mg, vi. 9	Above 90%	[166]
Rhodamine B dye, Mercury (Hg)	MoS ₂ /ZnO	i. Rh B 10 mg/L, iv. RhB 50 min, Hg 60 min, v. 25 mg for RhB, 0.1 g for Hg, vi. natural	RhB 95%, Hg 99.8%	[167]
Cu, Pb, Cd	Chitosan/Ag nanocomposites	i. 200 ppm, ii. 25 °C, iv. 250 min, v. 0.64%, vi. 5.5–6.5,	Cu 97%, Pb 88%, Cd 89%	[168]

i: pollutant concentration, ii: temperature, iii: reactor volume, iv: experimentation time, v: adsorbent/catalyst dose, vi: pH.

Both photocatalytic and electrocatalytic processes are part of advanced oxidation processes which have gained tremendous popularity for wastewater treatment. Their dye or heavy metal removal efficiency depends on the reaction conditions to some extent. Singaravadivel et al. [169] found Total Organic Carbon (TOC) removal efficiency to be 70% by electro-oxidation treatment and 67% by photocatalytic. Treatment by the photocatalytic process was faster than the other, but it produced photocatalyst-containing pollutants, which had to be treated before dumping to the environment, whereas no such treatment is required for electrocatalysis; thus, its' recyclability is quite feasible, having no excess chemical or produced sludge that can cause secondary pollution, so the environment was friendly. According to Suhadolnik et al. [170], toxic intermediate products are sometimes formed in photocatalysis before the final harmless products. If enough oxygen is not supplied to the system, incomplete conversion can occur with harmful intermediates. Controlling the extent of mineralization can be difficult as the reaction can be stopped if there is any oxygen deficiency. Though the thin film form of photocatalysts can be recycled easily, reusing the powder form is very difficult as it needs to be separated and treated, inducing an additional cost. However, the operating cost for photocatalysis is lower as it only requires solar light, which is a clean and economical light source; on the other hand, the electrocatalysis process needs expensive electrodes and electric energy [171]. This high energy consumption by the electrochemical method and difficulty scaling up has limited its application in the industrial sector [172]. Treated wastewater by the electrochemical process has large flocs which can be easily separated by sedimentation or filtration; thus, the produced water is clear, colorless, and odorless. The gas bubbles produced by this method carry the pollutants to the surface, which can then be removed from the water when they accumulate enough [173]. The electrochemical process sometimes can have a poisoning

effect which can have harmful consequences, but photocatalysis is usually non-toxic, so reliable if a high recombination rate of electron and hole can be controlled [174].

As both photocatalysis and electrocatalysis have their pros and cons, both of their disadvantages can be overcome if they can be used combinedly as photoelectrocatalysis processes. Electron-hole recombination can be suppressed by external electric potential and generate additional radicals that can assist in degrading more pollutants, achieving a faster mineralization rate [170].

3.3.3. Membrane Filtration

In the textile sector, membrane technology offers a wide range of applications. This method requires fewer chemicals, equipment, and energy as well as low capital cost, through which different kinds of dyes and contaminants can be removed from wastewater with the scope of reuse of a substantial amount of water. There are several types of membrane filtration (Figure 8). In general, wastewater treatment using MF and UF is inefficient, and further filtration is conducted using NF and RO [175].

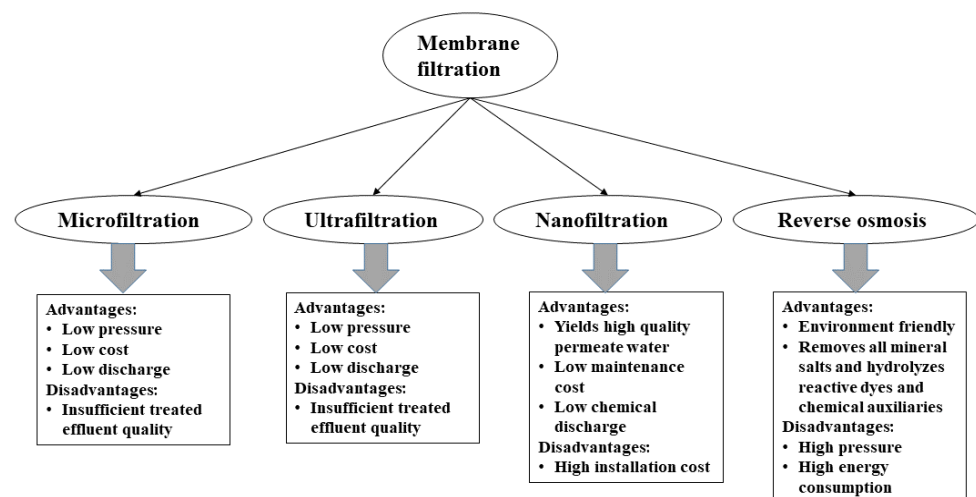


Figure 8. Different types of membrane filtration with respective advantages and disadvantages [175].

Microfiltration

Microfiltration membranes are made up of holes that are evenly distributed across the membrane and range in size from 0.1 to 10 μm on average. It separates macromolecules, colloids, and suspended particles from solution via a sieving process and is commonly employed for this purpose [176]. The usefulness of microfiltration in the treatment of textile wastewater is restricted due to the fact that it is analogous to more conventional methods of crude filtering [177].

Ultrafiltration

UF membranes have a typical pore diameter that falls between 2 and 10 nm, and they function best when subjected to a pressure gradient of 25 bar [178]. It is common practice to use UF for the removal of particles that are either undissolved or suspended in water, as well as for the retention of macromolecules and colloids in aqueous solutions. At the moment, ultrafiltration membranes are typically manufactured using a variety of synthetic polymers such as polyvinyl chloride (PVC), polyamides (PA), polyacrylonitrile (PAN), and other similar materials. In the case of the treatment of textile wastewater, ultrafiltration (UF) does not perform satisfactorily for direct use. This is due to the fact that dye molecules with a size that is smaller than the pore size of the UF membrane are allowed to pass through. There are examples of UF that have been enhanced with aggregation for the removal of dyes, but this is not the norm.

Nanofiltration

Nanofiltration is a promising method for treating textile effluent. Nanofiltration membranes are partially porous, having an average pore size of 1 nm. It is performed under a pressure gradient of 5–35 bars and can filter out substances such as small organic molecules and ions of size between 10^{-9} to 10^{-8} m. Compared to monovalent ions, NF membranes reject more divalent and trivalent ions because the NF membrane polymers mostly carry formal charges, excluding ions with higher valences from passing through [179]. The mechanism in which pollutants are rejected is primarily driven by steric and charge repulsion. The RO and UF classes of membranes are separated by the NF class of membranes. The most significant benefits of NF technology are that it requires little to no maintenance, has a low discharge volume, has a high solvent permeability, can easily be scaled up, is simple to clean with chemicals, and produces water of a high quality that satisfies the criteria for reuse. In the presence of salt and owing to operational difficulties such as fouling and salt breakdown, NF membrane may become difficult to work with and present a number of challenges. NF is often added to the textile wastewater treatment process after biological treatment or ultrafiltration and sometimes before reverse osmosis. This is conducted for the purpose of performance improvement [180].

Reverse Osmosis

In the reverse osmosis process, membranes are permeable to water but impermeable to salt or contaminant molecules. It is osmosis in reverse; that is, pressure is applied from the side of the high-concentration solution so that water passes through the semipermeable membrane to the low-concentration side (Figure 9). The semipermeable membrane does not let pollutant macromolecules and ions pass through. Though it is an environment-friendly treatment method with high pollutant removal efficiency, it requires a hydrostatic pressure gradient of 20–80 bar, so the energy consumption is high [181]. However, since textile wastewater is highly conductive, RO is often required for effective water recovery. Conventional biological and chemical treatment procedures are able to remove color and COD from the majority of wastewater. Textile wastewater treatment efficiency of various membrane filtration methods from different studies is shown in Table 7.

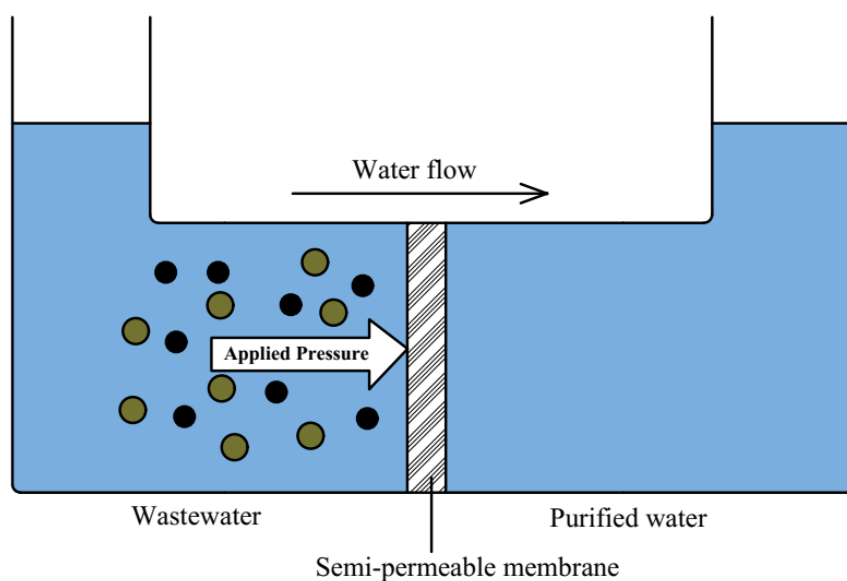


Figure 9. A schematic representation of wastewater treatment using reverse osmosis.

Table 7. Textile wastewater treatment efficiency of various membrane filtration methods from different studies.

Membrane Filtration Method	Type of Wastewater	Membrane Specifications and Applied Conditions	Removal (%)	Ref
Microfiltration	Textile dye-bath effluent	<ul style="list-style-type: none"> Ceramic MF membrane based on kaolin with water permeability of 1376 L/m²·h·bar Porosity 40.2%, pore diameter 0.27 µm 	TSS—100% COD—25% TDS—31% BOD—39% Turbidity—21% Sulfates—34% Chlorides—33% Color—26%	[182]
	Real textile wastewater	<ul style="list-style-type: none"> Ceramic-metal membrane Material—Kaolin, feldspar, sand 	Turbidity—98% COD—95%	[183]
	Textile dye	<ul style="list-style-type: none"> Polyethersulfone membrane with polyethilenimine and graphene oxide pH 6, 10 and dye concentration 10, 40 ppm 	Dye- (35.4–96.1)%	[184]
Ultrafiltration	Textile wastewater with dye/salt mixture	<ul style="list-style-type: none"> Reactive blue 2/Na₂SO₄ mixture Seven UF membranes with molecular weight cut-offs (MWCOs) from 6050 to 17,530 Da 	Desalination—99.84% Dye—97.47%	[185]
	Red and blue colored textile wastewater	<ul style="list-style-type: none"> Applied after bioremediation A polymeric membrane of cut off 13 kDa 	COD—90% Color—100%	[186]
	Textile dye-bath effluent	<ul style="list-style-type: none"> Applied prior to nanofiltration Polyethersulphone membrane and MWCO 0.02 µm 	Color—17% COD—52% TOC—32% TSS—64% Turbidity—82%	[187]
	Primary treated textile wastewater	<ul style="list-style-type: none"> Applied after primary screening, biological reactor and air flotation tank Ceramic membrane with 50 nm pore size Cross flow velocity 6 m/s, trans membrane pressure 2.05 bar 	COD—54.4% TDS—19.5% Conductivity- 42.4% Turbidity- 93%	[188]
Nanofiltration	Textile dye-bath effluent	<ul style="list-style-type: none"> Applied after ultrafiltration SR90 and NF90 polyamide membranes SR90 MWCO 200–300 Da, NF90 MWCO 100–200 Da 	SR90: COD—93% TSS—94.5% Turbidity—94% Color—87% NR90: COD—94% TSS—96% Turbidity—94% Color—98%	[187]
	Textile dye wastewater	<ul style="list-style-type: none"> Membrane of 16/64/20% weight of PEI/NMP (N-methyl-pyrrolidone)/Acetone formulation RR120 dye and 50 psi pressure 	Dye—81%	[189]
	Real textile wastewater	<ul style="list-style-type: none"> Optimal pressure and temperature of 10 bar and 40 °C Membrane area 2.5 m² and MWCO 200 Da Applied after coagulation-flocculation 	COD—57% Color—100% Salinity—30%	[190]

Table 7. Cont.

Membrane Filtration Method	Type of Wastewater	Membrane Specifications and Applied Conditions	Removal (%)	Ref
Reverse osmosis	Real textile wastewater	<ul style="list-style-type: none"> Applied after bioreactor 12 bar initial pressure 	Salt—97.1% Turbidity—98.5% Color—85.1%	[191]
	Real textile wastewater	<ul style="list-style-type: none"> Circular flat-sheet membrane with effective area 14.6 cm² 10 bar pressure 	COD—96.3%	[192]
	Textile dye	<ul style="list-style-type: none"> Composite polyamide membrane with active area 7.9 m² Dye concentration 65 mg/L Feed temperature 39 °C 8 bar pressure 	Acid red—97.2% Reactive black—99.58% Reactive blue—99.9%	[193]

4. Road towards ZLD: Resource Recovery from Wastewater

As a result of increased environmental awareness, rising costs of wastewater treatment, and difficulties associated with its disposal, the public's perception of wastewater is shifting from that of an "out-of-sight, out-of-mind" problem to that of an opportunity to recover valuable resources. This is occurring as a direct result of the combination of these factors. Figure 10 presents a visual representation of the ZLD concept's primary drivers as well as its many advantageous outcomes.

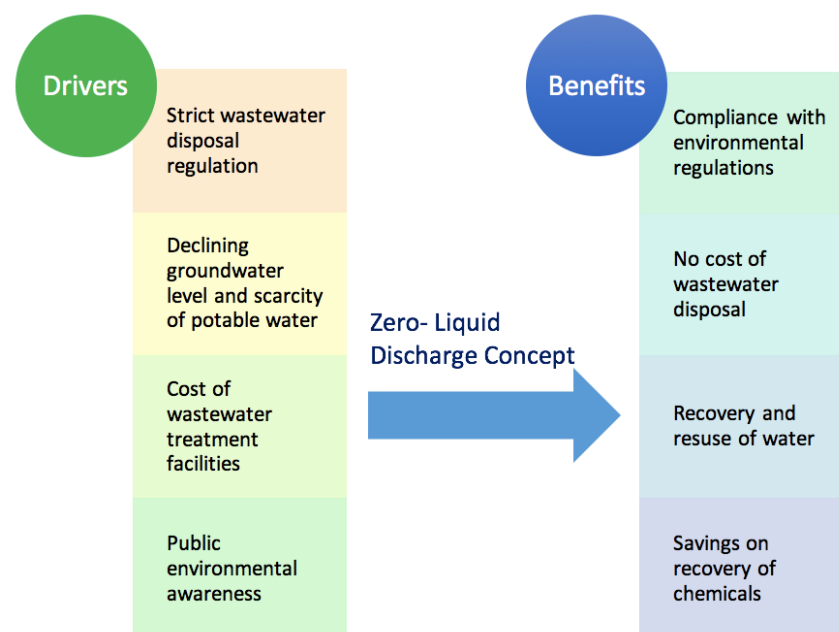


Figure 10. Drivers and benefits of the ZLD concept.

The reusing and recycling of wastewater may not only lower the amount of fresh water that is needed, but it can also allow for the reduction in waste and excess resources [21]. In addition, restrictions placed on the number of accessible resources are one of the factors driving the shift in emphasis from wastewater treatment to resource recovery. One of the businesses that make the largest use of both chemicals and water is the textile industry. As a result, it has the greatest potential for various intensive chemical recovery and water recycling alternatives. Because of restrictions imposed on available water supplies and rules governing wastewater, the recycling process has become indispensable to the industrial

sector. Before beginning the treatment process, recovery and recycling are exhausted as possibilities. Different techniques for dye, salt, and caustic recovery, along with their pros and cons, have been summarized in Table 8.

Table 8. Summary of different resource recovery techniques reported in the literature.

Resource Recovery Method	Removal %	Pros	Cons	Ref
Dye/ Salt recovery methods				
Hollow-fiber loose polyethersulfone NF membrane	-Congo red was found to be rejected by the membrane at a rate of 99.9% -More than 93% of NaCl salt was reported to be permeable	High fractionation efficiency of dye/salt combinations is achievable		[168]
Poly(ether sulfone) (PES) loose NF nanocomposite membranes	The following series of aqueous salt solutions were shown to have low rejection rates: MgSO ₄ (4.1%) is higher than Na ₂ SO ₃ (3.3%), MgCl ₂ (1.8%), and NaCl (1.2%)	Significant rejection of NF membranes to divalent salts achieved	In terms of thermal stability, chemical resistance, mechanical strength and permeability, polymeric membranes discussed are inferior to ceramic membranes.	[194]
Nanofiltration DL membrane with a negative surface	97.5% Na ₂ SO ₄ and 99.99% dye retained in feed	Significant retention of both salt and dye achieved		[194]
PES membrane with a tight ultrafiltration MWCO of 4700 Da	Anion dyes such as Direct Red 80, Direct Red 23, Congo Red, and Reactive Blue 2 show a rejection rate of over 98.9% and a desalination rate of up to 98%	Significant retention of both salt and dye achieved		[195]
Ceramic nano-filtration membrane with an MWCO of 900 Da	-Able to retain greater than 99% of the dye -Retained less than 10% of NaCl and less than 20% of the Na ₂ SO ₄	Significant retention of dye achieved but not of salt		[196]
Tight ultrafiltration (t-UF) ceramic membranes with TiO ₂ /ZrO ₂ skin layer with a mean pore size of 1.16 nm on porous Al ₂ O ₃ support	Higher rejection of dye molecules (>98%), and lower rejection of NaCl (10%) and Na ₂ SO ₄ (30%)	Compared to DK polymeric membranes, t-UF ceramic membranes exhibit higher permeability and higher rejection of dye molecules	Several of these methods have only been tried out on a small-scale basis. Therefore, further pilot-scale implementations in the textile sector are required to evaluate full-scale performance and feasibility	[197]
UP005+ NF200+ NF90	-Rejected 99.4 percent of color, 99.1 percent of COD, and 43.2 percent of the conductivity	Investigated different UF and NF membrane configurations, both in parallel and in series		[198]

Table 8. Cont.

Resource Recovery Method	Removal %	Pros	Cons	Ref
Caustic recovery methods				
Combination membrane design of ceramic membrane (first step) and polymeric membrane (second step)	91.3% recovery of sodium hydroxide from the process	Significant retention of sodium hydroxide achieved		[199]
Two-step membrane separation procedure: MF with 0.2- μ m pore size + UF with 100 kDa pore size and then using UF with 10 kDa pore size + NF with 200 Da pore size	- No NaOH was lost during the pre-treatment phase -Between 12% and 17% of the NaOH was retained during the second stage	Significant retention of sodium hydroxide achieved	-Nano-filtration membranes are prone to easy fouling, which may lead to reduced penetration efficiency	[200]
UF-NF integrated process	Able to recover at least 50% of the sodium	Installing NF after UF treatment has been shown to improve pollutant removal and caustic recovery efficiency compared to using UF alone	-Typical polymeric NF membranes can only be used with feed that has a very low NaOH content (0.1–0.4%) -Much of this research has only been conducted on a small scale in a lab	[201]
Tight UF membrane (GR95PP, AlfaLaval) and three NF membranes	-Recovered around 98–100% of the NaOH in the feed	NP010 NF is the best option		[202]
SelRo (MPT-34) NF membranes	NaOH recovery rate of 84% was achieved	Significant retention of sodium hydroxide achieved		[203]
UF membrane, an NF membrane, and a hybrid UF/NF membrane	At least 50% recovery was achieved in each instance	Significant retention of sodium hydroxide achieved for all configurations		[201]

In this context, we study the state-of-the-art for the recovery of two resources that are commonly utilized in the textile industry, namely salts and caustic solutions, in the following sub-sections of this article.

4.1. Dye/Salt Recovery

Salts are employed in the dyeing process to help in the fixing of colors onto the cloth. As a consequence, substantial levels of total dissolved solids (TDS) and chlorides are produced in the effluents, both of which are resistant to biodegradation. The dye bath and the first rinse bath are responsible for the emission of about more than 80 percent of these salts [180]. For example, the caustic content in effluent from mercerization processes is quite high. In the event that it is not adequately treated before being released into the sewage network, it has the potential to render the microorganisms that are used in the biological treatment procedures inactive [200]. It is recommended that mercerization water be reused due to the enormous volume and high alkalinity of the water produced by the mercerization process. In the circumstances such as these, it has been shown that treatment by thermal evaporation is the only viable option. Thermal evaporation is often considered an effective method for separating salt and dissolved solids from concentrated solutions and water from dye bath in textile industries. Permeate stream from membrane treatment is purified by evaporation. Streams with certain concentrations can be recycled, and condensate water is reused in the process. For example, in the caustic recovery process, after the evaporation

process, the caustic stream with the desired concentration is recycled in the mercerization process [200]. Studies regarding the field-scale assessment of the multiple-effect evaporator and solar evaporation pans alongside other primaries, secondary and tertiary treatments have been found [180]. Through evaporation, TDS concentrations of condensate water are lowered. There are several advantages of using a thermal evaporative treatment that include ease of construction, cleaning, maintenance, and low cost. However, this method has demerits such as foaming of products, drying up of water, and regular cleaning of the tube walls so that no contaminants are deposited.

Sustainable salt solution recovery from textile effluent may be accomplished in a number of various methods that avoid or mitigate the drawbacks of the evaporative process. Because of its distinct properties, such as its increased selectivity towards divalent/polyvalent ions, while permitting penetration for monovalent ions and tiny molecules of less than 100 Da, nanofiltration (NF) membrane has become a preferred option for this application. Dye molecules and salts (especially monovalent salts) may be partitioned by the NF membrane. This method not only prevents the discharge of harmful chemicals into the environment but also minimizes resource use, leading to cost savings [204]. By using a hollow-fiber loose polyethersulfone NF membrane, Chu et al. showed that a high fractionation efficiency of dye/salt combinations is possible. A dye (congo red, 0.1 g/L) was found to be rejected by the membrane at a rate of 99.9%, whereas more than 93% of NaCl salt (1 g/L) was reported to be permeable across the membrane. The findings of this study demonstrate the promise of loose NF for reclaiming salt solutions from textile wastewater. For their study, Tavangar et al. produced Poly(ether sulfone) (PES) loose NF nanocomposite membranes and looked at how well they desalinated actual textile effluent. The following series of aqueous salt solutions were shown to have low rejection rates: MgSO_4 (4.1%) is higher than Na_2SO_3 (3.3%), MgCl_2 (1.8%), and NaCl (1.2%). The significant rejection of NF membranes to divalent salts such as Na_2SO_4 , which is often found in dye products and wastewater, reduces salt recovery, notwithstanding the advantages. For instance, at 10 pressure and pH 4.4, He et al. employed a nanofiltration DL membrane with a negative surface to remove Reactive Brilliant Blue KN-R and Na_2SO_4 , retaining 97.5% Na_2SO_4 and 99.99% dye, respectively, in the feed. More multivalent salt ions may flow via ultrafiltration (UF) membranes because their pores are bigger than those of NF membranes. When trying to separate dyes and Na_2SO_4 , Lin et al. used tests using a PES membrane with a tight ultrafiltration MWCO of 4700 Da. Anion dyes such as Direct Red 80, Direct Red 23, Congo Red, and Reactive Blue 2 show a rejection rate of over 98.9% and a desalination rate of up to 98%. Ceramic membranes have been demonstrated to outperform polymeric membranes in terms of thermal stability, chemical resistance, and mechanical strength, as well as permeability [205]. Desalination of an Erichrome black T dye solution with NaCl/ Na_2SO_4 was studied by Chen et al., who found that a ceramic nano-filtration membrane with an MWCO of 900 Da was able to retain greater than 99% of the dye while retaining less than 10% of the NaCl and less than 20% of the Na_2SO_4 at an operating pressure of 3 bar. Tight ultrafiltration (t-UF) ceramic membranes were investigated by Xing et al. for the separation of dye and mixed salts (NaCl/ Na_2SO_4). These membranes included a $\text{TiO}_2/\text{ZrO}_2$ skin layer with a mean pore size of 1.16 nm on porous Al_2O_3 support. The authors showed that compared to DK polymeric membranes, t-UF ceramic membranes exhibit higher permeability, higher rejection of dye molecules (>98%), and lower rejection of NaCl (10%) and Na_2SO_4 (30%). Because of this, t-UF membranes are well-suited for desalinating textile wastewater for color and salt recovery. Researchers have looked at a wide variety of UF and NF membrane configurations, both in parallel and in series, to determine the most effective method of effluent treatment and resource recovery. To reject 99.4 percent of color, 99.1 percent of COD, and 43.2 percent of conductivity, Nadeem et al. employed a sequential setup of UP005+ NF200+ NF90. Moreover, some researchers have examined the solubility behavior of salts to understand better how to handle textile effluent. The influence of NaCl on the solubility behavior of Na_2SO_4 at different temperatures was studied by Bharmoria et al., along with the temperature dependence of the solubility transition of Na_2SO_4 . Both the solubility and

the solubility transition temperatures of Na_2SO_4 were shown to be lowered by the addition of NaCl , as predicted by the findings of this research. According to their findings, when the amount of NaCl in the solution was raised to 15% by weight, the solubility of Na_2SO_4 dropped from $3.5 \text{ mol}\cdot\text{kg}^{-1}$ to $1.72 \text{ mol}\cdot\text{kg}^{-1}$. The findings of this research are particularly useful since they provide light on the solubility of sodium sulfate, which is important in understanding how to separate and recover it from effluent textile streams.

4.2. Caustic Recovery

Mercerizing is a kind of alkaline treatment used in the textile industry during the preparation of cloth to achieve a permanent shine, to enhance the luster, hand, and other attributes of the fabric. Large amounts of caustic soda are used in this procedure. Therefore, recovering NaOH , which may be utilized in the causticization process, from the highly alkaline effluent from caustic main bath discharges might be an appealing possibility in the textile sector. In addition, caustic solution recovery contributes to one of the Textile BAT goals [206]. The recovery and reuse of highly alkaline caustic in the textile sector are not well covered in the literature, despite the fact that many researchers have examined color removal from textile wastewater [201]. The mercerization process consumes the most caustic solution; hence it is the primary subject of most writing on caustic recovery. The mercerization stage produces caustic effluent, which is hot, alkaline, and contains 1–5% sodium hydroxide. Earlier stages of fiber removal make membrane systems ideal for treating such effluents and recovering caustic chemicals. Small molecules and ions may pass through polymeric nano-filtration membranes without undergoing mercerization. However, many studies utilize an ultrafiltration/microfiltration pre-treatment step since nano-filtration membranes are prone to easy fouling, which may lead to reduced penetration efficiency. The following section details the numerous caustic recoveries from textile wastewater investigations that have been published in the literature. To recover caustic solution from caustic wastewater stream from the textile mercerization process, Yang et al. [207] employed a combination membrane design of ceramic membrane (first step) and polymeric membrane (second step). There was a 91.3% recovery of sodium hydroxide from the process, and the penetrated solution had a concentration of 4.2%. This solution could be recycled back into the process if an appropriate makeup solution were supplied. Researchers Tunç et al. looked into a two-step membrane separation procedure, first using micro-filtration (MF) membranes with a 0.2- μm pore size and ultrafiltration (UF) membranes with a 100 kDa pore size and then using UF membranes with a 10 kDa pore size and nanofiltration (NF) membranes with a 200 Da pore size. Despite the fact that no NaOH was lost during the pre-treatment phase, the findings demonstrate between 12% and 17% of the NaOH was retained during the second stage when NF was used, depending on whether MF or 100 kDa UF was used as a pre-treatment. Because of its greater chemical resistance than polymeric NF membrane, the ceramic membrane has been shown to have more potential for caustic recovery [208]. Additionally, typical polymeric NF membranes can only be used with feed that has a very low NaOH content (0.1–0.4%) [209]. With a UF-NF integrated process, Agtas et al. were able to recover caustic solutions using commercial ceramic NF (ATECH, 1000 Da). Installing NF after UF treatment has been shown to improve pollutant removal and caustic recovery efficiency compared to using UF alone. The UF-NF process was able to recover at least 50% of the sodium. The authors also conducted a cost-benefit analysis and discovered that recycling the caustic solution might reduce caustic consumption costs by 50%. Using a tight UF membrane (GR95PP, AlfaLaval) and three NF membranes, Yetis et al. studied caustic recovery from mercerizing wastewaters of a denim textile factory (NP010 and NP030, Microdyn Nadir, and MPF34, Koch Membranes). According to the authors, NP010 NF is the best option. After concentration, the resulting caustic stream recovered around 98–100% of the NaOH in the feed and had a concentration of 30–40 g/L, making it suitable for recycling. Choe et al. [203] use SelRo (MPT-34) NF membranes to research the recovery of caustic soda from the alkaline waste of polyester textiles. The optimal working temperature range for NaOH recovery was between 46 and 50 °C when it reached a rate

of 84%. Researchers Agtas et al. looked into ceramic membrane systems to learn more about the treatment of textile wastewater containing caustic chemicals and the possibilities for reusing the caustic compounds they extracted. For this, we used a UF membrane, an NF membrane, and a hybrid UF/NF membrane. The equipment used by the authors included a supervisory control and data acquisition (SCADA) system, three storage tanks, two pumps, and a UF/NF ceramic membrane. The pilot-scale plant has three possible configurations: using solely UF membranes, using UF and NF membranes together, or using NF membranes alone. It can operate in two modes: batch and continuous. Since at least 50% recovery was achieved in each instance, the resultant membrane permeation may be recycled by adding more sodium hydroxide to its composition. Several of the caustic and dye/salt recovery techniques described above have shown encouraging results. Much of this research, however, has only been conducted on a small scale in a lab, highlighting the need for larger pilot projects. Ultimately, this will allow for a more thorough analysis of the technical and financial viability of various resource recovery strategies.

5. Conclusions

In this review, we demonstrated a comprehensive literature analysis of sustainable textile wastewater treatment strategies, focusing on approaches that lead to zero liquid discharge (ZLD) and the subsequent recovery of important resources. The review includes a discussion of different stages of the textile processing operation and effluent characteristics in order to identify opportunities for implementing water management options. Next, different effluent treatment methods, with a particular focus on tertiary treatment methods, have been outlined. A logical diagram to guide the selection of possible treatment methods has been presented. Following BOD₅/COD₅ tests, secondary treatment is recommended for biodegradable wastewater, while advanced treatment is recommended for non-biodegradable wastewater. If the stream from the secondary treatment stage does not meet reuse guidelines, it needs to be sent to advanced treatment units. Finally, the streams need to be sent to the resource recovery section for the retention of valuable resources before discarding/ reusing the water.

Following this, an in-depth review of the state-of-the-art resource recovery techniques that may be applied in the textile industry to reclaim and reuse valuable resources, including caustic solutions and salts, has been presented. To reduce global water consumption, ZLD systems' incorporation into textile wastewater treatment is an important step. However, there are several characteristics of ZLD methods that prevent them from being used more widely. There are worries about the high energy requirements and initial investment in ZLD methods. The cost of energy and maintenance is far greater than that of more traditional methods of dealing with wastewater. Due to this, it is essential that research and development be directed toward the generation of methods that are more economically viable. Several ZLD approaches have only been adopted on a small scale. Therefore, further pilot-scale implementations of ZLD systems in the textile sector are required to evaluate full-scale performance and feasibility. The below sequential phases outline how facilities may help bring about a change toward more sustainable methods of water management and resource recovery.

1. Track water consumption at each stage of the production process (remember, you can't improve what you don't measure)
2. Identify opportunities for water and resource recovery from each stage, considering the various ZLD techniques available
3. Set a baseline for current performance and also set key performance indicators (KPI) to measure future performance
4. Aim for continuous performance improvements

The increased technical and economic viability of ZLD may hasten the transition to more sustainable water management, and future research should focus on creating energy-efficient and cost-effective membranes and other treatment technologies.

Author Contributions: Conceptualization, N.J., H.R. and M.S.I.; formal analysis, M.T., A.Z.S. and A.F.; writing—original draft and final paper preparation, N.J., M.T. and H.R.; writing—review and editing, M.N.P., M.S.I., Y.C. and V.N.; supervision, M.S.I. and V.N.; project administration, M.S.I. and V.N.; funding acquisition, M.S.I. and V.N. All authors have read and agreed to the published version of the manuscript.

Funding: We would like to express our sincere gratitude for the support from the Sanitary Environmental Engineering Division (SEED) and grants (FARB projects) from the University of Salerno, Italy, coordinated by V. Naddeo. Grant Number: 300393FRB22NADDE.

Institutional Review Board Statement: Not Applicable.

Informed Consent Statement: Not Applicable.

Data Availability Statement: The datasets generated during the current study are available from the corresponding author on reasonable request (Md. Shahinoor Islam, M.S.I.).

Conflicts of Interest: The authors declare no conflict of interest.

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