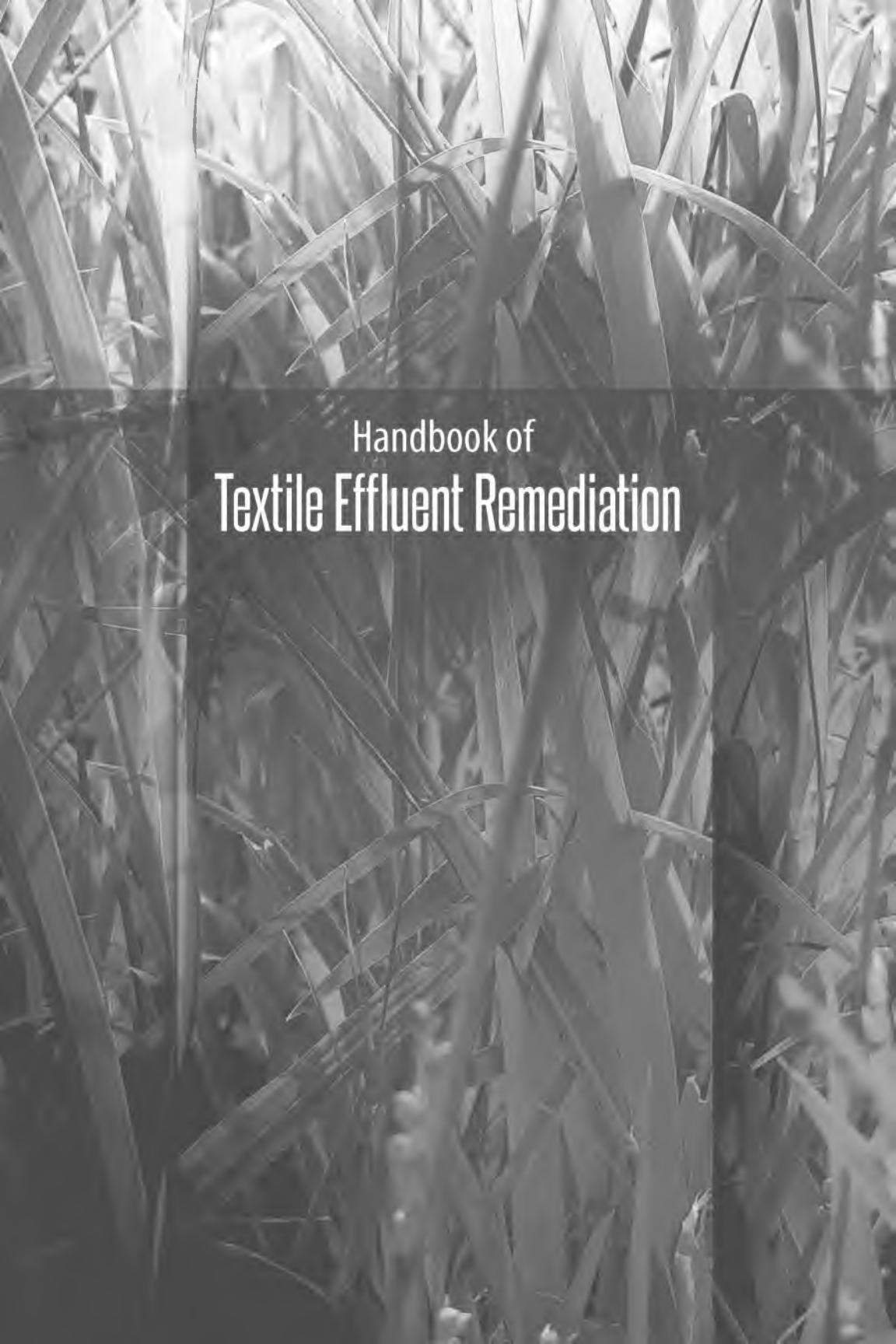


edited by Mohd Yusuf

Handbook of  
Textile Effluent Remediation





Handbook of  
**Textile Effluent Remediation**



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# Handbook of Textile Effluent Remediation

edited by  
**Mohd Yusuf**



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## **Preface**

Nowadays, textile units utilize a number of dyes, chemicals, reagents, and solvents to impart the desired quality to fabrics, and generate a substantial quantity of effluents/contaminants, which cause severe environmental problems if disposed of without proper treatment. In view of several surveys carried out through research papers, books, technical articles, and general reports published in high-repute academic societies, this book provides an in-depth look at the acceptable treatment techniques/methods for textile wastewater, like active ozonation, membrane filtration, and adsorption. Emerging and suitable treatment systems that work viably, efficiently, and economically have been discussed. In this context, the book provides an array of traditional as well as advanced treatment practices related to textile effluents. Needless to say, this book will be of immense use to global processors, academicians, consultants, etc., engaged in wastewater treatment.

**Mohd Yusuf**  
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## **Chapter 1**

# **Textile Effluents: Types and Prominent Hazards**

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According to surveys measuring natural resource use in all industries, textile dyeing and finishing mills use considerably more water than most—more than 200 tons of water for every ton of textiles produced. Many of the chemicals used in textile production are nonhazardous, but a relatively small proportion of these chemicals is potentially hazardous. Around 25% of the chemical compounds produced worldwide are used to a greater or lesser extent in the textile industry globally. More than 2000 different chemicals are used in textile processing, especially in textile wet processing, many of which are known to be harmful to human (and animal) health. Clean water is a finite resource that is becoming scarce. Once charged with chemical additives the water is expelled as wastewater, which, if untreated, may pollute the environment

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by virtue of the high temperature of the effluent; extreme pH; and/or contamination with dyes, diluents of dyes, auxiliaries, bleaches, detergents, optical brighteners, and many other chemicals used during textile processing.

Different impurities commonly present in water are grouped as suspended solids, dissolved mineral salts, organic and coloring matters, dissolved gases, bacteria, and other microorganisms. Some of the parameters of water that may change due to pollution are color, turbidity, dissolved solids, pH, dissolved oxygen (DO), adsorbable organic halogens (AOX), degradability of wastes in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD), and oils and grease.

## 1.1 Introduction

Industrialization has become an important factor to the development of a country's economy, through the establishment of plants and factories. However, the waste or by-products discharged from them are severely disastrous to the environment, contaminating the surface water, groundwater, and soil.

China has some of the worst water pollution in the world, with as much as 70% of its rivers, lakes, and reservoirs being affected; and the textile industry, an important sector of China's economy, with more than 50,000 textile mills in the country, contributes to some of this pollution. On the basis of Greenpeace's investigation, the report *Dirty Laundry* describes the problem of toxic water pollution resulting from the release of hazardous chemicals by the textile industry in China. The water pollution poses serious and immediate threats to both ecosystems and human health [1].

Dyes are creating a chemical Fukushima in Indonesia. The Citarum River is considered one of the most polluted rivers in the world, due in great part to the hundreds of textile factories lining its shores. According to Greenpeace, with 68% of the industrial facilities on the Upper Citarum producing textiles, the adverse health affecting the 5 million people living in the river basin and wildlife is alarming.

Little care was paid to Indonesia's water infrastructure when its textile boom began; proper framework for waste disposal was largely neglected. Clothing manufacturers dumped their chemicals into the river, making the Citarum nothing more than an open sewer containing lead, mercury, arsenic, and a host of other toxins. Greenpeace tested the discharge from one of the textile plants along the Citarum and found disturbing amounts of nonylphenol, an endocrine disruptor, which can be deadly to aquatic life. Greenpeace also found that the water was high in alkalinity—equivalent to that of lye-based drain openers—and had apparently not even received the most basic of treatments. According to Greenpeace the discharge is “highly caustic, will burn human skin coming into direct contact with the stream and will have a severe impact (most likely fatal) on aquatic life in the immediate vicinity of the discharge area” [1].

The menace caused by nonylphenol doesn't end at the Citarum River. The chemical remains in our clothes after they are produced and only comes out after a few washes. For this reason, the European Union member states have banned imports of clothing and textiles containing nonylphenol ethoxylates (it banned nonylphenol for its own textile manufacturing more than a decade ago). While these are not banned in the United States, the Environmental Protection Agency has identified eight safer alternatives to nonylphenol ethoxylates.

Altogether, more than half a trillion gallons of freshwater are used in the dyeing of textiles each year. The dye wastewater is discharged, often untreated, into nearby rivers, where it reaches the sea, eventually spreading around the globe. China, according to Yale Environment 360, discharges roughly 40% of these chemicals [2].

There are trends in developing countries to use sewage as fertilizer; this has gained much importance as it is considered a source of organic matter and plant nutrients and serves as a good fertilizer [3]. Farmers are mainly interested in general benefits of sewage, for example, it increases agriculture production and is a low-cost water source, effective way of effluent disposal, and source of nutrients and organic matter, but are not well aware of its harmful effects, like heavy metal contamination of soils and crops and quality problems related to health. Research has proven that long-term use of this sewage for irrigation contaminates soil and crops to such an

extent that it becomes toxic to plants and causes deterioration of soil [4].

The global textile and clothing industry is bound to be huge as it fulfills the second basic requirement of man. It is worth \$480 billion at present and is expected to reach \$700 billion shortly. This is because people are getting increasingly conscious of the way they dress. It has become a means to create an impression and represent the personality. Surveys show that nearly 5% of all landfill space is consumed by textile waste. Besides, 20% of all freshwater pollution is by textile treatment and dyeing. Surveys show that cotton consumes the highest amount of harmful pesticides and fertilizers, a majority of which fall on land while they are sprinkled on crops. Similarly, textile manufacturing units release hazardous waste onto nearby land [5].

In a textile processing plant, water is a vital raw material, not only for the boilers supplying steam for heating and drying purposes, but also for all the wet processes, such as scouring, bleaching, dyeing, printing, and finishing. The success of these processes largely depends on the quality of the water being used. Generally, water of two qualities has to be maintained separately—very pure quality for feeding to the boiler and moderately pure quality for processing purpose.

## 1.2 Impurities and Their Effects

It is necessary that the quality of effluent water be checked at regular time intervals. It is necessary to know details about different physicochemical parameters, such as color, temperature, acidity, hardness, pH, sulfate, chloride, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), and alkalinity, used for testing of water quality. Heavy metals such as Pb, Cr, Fe, and Hg are of special concern because they produce water or chronic poisoning in aquatic animals.

Different impurities commonly present in feedwater as well as in discharge or effluent water are as follows [6]:

- Suspended solids
- Dissolved mineral salts
- Organic and coloring matters

- Dissolved gases
- Bacteria and other microorganisms

The impurities affect the following characteristics of water and are, therefore, assessed regularly for feedwater as well as effluent water in textile industries.

### 1.2.1 Suspended Solids

Suspended solids make water turbid. Turbidity, an optical property of water, is a measure of the extent to which light is either absorbed or scattered by suspended materials in water. Both the size and surface characteristics of suspended materials influence the absorption and scattering of light through a water sample. The erosion of soil and the presence of excessive vegetable fibers and microorganisms may cause turbidity. Usually, domestic and industrial wastewater contains soap, detergent, and other emulsifying agents, which produce stable colloids and thus cause turbidity. Turbidity of water is not only aesthetically displeasing but also not acceptable to environmental engineers because the colloidal materials associated with turbidity provide absorption sites for chemicals as well as microorganisms that may be harmful. Turbidity reduces the efficiency of chlorination in water treatment plants and may interfere with light penetration and photosynthesis in natural water bodies.

### 1.2.2 Dissolved Mineral Salts

In surface and underground water, sodium chloride and sodium sulfate are commonly present. In addition, carbonates, bicarbonates, sulfates, and chlorides of calcium and magnesium may also be present in varying quantities. Iron salts may be present in considerable quantities, especially in underground water. Zinc and copper salts are occasionally present in trace quantities. Due to dissolved solids, especially calcium carbonate and calcium sulfate, scales are formed on the metal surface. Scale formation reduces the heat transfer rate as well as the thermal efficiency of the boiler plant. More serious problems, like failure of the water tube, may occur due to overheating. Corrosion may occur due to the presence of dissolved alkalis, acids, and salts and dissolved gases, like oxygen.

Iron salts are detrimental to textile processing in many ways. In scouring and bleaching, they impart yellow tints to white goods and may cause catalytic decomposition of bleaching agents and consequently degradation of the textile materials. In dyeing, iron may form a complex with some dyes, causing dulling of shades.

Estimation of solid content (ppm = parts per million) may be done in terms of total solids (TS), total dissolved solids (TDS), and suspended solids.

### **1.2.2.1 Total solids**

A known volume (100 mL) of water sample is taken in a dry-weighed evaporating disc and evaporated to about the dryness preferably on a sand bath. It is then transferred to an oven maintained at  $105^{\circ}\text{C} \pm 5^{\circ}\text{C}$  and kept for 1 hour. It is then cooled and weighed (g = grams).

$$\text{TS (ppm)} = \frac{\text{Weight of solid (g)} \times 10^6}{\text{Volume of sample (mL)}} \quad (1.1)$$

### **1.2.2.2 Total dissolved solids**

The same method and formula may be used for the estimation of TDS using water after filtration. Electrical conductivity also estimates the amount of total dissolved salts or the total amount of dissolved ions in the water. In marine observation, conductivity is measured by a temperature and conductivity recorder that can convert the measurement into salinity. In estuaries, salinity is an important factor for habitats of aquatic life.

### **1.2.2.3 Suspended solids**

Suspended solids (ppm) are the difference in the value of TS and TDS.

## **1.2.3 Dissolved Gases**

Gases like carbon dioxide, oxygen, nitrogen, ammonia, and hydrogen sulfide are found dissolved in varying quantities in water.

DO is one of the most important parameters. Its correlation with the water body gives direct and indirect information, for example, bacterial activity, photosynthesis, availability of nutrients, and stratification [7]. As summer progresses, DO decreases due to an

increase in the temperature and also due to increased microbial activity. The high DO in summer is due to an increase in the temperature, and the duration of bright sunlight has an influence on the percentage of soluble gases ( $O_2$  and  $CO_2$ ). During summer the long days and intense sunlight seem to accelerate photosynthesis by phytoplankton, utilizing  $CO_2$  and giving off oxygen. This possibly accounts for the greater quantities of  $O_2$  recorded during summer [8].

DO in a sample is measured titrimetrically by Winkler's method after 5 days of incubation at 293 K. The difference in the initial and final DO values gives the amount of oxygen consumed by the bacteria during this period, and the measure is termed as BOD.

The DO is the most important measure of water quality. A low level of DO recorded could result in the nonmaintenance of conditions favorable to aerobic organisms. This could lead to anaerobic organisms taking over, with the resultant creation of conditions making the water body uninhabitable to gill-breathing aquatic organisms.

#### 1.2.4 Alkalinity

The bicarbonate and carbonate salts present in water are responsible for the alkalinity of water. The amount of mineral acid consumed for the neutralization of a known volume of water is denoted as the index of alkalinity. Excessive alkalinity may interfere with dyeing or finishing processes and may corrode metallic surfaces. It may also cause foaming in the boiler followed by carryover of solid particles with steam.

A known volume (50 mL) is taken in a conical flask and a phenolphthalein indicator (four to five drops) is added. The solution is titrated against standard hydrochloric acid (preferably 0.1 N) until the end point (pH 8.3) is reached. The acid consumed at this stage is known as  $P$  alkalinity and is a measure of the carbonate present. If the end point is reached before titration, it may be concluded that carbonate is absent and alkalinity is due to the bicarbonate present. The sample after titration with phenolphthalein is titrated with methyl orange until the end point (pH 3.8) is reached. The total acid consumed is an index of total alkalinity,  $M$ , expressed as  $CaCO_3$ .

$$\text{Total alkalinity, } M \text{ (as CaCO}_3, \text{ ppm}) = \frac{\text{Volume of acid consumed}}{\frac{(\text{mL}) \times N \times 50 \times 10^3}{\text{Volume of sample (mL)}}}, \quad (1.2)$$

where  $N$  = normality of acid.

### 1.2.5 Metals

The contamination of metals is a major environmental problem, especially in the aquatic environment. Some metals are potentially toxic or carcinogenic even at very low concentrations and are, thus, hazardous to humans if they enter the food chain. Metals usually enter the aquatic system from natural or anthropogenic sources. Metal ions are distributed thoroughly during their transport in the different biotic and abiotic compartments of the aquatic ecosystems, such as fishes, water, sediments, and plants. Metals remain in contaminated sediments and may accumulate in microorganisms that in turn enter the food chain and eventually affect human well-being.

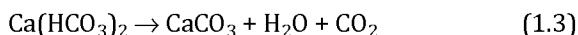
Rai and Tripathi [9] commented that most metals in the aquatic environment are in the form of particulate matter—they settle and accumulate in the bed sediments. The accumulation of contaminants in bed sediments and the remobilization of contaminants are the most important mechanisms of contaminant regulation in an aquatic ecosystem. Furthermore, under certain circumstances, such as deficit in the DO or decrease in the pH, the bed sediments can be another source of secondary water pollution when the heavy metals from the bed sediments are released.

### 1.2.6 Hardness

The presence of salts of calcium or magnesium in water is responsible for the hardness of water and leads to the formation of insoluble precipitates with soap. These may be deposited on the goods, thereby assisting in soil deposition and affecting handle (stiffening) of the cloth. Usually they are not deposited evenly and are one of the causes of poor leveling in subsequent dyeing. Moreover, these salts may precipitate some dyes during dyeing or form complexes resulting

in dulling of shades. Other metal salts, such as iron and strontium, may also contribute to hardness, but they are generally present in smaller amounts as compared to calcium and magnesium. Iron salts are, however, very harmful in textile dyeing and are responsible for dulling of shades. In effluent water, hardness may increase to an unacceptable level due to the incorporation of various metallic salts from impurities of the fibrous material or process chemicals.

Two types of hardness may be distinguished, temporary and permanent. Temporary hardness arises from bicarbonates and can be removed simply by boiling, when the bicarbonates precipitate as carbonates.



It is a contributory factor in the formation of scales in boilers, which are deposits, among other things, of calcium carbonate and magnesium hydroxide, the latter being a decomposition product of magnesium carbonate.



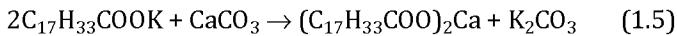
Permanent hardness is associated with sulfates and chlorides of calcium and magnesium. These are highly soluble in water, and expulsion of dissolved gases makes no difference in their solubility. These require chemical treatment for their removal. Water from most sources has both temporary and permanent hardness, but the proportion of the two varies.

### 1.2.6.1 Expression of hardness

Irrespective of the salts present, hardness is expressed in terms of  $\text{CaCO}_3$ . Hardness may be expressed in degrees or in parts per million. Units of hardness vary from country to country, and some of them are listed in Table 1.1. In British usage, water of  $0^\circ\text{--}4^\circ$  is soft,  $4^\circ\text{--}7^\circ$  is moderately hard,  $7^\circ\text{--}20^\circ$  is hard, and  $>20^\circ$  is very hard.

### 1.2.6.2 Estimation of hardness

The simplest method is based on titration with a standard soap solution, which depends upon the following reaction:



It follows that  $2 \times 282$  g of oleic acid is equivalent to 100 g of calcium carbonate.

**Table 1.1** Units of water hardness

<b>Unit (°)</b>	<b>Definition</b>	<b>Quantity in parts per million</b>
American	1 grain CaCO <sub>3</sub> /US gallon	17.1 as CaCO <sub>3</sub>
British/Clark	1 grain CaCO <sub>3</sub> /UK gallon	14.3 as CaCO <sub>3</sub>
French	1 part CaCO <sub>3</sub> /10 <sup>5</sup> parts water	10 as CaCO <sub>3</sub>
German	1 part CaO/10 <sup>5</sup> parts water	10 as CaO; 17.9 as CaCO <sub>3</sub>
Russian	1 part Ca/10 <sup>6</sup> parts water	2.5 as CaCO <sub>3</sub>

Source: [10]

A standard soap solution is prepared by dissolving pure oleic acid in alcohol and made neutral to phenolphthalein by stirring into concentrated potassium hydroxide solution until a pink color appears, which is finally discharged with just enough oleic acid. The solution is then diluted with a mixture of alcohol and water (2:1). The solution is standardized against calcium chloride. The soap solution is used, generally, to determine total hardness only. The test method is very simple, but the accuracy is limited [11].

More accurately, hardness is estimated by titration with standard EDTA (ethylenediaminetetraacetic acid) solution (disodium salt). A buffer is prepared by dissolving 6.75 g of pure ammonium chloride in 57 mL of ammonia and enough water to make 100 mL of the buffer. Buffer tablets may be used. An indicator is prepared by mixing 0.5 g Solochrome Black WDFA (ICI) or Eriochrome Black T (Geigy) (C.I. Mordant Black 11, 14645) (Colour Index number and structure number) with 4.5 g of hydroxylamine hydrochloride and the mixture is dissolved in 100 mL water. The dye, blue in alkaline solution (pH 10), forms a red complex with Ca or Mg ion. During titration, these metals preferably combine with EDTA to form the dye-complex (red). Consequently, the blue color of the dye reappears. A known volume (50 mL) of the water sample is taken in a conical flask. Two mL of the buffer and four to six drops of the indicator are added and titrated until the red or pink color of the solution turns blue.

$$\text{Total hardness (as CaCO}_3, \text{ ppm}) = \frac{\text{Volume of EDTA solution used (mL)} \times 10^6}{\text{Volume of sample (mL)}} \quad (1.6)$$

### 1.2.7 Total Chlorides

Chlorides are not usually harmful to people; however, the sodium part of table salt has been linked to heart and kidney disease. Sodium chloride may impart a salty taste at 250 mg/L. High concentrations of dissolved salts in water compromise its use for domestic or agricultural purpose. An excess of Cl<sup>-</sup> in inland water is usually taken as an index of pollution and can be provided across sanitary and industrial water. Depending upon the end user, there are maximum concentration limits recommended. Surface water with a chloride concentration below 25 mg/L belongs to the first class of quality, and water with a chloride concentration of 25–50 mg/L belongs to the second class of quality.

Chloride is estimated by titration with standard silver nitrate solution (0.1 N) using potassium chromate as the indicator. The end point is judged by the appearance of an orange precipitate of silver chromate.

$$\text{Total chlorides (as Cl}^{-}\text{, ppm}) = \frac{\text{Volume of silver nitrate (mL)} \times \text{N} \times 35.5 \times 10^3}{\text{Volume of sample (mL)}}, \quad (1.7)$$

where  $N$  = normality of silver nitrate.

### 1.2.8 Total Sulfates

The water sample is evaporated to dryness, and the solid is treated with concentrated hydrochloric acid to convert it into chlorides. The solution is again evaporated to dryness and redissolved with dilute hydrochloric acid. Ammonium chloride and ammonium hydroxide are added to precipitate metallic ions of iron, aluminum, etc. Ammonia is boiled off, and the solution is filtered. To the hot filtrate, concentrated hydrochloric acid and barium chloride are added and the solution is kept overnight to precipitate sulfates as BaSO<sub>4</sub>. The precipitate is filtered, washed, refiltered, and ignited with the filter paper, and the residue is weighed as BaSO<sub>4</sub>.

$$\text{Total sulfates (as SO}_4^{2-}\text{, ppm}) = \frac{96.06 \times \text{weight of BaSO}_4 \text{ (g)} \times 10^6}{\text{Volume of sample (mL)}} \quad (1.8)$$

### 1.2.9 Nutrients

For water quality evaluation, preconfirmation of the presence of matter created by the decomposition of wastes of animal origin is important. In polluted water, varied products can appear: C and S compounds, with a special importance being accorded to N compounds. Nitrogen may be in the form of nitrate, nitrite, ammonia, or ammonium salts or what is termed “albuminoid nitrogen” together with an organic proteinoid molecule. The differing forms of nitrogen are relatively stable in most river systems, with nitrite transforming into nitrate in well-oxygenated rivers and ammonia transforming into nitrite/nitrate. However, the process is slow in cool rivers, and a reduction in concentration may more often be attributed to simple dilution. All forms of nitrogen are taken up by algae, and elevated levels of nitrogen are often associated with overgrowth of plants. Thus high levels of nitrogenous compounds tend to lead at extreme variations in parameters, which in turn can degrade the ecological worth of the watercourse.

Ammonium is a nutrient for plants but can also have a toxic effect, especially on fish, when its concentration is higher than 0.2 mg/L. The toxicity of ammonia is dependent on pH and temperature and due to the added buffering effect, any additional toxicity is masked over pH = 8 [12].

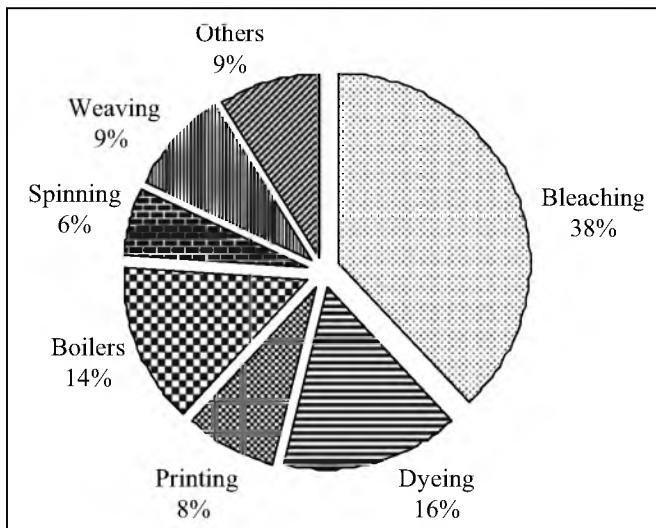
## 1.3 Water Consumption

Numerous studies by the Ahmedabad Textile Industry's Research Association (ATIRA) [6] show that the daily water consumption of an average-sized textile mill in India having cloth production of about 8000 kg/day is about 1.6 million liters.

The pattern of water consumption for the various processes/plants is illustrated in the pie chart in Fig. 1.1, which shows that the highest water consumption is in the bleaching department. ATIRA norms for water consumption in various stages of textile wet processing are shown in Table 1.2.

Impurities like iron, calcium, and magnesium salts are undesirable since they create problems in dyeing and finishing. By using water free from the above metallic ions, the damage in dyeing and finishing can be reduced. Since the volume of water utilized in the wet

processing of a mill is very high, mills generally cannot afford very sophisticated treatments, like partial or full demineralization. The precipitation process, like the soda-lime process, is unacceptable, due to the fact the soft water available from the process contains a large amount of suspended solids and occasionally the pH is very high. Hence, the mills use simple sodium ion exchangers for the treatment of water.



**Figure 1.1** Water consumption in a textile mill.

**Table 1.2** Water consumption in wet processing

Process	Liters/kg of material
Conventional bleaching	90
Continuous bleaching	70
Mercerizing	25
Cloth dyeing (jigger)	45
Cloth dyeing (continuous)	35
Yarn dyeing (package)	60
Printing	100
Finishing	15

Source: [13]

Impurities lead to scale formation and/or corrosion depending on the composition of the impurities. Scale formation, in turn, leads to overheating of water tubes. These result in lower heat transfer rates from the metal surfaces and also at times failure of and breakdown in steam generation systems. Other consequences of impurities are carry-over of solids in steam, priming, and foaming.

## 1.4 Effects of Effluent Characteristics

The effect of pollution on effluent water may be physical, chemical, and biological. The color, turbidity, taste, and odor are heavily affected by contamination, and the water becomes unfit for domestic consumption. The change in pH and salt content makes the water corrosive for industrial and boiler uses.

A variety of substances, the majority of which are organic, are oxidized biochemically in the receiving water bodies and, thereby, reduce the amount of DO available. Biodegradable organic matters are utilized by natural microorganisms during metabolic processes as their source of food and energy. Municipal wastewater, industrial effluents, and agricultural (irrigation) return water are some of the sources of oxygen demanding substances. Some biodegradable substances are starch, fat, protein, acid, alcohol, aldehyde, and ester. Aerobic metabolism of aquatic microorganisms predominates when oxygen is available. The end products of such metabolism are more or less nonobjectionable. But as soon as the DO drops, fish and other aquatic life forms are threatened and in extreme cases, killed. Subsequently in an oxygen-depleted environment, very quickly anaerobic metabolism commences, utilizing the remaining food or substrate. The end product of such anaerobic metabolism is undesirable, and the resulting odor, taste, and color reduce the acceptability and attractiveness of water.

Nonbiodegradable or refractory substances are resistant to biochemical degradation; some of them are even hazardous. Examples of such refractory substances are tannic acid, lignic acid, cellulose, and phenols. Some polysaccharides and benzene are nonbiodegradable. Alkyl benzene sulfonate (ABS), widely used in the manufacture of detergents, is nonbiodegradable, while its substitute linear alkyl sulfonate is biodegradable and thus ecofriendly.

Nutrients include all inorganic substances required by aquatic life forms for their growth in macro- or microquantities. The nutrients of major concern are nitrogen and phosphorous, while those like calcium, iron, manganese, and boron are also added to the aquatic environment. In terms of water quality, these may be considered as pollutants when they encourage excessive growth of aquatic plants, particularly algae. The process of nutrient enrichment is known as "eutrophication." Any uncontrolled discharge of phosphates is likely to cause eutrophication.

#### 1.4.1 Adsorbable Organic Halogens

Only a few natural organic substances contain halogens in their molecules, and chlorinated organic compounds are usually synthetically produced. Because of their manifold favorable qualities, they have found widespread acceptance in households and industry throughout the world. Unfortunately, their environmental risk is also considerable. Most of them are resistant to biodegradation. They are lipophilic and concentrate in fatty tissues. In addition to being acutely toxic to human beings, many organohalides are proven or suspected carcinogens.

In the strictest sense of the term, AOX is a measured value for organically bound chlorine, bromine, and iodine in a given substance. It cannot be ruled out that in the future, fluorine compounds will also be included in the list of AOX donors. When selecting products, textile finishers insist on being informed about the theoretical AOX value of a product. This indicates its theoretically calculated halogen content.

In the early 1970s, Kuhn and Sontheimer in Germany developed the AOX method for the analysis of organohalogens, consisting of adsorption on activated carbon, rinsing off of inorganic chlorides, pyrolysis of the organohalogens, and microcoulometry. The result is expressed in milligrams of chlorine per liter, regardless of the actual composition (chlorine, bromine, or iodine). The AOX method was standardized first in Germany (DIN 38409H14). Having the highest recovery rates and being most practicable, this method of determination has meanwhile come into worldwide use. Federal effluent law sets a threshold value of 100 µg/L AOX for discharge into surface water and permits a discharge of 0.5 mg/L of AOX into

sewage plants. A criticism often raised is that the AOX method does not differentiate between hazardous and nonhazardous substances, as there is no quick screening test for such differentiation. Bleaching is the main source of AOX in cotton processing. Pretreatments like alkaline boiling significantly reduce the AOX level. AOX concentrations after bleaching are higher if the cotton contains greater amounts of impurities. In the chlorine-Hercosett (Hercules) process of shrink-proofing wool, the AOX concentration may be as high as 39 mg/L in the effluent, representing an average AOX load of 350 g/ton of wool processed. In the dichloroisocyanuric acid (DCCA) method of shrink proofing, the continuous process yields high AOX values due to excess reagent and discontinuous batch processes give lower AOX concentrations, that is, below 10 mg/L [14].

In dyeing, reactive dyes and other dyes containing halogens in the chromophore and/or reactive group may increase the AOX level. In dyes, halogens are deliberately introduced to achieve desirable properties. The presence of halogen atoms may affect shade, light fastness, other end-use fastness properties and application characteristics of dyes. It is virtually impossible to attain the present state of the art in every case exclusively with halogen-free products. Among the reactive dyes, certain reactive groups are based on halogenated heterocycles. A halogen atom that is split off during covalent bond formation cannot be considered an AOX-active halogen. The AOX value (Cl in mg/L) of a residual dyebath may be calculated as follows:

$$\text{AOX} = \frac{C \times (100 - E) \times H \times 35.5}{10 \times V \times M}, \quad (1.9)$$

where  $C$  = concentration of dye in g/L,

$E$  = % exhaustion of dye,

$H$  = theoretical halogen content %,

$V$  = bath volume in liters, and

$M$  = molecular weight of halogen.

For 2% dyeing in a dyebath with an  $M:L$  ratio of 1:10 and 95% exhaustion of a dye of theoretical halogen content of 5%, the AOX concentration in the residual bath is estimated to be 5 mg/L from the above equation. On the basis of experience published in the literature, it must be assumed that discoloration is necessary

whenever the dye concentration in the wastewater released to the treatment plant exceeds 5 mg/L.

Simple filtration reduces AOX significantly. Microfiltration yields a reduction of up to 40%. Flocculation reduces AOX by about 50%, but large amounts of flocculating agents are required and the AOX-containing floc would have to be disposed of or incinerated. Adsorption on charcoal is effective but expensive [15].

According to an estimate in 1977 [16], about 40,000 to 80,000 tons of dyes and 1500 to 1800 tons of pigments are discharged in a year by the textile processing units due to incomplete exhaustion, washing operation, etc. About 15% of the total world production of colorants is lost in the synthesis and processing of colorants. About 10%–20% of dyes are lost in residual liquor due to incomplete exhaustion. For water-insoluble pigments, the loss is only 1%–2%. One of the major factors determining the release of a dye to the environment is its degree of fixation on the substrate. The fixation, on the other hand, is clearly dependent on individual circumstances and governed by several factors, including depth of shade, application method, and liquor ratio. It is, therefore, impossible to give a definite set of figures. A tentative summary, given by Cooper [17], is shown in Table 1.3.

**Table 1.3** Estimated degree of fixation of various dyes on fibers

Dye class	Fiber	% Fixation	% Loss in effluent
Acid	Polyamide	80–95	5–20
Basic	Acrylic	95–100	0–5
Direct	Cellulose	70–95	5–30
Reactive	Cellulose	50–90	10–50
Sulfur	Cellulose	60–90	10–40
Vat	Cellulose	80–95	5–20
Metal complex	Wool	90–98	2–10
Disperse	Polyester	90–100	0–10

Source: [17]

The problem of colored effluent is mainly encountered while dyeing cellulosic fibers, which account for almost 50% of the total

fiber consumed by the textile industry. The table shows that as much as 50% of reactive dyes used may be lost to the effluent.

The dyes are not truly water pollutants since the biological effects are negligible. However, some azo dyes, for example, benzidine-based direct dyes, are easily reduced to colorless primary organic amines, which are more toxic than the original dyes.

The environmental problems posed by dyes are rather moderate in their impact, but great complexities arise due to the variation in chemical structures and properties of a few thousand dyes in use. The problem is enhanced by the fact that many auxiliaries used during dyeing, such as cationic fatty acid polymers and quaternary mono-, di-, and trialkyl ammonium salts, are not biodegradable and are difficult to remove.

Extensive tests indicate that the dyes are generally absorbed to the extent of 40%–50% by the biomass and are thus partially eliminated in sewerage plants; practically no biodegradation takes place. The large dye molecules have high affinity for various materials, and some are only sparingly water soluble. Porter and Snider [18] showed that most of the textile dyes are nonbiodegradable. Dyes are required to show a high degree of chemical and photolytic stability in order to fulfill the fastness requirements of textile materials. Due to such stability, they are not readily degraded under the aerobic conditions prevailing in the biological treatment plants. Therefore, unless color is removed by chemical or physical means, it may pass with the discharge water and lead to public complaint even if the concentration of the dye is as low as 1 mg/L. Unnatural colors, like red and purple, usually cause most concern; blue, green, and brown colors are less objectionable.

While colored organic substances generally impart only a small fraction of the total organic load in wastewater, their high degree of color is easily detectable and detracts from the aesthetic value of streams, rivers, etc. As far as the public is concerned, the removal of color is often much more in demand than the removal of soluble, colorless organic substances, which usually contribute more to increase the BOD of the wastewater. Small quantities of dyes (less than 1 ppm for some dyes) are visible in water and so give rise to concern. Most dyestuffs have a mammalian toxicity low enough not to cause problems.

Dyestuff manufacturing units are more polluting. Many of the dyestuff intermediates are toxic, and some are even carcinogenic. Dyestuff manufacture involves sulfonation, nitration, reduction, aminolysis, diazo coupling, etc., which account for large organic and inorganic chemical inputs. The combination of these processes generates diverse liquid, gaseous, and solid pollutants that eventually migrate to our ecosystem. The injurious biological effects of the waste products as listed by Roy Choudhury [19] are as follows:

- The suspended matters slowly settle at the bottom of rivers, destroying various plants under the sea and thereby killing fishes, which consume these plants as food.
- Materials having an oxygen demand reduce the DO content of the stream to a point where fishes cannot survive.
- Acidity or alkalinity of the discharge water affects the fish life; most fishes require a pH value of 6.4 to 8.4.
- Freshwater fishes cannot tolerate a sudden change in osmotic pressure due to an increase in salinity. About 7000 ppm of sodium chloride is usually lethal for freshwater fishes.
- Constant accumulation of toxic substances may kill fishes. High carbon dioxide concentration in water is also fatal for fishes.

## 1.5 Degradability of Wastes

There may be three cases of biodegradability: readily biodegradable, inherently degradable, and bioeliminable.

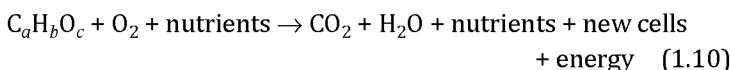
- A substance may be readily biodegradable, which is easily degraded in natural watercourses.
- Inherently degradable substances show very good biodegradation in wastewater treatment plants.
- Bioeliminable substances show good eliminability in the simulated conditions of a wastewater treatment plant.

The degradability of the waste chemicals can be measured by two parameters, one measuring the oxygen demanded (BOD) and one measuring that consumed during degradation (COD), also known as the dichromate value (DV) [11].

### 1.5.1 Biological Oxygen Demand

BOD is the amount of DO needed (i.e., demanded) by aerobic biological organisms to break down the organic material present in a given water sample at a certain temperature over a specific time period. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20°C and is often used as a surrogate of the degree of organic pollution of water [20].

BOD is the amount of O<sub>2</sub> used in the metabolism of biodegradable organics as follows:



Under normal conditions, the oxygen absorbed by bacteria is replaced by fresh DO derived from the air. The total amount of oxygen absorbed over a period of 5 days at a temperature at which bacteria can breed is a very good pragmatic measure of the objectionable nature of the effluent. This is measured by estimating BOD.

BOD is determined by estimating the DO in water both before and after incubation at 20°C for 5 days. The difference between the two values multiplied by the dilution factor gives the BOD. A measured quantity of the sample under investigation is diluted with well-oxygenated water so that not more 50% of the oxygen present will be absorbed by the end of 5 days. The mixture is taken in a 250 mL stoppered bottle in such a way that no air bubble is trapped at the top. The DO is measured by adding 1 mL of a saturated solution of manganese chloride, introduced by a pipette reaching nearly to the bottom of the bottle, and similarly 1 mL of a 33% solution of sodium hydroxide containing 10% of potassium iodide is added. Finally, the mixture is acidified with hydrochloric acid. Iodine is liberated in a quantity equivalent to that of DO and is titrated with a centinormal sodium thiosulfate (0.248 M) solution, 1 mL of which is equivalent to 0.00008 g of oxygen.

### 1.5.2 Chemical Oxygen Demand

In environmental chemistry, the COD test is commonly used to indirectly measure the amount of organic compounds in water. Most

applications of COD determine the amount of organic pollutants found in surface water (e.g., lakes and rivers) or wastewater, making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution.

The dichromate test to measure COD is based on the amount of potassium dichromate used in oxidizing the organic matters in water. In a flask, 10 mL of a water sample is taken. To avoid interference from chlorine, mercuric chloride is added, which forms a complex with chlorine. Silver sulfate is also added as a catalyst to promote oxidation of low-molecular-weight fatty acids. To this, 5 mL of a 0.020833 M dichromate solution is added and the mixture is boiled gently under a reflex condenser for 2 hours. After cooling, the residual dichromate is determined by titration with a standard ferrous ammonium sulfate solution, using ferror as an indicator. A blank test using pure water as a sample is also to be carried out. COD can be measured much faster than BOD.

Essentially BOD is the indirect measure of total biodegradable organic matters in water. In spite of low precision, the test is widely used for measuring organic matters in water because of the direct conceptual relationship between the BOD and the oxygen depletion potential of the waste. COD tests are used to quantify the total organic substances in water. In fact, COD is the oxygen equivalent of the amount of potassium dichromate required to oxidize the organic fraction of the wastes, under acidic conditions.

Both BOD and COD are key indicators of the environmental health of surface water supply. They are commonly used in wastewater treatment but rarely in general water treatment.

Biodegradability is the ratio of BOD and COD expressed as a percentage. If the biodegradability of wastewater is greater than 0.6, the waste can be treated biologically. When the ratio is less than 0.3, other methods are suggested for treatment. But when the ratio varies between 0.3 and 0.6, acclimatization of seed microorganisms is needed for effective biological treatment. Acclimatization involves gradual exposure of the waste in increasing concentrations to the seed or initial microbiological population under controlled conditions.

### 1.5.3 Total Organic Carbon

This method measures the organic carbon existing in wastewater by injecting a sample of the wastewater into a special device in which the carbon is oxidized to carbon dioxide and then the carbon dioxide is measured and used to quantify the amount of organic matter in the wastewater. This method is used only for small concentrations of organic matter.

## 1.6 Industrial Discharge

The contaminant from a discharge is directly related to the nature of the industry. For example, in the textile industry, the discharge usually has high COD and BOD and a strong color; the tannery industry, on the other hand, produces discharges that have high concentrations of metals such as cadmium.

## 1.7 Pollution by the Textile Industry

The textile industry has been cited as the most ecologically harmful industry in the world [21], while an argument was presented to CNN saying that water pollution is a major issue in China and that its textile industry, a large water user, has traditionally experienced wastewater problems [22]. In some cases, wastewater with extreme pH values and temperatures as well as high chemical loading is discharged (largely untreated) into groundwater.

The textile industry uses millions of gallons of water every day. The problem does not rest in the high usage, though! The waste is not treated to remove pollutants from it before it is disposed of into water bodies. The wastewater usually contains polybrominated diphenyl ethers (PBDEs), phthalates, organochlorines, lead, and many other chemicals that cause severe health problems and diseases in human beings.

The liquid effluents released by the textile industry are the most disturbing area of concern. This is because the toxic materials released through liquid waste are vast in quantity. They consist of chemicals such as formaldehyde (HCHO), chlorine, and heavy metals. Besides, they are disposed of into water bodies that reach

faraway areas and this water is used by a large number of people for drinking or for daily activities. These effluents need to be treated to reduce their toxic content before being released into water bodies.

Air pollution caused by the textile industry is also a major cause of concern. Boilers, thermo packs, and diesel generators produce pollutants that are released into the air. The pollutants generated are suspended particulate matter (SPM), sulfur dioxide gas, oxide of nitrogen gas, etc. The nearby areas with human population get affected adversely owing to the release of toxic gases into the atmosphere [23].

### 1.7.1 Usage of Chemicals

Around 25% of the chemical compounds produced worldwide are used to a greater or lesser extent in the textile industry globally [1]. As many as 2000 different chemicals are used in textile processing, especially in textile wet processing, many of which are known to be harmful to human (and animal) health. Some of these chemicals evaporate, some are dissolved in the treated water that is discharged into the environment, and some are retained in the fabric. A list of the most commonly used chemicals, some of which are involved in fabric production and linked to human health problems that vary from annoying to profound, have been published by the National Institute for Environmental Health Sciences (part of the US Department of Health and Human Services) [24].

Broadly, the restrictions concern the presence of the following chemicals on textiles beyond prescribed limits.

- Prohibited amines in azo dyes
- Chlorinated phenols
- Formaldehyde
- Extractable heavy metals
- Residual pesticides
- Allergenic dyes
- Chlorinated benzene and toluene compounds
- Phthalates
- Organotin compounds

There has been a significant increase over the past few years in the use of ecolabels, that is, environmental labels attached to a

variety of products to attract the attention of consumers to the environmentally positive features of the products. Generally, these labels are voluntary and mostly used for the promotion of the products on the basis of their environmentally friendly characteristics. In the case of textiles and clothing there are for the time being no ecolabels the use of which has been enforced by mandatory rules.

### 1.7.2 Colorants

Until the middle of the nineteenth century, the dyeing of textiles was based on natural products, but within 50 years of Perkin's discovery of mauveine in 1856, synthetic dyes accounted for over 90% of the dyes used, a spectacular change initiated by the relatively new science of organic chemistry [25].

Azo colorants are used to color textile fibers, leather, plastics, papers, hair, mineral oils, waxes, foodstuffs, and cosmetics. "Azo dye" is the collective term used to describe a group of synthetic dyes that rose to prominence in the 1880s and now comprise 70% of all organic commercial dyes. Azo dyes are popularly used because they dye cloth at 60°C, while azo-free dyes require 100°C. Also, azo dyes offer an extensive range of colors, better color fastness, and four times the intensity of the closest alternatives, making them invaluable to the textile industry.

However, under certain (reductive) conditions the azo group can cleave, producing potentially dangerous substances known as aromatic amines. These conditions are met in the digestive tracts and some organs of animals, including humans [26]. Twenty-four aromatic amines have been confirmed as, or implicated to be, carcinogens in humans, and as many as 5% of azo dyes can cleave to form these dangerous compounds [27a]. They can be present in dyed products and in the environment due to incomplete synthesis or degradation of azo dyes.

Instigated by the German azo ban, measures were taken in 2002 by the European Commission and other regulatory bodies worldwide to prohibit the marketing of products containing certain restricted azo dyes in articles that may come into contact with skin for a prolonged period of time. However, little equivalent regulation oversees the expulsion of hazardous dyes, restricted or not restricted, into the environment at the initial point of use, largely as waste from dyeing

factories, despite mounting evidence that this continued practice is damaging local ecosystems and is potentially detrimental to human health and well-being. The dyestuff lost through the processes of the textile industry poses a major problem for wastewater management. An estimated 200,000 tons of dyestuff is expelled into the global environment every year [27b]. The concentration of azo dyes in textile effluents can reach 500 ppm.

Through the dyeing process it has been calculated that colorant loss to the environment can be as high as 50%. Color is the first wastewater contaminant to be recognized, since a very small amount of azo dye in water (<1 ppm) is highly visible.

Scientific study in 1992 initially ascertained that occupational exposure to some aromatic amines, particularly benzidine, 2-naphthylamine, and 4-aminobiphenyl, dramatically elevates bladder cancer risk [28]. In one German dye plant, 100% of the workers (15 in number) involved in distilling 2-naphthylamine developed bladder cancer [29].

1,4-Diamino benzene is an aromatic amine whose parent azo dyes can cause skin irritation, contact dermatitis, chemosis, lacrimation, exophthalmos, permanent blindness, rhabdomyolysis, acute tubular necrosis supervene, vomiting gastritis, hypertension, and vertigo. Upon ingestion, it can cause edema of the face, neck, pharynx, tongue, and larynx, along with respiratory distress [28].

Aromatic amines can be mobilized by water or sweat, which aids their absorption through the skin and other exposed areas, such as the mouth. Absorption by ingestion is faster and so potentially more dangerous, as more dye can be absorbed in a smaller time frame. Water-soluble azo dyes become dangerous when metabolized by liver enzymes.

Azo dye release in an industrial effluent can also have an impact on human health in certain countries. In 2007, a study identified an azo dyeing plant as one of the sources of mutagenic activity detected in the Cristais River in Brazil, a source of drinking water for 60,000 locals. Though the drinking water was treated in a plant 6 km downstream of the discharge site, testing confirmed the presence of carcinogenic aromatic amines. When laboratory rodents consumed industrial effluent at 1%-10% concentration, an increase in pretumor lesions of the colon was observed [21].

### 1.7.3 Water Usage

Clean water is a finite resource that is becoming scarce and is used at every step of the wet processing sequence both to convey the chemicals into the material and to wash them out before the beginning of the next step. Once charged with chemical additives the water is expelled as wastewater, which, if untreated, may thermally pollute the environment by virtue of the high temperature of the effluent; extreme pH; and/or contamination with dyes, diluents of dyes, auxiliaries, bleaches, detergents, optical brighteners, and many other chemicals used during textile processing [30].

Problems are at their worst when there is inappropriate or incomplete effluent treatment or when polluted water is directly discharged without treatment, leading to polluted surface water and polluted aquifers [31]. As a result, any heavy metal constituents in effluents result in pollution, with both negative ecological impacts on the water body environment and deterioration of human health.

### 1.7.4 Pollution by Heavy Metals

Heavy metals have been defined as metals with elemental densities higher than 7 g/cm<sup>3</sup> [32]. Subsequently, the definition has been modified by various authors. However, the term “heavy metal” has never been defined by any authoritative body, such as the International Union of Pure and Applied Chemistry (IUPAC), and in any case, density is not of great significance in relation to the reactivity of a metal. A more useful definition is that heavy metals are the group of metals with atomic numbers between 22 and 34 and 40 and 52 and members of the lanthanide and actinide series that have a specific gravity four to five times greater than that of water [33]. With regard to toxicity, differentiation between metals depends upon the chemical properties of the metals and their compounds and upon the biological properties of the organisms at risk [34]. Heavy metals are some of the most harmful ecologically. In the case of humans, they may enter the body through food, water, or air or by absorption through the skin and exhibit a tendency to bioaccumulate, with many forming lipid-soluble organometallic compounds that accumulate within cells and organs, thereby impairing their functions.

Among many possible sources of heavy metals in textile operations are incoming fibers, water, dyestuffs (heavy metals are constituents of some classes of dyes and pigments), auxiliaries, finishing, chemical impurities, and the plumbing fittings used in dyeing and finishing plants [35]; heavy metals may also be found in plant fibers due to absorption from the soil in which they are grown. Once absorbed by humans, heavy metals tend to accumulate in internal organs such as the liver or kidneys, with serious effects on health, particularly when high levels of accumulation are reached. For example, high levels of lead can seriously affect the nervous system. The heavy metals typically referred to are antimony (Sb), arsenic (As), cadmium (Cd), chromium (VI), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), silver (Ag), tin (Sn), titanium (Ti), and zinc (Zn), many of which can be found in effluents from textile operations [36].

Both cadmium and lead are classified as carcinogens. Cadmium has been restricted in Europe for a long time. Cadmium and cadmium oxide were classified as carcinogens and aquatic acute and chronic toxic. Since December 31, 1992, cadmium has been prohibited under the Council Directive 76/769/EEC of the European Union (regulation concerning the registration, evaluation, authorization, and restriction of chemicals, henceforth REACH) [37]. Lead is restricted in the United States under the Consumer Product Safety Improvement Act (CPSIA) [38], and children's products that contain more lead than 600 ppm have been banned in the United States since February 10, 2009, while the permissible lead content in paint and similar surface-coating materials for consumer use is reduced from 600 ppm to 90 ppm; there are similar European regulations controlling the content [39].

Chromium (VI) is an undesirable by-product generated during the leather-tanning process whenever chrome tanning is employed. Chromium (VI) is a strong oxidant and a skin irritant and is classified as a carcinogen that needs to be controlled [40]. Nickel is found in alloys used for metal accessories on garments, such as buttons, zippers, and rivets. Some people are allergic to nickel and may experience serious skin irritation on coming in contact with nickel-containing accessories for an extended period. The release of nickel is restricted under the EU REACH Regulation (EC) No 1907/2006, Annex XVII [41].

The health hazards associated with some heavy metals and metalloids (e.g., arsenic) are listed in Table 1.4 [42].

**Table 1.4** Health hazards associated with some heavy metals and metalloids used in the textile industry

Metal/Metalloid	Associated health hazard
Lead (Pb)	Damage to the brain, nervous system, and kidneys and in mild cases, insomnia, restlessness, loss of appetite, and gastrointestinal problems
Mercury (Hg)	Damage to the brain
Cadmium (Cd)	Disorders of the respiratory system, kidneys, and lungs
Chromium (Cr)	Skin and respiratory disorders, ulceration of the skin, and cancer of the respiratory tract on inhalation
Arsenic (As)	Skin cancer, hyperpigmentation, kurtosis, and black foot disease

Heavy metals that have been transferred to the environment are highly toxic and can bioaccumulate in the human body, aquatic life, and natural water bodies and also possibly get trapped in the soil [43].

Heavy metals enter the environment through wastewater from different branches of the textile industry, in particular from discharged spinning baths, from man-made fiber-manufacturing plants, and from discharged effluents from dyeing machines, but while it contributes, the textile industry is not the only source of this type of pollution [44]; significant amounts of heavy metals enter the environment in many cities from vehicle emissions, and solid industrial wastes also contribute to contamination. Several other sources contribute to trace metal impurities, such as:

- Natural levels in our environment
- Impurities in reactants or raw materials
- Use of metal catalysts or reactants
- Corrosion of manufacturing plant equipment

Limits on heavy metal content do not apply to a product containing a listed metal as an inherent part of the molecular structure or formula, such as a metal-complex dye [45].

## 1.8 Quality of Textile Effluents

Textile mills discharge large quantities of effluent water into the public sewerage system or the surface water on open land that is to be treated up to certain tolerance limits. An average-sized mill having cloth production of about 8000 kg/day discharges about 1 million liters of effluent water per day. The characteristics of effluent water vary widely among various wet-processing sections. The desizing process consumes less water, but the effluents of this process are characterized by a high BOD value, high amounts of TDS, and a significant amount of suspended solids (mostly in colloidal form). Scouring effluents have high BOD and COD values, high temperatures (70°C–80°C), pH as high as 10–12, high amounts of cations in the form of sodium, and high amounts of TDS. Effluents from the dyeing section have high temperatures, high amounts of solids, high COD, pH normally above 7, and a high amount of sodium ion content.

Composite waste from an integrated cotton textile mill may contain several chemicals, predominantly starches, dextrins, gums, glucose, carboxymethyl cellulose, gelatin, waxes, pectins, alcohols, fatty acids, mineral and organic acids, soaps, detergents, sodium hydroxide, carbonates, sulfides, chlorides, sulfates, bleaching agents (peroxide and chlorine compounds), dyes, pigments, etc. The pH varies between 4 and 12, and also the color varies due to the presence of various dyes. The actual values of the various effluent parameters vary widely from unit to unit, but tentative ranges for a few parameters reported [46] are BOD 200–1800 mg/L, TS 1000–1600 mg/L, suspended solids 30–300 mg/L, alkalinity 300–900 mg/L, and chromium 0–25 mg/L.

The characteristics of composite effluents from various textile mills have been estimated by ATIRA [6]. The approximate range of values is shown in Table 1.5. Another study [47] reported pollution loads of various sectors of the textile industry as shown in Table 1.6.

Sizing agents are used to strengthen the warp yarns before weaving, which are subsequently removed before dyeing by a process known as desizing. Sizing units significantly increase the pollution load. The fungicide pentachlorophenol is used to prevent mildew formation. However, it is prohibited in effluents and must largely be eliminated at source. The BOD/COD data of various sizing

agents are given in Table 1.7. The effluent composition and the nature of pollutants in various steps of textile chemical processing are shown in Table 1.8.

**Table 1.5** Characteristics of composite effluents estimated by ATIRA

Characteristics	Estimated range
pH value	6.7–9.5
Total alkalinity, mg/L	500–796
TDS, mg/L	2180–3600
Suspended solids, mg/L	80–720
BOD, 20°C, 5 days, mg/L	60–540
COD, mg/L	592–800
Chlorides (as Cl) mg/L	488–1390
Sulfates (as SO <sub>4</sub> ) mg/L	47–500
Calcium (as Ca) mg/L	8–76
Magnesium (as M) mg/L	7–53
Sodium (as Na) mg/L	610–2175

**Table 1.6** Characteristics of effluents from different textile sectors

Characteristics	Cotton	Synthetic	Wool scouring (dyeing)
pH	8–12	7–9	3–10 (5–10)
BOD	150–750	150–200	5000–8000 (500–600)
COD	200–2400	400–650	10 <sup>4</sup> –2 × 10 <sup>4</sup> (1700–2400)
Alkalinity	180–7300	550–630	80–100 (240–300)
Phenol	0.03–1	-	-
Oils and grease	4.5–30	-	2000–2500 (400–500)
Suspended solids	35–1750	50–150	5000–6000 (500–700)
TDS	2100–7700	1060–1080	10 <sup>4</sup> –1.3 × 10 <sup>4</sup> (800–1000)

The quantities are in mg/L. The bracketed quantities are for wool dyeing units.

*Source:* [47]

When textile mill effluents are discharged into inland surface water and public sewerage and on to land for irrigation purpose, the tolerance limits for various substances (in mg/L, maximum

permissible) and parameters commonly encountered in the effluents are specified by the Bureau of Indian Standards as given in Table 1.9.

**Table 1.7** Pollution load of sizing agents

Agents	COD (mg O <sub>2</sub> /g)	BOD (mg O <sub>2</sub> /g)
Starch	900–1000	500–600
CMC	800–1000	50–90
PVA	1700	30–80
Polyacrylates	350–1650	50
Galactomanans (Guar gum)	1000–1150	400
PET dispersions	1600–1700	50
Protein based	1200	700–800

**Table 1.8** Effluent characteristics of textile industry processes

Process	Effluent composition	Pollutant nature
Sizing	Starch, waxes, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVA), wetting agents, fungicide (pentachlorophenol)	High BOD and COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins	High BOD, COD, suspended solids, and TDS
Bleaching	Sodium hypochlorite, chlorine, caustic soda, hydrogen peroxide, acids, surfactants, sodium silicate, sodium phosphate, short cotton fiber	High alkalinity and suspended solids
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD, and high DS
Dyeing	Dyestuffs, urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents	Strongly colored, high BOD and DS, and low suspended solids and heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross linkers, reducing agents, alkali	Highly colored, high BOD, oily appearance, suspended solids, and slightly alkaline

**Table 1.9** Tolerance limits of various substances (mg/L, maximum) as industrial effluents for discharge to various destinations

Characteristics	ISW <sup>a</sup>	PS <sup>b</sup>	AL <sup>c</sup>
pH	5.5–9	5.5–9	5.5–9
Temperature, °C	40	45	-
Suspended solids	100	600	200
Dissolved solids (inorganic)	2100	2100	2100
Chloride (as Cl)	1000	1000	600
Sulfate (as SO <sub>4</sub> )	1000	1000	1000
Sulfide (as S)	2	-	-
BOD, 20°C, 5 days	30	350	500
COD	250	-	-
Oil and grease	10	20	10
Lead (as Pb)	0.1	1	-
Copper (as Cu)	3	3	-
Zinc (as Zn)	5	15	-
Chromium (as Cr <sup>6+</sup> )	0.1	2	-
Total chromium (as Cr)	2	2	-
Residual chlorine	1	-	-
Dissolved phosphates (as P)	5	-	-
Phenolic compounds	1	5	-
Free ammonia (as NH <sub>3</sub> )	5	-	-
Total Kjeldahl nitrogen	100	-	-

(IS: 2490, part I, 1974, amended in 1985, Bureau of Indian Standards)

<sup>a</sup>ISW: Inland surface water<sup>b</sup>PS: Public sewerage<sup>c</sup>AL: Agricultural land

## 1.9 Classification of Textile Wastes

Wastes generated in the textile industry can be classified into four categories:

- Hard to treat
- Hazardous or toxic

- Dispersible
- High-volume wastes

### 1.9.1 Hard-to-Treat Wastes

These include primarily colors, metals, phenol, toxic organic compounds, phosphates, etc. Hard-to-treat wastes also include nonbiodegradable organic materials, such as certain surfactants and solvents.

These can resist the biological effluent treatment process, pass through standard activated sludge systems, and produce aquatic toxicity when the effluent-treated water is discharged downstream. Since the primary problem associated with these wastes is toxicity, they can also be included in the hazardous or toxic category.

### 1.9.2 Hazardous or Toxic Wastes

These are generally a subgroup of hard-to-treat waste and include materials such as metals, chlorinated solvents, nonbiodegradable surfactants, and volatile organic materials. Some of these wastes can also come from nontextile processes such as machine cleaning and boiler chemicals.

### 1.9.3 Dispersible Wastes

Examples are the waste stream from continuous operations, print pastes, wastes from back coating operations, and batch dumps of unused process chemicals. Thus, the sources of dispersible wastes are widespread in textile wet processing.

### 1.9.4 High-Volume Wastes

The most common high-volume wastes are the wash water from preparatory, dyeing, and printing operations and the exhausted dyebaths. These can be reduced by recycling processes and equipment modification.

## 1.10 Control of Effluent Quality

Before the treatment of an effluent, certain steps or precautions are to be taken to minimize the pollution load. Some are discussed below.

### 1.10.1 Equalization

Effluent characteristics like pH, temperature, BOD, and alkalinity vary widely from time to time depending on the textile wet processes carried out at different times. To even out such dynamic characteristics, the effluents are held for several hours (say 8–16 hours) or a few days, depending on the capacity of the treatment plant and the quantity of effluent generated. Equalization also brings about self-neutralization of different alkaline and acidic streams. Pollution may also be diluted when concentrated and dilute streams are mixed together. The effluent may be optionally screened to remove floating matters like fibers and linters before being taken into an equalization tank.

### 1.10.2 Recovery of By-products

The effluent load can be reduced considerably if some of the polluting chemicals present in the effluents can be recovered, for example, recovery of caustic soda from mercerization waste. Costly dyes can be recovered from dye-house waste by dialysis, reverse osmosis, and other techniques. Heat from the wastewater can be used for preheating, thereby reducing the temperature of the discharge water.

### 1.10.3 Ecofriendly Reactions

Reactions that have minimum environmental impact can be achieved by replacing conventional toxic metal-based catalysts with ecologically acceptable organic catalysts or enzymes and may be described as ecofriendly reactions; related concerns that would also need to be addressed are as discussed below.

### 1.10.3.1 Waste minimization

Industrial processes should show maximum efficiency with reactions generating maximum yields in order to produce minimum waste. In the chemical industry, some waste is unavoidable because energy is required to break the chemical bonds in the starting materials of a reaction. If the energy input is not balanced by the energy generated from the chemical bonds being formed in the product (which is often the case), then extra bonds must be created, usually in a by-product. Some by-products can be used as feedstocks for further reactions, but many by-products are insufficiently reactive or too dilute to be recycled economically.

The Sheldon factor of environmental acceptability, or E-factor, assesses how green a chemical process is by measuring the amount of waste generated as a ratio of the mass of waste to that of product [48]. In fact, the easiest way to assess the extent to which a chemical process can be considered green is to measure the amount of waste generated. From the balanced chemical equation for a process, the theoretical quantity of waste can be calculated per unit mass of starting material, assuming that the product yield is 100%. However, in reality, most reactions give lower yields and the actual amount of waste is higher than the theoretical value. Thus, processes are assessed using their E-factors [49]. All processes should aim for the lowest possible E-factor; for truly green processes, the E-factor should be zero.

### 1.10.3.2 Product substitution

Products with reduced toxicity and increased biodegradability should be substituted for environmentally harmful chemicals [49]. By suitable modification of the processes and by using more ecofriendly chemicals, the quality of wastewater can be improved. By using carboxymethylcellulose and polyvinyl alcohol instead of starch in sizing, mineral acids instead of enzymes in desizing, mineral acids and ammonium sulfate instead of acetic acid, synthetic detergents instead of soap, emulsions instead of gums in printing, and durable finishes instead of temporary finishes, the BOD load can be reduced considerably. Dyes having high exhaustion power minimize residual dye in the effluent.

### 1.10.3.3 Greener solvents

Flammable, toxic, and volatile solvents with the potential to pollute the atmosphere need to be substituted with more ecofriendly solvents [50] or with solvent-free chemical syntheses.

### 1.10.3.4 Harmless chemicals

Perhaps the greatest challenge facing the “green chemist” is the eventual elimination of all environmentally harmful chemical products. In other words, when designing compounds for a particular application, synthetic chemists need to ensure low toxicity and rapid biodegradability while retaining the desired effect, but chemists are as yet unable to predict both chemical and biological properties of compounds from their chemical structures.

The attention given to sustainable (green) chemistry can be categorized into the following three focus areas [51]:

- Alternative synthesis routes—greener synthetic pathways
- Alternative reaction conditions—the use of greener reaction conditions
- The design of alternative, safer, less toxic, or less hazardous chemicals

Catalysis cannot only help to make chemical processes greener (e.g., by replacing reagents or by enabling more efficient processes) but also reduce the environmental impact and process costs. Heterogeneous catalysts and reagents may be chosen so that they can be separated easily (and reused) at the end of a process [52].

### 1.10.4 Loss of Chemicals

Many a time, spillage and leakage may cause several raw materials to spread into the drainage or discharge route. Reduction of such wastage will reduce the pollution load significantly.

### 1.10.5 Segregation

Sometimes, it is beneficial to segregate waste streams containing highly toxic or specific chemicals that can be treated separately and more efficiently. For example, dye liquors from the dyeing section

can be separately treated with coagulants and/or absorbents before they are diluted or mixed with the main stream of discharge water.

## 1.11 Pollution Control Strategies

There are two major pollution control strategies that could be followed [53]:

- Cleaner production techniques and processes
- End-of-pipe treatments

### 1.11.1 Cleaner Production Techniques

A comprehensive integrated approach is required to tackle the problems of pollution. Reduction in the use of water and other raw materials, along with waste minimization and elimination, whenever and wherever possible, should be the highest priority. This implies that all types of resources, along with entire product life cycle, should be used as optimally as possible to reduce environmental impacts. In a textile process, this can mean using a nontoxic raw material as a substitute, reducing water flow, or changing operational parameters.

Simple, good housekeeping measures can deliver cleaner processes. The entire existing process technology should be reviewed to evaluate the choice of process, the processing sequence, and equipment used. Examples of such options are water conservation by countercurrent washing; recovery of chemicals such as caustic soda, dyes, and grease; and replacement of high-BOD chemicals with low-BOD ones. Textile equipment manufacturers are becoming more aware of the need to conserve water, chemicals, and energy.

Many new production technologies have been developed. An example of such process and equipment change is modification of equipment for washing, dyeing, printing, and drying.

### 1.11.2 End-of-Pipe Treatment

Having reviewed the production processes to eliminate and reduce waste as much as possible, it is necessary to select the best effluent treatment strategy. Segregation and separate treatment of specific effluent streams is more efficient than attempting to treat combined

and complex effluents. Such strategy will often provide opportunities to reuse water or recover chemicals and reduce the size of the treatment plant. Combined chemical and biological treatment is one of the most commonly employed methods for liquid wastewater treatment in the textile industry. In such instances, flow equalization tanks and appropriate pretreatment units must be constructed to remove toxic substances such as chemical additives and dyestuffs in the waste stream and to ensure the proper operation and maintenance of any biological unit.

Residues from textile operations include sludge from biological or physicochemical units and waste materials from the production process. Disposal alternatives include a range of options, such as compaction, land filling, and anaerobic digestion or incineration.

For practical implementation the relative emphasis on these various strategies may vary. Existing old textile mills or small units with mostly batch or semimechanized operating methods have few opportunities for new, cleaner equipment. Better housekeeping, minimization of chemical and water usage, recycling of water, and low-cost technologies for end-of-pipe treatments such as aerated lagoons or common effluent treatment plant may be the most practical approaches. The new state-of-the-art textile mills preferably follow continuous methods of operations. Such units will prefer environmentally sound processes and equipment.

### **1.11.3 Sludge Treatment and Disposal**

During the biological treatment of an effluent, sludge is formed. If the amount of sludge formed is small, it may be recycled or can be used in lagoons. In the case of a substantial quantity of sludge, it may be subjected to aerobic digestion. The digested sludge may be thickened by a gravity thickener. The supernatant from this process should be returned to the aeration tank, and the thickened sludge may be dewatered. The liquid taken off may be returned to the rapid mix tank of the chemical coagulation process. Sludge from the centrifuge is best disposed of to a sanitary on- or off-site landfill facility.

Apart from sludge, other residues from textile processes are solid wastes such as cans, rejected fabric pieces, and willow dust. These are generally carted away to a landfill site or incinerated

either on-site or away from the site of the production activity. During incineration, adequate air pollution control measures must be taken to control particulate and scrub flue gases.

## 1.12 Future Trends

Characteristics of organic, inorganic, and synthetic chemical elements are well documented in literature. Research on the synthesis of new green chemical elements for industry application is important to replace the original materials in order to ensure a sustainable environment.

According to Horstmann, a systematic approach to shift the average production toward clean technology should be followed as per the following sequence [54]:

Avoid > Reduce > Reuse > Recycle > Biodegrade

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## **Chapter 2**

# **Textile Industry and Effluents: Present Scenario, Governing Laws, and Initiatives toward the Road Ahead**

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The textile industry is a diverse industry, not only in terms of the final product range, but also in terms of raw materials, processes, products, and equipment, and additionally addresses an extremely complex supply chain. This industry, which caters to one of the basic needs of mankind, has far-reaching environmental impacts, not only in terms of the discharge to the environment and surroundings, but also in terms of depletion of natural resources due to the consumption of large amounts of water and energy. These impacts have been realized for the last few decades, and various stringent regulations have been implemented by legal entities and also through the efforts of organizations like Greenpeace International, whose investigation into the apparels of famous brands identifying the presence of

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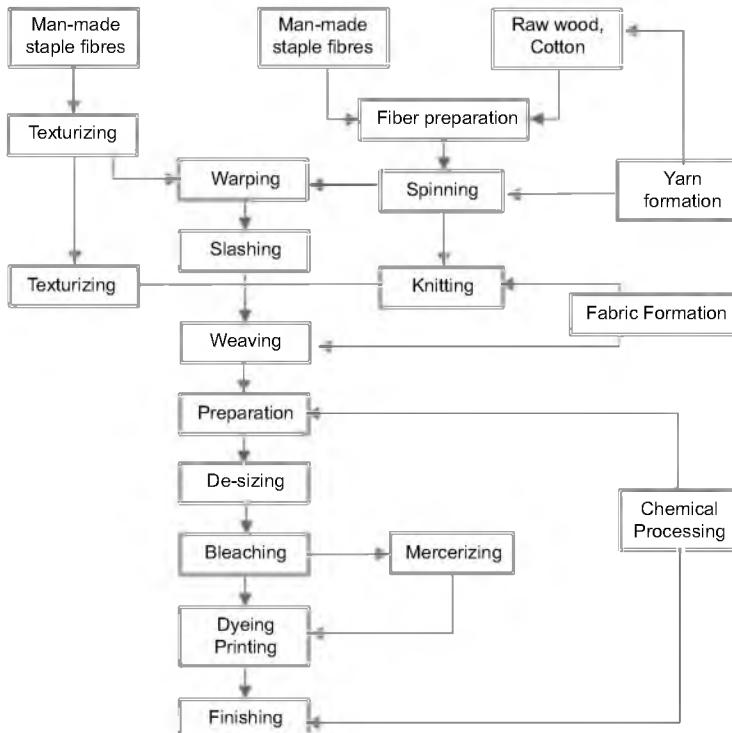
harmful chemicals has shocked the global consumer. The awareness created by Greenpeace International forced brands to review their supply chains and work toward ZDHC by 2020. This chapter will deal in detail with conventional textile processes, characteristics of textile effluents, conventional effluent treatment, new technologies for ET, new challenges and norms for textile effluents, ZLD/ZDHC, and the future of textile effluent treatment.

## 2.1 Introduction

The textile industry consumes large amounts of water and chemicals, right from the cultivation of the fibers to the multitude of process cycles for wet processing of textiles to obtaining the final finished textile products procured by the consumer. The chemical reagents used in these processes are diverse in their chemical composition, ranging from inorganic compounds to polymers and organic compounds. Moreover, the industry suffers from excessive water consumption due to the repeated wash cycles that dyed fabrics require to remove residual dyes from their surfaces. There are more than 100,000 commercially available dyes, with over  $7 \times 10^5$  tons of dyestuffs produced annually. Due to their chemical structure dyes are resistant to fading on exposure to light, water, and many chemicals. Dyes generally present in these effluents are in concentrations of 10–15 mg/L. The presence of even low concentrations of dyes and auxiliaries in the effluent is highly visible and undesirable due to which the textile industry is facing a lot of problems. Color is usually noticeable at concentrations above 1 mg/L and has been reported in effluents from textile manufacturing processes at concentrations exceeding 300 mg/L. Dark colors in water streams reduce light penetration, affecting the growth of plants and adversely impacting other forms of wildlife. Additionally, colors cause an aesthetic problem for the surrounding land and water bodies in which they are disposed of after use.

Today across the globe, regulations for industrial effluents are being updated and strictly enforced and the demand for more efficient wastewater treatment systems is steadily on the rise. Because industrial textile effluents come from a large number of

textile chemical processes and finishing and contain several types of pollutants, such as dispersants, leveling agents, salts, carriers, acids, alkali, and various dyes (see Fig. 2.1 and Table 2.1), a holistic approach is required for efficient treatment of these trade effluents and for efficient water recovery.



**Figure 2.1** Sequence of the process involved in the finishing of textiles.

Textile waste effluents pose a challenge in terms of treatment because they are highly variable in composition. The strong color of the textile wastewater is the most notorious characteristic of the textile waste effluent. The color in the effluent, if not rightly addressed, would have a severe negative impact on the aquatic environment on discharge into water bodies owing to its resultant turbidity and high polluting characteristics. Hence, decolorization is an integral part of the textile waste treatment process.

**Table 2.1** Different textile processes and characteristics of their associated effluents

S. No.	Unit process	Possible pollution in the wastewater	Nature of wastewater
1.	Desizing	Starch, glucose, carboxyl methyl cellulose, polyvinyl alcohol, resins, and fats and waxes	High BOD
2.	Scouring	Caustic soda, waxes and grease, soda ash, sodium silicate, and fragments of cloth	Strongly alkaline, dark color, and high BOD
3.	Bleaching	Hypochlorite, chlorine, and caustic soda	Alkaline
4.	Mercerizing	Caustic soda	Strongly alkaline and low BOD
5.	Dyeing	Various dyes; mordants; and reducing agents like sulfides, hydrosulfites, and other chemicals like acetic acid and soap	Strongly colored and high BOD
6.	Printing	Colors, starch, gums, oil, china clay, mordants, acids, metallic salts, etc.	Highly colored, fairly high BOD, and an oily appearance
7.	Finishing	Traces of starch, tallow, common salt, glauber salt, etc.	Slightly alkaline and low BOD

Source: [1-3]

Before we start navigating through the different processes involved in the treatment of effluents from the textile industry, we would like to define some commonly used terms a new learner would frequently encounter in the effluent treatment processes (ETPs).

## 2.2 Terms and Definitions

### 2.2.1 Biochemical Oxygen Demand

This represents the oxygen required by bacteria present in an effluent for their growth. They will seize upon any oxygen available and thus

deplete the oxygen level of any water body into which the effluent is let out, thereby making the entire water unfit for consumption. Biochemical oxygen demand (BOD) is measured as grams of oxygen utilized by microorganisms in the biochemical oxidation of organic matter. Noncarbonaceous matter such as ammonia can also be utilized; ammonia oxidizes to nitrites and nitrates. The nitrogenous oxygen demand caused by autotrophic bacteria is called second-stage BOD.

### 2.2.2 Chemical Oxygen Demand

The chemicals present in an effluent also rapidly deplete any oxygen present in the water into which the effluent is let out. Even when there are no such volumes of water into which the effluent can be let out, in due course the bacteria get accustomed to the impurities present and start decomposing the chemicals into obnoxious compounds, which may be harmful to health. Chemical oxygen demand (COD) is the amount of oxygen, equivalent of organic matter, which can be oxidized by using some chemical-oxidizing agents in acid media.

### 2.2.3 Theoretical Oxygen Demand

Organic matters are combinations of carbon, hydrogen, oxygen and nitrogen, proteins, fats, carbohydrates, etc. The theoretical oxygen demand (THOD) can be determined from the chemical formula of a compound, if it is readily available. THOD determination is based upon the oxygen consumed at different steps of oxidation.

1. Carbon atoms are oxidized to  $\text{CO}_2$ , while nitrogen is oxidized to ammonia.
2. The ammonia is oxidized to nitrites.
3. The remaining ammonia is oxidized to nitrates.

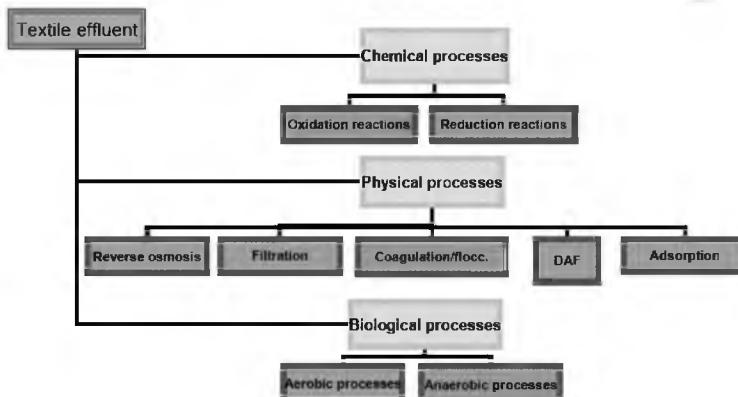
The method is the sum of oxygen required for all three steps.

The THOD represents the worst-case scenario. The actual oxygen demand of any compound depends on the biodegradability of the compound and the specific organism metabolizing the compound.

## 2.3 Textile Effluent Treatments

### 2.3.1 Adsorption

Industrial wastewater treatment covers the mechanisms and processes used to treat wastewater that is produced as a by-product of industrial or commercial activities, especially of textile-related industries. In the current era of ecopreservation, ETPs use various chemical, physical, and biological methods (Fig. 2.2). Adsorption [4–7] is a rapid phenomenon of passive sequestration separation of adsorbate from an aqueous/gases phase onto a solid phase. The most common industrial adsorbents are activated carbon, silica gel, and ammonia, because they present an enormous surface per unit weight (Tables 2.1 and 2.2). Activated carbon is produced by roasting the organic material to decompose it to granules of carbon. Silica gel is a matrix of hydrated silicon dioxide and hydroxide (Fig. 2.2). The most conventional adsorption systems use activated carbon, which, although expensive and necessitates regeneration, is an excellent material for adsorption.



**Figure 2.2** Flow diagram of common ETPs.

#### 2.3.1.1 Activated charcoal

Activated charcoal is a widely used adsorption technique. It is most effective with volatile organic compounds (VOCs), which can be readily and effectively adsorbed on to the surface from a waste

**Table 2.2** Different methods for treating textile process house effluents

Method	Working principle	Shortcomings
NaOCl	It is used as an oxidizing agent.	Aromatic amines and chlorine are released.
Ozonation O <sub>3</sub> (alone)	Ozone is used as an oxidizing agent.	It suffers from the short half-life of ozone and sensitivity to pH, salts, and electrolytes.
H <sub>2</sub> O <sub>2</sub> (alone)	It is used as a strong oxidant.	It is ineffective for complex dyes.
Electrochemical destruction	It employs electrochemical disintegration of dyes.	It is very expensive.
Activated carbon	It is used as an absorption medium for dyes.	It is very expensive and specific to a particular dye.
Peat	Its cellular structure is used for effective adsorption.	Specific surface areas for adsorption are lower than activated carbon.
Wood chips	They contain cellulose and are used for chemisorption of the dyestuffs.	They require long retention times.
Silica gel	It is used as an adsorption medium for dyes in the effluent.	The side reaction prevents commercial applications.
Membrane filtration	It clarifies, concentrates, and separates dyes continuously using polymeric membranes.	There is concentrated sludge production.
Ion exchange	Wastewater is passed over an ion exchange resin until exchange sites are exhausted.	This method is not effective for all dyes.
Irradiation	The wastewater is irradiated in the presence of a large amount of dissolved oxygen.	It requires a lot of dissolved oxygen.
Biotreatments	Microbes such as white rot fungi are used for dye decolorization.	A slow process, it is not economical.
Electrokinetic coagulation	Coagulating agents like FeCl <sub>3</sub> and FeSO <sub>4</sub> are used.	There is high sludge production.

stream. A VOC is also capable of rapid and efficient desorption and so the activated charcoal, which itself has a high unit cost, can be reused a number of times. However, although molecules of colored materials are reasonably well adsorbed on to the charcoal, desorption of this large and inert molecule is extremely difficult. Regeneration costs therefore soar, either because the incineration required for desorption is significant or because disposal costs are high.

The technique is most effective with relatively small volumes on short time scales so that interchange can take place. Due to the technical problems of desorption/regeneration and cost consideration this technique is not always viable.

### **2.3.1.2 Natural adsorbents**

The use of a natural clay, bagasse pith, and maze cob as adsorbents has been studied and found to be economically attractive for the removal of dyestuffs from aqueous solutions. These natural adsorbents are recommended as effective and cheap materials for dyestuff removal from textile effluents as compared to activated charcoal. These materials are so cheap that regeneration is not necessary. But the challenge lies in disposing of these natural adsorbents after use, and the only path of disposal is to use them as boiler fuels in the industry.

### **2.3.1.3 Silica gel adsorbent**

Silica gel may be employed as an adsorbent for the removal of basic dyes. In the application of silica gel for large-scale treatment of wastewater the manner in which the silica gel comes in contact with the effluent is of particular importance. Silica gel was found to be useful in decreasing the dye concentration in an effluent. Although this method was economically feasible, other side reactions, such as air binding and fouling with the particulate matter, prohibited silica gel being used as an adsorbent commercially.

## **2.3.2 Ion Exchange Methods**

In the ion exchange method, the wastewater is passed over the ion exchange resin until the available exchange sites are saturated. The process can remove both dye cations and dye anions from the

effluent. A combined process involving adsorption on the synthetic polymers and ion exchange may be used to decolorize the dye wastes. The process has several operating and performance advantages. The polymeric adsorbent loaded with the dye waste is regenerated with a solvent such as methanol. There is no loss of adsorbent on regeneration, and the solvent is reclaimed for reuse, minimizing the operating cost [3, 6].

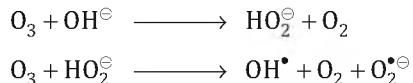
### 2.3.3 Membrane Technology

Membrane technology can be further subdivided into three categories: ultrafiltration, nanofiltration, and reverse osmosis (RO). Ultrafiltration is of no use in color removal as the membrane hole size is too large to prevent dye molecules from passing through. On the other hand both nanofiltration and RO membranes are effective in separating large dye molecules from an effluent. The colored dye molecules are concentrated on one side of the membrane while allowing the water to pass through. It actually separates all large molecules, not only dye molecules, and the extent of filtration depends on the size of the nanofiltration and RO membrane used. The technique is capable of treating large volumes fairly quickly, but capital cost is high. Cleaning the membrane can also cause problems if the relationship between molecular size and membrane pore size is not correct. RO can remove all types of the dyes from wastewater [5, 8].

### 2.3.4 Advanced Oxidation Processes

#### 2.3.4.1 Treatment of textile effluents by ozonation

Ozone decomposition occurs in a chain process that can be represented by the following fundamental reactions:



Ozone is very effective for decolorizing dye wastewater because it attacks the conjugated double bonds often associated with color. There are two different pathways for ozone reactions: indirect and

direct. Indirect reactions are dependent on radicals formed by the reactions between ozone and an initiator, typically  $\text{OH}^-$ . The product of this reaction is called a hydroxyl radical. A hydroxyl radical is characterized as being highly unstable, reacting with electron-dense clusters in other molecules (such as the double and triple bonds in amines). The reactions undertaken by hydroxyl radicals are extremely fast, with typical reaction constants in the range of  $10^8$ – $10^{10} \text{ M}^{-1}\text{S}^{-1}$ . The formation of hydroxyl radicals is deeply influenced by the pH of the system as well as the concentration of radical scavengers, such as carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3$ ). The reactions that make up the direct pathways are numerous and complex. The direct reactions are much slower than the indirect reactions, typically in the  $10^6 \text{ M}^{-1}\text{S}^{-1}$  range [9, 10]. Ozone reacts selectively with nucleophilic centers, such as unsaturated bonds in the target organic molecule, resulting in ozone being incorporated into the target and breaking of the attacked bond.

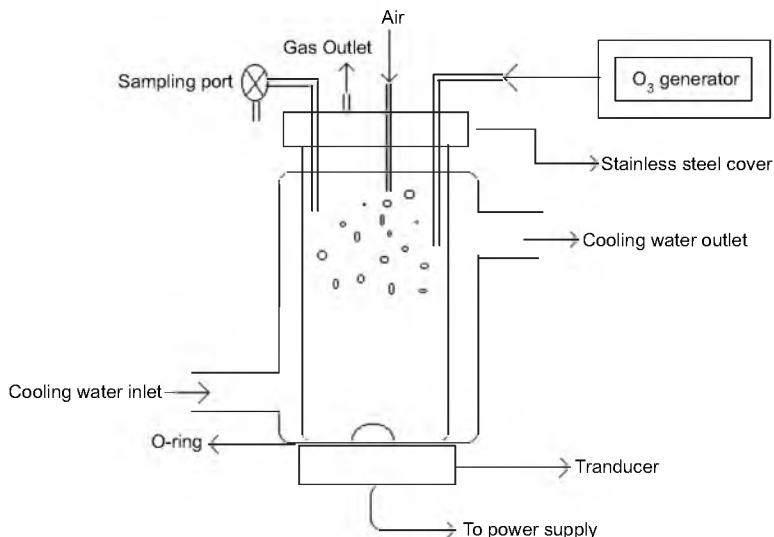
There are three fundamental mechanisms that apply to the oxidation of organic compounds reacting with ozone:

- The addition mechanism that occurs with organic compounds containing aliphatic unsaturated compounds, such as olefin.
- The ozonide mechanism in which ozone can add across a double bond to form an ozonide. This reaction occurs readily in nonaqueous solvents, but as soon as water is added, the ozone hydrolyzes to other products, with cleavage of the former double bond.
- The substitution mechanism involves replacement of one atom or functional group with another. This specific reaction also can be viewed as an insertion reaction, whereby oxygen is inserted between the ring carbon and hydrogen to form the hydrogen group on the ring; oxidation also can involve cleavage of carbon–carbon bonds to produce fragmented organic compounds [11–13].

Figure 2.3 provides a schematic representation of the experimental setup for the ozone treatment process.

The reactivity of ozone decreases with increasing content of nitrogen in heterocyclic ring systems. This is of importance if reactive dyes based on heterocyclic systems like triazines, pyrimidines, or quinoxilines are present. Ozone demand for decolorization is

greatly reduced by the elimination of suspended solids since these are the ingredients that contribute toward the COD of the effluent and so consume large amounts of ozone before the ozone acts on the colored material. Ozonation is observed to be relatively ineffective in reducing the COD concentration, especially for medium- and high-strength effluents. The reason is that the structured polymer dye molecules in these wastes are oxidized by ozone and produce small molecules such as acetic acid, aldehydes, and ketones instead of  $\text{CO}_2$  and water. These small molecules increase the COD content in the effluent rather than decreasing it. However, in conjunction with the chemical coagulation, the COD reduction is as high as 70% [3, 7, 14].



**Figure 2.3** Schematic diagram of the ozone treatment process: experimental setup.

Ozone wastewater treatment is a method that is increasing in popularity. An ozone generator is used to break down pollutants in the water source.

- The generator converts oxygen into ozone by using ultraviolet (UV) radiation or by an electric discharge field.
- Ozone is a very reactive gas that can oxidize bacteria, molds, organic material, and other pollutants found in water.

- Using ozone to treat wastewater has many benefits:
  - It kills bacteria effectively.
  - It oxidizes substances such as iron and sulfur so that they can be filtered out of the solution.
  - There are no nasty odors or residues produced from the treatment.
  - Ozone converts back into oxygen quickly and leaves no trace once it has been used.
- The disadvantages of using ozone as a treatment for wastewater are:
  - The treatment requires energy in the form of electricity; this can cost money and cannot work when there is no power.
  - The treatment cannot remove dissolved minerals and salts.
  - Ozone treatment can sometimes produce by-products, such as bromate, that can harm human health if they are not controlled.

#### **2.3.4.2 Gamma ray irradiation**

Azo dye containing wastewater is decolorized by gamma ray irradiation in the presence of  $N_2O$  or hydrogen peroxide. The gamma ray irradiation can also be done in the presence of a hydroxyl compound. Aqueous organic waste effluents containing dye material are decolorized, degraded, and rendered more biodegradable by subjecting them to penetrating ionizing radiations from  $CO_{60}$  or any other source of penetrating rays in the presence of oxygen and multivalent cation such as  $Fe^{++}$  and  $Fe^{+++}$ . Desirably a chlorine ion is incorporated into the waste during treatment. The process is applicable to acidic, neutral, or alkaline wastes. However, the radiation's effect is enhanced if the pH is adjusted to the 9–12 range [2, 14].

#### **2.3.4.3 Decolorization of dyes using $UV/H_2O_2$ photochemical oxidation**

Although no treatment technology used today has universal application, chemical oxidation technology seems to hold the

potential for future use in the textile industry. Sufficient work has been performed using combinations of either UV or H<sub>2</sub>O<sub>2</sub> with other chemicals/techniques to suggest that the UV/H<sub>2</sub>O<sub>2</sub> system [9] could decompose textile effluents efficiently, particularly exhausted dyebaths. These studies suggest that not only can textile effluent be decomposed, it can be decolorized as well.

Photodegradation by UV/H<sub>2</sub>O<sub>2</sub>, in generalized terms, is an attempt to accelerate nature's own degradation process through the use of chemicals and radiant energy. Through UV/H<sub>2</sub>O<sub>2</sub> treatment, contaminants can be completely oxidized to form carbon dioxide and water, both nonharmful by-products.

Three advantages of UV/H<sub>2</sub>O<sub>2</sub> photochemical oxidation are significant to the textile industry.

- Sludge formation, handling, and disposal may be avoided.
- Air emission permits could potentially be eliminated.
- Offensive odors typically associated with waste treatment could be avoided.

UV light causes the dissociation of H<sub>2</sub>O<sub>2</sub> into two hydroxyl radicals, represented in the chemical reaction below, which cause the chemical oxidation of organic materials. Hydroxyl radicals degrade organics by abstracting protons to yield organic radical compounds. These compounds are extremely reactive and are subject to further oxidation. UV light alone has the ability to degrade organic compounds, but when UV light and H<sub>2</sub>O<sub>2</sub> are combined, the overall oxidative reaction potential is greatly enhanced.



An example of an UV/H<sub>2</sub>O<sub>2</sub> oxidation system in use today is the peroxpure chemical oxidation treatment technology. Peroxpure treatment uses medium-pressure mercury vapor lamps and H<sub>2</sub>O<sub>2</sub> to oxidize organic compounds found in water. The technology produces no air emissions, generates no sludge, and requires no further processing, handling, or disposal.

#### **2.3.4.4 Effluent treatment by a UV/ultrasonic/peroxide system**

The decolorization of reactive dyeing wastewater with UV radiation and ultrasonic vibration in the presence of hydrogen peroxide has

been investigated by the batch operation system. An UV/ultrasound system consisting of a stainless-steel reactor [10] equipped with UV lamps and ultrasonic transducers for batchwise operation was used to evaluate the treatment performance of decolorization. The dyeing wastewater was exposed to the UV/ultrasound-combined photoreactor at varying pH values with a suitable peroxide dosage rate. Higher pH values favor faster dye degradation. During the process, the pH value in the wastewater decreases gradually, mainly due to the generation of hydrogen ions or some organic acids.

Peroxide photolysis is pH dependent, and as such the reaction rate would increase when more alkaline conditions are used. The dosage of peroxide is the key parameter for the decolorization of dyeing wastewater, having a direct impact on the treatment performance. The rate of decolorization was increased by the addition of increasing amounts of the initial peroxide dosage. However, a dosage greater than 0.2 mL/L peroxide lowered the rate of photodegradation, which, in turn, reduced the color removal efficiency. Ultrasound, in combination with UV, improves the initial reaction rate and the overall dye removal efficiency [11, 14–16]. Ultrasound may increase the oxygen uptake and transfer rates. Results indicated that high levels of pH enhance the rate of dye degradation due to the generation of free hydroxyl radicals, with excessive dosage of peroxide reducing dye degradation, and the final products of the decolorization process were completely soluble in H<sub>2</sub>O and, therefore, no sludge was formed in the decolorization process.

#### **2.3.4.5 Oxidative degradation of dyes and surfactant in the Fenton and photo-Fenton treatment of dye-house effluents**

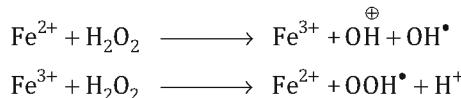
Fenton discovered in 1894 that several metals have special oxygen transfer properties that improve the use of hydrogen peroxide. Actually, some metals have a strong catalytic power to generate *highly reactive hydroxyl radicals*. Since this discovery, the iron-catalyzed hydrogen peroxide has been called Fenton's reaction. Nowadays, Fenton's reaction is used to treat a large variety of water pollutants, such as phenols, formaldehyde, BTEX (benzene, toluene, ethylbenzene, xylene), pesticides, and rubber chemicals [12, 13, 16].

This process may be used to treat wastewater, contaminated soils, and sludges, with the following actions:

- Organic pollutant destruction
- Toxicity reduction
- Biodegradability improvement
- BOD/COD removal
- Odor and color removal
- Destruction of resin in radioactive contaminated sludge

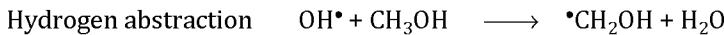
#### **2.3.4.5.1 Fenton reaction mechanism**

On addition of hydrogen peroxide and iron, they react together to generate some hydroxyl radicals as per the following reactions:



The typical range for the iron dose is 1 part of Fe per 5–25 parts of  $\text{H}_2\text{O}_2$ .

The hydroxyl radicals so generated react with the pollutants and oxidize them. The hydroxyl radicals can react via four kinds of reactions with the pollutants:

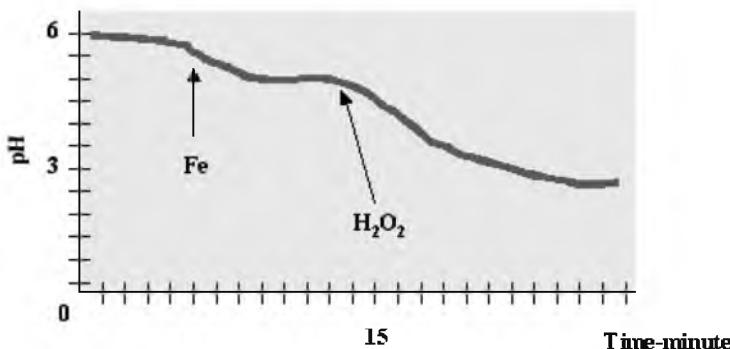


During Fenton's reaction all the parameters are adjusted to promote the first two kinds of reactions between the pollutant and the hydroxyl radicals.

#### **2.3.4.5.2 Requirements of the reaction**

- pH adjustment to 3–5. If the pH is too high the iron precipitates in  $\text{Fe}(\text{OH})_3$  and will decompose the  $\text{H}_2\text{O}_2$  to oxygen. Basically, the optimal pH occurs between 3 and 6. It's really important to pay attention to the double pH drop due to the addition of iron and  $\text{H}_2\text{O}_2$ , as you can see in the chart in Fig. 2.4. Indeed,

the  $\text{FeSO}_4$  catalyst containing residual  $\text{H}_2\text{SO}_4$  and the addition of  $\text{H}_2\text{O}_2$  are responsible for the fragmentation of organic material into organic acids.

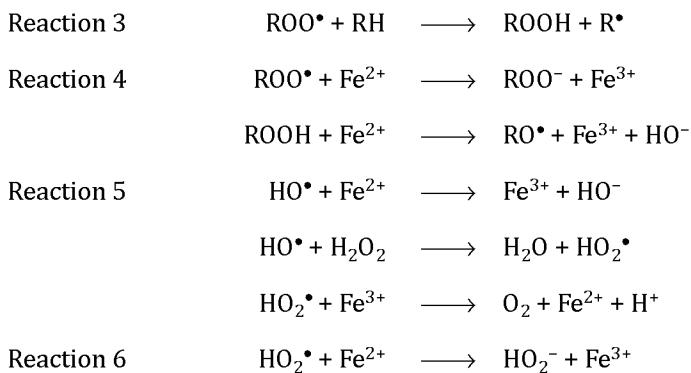


**Figure 2.4** Double pH drop due to the addition of  $\text{Fe}$  and  $\text{H}_2\text{O}_2$ .

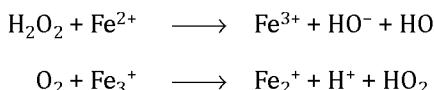
- Addition of the iron catalyst as a solution of  $\text{FeSO}_4$ .
- Slow addition of  $\text{H}_2\text{O}_2$  to control the increase of pH and temperature during the reaction. It is better to complete the reaction step by step with continuous adjustment.

The combination of hydrogen peroxide and an iron (II) salt known as Fenton's reagent is an effective oxidant for various organic substrates because the hydroxyl radical formed can rapidly oxidize most organic substances (Reaction 1). The organic radicals react rapidly with environmental molecular oxygen to form organic peroxy radicals (Reaction 2). The organic peroxy radicals can abstract hydrogen atoms from organic substrates, producing organic hydroperoxides and other organic radicals (Reaction 3). In the presence of iron (II) ions, some peroxy radicals can also undergo reduction (Reaction 4). On the other hand, in the presence of iron salts, the decomposition of hydroperoxides produces chain-continuing radicals (Reaction 5). Moreover, hydrogen peroxide decomposition catalyzed by iron salts in a dilute acid solution can occur according to Reaction 6.





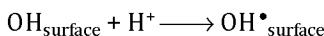
#### Overall Reaction



Fenton's reagent shows a powerful degradation action on refractory organic substances such as aromatic compounds, dyes, and surfactants. In some cases strong COD reduction is achieved, showing extended bond degradation. Therefore, Fenton's reagent can improve biological degradation of organic compounds by reducing their molecular size and is generally utilized as a stage before a biological treatment.

#### 2.3.4.6 $\text{TiO}_2$ -mediated catalytic oxidation

The UV/ $\text{TiO}_2$  method treats textile bath effluents contaminated with reactive dyes usually used in the textile industry. The photo-oxidizing power of titanium dioxide can be harnessed to decolorize and mineralize synthetic dyes. Sunlight energy (UV; around 360–380 nm) excites titanium dioxide particles, creating a photogenerated electron and a highly oxidizing hole in the conduction and valence bands of the semiconductor. The electron can be scavenged by oxygen and hole can react with surface-bound OH on  $\text{TiO}_2$ , creating a highly reactive radical  $\text{OH}^\bullet$  that can completely decolorize and mineralize the dye effluent [9, 16].



## 2.4 Chemical and Biological Treatments for Textile Effluents

### 2.4.1 Treatment of Textile Effluents Using Sodium Alginate as the Flocculant

Use of polymeric flocculants for clarification of industrial effluents is slowly gaining importance due to their ecofriendliness, abundant availability, cost effectiveness, nontoxicity, and usually inert behavior to pH changes. Natural water-soluble polysaccharides have the capability of flocculating small particles and of causing turbulent drag reduction. Natural polymers such as starch, sodium alginate, amylopectin, guar gum, and chitosan find extensive application as flocculants [9, 17, 18]. Sodium alginate is a sodium salt of algin (alginic acid), a polymer consisting of  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid.

Flocculation studies of sodium alginate gum were conducted by a standard jar test. Beakers of 1 L capacity, each equipped with a variable-speed (0–100 rpm) agitator, were used. Wastewater was added to the beaker and the polymer solution was added into it by means of a syringe. The agitator was first adjusted to 100 rpm for 1 min. and then continued for a total of 10 min. at 50 rpm. The agitator was subsequently stopped, and the wastewater was allowed to settle for 1 h. Flocculation efficiency was seen at pH values of 4.7 and 9.2. With an increase in the polymer dose, the percentage removal of solid waste increased; after a certain dose of polymer, a decreasing trend in solid removal was seen. The optimal amount of dose of flocculants in the suspension caused larger amounts of suspended solids to aggregate and settle. However, an overoptimal amount of dose of flocculants in suspension caused the aggregate particle to redisperse and can also disturb particle settling [19]. Maximum solid removal was seen after the first hour of contact time using the best polymer dose. Maximum solid removal was observed at a particular time duration in the effluent. After this duration a reverse trend was seen.

The flocculation efficiency of the gum was found to be maximum at alkaline pH 9.2 at its optimized concentration. The maximum solid removal was seen after 3 h of contact time at pH 9.2. There

are metals like Zn, Mn, Ni, Cu, Cd, Al, and Fe usually present in the textile effluent. It may be suggested that at alkaline pH the metal ions precipitate in the form of hydroxides. Therefore, the presence of these metals in the ionic form increases the adsorption capacity of the polymer and also increases the percentage of solids settled. Natural polysaccharide sodium alginate is a very effective flocculant, capable of removing 91% of solids in nearly 3 h at pH 9.2. It is also a very good dye removal agent, which is proved by UV-visible spectrophotometric analysis of the textile effluents before and after treatment.

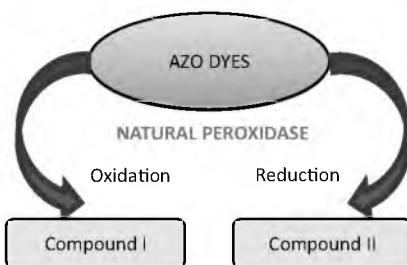
#### 2.4.2 Decolorization of Dye Wastewater by Selective Fungi (Enzymes)

Not all dyes currently used can be degraded or removed with physical and chemical processes, and sometimes the degradation products are more toxic. Several combined anaerobic and aerobic microbial processes are believed to enhance the degradation of dyes, but under aerobic conditions, azoreductases usually cleave azo dyes into the corresponding amines, many of which are mutagenic or carcinogenic.

Certain enzymes, such as laccase, lignin peroxidase (LiP), and manganese peroxidase (MnP), are known to be capable of cleaving aromatic rings. These enzymes have the potential for destroying color-producing compounds such as dyes.

White rot fungi organisms degrade lignin and cause rotting wood. Many white rot fungi, including *Phanerochaete chrysosporium*, *Pycnoporus cinnabarinus*, *Pleurotus ostreatus*, and *Trametes versicolor*, have been found to be efficient in degrading dyes. The fungus *P. chrysosporium* aerobically degrades azo dyes. The effectiveness of *P. chrysosporium* in decolorizing the dyes varies depending on the structure and complexity of the dye and nitrogen availability in the medium [18–21]. White rot fungi degrade dyes by means of oxidation, by a process similar to lignin degradation typically associated with enzymes. For the metabolic activity glucose is required and the rate of decolorization decreases with decreasing glucose concentration. The fungus *P. chrysosporium* can produce two families of nonspecific extracellular peroxidases, LiP and MnP, during the secondary metabolism in response to nitrogen or carbon

starvation. LiP and MnP are implicated in the azo dye degradation by *P. chrysosporium* coincides with the production of peroxidase, which are known to decolorize azo dyes [22–24]. The catalytic cycles of LiP and MnP are similar to those of other peroxidases. The hydrogen peroxide produced by microorganisms oxidizes the native enzyme, and an oxidizing state (compound I) is produced. Compound I can be reduced in two steps to form a second oxidized state (compound II) and then the native enzyme to complete the cycle. LiP catalyzes the oxidation of nonphenolic aromatic compounds, such as veratryl (3,4-dimethoxybenzoyl) alcohol. MnP catalyzes the Mn<sup>+2</sup> to Mn<sup>+3</sup>, and the high oxidation potential of Mn<sup>3+</sup> can oxidize many phenolic compounds. The catalytic cycle of *P. chrysosporium* LiP and MnP is shown in Fig. 2.5.



**Figure 2.5** Catalytic cycle of *P. chrysosporium* LiP and MnP.

Many azo dyes can reduce compound I of LiP to compound II, and the dyes themselves are oxidized and decolorized. The typical amount of dye, enzyme preparation, and buffer (0.1 M sodium acetate, pH 5) is incubated on a rotary shaker at 50°C for 5 h. Decolorization is followed spectrophotometrically at the maximum absorbance of the dye. A decrease in absorbance shows the removal of color.

#### 2.4.2.1 Advantages

This method gives a way to decolorize textile effluents that eliminates the need for inorganic oxidizing agents such as ozone or precipitating agents such as polymeric flocculants. Using this method the removal of color from textile wastewater will be environmentally friendly and much less costly than the current oxidation and precipitating methods [25].

#### 2.4.2.2 Disadvantages

The specific enzyme approach may determine the rate of reaction, which can be slow unless conditions of pH and temperature are optimal. It is very difficult to commercially produce LiP and MnP enzymes [15].

#### 2.4.3 Sludge Color Removal of Textile Effluents Using the Upflow Anaerobic Reactor

The uptake anaerobic sludge blanket (UASB) reactor consists of a polyvinyl chloride (PVC) column. The reactor is equipped with several sample ports. The reactor has a water jacket to provide temperature control. To measure the volume of biogas produced the outlet at the top of the reactor is connected to a gas washing flask that contains a solution of potassium hydroxide [17].

In a reported procedure [18] the reactor was fed with a synthetic medium consisting of glucose and sucrose as a carbon source. Macro- and micronutrients were added. After inoculation of the seed sludge the reactor was acclimatized for 3 months. The sludge bed height was 30%–50% of the reactor height. Results show that some of the dyes are readily reduced under anaerobic conditions even at a high concentration of 700 mg/L. The average removal efficiency for acid dyes using this method was between 80% and 90% and that for direct dyes was 81%. The removal of the color occurs predominantly at the bottom of the reactor.

#### 2.4.4 COD, Color, and Sludge Reduction Using the Immobilized Microbe Bioreactor

Although textile effluents contain numerous compounds, there are two or three main compounds that contribute to high COD and BOD. Polyvinyl alcohol (PVA) is a sizing agent widely used in the textile industry and is difficult to biodegrade. Without a long resonance time and good contact between the microbes and these materials, degradation and color reduction will not occur. Immobilized microbe bioreactor (IMBR) technology is able to treat these components.

IMBR needs the increased contact between microbial populations. This is done through the use of the solid, but porous, matrix to which a tailored microbial consortium of organisms can be attached. In

addition to enhancement of waste contact, IMBR systems control various physicochemical parameters, including pH, temperature, dissolved oxygen, and nutrient addition. IMBR technology has proven to be a mature method for treating textile effluents. It is reported that batch treatment with nutrient addition over a 24 h time period was sufficient in most cases for a greater than 75% COD reduction and color removal. No odor or sludge was formed throughout the treatment. The IMBR system must be designed specifically for each plant on the basis of the needs and desires [19, 26].

## 2.5 Some Alternate Treatment Methods

### 2.5.1 Use of Apple Pomace and Wheat Straw

Dyes can be removed by biosorption on apple pomace and wheat straw [17]. The study by Gonçalves et al. [17] revealed that the adsorption does not depend on the pH but on the initial concentration of the colored solution. The experimental results showed the following:

- The percentage of the dye removed is low at concentrations of 10–40 mg/L when compared to that for a higher concentration range (50–200 mg/L).
- The optimum particle size of the adsorbent for color removal is 600  $\mu\text{m}$ .
- Apple pomace has a greater capacity to adsorb the reactive dyes taken for the study compared to wheat straw. It also removes the dye at a faster rate than straw.
- For both adsorbents, the concentration of the dye remaining in the solution decreases with time until a point is reached when no more dye can be adsorbed onto the sorbent.

### 2.5.2 Use of Chitin as an Adsorbent for Color Removal

Chitin is the second-most-abundant organic material on the earth. Chitin and its derivative chitosan have been researched extensively all over the world, but it has yet to make an impact as a marketable product. Both of these materials have been shown to have very high affinity for dyes, metals, and certain surfactants. Utilization of chitin for color removal can produce two advantages: (i) in identifying a

viable method for purifying dye wastewater and (ii) in discovering ways to use previously wasted natural resources [26, 27]. After use for color removal, this spent sorbent still finds further use as a fibrous material for paper making.

Chitin is a polysaccharide very similar to cellulose, being composed of poly-2-acetamido-2-deoxy-D-glucose. It is a white, flaky material that does not melt and is insoluble in water, dilute acid, cold alkali, and organic solvents. Sorption is influenced by many physicochemical factors, including dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and time.

Chitosan is obtained when chitin is subjected to strong caustic soda and heated, which removes the *N*-acetyl group. It is insoluble in water and most common solvents, but it is soluble without degradation in weak acids, such as 5% formic acid and acetic acid. Due to its unique molecular structure chitosan has an extremely high affinity for many classes of dyes, including disperse, direct, reactive, acid, vat, and sulfur. The rate of diffusion of the dyes in chitosan is similar to that in cellulose. The only class for which chitosan has a low affinity are basic dyes.

The sorption of the dyes is exothermic in nature, which increases the temperature. The increase in temperature leads to an increase in the dye sorption rate but diminishes total sorption capacity. The wastewater pH is another important factor, because at low pH chitosan's free amine groups get protonated, causing them to attract the cationic dyes. The dye-binding capacity of chitin decreases above pH 7. Chitosan can be put into fibers, which would help to improve their absorption kinetics. A moderately cross-linked fiber was found to have binding capacity for a dye acid orange II. The capacity decreases with increasing temperature and pH. The cross-linked fiber can be regenerated by treatment with NaOH. Chitosan can also be cast into membranes and then cross-linked to produce filters with good physical and chemical stability and high water permeability. Such membranes would be expected to have very rapid dye adsorption kinetics in addition to good capacity [28].

The adsorption of dyes in some natural materials containing chitin, namely squid (*Loligo vulgaris*) and sepio (*Sepia officinalis*) pens and *Anodonta* shells, has been studied in detail. In continuation, experiments in a packed column at 20°C with natural materials showed large internal resistance to mass transfer. To improve the

adsorbents' performance, the materials were subjected to chemical treatments, like demineralization and/or deproteinization [7, 9, 11, 28]. Demineralization of *Anodonta* shell and sepio pen and deproteinization of squid pen improved their adsorption capacities and the performance in the continuous operation.

### **2.5.3 Chemically Modified Cellulose and Lignocellulose for Color Removal**

Derived products of cellulose of lignocellulose have got very good dye-binding properties. Quaternary ammonium groups can be introduced into the cellulose and lignocellulose, which introduces a permanent positive charge into the substrate, making it a very effective adsorbent for acid dyes. Cellulose can be modified with the *N*-methyl derivatives of tris- and bis-(2-carbamoylehtyl) ethylamine to enhance acid dye adsorption, which decreases with increasing pH. The dye can be readily removed from cellulose with NaOH.

### **2.5.4 Textile Effluent Treatment with a Root Zone System**

In the reported root zone system [17, 20] sulfur compounds, reactive dyes, ammonia, sulfur, and chlorinated hydrocarbons were removed. Additionally, there was significant removal of heavy metals present in the textile effluent. Surface architects perfectly designed the root zone system, which looks like a garden rather than an effluent treatment plant. In this system nearly 2000 kinds of friendly bacteria thrive around the roots of *Phragmites australis*. The plant has got the remarkable property of absorbing CO<sub>2</sub> from the atmosphere through its leaves and pumping O<sub>2</sub> through its roots. The oxygen so liberated is utilized for the metabolic activities of the bacteria for the decomposition of the organic pollutants of the effluents. *P. australis* is unaffected by temperatures up to 45°C; a further increase in temperature is detrimental to the species.

Care taken during the experiment:

- The pH of the effluents to the system was maintained at neutral.
- The debris and wilted leaves were periodically removed.
- Adequate sunshine was ensured.

Here are the salient advantages of the system:

- There is no power cost.
- There is no cost of chemicals.
- There is no operating cost.
- A huge investment is not required in the machinery.
- There is no generation of solid waste, which is likely to be generated in the conventional method of primary setting with inorganic salts like ferrous sulfate, calcium carbonate, and polyacrylamide-based polyelectrolytes.
- *P. australis* is very adaptive and unaffected by occasional shock loads of effluents.
- Apart from removal of organics, improvement in turbidity is also seen in this system.

One certain disadvantage of the system is the requirement of a large amount of space.

### **2.5.5 Adsorption/Bio-oxidation Process for the Treatment of Textile Dyeing Wastewater**

The adsorption/bio-oxidation process developed in Europe uses physical, biochemical, and biological reaction mechanisms to reduce a very wide spectrum of organic pollutants, including the complex chemical compounds that are found in textile processing wastewater. This process is categorized as a dual-stage activated sludge treatment system. It involves adsorption as a first stage, with a very high food-to-microorganism (F/M) ratio and a short retention time, followed by a second stage for biological oxidation, the bio-oxidation stage [17, 29]. Typically, 50%-80% of the pollutants entering the wastewater treatment facility are removed in the adsorption stage at a retention time of 30 min. This rapid removal in the first stage is based primarily on adsorption as the main pollutant removal mechanism. It was found that the adsorption capability of activated sludge increases with an increase in the F/M ratio. Since the ratio is very high for the first stage in the process and the sludge is low, bacteria proliferate rapidly and are available for adsorption. The activated sludge, which consists of these bacteria and inorganic substances, forms the flocks and facilitates the adsorption in the first stage. The adsorption removal mechanism is responsible for 80% of

the total pollutant removal. Some of the activated sludge of the first stage with the adsorbed pollutants is withdrawn from the first stage clarifier, and the remainder is recycled back as activated sludge. The waste sludge withdrawn from the system settles easily [30]. After thickening, it is disposed of. The second stage (bio-oxidation) fulfills the function of the polishing stage. It is operated like a typical aerated activated sludge treatment system.

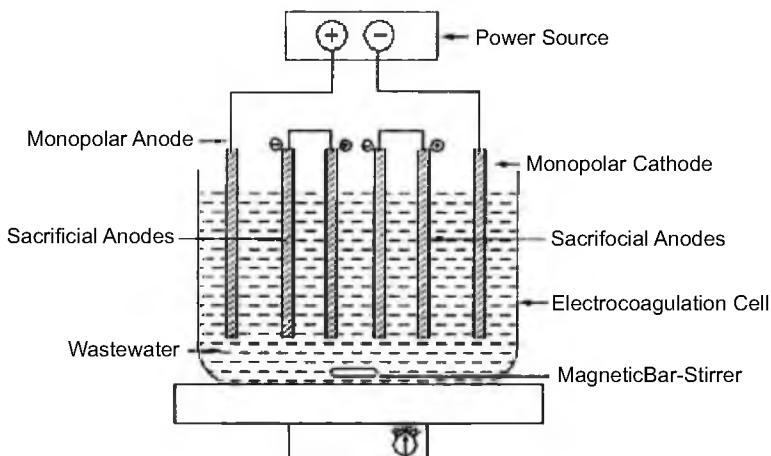
The unique operation of the adsorption stage yields the following features:

- Very high bacterial activity
- High BOD/COD removal
- Excellent handling of toxic, nontoxic, and pH shock loads
- Generation of easily settling sludge
- Reduced chemical requirements
- Destruction of difficult-to-decompose substances

## **2.6 Electrochemical Technology for Wastewater Treatment**

The process involves the use of a sacrificial iron electrode. Electrocoagulation (EC), the passing of electric current through water, has proven very effective in the removal of contaminants from water. EC systems have been in existence for many years (Dietrich, patented, 1906) using a variety of anode and cathode geometries, including plates, balls, fluidized bed spheres, wire mesh, and rods and tubes [31]. In the past few decades EC has been used for the treatment of defluorination of water and water containing foodstuff waste, oil waste, dyes, suspended particles, chemical and mechanical polishing waste, organic matter from landfill leachates, synthetic detergent effluents, mine waste, and heavy metal-containing solution. EC has become one of the affordable wastewater treatment processes around the world by reducing electricity consumption and miniaturizing the needed power supplies. EC offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions. EC removes metals, colloidal solids and particles, and soluble inorganic pollutants from aqueous media by introducing highly charged polymeric metal hydroxide species [25, 32].

EC uses a proprietary treatment chamber and electricity to treat a wide range of differing waste streams containing heavy metals, viruses, bacteria, pesticides, arsenic, methyl tertiary-butyl ether (MTBE), cyanide, BOD, total dissolved solids (TDS), and total suspended solids (TSS). It is used to treat municipal, industrial, and commercial wastewater. An EC reactor is made up of an electrolytic cell with one anode and one cathode. The EC system essentially consists of pairs of conductive metal plates in parallel, which act as monopolar electrodes. To operate, an EC reactor requires direct current, a power source, a resistance box, and a multimeter (Fig. 2.6).



**Figure 2.6** Bench-scale EC reactor with monopolar electrodes in series connection.

The conductive metal plates are commonly known as “sacrificial electrodes.” The sacrificial anode lowers the dissolution potential of the anode and minimizes the passivation of the cathode. The sacrificial anodes and cathodes can be of the same or of different materials. The monopolar electrodes with cells are arranged in series. In a series cell arrangement, a higher potential difference is required for a given current to flow because the cells connected in series have higher resistance. During electrolysis, the positive side undergoes anodic reactions, while on the negative side, cathodic reactions are encountered. The coagulation process will be initiated

by neutralization of the charges of the particles by released ions. The released ions remove undesirable contaminants either by chemical reaction and precipitation or by causing the colloidal materials to coalesce, which can then be removed by flotation. Water containing colloidal particulates, oils, or other contaminants moves through the applied electric field; there may be ionization, electrolysis, hydrolysis, and free-radical formation, which can alter the physical and chemical properties of water and contaminants. The reactive and excited state causes contaminants to be released from the water and destroyed or made less soluble.

Within the EC reactor, several distinct electrochemical reactions are produced independently.

- **Seeding:** It results from the anode reduction of metal ions, which become new centers for larger, stable, insoluble complexes that precipitate as complex metal ions.
- **Emulsion breaking:** It results from the oxygen and hydrogen ions that bond with the water receptor sites of oil molecules, creating a water-insoluble complex separating water from oil, driller's mud, dyes, inks, etc.
- **Halogen complexing:** The metal ions bind themselves to chlorines in a chlorinated hydrocarbon molecule, resulting in a large, insoluble complex separating water from pesticides, herbicides, polychlorinated biphenyls (PCBs), etc.
- **Bleaching:** This is caused when the oxygen ions produced in the reaction chamber oxidize dyes, cyanides, bacteria, viruses, biohazards, etc. Electron flooding of the water eliminates the polar effect of the water complex, allowing colloidal materials to precipitate, and the increase of electrons creates an osmotic pressure that ruptures bacteria, cysts, and viruses.
- **Oxidation reduction:** These reactions are forced to their natural end point within the reaction tank, which speeds up the natural process that occurs in wet chemistry.

Advantages of EC are as follows:

- Removes heavy metals as oxides that pass the toxicity characteristic leaching procedure (TCLP)
- Removes suspended and colloidal solids

- Breaks oil emulsions in water
- Removes fats, oil, and grease
- Removes complex organics
- Destroys and removes bacteria, viruses, and cysts

Benefits of EC are as follows:

- It is supplied as a skid-mounted unit, fully assembled for inlet/outlet and backwash connections.
- It has low operating costs.
- It has low power requirements.
- Minimal chemical additions are required.
- It involves low maintenance.
- Sludge is minimized.

Disadvantages of EC are as follows:

- The sacrificial electrodes are dissolved into wastewater streams as a result of oxidation and need to be regularly replaced.
- The use of electricity may be expensive in many places.
- An impermeable oxide film may be formed on the cathode, leading to loss of efficiency of the EC unit.
- High conductivity of the wastewater suspension is required.
- Gelatinous hydroxide may tend to solubilize in some cases.

## 2.6.1 Applications of EC

### 2.6.1.1 Groundwater cleanup

EC is extremely effective in the removal of naturally occurring salts in well water, as well as the separation of iron, magnesium, calcium, metals, nitrates, and sulfur. EC is also well suited for the reclamation of groundwater that has been contaminated with heavy metals, high-molecular-weight hydrocarbons, and halogenated hydrocarbons.

### 2.6.1.2 Surface water cleanup

EC is used to remove bacteria, viruses, and cysts from surface water, thereby rendering contaminated waste streams into potable water. EC is particularly effective in the removal of life-threatening contaminants, such as *Giardia* and *Cryptosporidium*.

### **2.6.1.3 Process rinse water and wash water**

EC routinely treats process and rinse water from electroplating, computer board manufacture, textile industry, paint rinse water, steel production, mining industry, automotive industry, equipment repair industry, stack wash water, and pulp and paper. In most cases, the treated water can be recycled and reused.

### **2.6.1.4 Sewage treatment**

EC has proven effective in treating sewage water, sewage sludge concentrations, and sewage sludge metal fixation sufficiently to enable land application.

### **2.6.1.5 Cooling towers**

EC is used to pretreat water entering towers as well as blow down water to remove algae, suspended solids, calcium, and magnesium buildup, thereby eliminating costly replacement water.

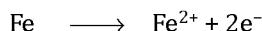
### **2.6.1.6 Water pretreatment**

Water pretreatment with EC has proven effective in removing bacteria, silica, and TSS prior to polishing with reverse osmosis (RO), ultrafiltration, nanofiltration, and photocatalysis.

When direct current is passed through a cell  $\text{Fe(OH)}_2$  is produced. It is hypothesized that the large surface area of  $\text{Fe(OH)}_2$  can adsorb organic compounds and that adsorption is the pathway for dye removal. Researchers have found that the process removes the color efficiently; color reduction of 75% to 100% has been achieved with a wide variety of dyes. The process effectively reduces the organic load toxicity. Decrease in COD, total organic carbon (TOC), BOD, and toxicity to *Daphnia magna* has been reported [11, 32]. Removal of dye and other dyebath constituents has been established with electrochemical treatment by an aluminum electrode. Adsorption has been accepted as the main mechanism of dye removal of this process.

Electrochemical treatment was done with laboratory-scale iron electrode (L-cell). The L-cell is made up of three plates of cold-rolled carbon steel separated by a 1/8-inch gap. The reaction that takes place when current is passed through the electrode may be summarized as follows:

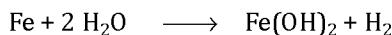
Anode (oxidation)



Cathode (reduction)



Overall



Forty mL of the solution is placed in a 60 mL beaker for treatment. To provide a conductive environment for the L-cell 0.4 gm of NaCl is added to each solution made with deionized distilled water. Preliminary experiment with acid dyes in the electrochemical system indicates that the process does not remove the dye efficiently unless salt is added.

## 2.7 Regulations in India and Voluntary Initiatives from Brands

### 2.7.1 Zero Liquid Discharge

Most industrial processes generate a wastewater stream. The objective of a zero liquid discharge (ZLD) system is to recover and reuse all water, avoiding any liquid discharge to the ground or environment. In other words, it is a wastewater treatment process developed to completely eliminate all liquid discharge from a system. The goal of a ZLD system is to reduce the volume of wastewater that requires further treatment, economically process wastewater, and produce a clean stream suitable for reuse [17, 33, 34]. Companies may begin to explore ZLD because of ever-tightening wastewater disposal regulations, company-mandated green initiatives, public perception of industrial impact on the environment, or concern over the quality and quantity of the water supply.

The rise of ZLD can be traced back to the United States in the 1970s, when power plant discharge increased the salinity of the Colorado River and thus created the regulatory context to push for ZLD in the United States. At that time, new industrial projects seeking approval for discharge agreement could take several years; with ZLD, the timetable was cut to mere months. ZLD technology

has taken hold and evolved significantly—in the United States and around the world—over the last four decades.

### **2.7.1.1 The global goal of zero**

Today, there are a rising number of evaporator/concentrator systems worldwide at work in a wide range of industries. Global construction of ZLD equipment represents an average of US\$100–200 million of investment annually according to industry analysts. ZLD technology has been mostly developed in Western countries for power plants but continues to spread to drought-stricken regions such as the Middle East and high-pollution-sensitive environments.

Generally, ZLD systems are mandated where severe environmental constraints exist and/or where strong environmental regulations are enforced—either due to a resource-intensive industry process, such as coal processing or petrochemical and mining, or due to water scarcity in the region. In coal-rich but dry northwest China, for example, ZLD is an ideal solution for water recovery and mitigating resource depletion.

In India, water is a key priority, with US\$20 billion set aside for sewage treatment, irrigation, and the recycling of water resources over the next five years. The establishment of the National Bureau of Water Use Efficiency (NBWUE) has been proposed with the objective of achieving a 20% increase in water use efficiency by March 2017. As part of this ambitious initiative, ZLD systems are mandatory for all inland thermal power units.

ZLD guidelines were recently introduced for four industrial sectors—textile (wet processing), distilleries, pulp and paper, and tanneries—in India. Since March 2015, when the Central Pollution Control Board (CPCB) issued notifications to nine state pollution control boards of states along the Ganga basin, a series of notices have been sent to factories asking them to submit action plans for achieving ZLD or face severe penalties (including shutdown). The ZLD mandate has helped increase the focus of the industry on water, which has traditionally been an underpriced resource. However, uniform policy across different regions in the country is key to the widespread adoption of ZLD since high operating costs (which impact end product cost) will make factories shift to other areas (and pollute freely there) to stay competitive rather than installing ZLD plants in their facilities [7, 17].

### 2.7.1.2 Cost is high but not as significant as compliance

While the ZLD technology has been available and mandated in industries in Europe since the 1980s, it is still at a relatively nascent stage in India. This is because ZLD systems are associated with high capital investments and even higher operating expenses. More than 90% of this operating cost is incurred during evaporation, which is a very energy-intensive process. This is because, after various stages of filtration, chemical treatment, and separation of water from chemicals following RO, the RO reject is first evaporated and then condensed to recover the water.

There is no single treatment technology that is better than others in achieving ZLD in all the given industries as it depends on the quality of and contaminants in the waste stream. Therefore, there is confusion about ZLD as a whole as it is not a single system but a combination of various treatment processes that may vary from industry to industry. This is due to the fact that the type of technology depends upon the quality of the effluent and the process water quality requirement.

Apart from this in some cases this cost can be offset by resource recovery, that is, salt and other chemicals that can be reused in the process. In the textile industry, for example, there is enough scope to recover salts and brine solution, which can be reused in the manufacturing process and reduce the impact of treatment cost on the overall cost of production.

A key issue to consider is that this mandate will drive water efficiency measures in the Indian industry. Lesser wastewater means lesser treatment cost, and thus improving water use efficiency will have significant benefits, especially for industries like sugar and pulp and paper industry, which have a considerably large water footprint. It is unviable for these industries to implement ZLD at their current levels of water use. Considering this, the CPCB has issued only water conservation norms for both industries, which will help them move to ZLD in the future. The key is that there is a gradual transformation of the way water is viewed in India due to the ZLD mandate. Today water is an underpriced resource in most of the country and toxic wastewater is discharged without much consideration. This shift in focus around addressing water pollution and scarcity will lead

to water being viewed as a shared resource in an ecosystem where polluters will have to pay for cleaning up their waste.

## **2.7.2 Zero Discharge of Hazardous Chemicals**

Zero discharge of hazardous chemicals (ZDHC) was started in 2011, mostly as a response to Greenpeace's Detox campaign. Greenpeace International had conducted four investigations into the use of hazardous chemicals in the textile supply chain. These reports found persistent, hazardous chemicals in the discharges from textile manufacturing facilities in China, Mexico, and Indonesia—all suppliers of big sportswear and fashion brands [35].

Greenpeace International also conducted several investigations into the presence of hazardous chemicals in clothing. After testing garments from international clothing brands made and sold in a number of countries around the world, the presence of a number of these substances was found in the fabric of the clothes [34].

This body of evidence forms the basis of Greenpeace's Detox campaign, directed toward global sportswear and fashion companies, challenging them to eliminate all hazardous chemicals from their supply chains and products. A number of brands—including many of those directly challenged by Greenpeace and hundreds of thousands of people around the world—took up the challenge and made individual commitments to ZDHC by 2020. In doing so, they publicly committed to eliminating the use and release of such persistent hormone-disrupting chemicals into our waters via their production processes.

Initially a joint roadmap was established to demonstrate the collaborative efforts and an agreement on the steps needed to lead the apparel and footwear industry toward ZDHC for all products across all pathways by 2020. The ZDHC membership has grown from 6 brands in 2011 to a total of 63 contributors today, divided into three categories: 23 signatory brands, 27 value chain affiliates, and 13 associates.

The group is diverse and includes:

- Brands from Europe and the United States
- Sportswear, luxury, and fashion brands
- Multibillion-dollar companies as well as small, niche brands

### 2.7.2.1 Guiding principles of ZDHC

Apparel and footwear supply chains are long and complicated and continuously moving into developing countries where labor is cheap. This means manufacturing facilities and workers may lack the knowledge and training necessary to implement a chemicals management program. Companies committed to ZDHC have established and implemented the following competencies to drive their work:

- Capture and share best practices.
- Use management systems thinking.
- Maintain open, transparent communication.
- Engage with stakeholders across different regions and cultures.

The ZDHC approach is unique and holistic because it talks about chemical management as the precursor to ZDHC. The emphasis is on understanding and controlling the input chemicals so that no hazardous chemicals are released down the line. The ZDHC platform has initiated a bunch of innovative approaches and recently released its norms for effluent release.

### 2.7.2.2 Focus areas of the updated joint roadmap

The ZDHC program provided a joint roadmap update in late 2015. The update transitions seven work streams into four focus areas to strategically support all elements of the supply chain in adopting improved chemical management practices [7, 34]. Comparative aspects are presented in Table 2.3 with respect to ZLD and ZDHC.

- **Wastewater quality:** The roadmap has benchmarked the existing standards and existing data at facilities and has now come up with a guidance document and promotes the inclusion of functioning wastewater treatment plants at manufacturing facilities.
- **The MRSList:** The ZDHC forum has updated the MRSList (Manufacturing Restricted Substances List) to include leather-processing chemicals. In addition, it has aligned on a conformance process, engaged stakeholders, and scaled the tool.

**Table 2.3** Comparison between ZLD and ZDHC

ZLD	ZDHC
It is limited to the discharge of hazardous chemicals in wastewater only.	It considers discharge of hazardous chemicals across all pathways, that is, end products, wastewater, sludge, and air.
It is an “end of pipe” solution to prevent pollution of the environment.	The focus is on the management of input chemicals (by the use of MRSI) so that hazardous chemicals are screened for restricted substance.
It prohibits the discharge of wastewater (inclusive of hazardous chemicals) to the surrounding environment by a factory.	Discharge of wastewater is not prohibited, but the stipulation is on the presence of hazardous chemicals, which should be below the detection limit of the testing laboratory.

- **The process:** The forum has defined a process for finding safer alternatives, developed a process to add substances to and remove substances from the research list, and engaged with stakeholders to find alternatives to chemicals of concern.
- **Audit protocol:** The forum will align the audit protocol with the Higg Index, develop and finalize an assessment process, and engage groups to promote the adoption and use of the audit protocol.

In addition to these four focus areas, the program has also established work that cuts across all focus areas, notably:

- Data and disclosure
- Training

The ZDHC program has identified 11 chemicals of concern, namely:

- Alkyl phenol ethoxylate
- Halogenated flame retardant
- Chlorinated solvents
- Chlorinated phenols
- Chlorophenols

- Heavy metals
- Organotin compounds
- Perfluoro-octanic acid (PFOa) and perfluoro-octane sulfonic (PFOS)
- Phthalates
- Short-chain chlorinated phenols
- Azo dyes

## 2.8 Conclusion

During the past two decades, there has been a growing consciousness among people across the globe about clean processes, environment, and water management. As population has grown and natural resources have become scarce the consciousness has turned into a persistent need and the governing bodies have realized the same. In response to that the laws and regulations regarding effluent treatment have become more stringent. The lack of implementation of the reported processes is due to high cost, low efficiency, and also the high cost of recovery. The basis to make a pollution control technology more efficient and effective is to integrate innovative and conventional water treatment technologies in combined processes with improved performance and lower cost. With environmental rules becoming more stringent than ever, innovative technology is the only weapon to counter this, the focus being on consistently exerting to develop new techniques and applying newer methods that are benign to nature and mankind.

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## **Chapter 3**

# **Ecological Impacts of Azo Dyes and Environmental Considerations**

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In general, dyes may be defined as those substances that, when applied to a substrate, impart color to the applied substrate through a process by which they adhere to compatible surfaces by physical adsorption that, at least temporarily, destroys any crystal structure of the colored substance. In this phenomenon, the formation of new covalent as well as weak bonding occurs by interaction between substrate and dye molecules. However, textile and other dye-related industries consistently produce wastewaters of very complex contents, which pose a serious hazard to the environment. Toxic effluents containing discharge from such industries have several adverse effects on water resources, aquatic life, and soil fertility. The chapter provides an overview of the ecological impacts and prominent hazards associated with the use of azo-based dyes in

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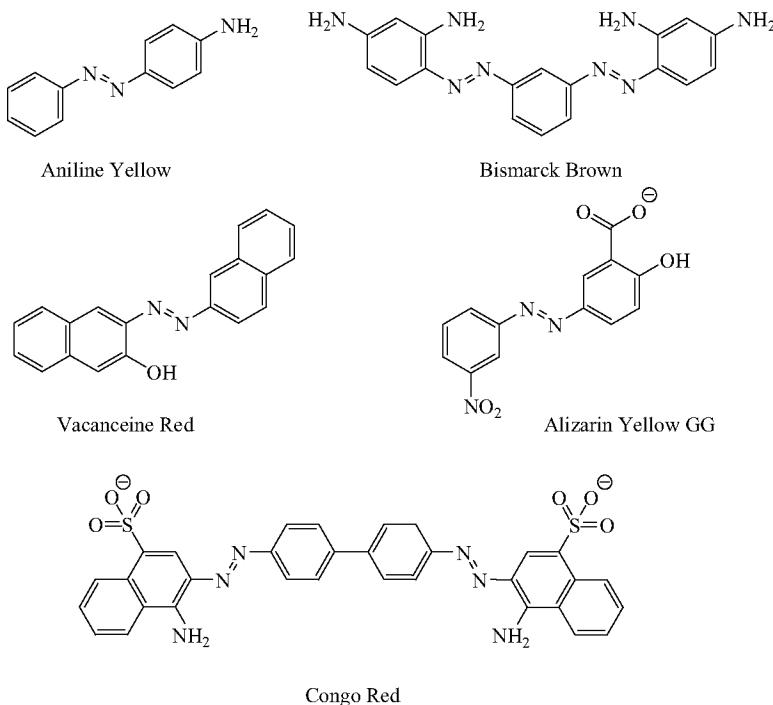
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the textile industry, with a particular emphasis on wastewater contamination.

### 3.1 Azo Dyes: An Overview

Until the middle of the nineteenth century, all dyes came from natural sources, including vegetable and animal extracts/products. In the Ancient Stone Age, descriptions have shown that people applied various powders made up of colored minerals to their hair and body parts to gain magical powers while hunting as well as for occasional dressing. Spectroscopic analysis has shown that Egyptian mummies are wrapped in cloth dyed with biocolorants. Also, nails of Egyptian mummies were painted with henna paste. Alexander the Great is thought to have deceived the Persians into thinking that his army was wounded, by sprinkling his soldiers with a red dye, probably madder extract [1–3].



**Figure 3.1** Chemical structures of some common azo dyes.

In 1856, Sir William Henry Perkin, while experimenting with coal tar in the hope of finding a cure for malaria, discovered the first violet synthetic dyestuff, which he called mauve, and a new industry began: synthetic color manufacturing. The first important event in the history of azo pigments was the discovery of diazotization reaction by P. Gries in 1858. The first azo dyes were synthesized by Mene (aniline yellow) in 1861 and by Martius (Bismarck brown) in 1863. In 1875, Caro and Witt synthesized chrysoidine badische anilin & soda-fabrik (BASF, Germany) through a reaction sequence of diazotization and coupling conversion. In 1980, Thomas and Holliday developed vacanceine red; and Böttiger synthesized Congo red (direct red 28) in 1984 [1, 4]. The chemical structures of some common azo dyes are represented in Fig. 3.1.

## 3.2 Types of Azo Dyes

Azo dyes, with respect to both number and production volume, are the largest group of colorants, constituting about 70% of all organic dyes produced in the world. Due to the complexity of the chemical names, they are only rarely referred to by their IUPAC (International Union of Pure and Applied Chemistry) or CAS (Chemical Abstracts Service) nomenclatures. Technical literature has adopted the classification of azo pigments either by the chemical constitution or by the color produced. For example, in the Colour Index system, azo colorants are provided with numbers ranging from 11000 to 39999 in correspondence with the chemical classes (Table 3.1) [1, 5].

**Table 3.1** Colour Index-based nomenclature of azo colorants

Number of azo groups	Chemical class	Colour Index numbers
1	Mono-azo	11000–19999
2	Bis-azo	20000–29999
3	Tris-azo	30000–34999
<i>n</i>	Poly-azo	35000–36999
1 to <i>n</i>	Azoic	37000–39999

### **3.3 Toxicological and Carcinogenicity Aspects**

Effluents from textile dyeing industries are a serious environmental concern. In addition to being toxic, dye effluents contain chemicals that are carcinogenic, mutagenic, or causative to a number of health-related problems. Undoubtedly, dyes also inhibit several biological processes that are ecologically very important. For example, they can inhibit algal photosynthesis by reducing the penetration of light. Consequently, these dyes have been reported to inhibit chemical oxygen demand reduction and respiratory activities of microbial world in aquatic systems. This may result in inhibition or alteration of microbial processes like wastewater treatment systems and natural biogeochemical cycles [6–8]. Azo dyes constitute a significant fraction of textile dyes and are toxic as well as carcinogenic. For example, they cause a variety of chronic effects/disorders. Some azo dyes have been linked to bladder cancer in humans and to splenic sacromas, hepatocarcinomas, and nuclear anomalies in experimental animals and to cause chromosomal aberration in mammalian cells [9]. The majority of azo dyes show LD<sub>50</sub> values in the range of 250–2000 mg/kg body weight. On the basis of toxicological and carcinogenicity prospects, the European Union (EU) had made essential criteria and classified dangerous substances, including azo dyes. Reactive brilliant red, an azo dye, can inhibit the functioning of human serum albumin by binding to it and causing a conformational change or even precipitation. In addition, the International Agency for Research on Cancer (IARC) reported the presence of 4-aminobiphenyl and 2,4-diaminoazobenzene as impurities in direct black 38 dye [1, 3, 10]. Table 3.2 represents the CAS-based numbers and IARC-based classification regarding harmful constituent aromatic amines, many of which show very high levels of acute and chronic toxicity and carcinogenicity.

**Table 3.2** The 22 aromatic amines that cause highly adverse responses in humans, like cancer, and banned by European Union Commission

Amine residues	CAS number	IARC classification	Chemical structures
4-Aminodiphenyl	92-67-1	Group 1	
Benzidine	92-87-5	Group 1	
4-Chloro-o-toluidine	95-69-2	Group 2A	
2-Naphthylamine	91-59-8	Group 1	
4-Amino-2',3-dimethylazobenzene	97-56-3	Group 2B	

(Continued)

**Table 3.2** (Continued)

Amine residues	CAS number	IARC classification	Chemical structures
2-Amino-4-nitrotoluene	99-55-8	Group 3	
4-Chloroaniline	106-47-8	Group 2B	
2,4-Diaminoanisole	615-05-4	Group 2B	
4,4'-Diaminodiphenylmethane	101-77-9	Group 2B	
3,3'-Dichlorobenzidine	91-94-1	Group 2B	
3,3'-Dimethoxybenzidine	119-90-4	Group 2B	

Amine residues	CAS number	IARC classification	Chemical structures
3,3'-Dimethylbenzidine	119-93-7	Group 2B	
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	838-88-0	Group 2B	
4-Cresidine	120-71-8	Group 2B	
4,4'-Methylene-bis-(2-chloroaniline)	101-14-4	Group 2B	
4,4'-Oxydianiline	101-80-4	Group 2B	

(continued)

**Table 3.2** (*Continued*)

Amine residues	CAS number	IARC classification	Chemical structures
4,4'-Thiodianiline	139-65-1	Group 2B	
2-Aminotoluene	95-53-4	Group 2B	
2,4-Diaminotoluene	95-80-7	Group 2B	
2,4,5-Trimethylaniline	137-17-7	Group 3	
2-Methoxyaniline	90-04-0	Group 2B	
4-Aminoazobenzene	60-09-3	Group 2B	

### 3.4 Ecological Legislations

In accordance with ecological legislations, there is as yet no international consensus concerning discharging textile effluents, including azo dyes, and there is no official document listing the different effluent limit values applied in different countries. Many developed countries establish limits. For example, the United States, European nations, Canada, and Australia enforce environmental legislations. Some countries (e.g., Thailand) follow the legislative system of the United States, while countries like Turkey and Morocco follow the EU model [1, 10]. In China pollution has been controlled to a significant extent in order to manage environmental problems. In other nations, including India, Pakistan, and Malaysia, effluent contamination limits are recommended, not mandatory. The EU banned azo dyes based on 22 aromatic amines by its directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (Table 3.2). It was later amended to include two more azo dyes and testing methods for the banned compounds, through the directives 2002/61/EC 2003/3/EC and 2004/21/EC [11–14]. The Ministry of Environment and Forests in India also called for a three-year phaseout of the use of benzidine-based dyes in a notification published in January 1990 in the *Gazette*. As per this notification, handling of 42 benzidine-based dyes was prohibited 1993 onward. In March 1997, the handling of 70 more azo dyes was prohibited [1, 6, 15]. However, the use and manufacture of benzidine-based dyes still continues in India, China, Korea, Taiwan, and Argentina. Several recent studies have demonstrated water contamination resulting from continued discharge of mutagenic textile and dye-house effluents in these countries. Therefore, the probability of health issues from azo dye poisoning and severity of cancer-related disorders demand stringent responses.

### 3.5 Conclusion and Future Considerations

Globally, environmental pollution occurs chiefly by the action of textile effluents, one of the major threats nowadays. During textile processing, inefficiencies in dyeing result in large amounts of the

dyestuff being directly lost to wastewater, which ultimately finds its way to the environment. Azo dyes have been proven to be toxic for living species of the aquatic ecosystem as the degradation of azo dyes produces benzidine and other aromatic amines, which are associated with toxicological as well as carcinogenic consequences. The increasing complexity of and difficulty in treating textile effluents has led to a constant search for new methods that are effective and economically viable. To ensure suitable materials for textile coloration, they should adhere to the technical, ecopreservation, economic, and ecological requirements of the twenty-first century, with sustainability being the priority. In this regard, the research and development sector needs to join the *race to the green* using environmentally valued materials.

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## **Chapter 4**

# **Textile Effluent Treatment Using Adsorbents**

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Textile effluent consists of a wide range of organic compounds and contaminants that cause environmental pollution if left untreated. Various methods are used simultaneously or independently to treat the effluent. One of the important methods is the use of adsorbents. Nonbiodegradable organic compounds, color compounds like dyestuffs, aromatic compounds, chlorinated organic compounds, and pesticides can be removed by using adsorbents. Adsorbents consist of minute pores, in which the contaminants are held by van der Waals forces. Most of the nonpolar organic molecules are readily adsorbed by adsorbents. Effective usage of adsorbents lowers the concentration of dissolved organics present in the effluent. Different types of adsorbents, like activated carbon, bioadsorbents, biomass,

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microbial biomass, and inorganic adsorbents, have been used in treating textile effluents.

In this chapter, characteristics of effluents, overview of different methods of treatment, treatment of effluents using adsorbents, types of adsorbents, mechanism of adsorbents, application of adsorbents, advantages and limitations of adsorbents, and studies conducted on the treatment of effluents using adsorbents are discussed.

## 4.1 Introduction

Chemical processing of textiles is one of the most important and unavoidable steps in manufacturing textiles and garments for various applications. It often includes processing of fibers and yarns and dyeing and finishing of fabrics with various processes and finishes. Processes that create effluents are broadly classified into the following categories:

- Sizing
- Desizing
- Scouring/Degumming
- Bleaching
- Mercerization
- Dyeing
- Printing
- Finishing

Sizing is the process of imparting additional strength and enhancing abrasion resistance of warp yarns, thereby improving the weavability of warp yarns. In this process, a thick paste of starch and other essential ingredients (hygroscopic agents, antimicrobial agents, and weighting agents) is applied to the warp sheet in various quantities depending on the linear density of the yarn and application of the fabrics for various end uses. Since it is applied in a paste form, the effluents generated in this process are limited to a lesser extent in terms of quantity with high concentrations.

Desizing is the process of removing the applied size ingredients after fabric formation through weaving and prior to further wet processing of fabrics, which obviously generates huge amounts of effluents with organic and inorganic pollutants.

Scouring, or degumming, is the process removing unwanted natural substances from the surface of fibers that were meant for certain designated functions during fiber formation and preparing the fabrics for mercerization (in the case of cotton and its blends), bleaching, dyeing, and finishing.

Bleaching is the process where the natural coloring substances from the fibers are removed. Dyeing and printing are meant for the coloration of textile materials to various extents, and ever since the coloration of materials has been initiated, thousands of dyes are manufactured all over the world. The production of dyes is estimated to be around 700,000 tons per year, which includes more than 100,000 commercially available dyes [1]. The detailed breakdown of the market share of dyes in the year 2011 is shown in Table 4.1.

**Table 4.1** Market potential of certain classes of dyes

Class of dye	World market (in tons)
Direct dyes	181,998
Indigo dyes	121,000
Acid dyes	680,000
Disperse dyes	570,000

Source: [2]

Two to twenty percent of the dyes used in the coloration of fabrics are directly discharged into effluents [3], depending on the process conditions employed; and 100 to 300 L of water is used and released as effluent for every kilogram of fabric processed, under normal process conditions [2]. During the above processes, many chemicals and auxiliaries are used, of which some of the important chemicals are [3]:

- Sizing agents with a high proportion of starch
- Acids
- Alkalies and detergents
- Oils (used as lubrication aid)
- Bleaching agents
- Dyes, dye-fixing agents, and inorganic chemicals auxiliaries

- Special chemicals (softeners, antifoaming agents, antimicrobial agents, wetting agents, soil release agents, etc.)

These processes are important to enhance the appearance, comfort, and functionality of textile materials. But in recent years, due to the increase in population and lifestyle improvement, the consumption of textile materials has increased enormously, leading to increases in wet processing and effluents, with the following threats to society:

- Color in water
- Toxicity
- Carcinogenic substances
- Mutagenicity

In this chapter, a detailed review of the characteristics of effluents, different methods used in effluent treatment, treatment of effluents using adsorbents and different types of adsorbents used in effluent treatment, mechanism of adsorbents in removal of pollutants, and advantages and limitations of different adsorbents, along with a few case studies, are presented.

## 4.2 Characteristics of Textile Effluents

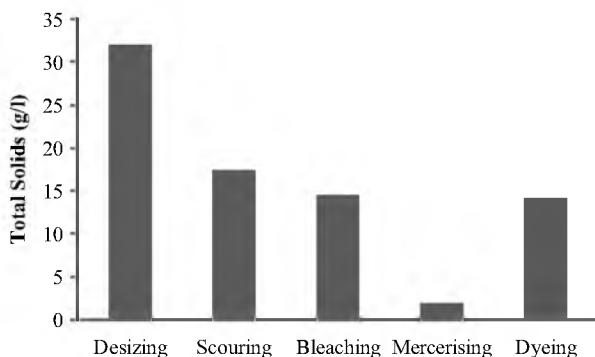
The effluents generated from textile treatment can be characterized by appearance, chemical contents, degradability, and the extent of harmful effects associated with the environment. The following are the most important characteristics of effluents released by the textile industry:

- Color
- Heavy metals
- Total dissolved solids (TDS)
- Total suspended solids (TSS)
- Total solids (TS)
- pH
- Biochemical oxygen demand (BOD)
- Chemical oxygen demand (COD)
- Other potential hazards

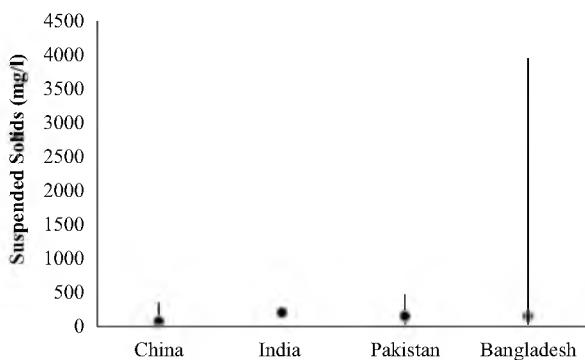
On the basis of the biodegradability of the pollutants, effluents can be classified into five categories, from 1 to 5, where Category 1 stands for less harmful while Category 5 stands for the presence of severe pollutants. Alkalies, mineral acids, oxidants, and salts used in the pretreatment processes or any other wet processing treatments and inorganic pollutants that are relatively inoffensive in nature are classified under Category 1. Washed-out starch from desizing; oils, fats, and waxes that are removed during the process of scouring; organic acids; biodegradable surfactants; and reducing agents are easily biodegradable in nature, with moderate to high BOD contents, and are classified under Category 2. Effluents that are generated from man-made or synthetic fibers' manufacturing and dyeing consist of colored particles, optical brightening agents, fiber waste, polymeric waste from fiber spinning, spin-finish (formulations) and resins, etc., which are difficult to biodegrade and are classified under Category 3. Certain special chemicals or additives that are difficult to biodegrade and have moderate BOD, such as polyvinyl alcohols, emulsions, and oils, are classified under Category 4. Chemicals that belong to Category 5 are very difficult or not possible to degrade by conventional biological treatments and the pollutants have low BOD. These include residues such as formaldehyde, catalysts, retarders, and salts of heavy metals [3].

#### 4.2.1 TS, TDS, and TSS

Textile effluents (wastewater), in general, are characterized in terms of TS, TDS, and TSS. TSS are measured by filtering the effluents through a standard filter, and the resultant mass of residue is used for calculation. TS are identified by evaporating the water from effluents at a particular temperature and calculating the residue content. TDS in the effluent are calculated by subtracting the TDS from TS [4]. Figure 4.1 shows the average TS present at different stages of effluent generated from various preparatory processes and dyeing of fabrics [2], while Fig. 4.2 shows the TSS observed in four different countries of Asian region [4] who are the major producers of textile materials.



**Figure 4.1** Characterization of effluents—total solids [2].

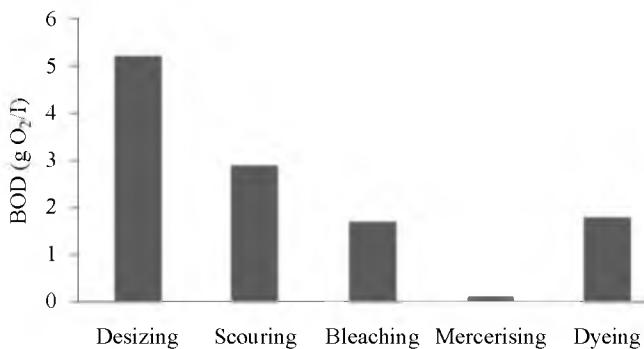


**Figure 4.2** Characterization of effluents—total suspended solids [4].

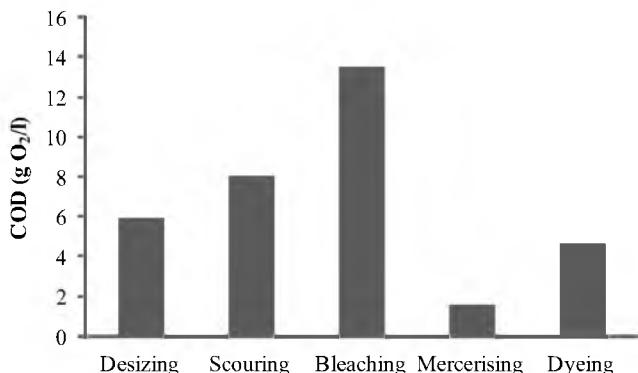
#### 4.2.2 Oxygen Demand

The amount of oxidizable organic substances or pollutants present in effluents can be characterized in terms of BOD and COD. BOD is the measure of the amount of dissolved oxygen required by the microorganisms to break down the organic matter present in the effluent under aerobic conditions, usually evaluated over the period of time and at a particular temperature. This process helps to determine the size of the effluent treatment plant required and thereby the quantity of dissolved oxygen required in the plant at various stages. The assessment of BOD takes a longer time, depending on the point of generation to discharge, to oxidize the

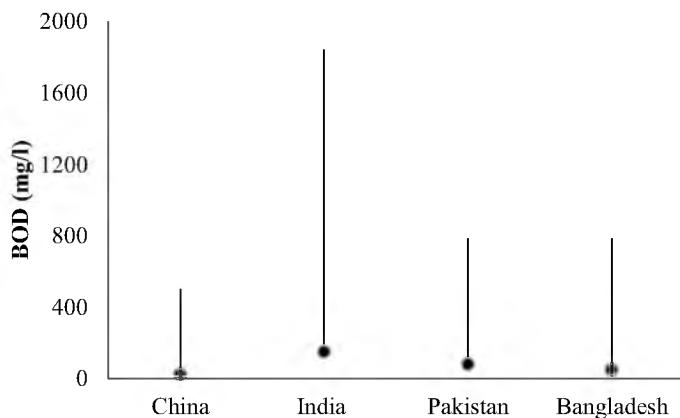
organic matters. And since BOD calculation is a time-consuming process, many a time, an alternate approach, chemical means, is adopted by the industry. COD is the measure of total quantity oxygen/equivalent required to oxidize all organic substances into carbon dioxide and water using chemical means. Figures 4.3 and 4.4 show the approximate BOD and COD of the effluents at different stages of fabric processing [3]. Figures 4.5 and 4.6 show the approximate BOD and COD of the effluents generated in four different counties, as reported. Figure 4.7 shows the percentage of total organic material available at each stage of the processing in which most of the contents are oxidizable [4].



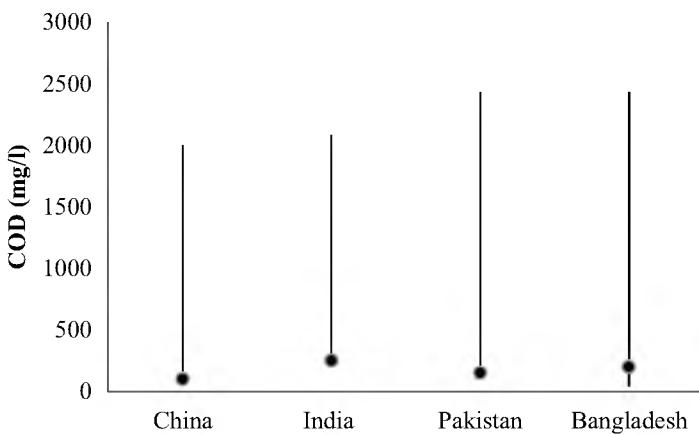
**Figure 4.3** Characterization of effluents' biological oxygen demand [3].



**Figure 4.4** Characterization of effluents' chemical oxygen demand [3].



**Figure 4.5** BOD of effluents in the Asian region [3].

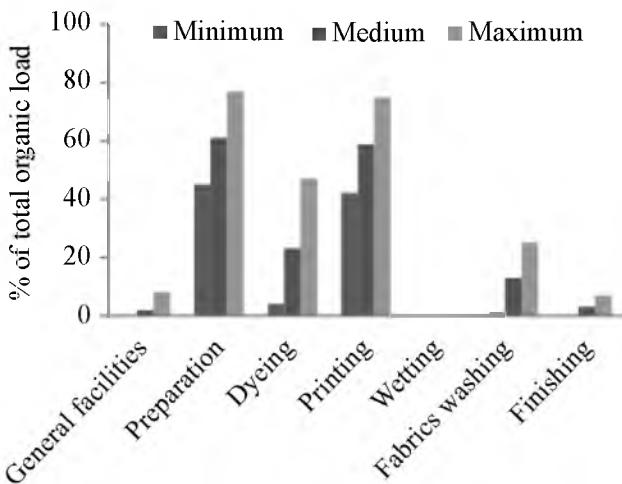


**Figure 4.6** COD of effluents in the Asian region [3].

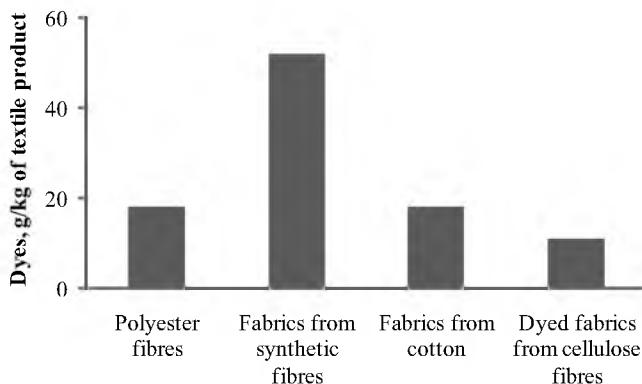
#### 4.2.3 Color

The color of an effluent, due to residues arising from dyeing, affects the environment in two aspects: (i) the appearance of the effluent because of the color of dyes and (ii) the breakdown of dyes, which creates toxic substances during the breakdown process, such as

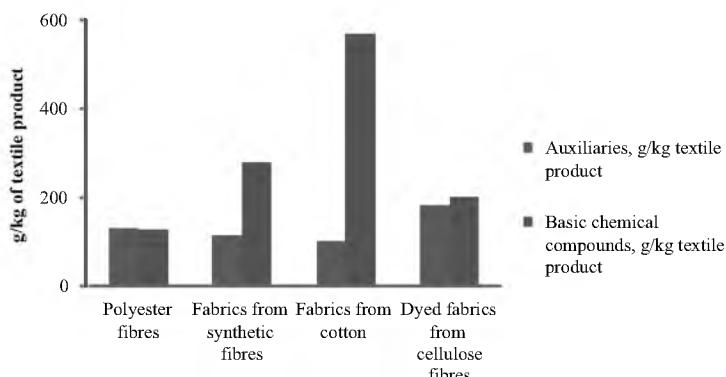
carcinogenic compounds, which get released into the environment. Hence, the removal of dyes and coloring matters from effluents becomes obvious and essential [5]. Figures 4.8 and 4.9 show the amount of dyes and other chemicals used in textile materials, respectively. Figure 4.10 shows the amount of residual dyes in the effluent, observed for various classes of dyes.



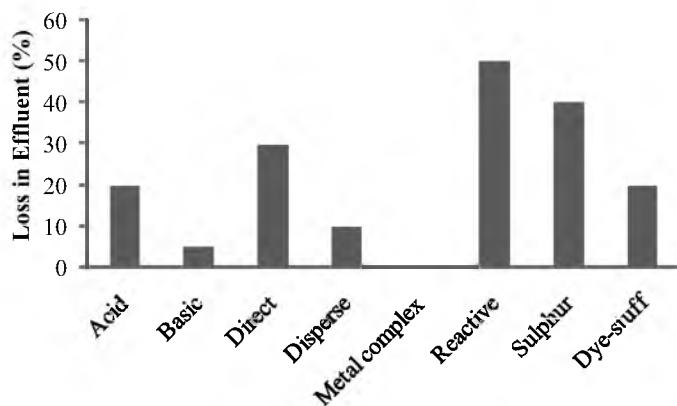
**Figure 4.7** Organic load at different stages of processing [3].



**Figure 4.8** Dye effluents from textile treatment plants [3].



**Figure 4.9** Auxiliaries and basic chemicals in effluents [3].



**Figure 4.10** Residual dyes in effluents [3].

### 4.3 Effluent Treatment Methods: An Overview

Many methods are used for the treatment of effluents based on physical, physicochemical, and biological treatments and combinations of these methods. Various stages of effluent treatment are classified into three categories—pretreatment, main treatment, and posttreatment processes—which are shown in Table 4.2. Some of these treatments are versatile in nature, which can be used at more than one stage of processing the effluents.

**Table 4.2** Effluent treatment methods used in different stages

<b>Treatment stage</b>	<b>Method of treatment</b>
Pretreatment	Precipitation, coagulation-flocculation Electrokinetic coagulation Fenton process Adsorption using activated carbon Adsorption using peat Adsorption using coal ashes Adsorption using wood chips Adsorption using silica gels Electrochemical oxidation Sonication Redox mediators
Main treatment	Precipitation, coagulation-flocculation Electrokinetic coagulation Fenton process Ozonation Ion exchange Anaerobic biological treatment process Advanced oxidation process Membrane filtration
Posttreatment	Oxidation with hypochlorite Adsorption using activated carbon Irradiation Photochemical process Aerobic biological treatment process Single cell (Fungal, algal, and bacterial) Photocatalysis Enzymatic treatment

Even though these treatments are classified into three different stages, it is not necessary for the treatments to be restricted to only these categories. On the basis of the nature of effluents, type and location of industry, and availability of treatment methods, combinations of the effluent treatment process can be designed. The following sections describe different methods of effluent treatment used by the industry.

### 4.3.1 Physical Methods

#### 4.3.1.1 Adsorption

Adsorption is one of the most effective methods of effluent treatment in textile industries and is one of the most economical methods among all the effluent treatment processes. In this method, an adsorbent is used to collect dye particles and other dissolved substances on the surface of the solid and porous adsorbent. Adsorption is the result of two different mechanisms, namely adsorption and ion exchange. The extent of the second mechanism depends on the type of adsorbents used in the treatment, and the only limitation of the adsorption process is the finite capacity of the absorbent for each compound present in the effluent. Once “spent,” the adsorbents must be replaced [5–8]. The following are some of the key factors influencing dye adsorption [5]:

- Surface area of the adsorbent
- Particle size of the dye and other solid materials
- Dye/adsorbent interaction
- Contact time of effluent with adsorbent
- Temperature and pH of the effluent

Activated carbon, a widely used adsorbent, can adsorb large, negatively charged dye particles. Granular or powdered activated carbon with a specific surface area in the range of 500 to 1500 m<sup>2</sup>/g, a pore volume of 0.3 to 1 cm<sup>3</sup>/g, and a bulk density of 300 to 550 g/L can be used appropriately in a column or batchwise treatment. Adsorbents are capable of removing pollutants at a pH range of 2 to 11 and effluent temperatures between 0°C and 100°C. Once the activated carbon is saturated with pollutants, it needs to be reactivated, which often results in a loss of 10% to 15% of its adsorption capacity [3].

#### 4.3.1.2 Irradiation

The irradiation method of effluent treatment is a simple and efficient treatment that uses gamma rays or electron beams to disinfect the microorganisms present in the effluent. Few reports are available to prove that natural sunlight can also act as a source of irradiation for effluents that consist of dyes, for a period of 6 to 48 h, during which

a natural photolysis reaction takes place. To speed up the photolysis process, artificial radiation may be used, such as monochromatic UV light. Since this type of treatment consumes a high quantity of dissolved oxygen, adequate supply of oxygen is essential for this process. The COD, total organic carbon (TOC), and color of effluent can be reduced by 65%, 34%, and 85%, respectively, during treatment, when 15 kilogray (kGy) gamma rays are used during irradiation. In recent years, most of the commercially available dyes have exhibited good performance in terms of light fastness, and research on photodegradation of organic dyes is highly analyzed nowadays [3].

#### **4.3.1.3 Membrane process**

Membrane processes facilitate in-plant treatment of effluents discontinuously, which separates the residual dyes and reduce the BOD. There are many types of membranes available for effluent treatment, namely microfilters, ultrafilters, nanofilters, and membranes for reverse osmosis, which can be selected on the basis of the quality of effluent to be treated and the nature of pollutants present in the effluent. Table 4.3 shows the different types of filters, their functions, and the process conditions used in membrane processes.

##### **4.3.1.3.1 *Microfiltration***

This type of filter is for the treatment of pigments and effluents arising from rinsing processes and is used as the preliminary step for nanofiltration or reverse osmosis. The pore size of the membranes used in the ultrafiltration process, which are typically low-pressure membranes, ranges from 0.1 to 1 micron, and the membranes are meant for a transmembrane pressure range of 20 to 100 psi. These filters can handle effluent transport velocities ranging from 20 to 100 cm/s, capable of offering high resistance to chemicals and heat [3, 9].

##### **4.3.1.3.2 *Nanofiltration***

Nanofiltration is more effective when it is used in combination with adsorption processes. If the textile effluents are left as is to the environment, harmful effects were reported if the color and

**Table 4.3** Different types of filters used in effluent treatment

Type of filtration	Purpose	Treatment	Material or polymer used to produce the membrane	Process conditions
Microfiltration	Pretreatment for nanofiltration or reverse osmosis	Pigment and subsequent rinsing	Poly(ether sulfone), poly(vinylidene fluoride), poly(sulfone), poly(vinylidene difluoride), polycarbonate (PC), polypropylene (PP), polytetrafluoroethylene (PTFE)	Pressure: 20–100 PSI Velocity: 20–100 cm/s
Ultrafiltration	Pretreatment for reverse osmosis or used in combination with a biological reactor	Separation of macromolecules and particles	Polysulfone, PP, nylon-6, PTFE, polyvinyl chlorides (PVCS), acrylic copolymers	-
Nanofiltration	Retention of low-molecular weight organic compounds, divalent ions, large monovalent ions, and hydrolyzed reactive dyes	Textile effluent decolorization	Cellulose acetate, aromatic polyamides, ceramics, carbon-based membranes, zirconia	NF flux rates: 5–30 GFD Pressure: 8 bar
Reverse osmosis	Ionic compounds, hydrolyzed reactive dyes, and chemical auxiliaries	-	Cellulose acetate, aromatic polyamides, inorganic materials	Pressure: 500–1000 PSI Cross flows: 20–100 cm/s RO fluxes: 5–15 GFD

Source: [3, 6]

concentrations of the salts are on the higher side. It is reported that 70% to 90% of dyes from effluents are removed using the nanofiltration process. Situations in which the accumulation of dissolved solids is reported, nanofiltration can be the best alternative in effluent treatment [10].

### 4.3.2 Chemical Treatment: Oxidative Treatment

Chemical oxidation is the process of converting pollutants to less harmful and less hazardous compounds by using oxidizing agents other than oxygen/air or bacteria. Chemical oxidation is preferred when biological treatment is not a part of the effluent treatment plant and when small quantities of effluent are to be treated. Chemical oxidation process reduces COD, color, and toxicity of soluble and insoluble dyes effectively. Since most of the commercially available dyes are not affected by mild oxidation conditions, stronger oxidizing agents, such as ozone, chlorine, chlorites, Fenton's reagent, and UV/ozone combinations, may be used for the treatment. Hydrogen peroxide can be used in the oxidization of dyes in two different systems, homogeneous systems with the use of UV light and heterogeneous systems with or without the use of UV light [11]. A catalyst can also be used to speed up the reaction, usually Fenton's reagent, which activates the hydrogen peroxide by iron salts to form perhydroxyl radicals, which have almost double the time oxidation potential than  $\text{H}_2\text{O}_2$  has [3, 11, 12]. Table 4.4 shows the oxidation potentials of some of the important oxidizing agents.

**Table 4.4** Oxidation potential of oxidizing compounds

Compound	Oxidation potential (eV)
$\text{H}_2\text{O}_2$	1.80
HO	3.06
Ozone	2.07

#### 4.3.2.1 Ozonation process

Ozone can decompose some of the textile dye molecules and other organic pollutants by cleavage of the aromatic rings. The main advantage of the ozonation process is that the ozone can be treated in its gaseous form, which will not increase the volume of the effluent.

But destabilization of ozone might take place, in approximately 20 min., depending on various factors, including pH, temperature of the effluent, and the presence of salts [3, 11].

#### **4.3.2.2 Oxidation with sodium hypochlorite**

Sodium hypochlorite attacks the amino group of the dye molecule and causes the cleavage of the azo bond by chloride ions. It results in an increase in the concentration of chlorine, which helps in dye removal and neutralization, that is, the reduction of pH. However, this method is not suitable for effluents that contain disperse dyes [11].

#### **4.3.2.3 Photochemical oxidation**

Dye molecules are decomposed into lower-weight organic molecules, even to the extent of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , using  $\text{H}_2\text{O}_2$  during UV irradiation. The by-products produced in the process vary on the basis of the initial material, that is, the composition of the effluent and the extent of decolorization [3, 11]. The following are some of the important parameters that influence the treatment.

- Composition of the dyebath
- Structure of the dye in the effluent
- Intensity of the UV irradiation
- pH of the effluent

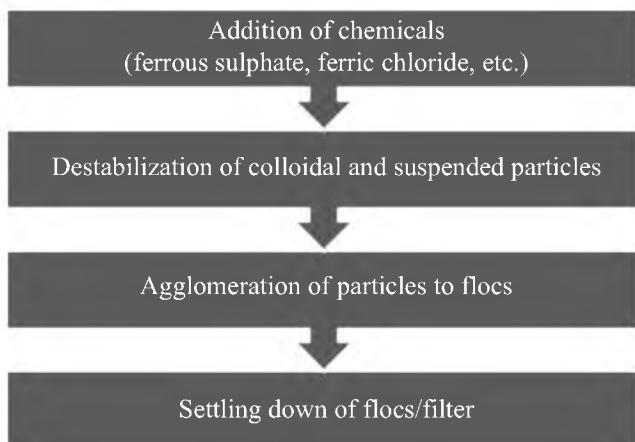
#### **4.3.2.4 Electrochemical oxidation**

It is one of the most powerful and advanced processes of effluent treatment, particularly for the acid, disperse, and metal complex classes of dyes. Hypochlorite ion or hypochlorous acid is the principal oxidizing agent involved in the electrochemical oxidation process, which is provided from chloride ions [11]. Here are some of the advantages of the electrochemical oxidation process:

- Unwanted by-products are eliminated.
- It involves easy operation and simple setup of equipment.
- It involves low-temperature treatment.
- Emissions are minimum.
- It is easy to scale up.

### 4.3.3 Coagulation: Flocculation and Precipitation

Some of dyes, such as reactive dyes, in the dissolved form, carry negative residual charges with them, where a positively charged polymeric substance can be used to form a precipitate of the colored particles, which can be agglomerated using suitable electrolytes or polyelectrolytes [11]. The following flowchart (Fig. 4.11) shows the sequence of principal operations involved in the coagulation–flocculation process:



**Figure 4.11** Flow diagram of the flocculation process.

### 4.3.4 Ion Exchange

The effluent is processed over the ion exchanger until the saturation of available sites for the exchange of ions. It is a reversible process, and all the exchangers can be reused. The only disadvantage of this process is the cost of organic solvents. These are expensive and not suitable for nonionic dyes, like disperse dyes [3, 11]. The main advantages of this process are:

- Removal of soluble dyes from the effluent
- Complete regeneration of the adsorbent
- Reclamation of the solvent after use

## 4.4 Types of Adsorbents

The effectiveness of textile effluent treatment has been always associated with the use of adsorbents in the process. Huge varieties of adsorbents have been studied by researchers for their efficiency in textile effluent treatment [13–29]. Activated carbon, clay minerals, silica gel, and agricultural and industrial wastes are some of the adsorbents used for the treatment of textile effluents. Activated carbon is the oldest and most traditional adsorbent used to treat wastewater. Coal has been the most common raw material used for the manufacture of activated carbon [14, 15]. The use of coal in the manufacturing of activated carbon leads to high costs, and so huge varieties of industrial wastes and agricultural wastes are used for the manufacturing of activated carbon as low-cost alternatives [16]. Some of the agricultural wastes used in the manufacturing of activated carbon are coconut shells [17], rice straw [18], rice husk [19, 20], nutshells [21, 22], coir pith [23], sawdust [24], bamboo wastes [25], and fruit and vegetable peels [26–29].

Among the low-cost alternatives, coconut shells are commercially used by most of the textile effluent treatment industries [17]. Activated carbon's efficiency is highly influenced by factors such as porosity, distribution of pore size, surface area, and bulk density. The selection of activated carbon depends on the pH of the effluents and the density and size of the particles to be separated. Organic pollutants, inorganic pollutants, and heavy metals are effectively removed with the use of activated carbon as an adsorbent [14–29].

The use of naturally available adsorbents has always found a place in effluent and wastewater treatment. Clay-based minerals are one such natural substance formed by chemical weathering of rocks and are basically negatively charged ionic adsorbents [30–32]. These are kaolinite and montmorillonite, mainly composed of layers of silica and alumina in a ratio of 1:1 and 2:1, respectively. Researchers have studied the adsorbent efficiency of kaolin, zeolite, and bentonite for the removal of color from textile effluents. Aluminum salts that cause various direct and indirect health hazards have been replaced by bentonite to treat effluents [31]. Combinations of two or more clay

minerals have also been studied for the treatment of textile effluents. Clay minerals in natural form or modified natural form, alone or in combinations with metal oxides to form nanocomposites, are used in the removal of organic compounds, inorganic compounds, and heavy metals [32].

Silica gels, with their high surface area, act as good adsorbents under moistened conditions, in original or modified forms. Due to high porosity and pore volume, their adsorbent efficiency has always been superior compared to many adsorbents [33]. Basically, silica gels are classified on the basis of the density of the gels [34].

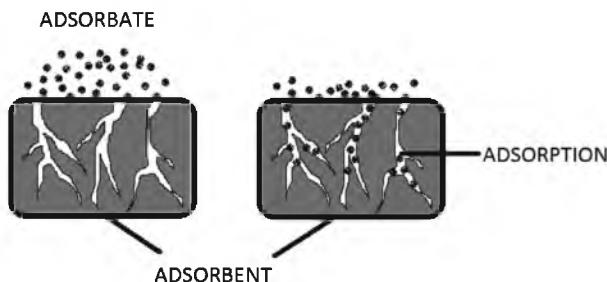
An abundance of agricultural wastes is found to give an economical solution to wastewater treatment. Wastes, being a cheap resource, can be effectively used as low-cost adsorbents. Wastes like sugarcane husks, peanut hulls, rice hulls, and wheat husks have been found to be effective in treating textile effluents [35]. These wastes are found to be effectively utilized in the form of activated carbon or when ground to dry powder directly to treat effluents. Agricultural wastes are washed and dried at around 80°C-100°C and ground into fine powders, with particle sizes ranging from 250 to 500 µm [21].

Industrial wastes in the form of organic or inorganic mixture or combinations of organic and inorganic mixtures are found to aid wastewater treatment. Among them, wastes from the fertilizer industry in the form of carbon slurry [36], wastes from steel plants in the form of slag, furnace dust, carbonaceous residues from petroleum refining industries, wastes generated from vehicle tires, and carbonized wool wastes have been used by researchers to treat wastewater in order to remove organic and inorganic pollutants. Sawdust and cotton wastes are converted into activated carbon and effectively used to treat effluents [37].

## 4.5 Mechanism of Adsorbents

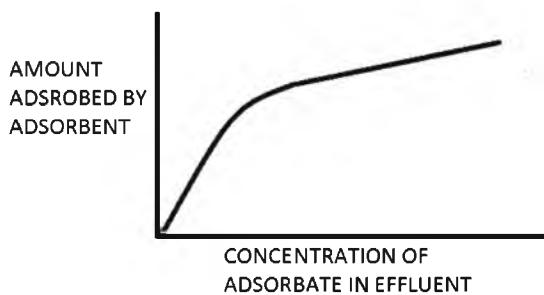
Adsorption, being a surface phenomenon, has given the best results in the treatment of textile effluents. Adsorption, being a physisorption and chemisorption process, aids in the removal of organic pollutants, inorganic pollutants, and heavy metals by its simple working

principle. The adsorption phenomenon is best explained through adsorption isotherms, and its efficiency is highly influenced by the adsorbent characteristics and the size of the adsorbates. The simple working principle of an adsorbent is shown in Fig. 4.12 [38].



**Figure 4.12** Mechanism of adsorption.

Most of the adsorbents used for wastewater treatment have been analyzed by researchers for kinetics and equilibrium properties [39, 40]. It can be seen (Fig. 4.13) that the absorbing medium consists of fixed sites to accommodate the adsorbates. After a certain level of adsorption, the amount of adsorbates adsorbed by the adsorbent falls gradually. This may be due to the saturation of pores within the adsorbent and thus a decrease in the sites, and at this stage, the adsorbent requires, possibly, reactivation.



**Figure 4.13** Langmuir adsorption isotherm [39].

Some of the reported research studies on adsorption isotherms of adsorbents like bamboo-activated carbon, coconut husk-activated carbon, fly ash, chitin adsorbent, hazelnut shell-activated carbon, and natural clay tend to follow the Langmuir model [39, 40].

## 4.6 Advantages and Limitations of Adsorbents

### 4.6.1 Advantages

The advantages of using adsorbents for wastewater treatments are:

- Simplicity of the working mechanism for the removal of organic and inorganic impurities
- Cost-effective solutions
- Availability of a wide range of adsorbents
- Possibility of desorption and reuse of adsorbents

### 4.6.2 Limitations of Adsorbents

Adsorbents have proved to be effective in the treatment of wastewater. Among all the adsorbents discussed, activated carbon is found to be the commercial adsorbent used in abundance by most of the industries [41]. The value of activated carbon in the global market was about USD 4.74 billion in 2015 and is expected to reach about USD 8.12 billion by 2021 [42].

Investigations on disposal or regeneration of adsorbents show that they have a great impact on environment and health [42]. Adsorbents adsorb the adsorbates, and thus adsorbates are present within the adsorbents undisturbed, and this makes the adsorbents themselves environmental hazards [43]. The adsorption capacity of an adsorbent decreases on usage and gets exhausted over a period of time. The exhausted adsorbents have to be either disposed of or regenerated for the possible reuse. Efficiency of the adsorption capacity reduces to some extent on reuse [44]. On disposing of adsorbents, they add to the pollution load, and on regeneration, the adsorbents are desorbed. Regeneration can be done thermally, using an inert gas, steam, and microwave, or can be done nonthermally by solvent extraction methods, ion exchange, ultrasound, and supercritical fluid extraction methods. In the case of disposal, degradation of adsorbents is achieved by chemical, electrochemical, and microbial methods. Nevertheless, the spent adsorbents contribute to the following problems [44]: (i) spent adsorbents pose a solid pollution hazard, (ii) regeneration of adsorbents leads to the release of toxic substances into the environment, (iii) pollutants

present in adsorbents may undergo exothermic reactions, leading to a fire hazard, and (iv) the presence of organic pollutants within the adsorbent may support unwanted microbial growth. Limitations of various regeneration processes are shown in Table 4.5.

**Table 4.5** Limitations of adsorbent regeneration methods

Process	Types of regeneration	Process principle	Limitations
Microbial		Microbes are used to degrade the pollutants present in the adsorbents.	It is applicable only for biodegradable pollutants.
			Biodegradation of pollutants often causes a foul smell.
			The process is slow.
Regeneration/ Desorption	Thermal	Thermal energy in the form of inert gas, steam, and microwave is used to desorb the adsorbents.	Optimum process conditions are to be strictly maintained for good results.
			It disturbs the pore structure, thus reducing the adsorption capacity.
			Reaction of thermal energy with pollutants may cause air pollution.
Chemical		Solvents and chemical reagents such as phosphoric acid are used for regeneration of adsorbents.	It is costlier due to high energy consumption.
			It alters the surface property of adsorbents.
			Insoluble adsorbates cannot be removed efficiently.

*Source:* [44]

## 4.7 Studies Conducted on the Treatment of Effluents Using Adsorbents

Researchers have studied various adsorbents [19, 34, 36, 38–40, 45–50] and their applications in effluent treatment. Some of the research highlights are stated below.

### 4.7.1 Activated Carbon

Simate et al. [45] studied coal-based adsorbents for the treatment of water and wastewater to facilitate the removal of heavy metals. Coal-based activated carbon was analyzed for its surface characteristics, such as porosity, surface area, and pore structure. Core fly ash, due to its surface negativity, aided in the efficient removal of Cr<sup>6+</sup> from effluents. Studies on zeolite derived from coal fly ash have also been found to be effective in the removal of ammonium ions and heavy metals from effluents.

Nagarethinam and Mariappan [39] made a comparative study between commercially available activated carbon and activated carbon prepared using coconut shell, bamboo waste, rice husk, groundnut shell, and straw carbon, with methylene blue as the adsorbate. Adsorption isotherms of all the adsorbents were found to be similar and fit into the Langmuir adsorption isotherm. Among the prepared activated carbons, the researchers found that straw carbon had the maximum adsorption capacity and bamboo dust carbon had the minimum adsorption capacity [39]. The adsorption capacities of the adsorbents were found to be in the order of straw carbon > rice husk carbon > coconut shell carbon > groundnut shell > bamboo dust carbon.

Balasubramani and Sivarajasekar researched the removal of organic pollutants using coconut shell-based activated carbon [38]. It was found that coconut-activated shells were effective in the removal of rhodamine B from textile effluents.

Sodeinde and Eboreime further add research inputs suggesting the removal of methylene blue and Congo red by using coconut shell-activated carbon [40]. In this study, the researchers used the activated carbon produced using coconut shells by treating the shells at 600°C in a muffle furnace. The carbonized shells were

further crushed into small particles 1 nm, 50 nm, and 500 nm in size [40]. The effluent was treated for about 120 to 180 min. at a pH of 6 in room temperature to achieve optimum results.

Studies on the adsorption of reactive dyes from textile effluent using coir pith-based activated carbon were reported by Santhy and Selvapathy [16]. Coir pith-activated carbon was prepared by treating coir pith with concentrated sulfuric acid, followed by drying it in an air oven at  $105 \pm 5^\circ\text{C}$  for 24 h, followed by washing it using 2% sodium bicarbonate. The coir pith was then carbonized at  $900^\circ\text{C}$  for 30 min. and used for the removal of reactive orange 12, reactive blue 4, and reactive red 2. Studies show that the removal of reactive dyes from effluents was effective at acidic pH, leading to a significant reduction in COD.

#### **4.7.2 Clay Minerals**

Syafalni et al. [46] carried out research using bentonite and combinations of bentonite with zeolite, alum, and limestone. Mixtures were studied at different ratios: 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, and 90:10. The research mainly concentrated on the adsorbent efficiency of bentonite, bentonite-zeolite adsorbent mixture, bentonite-alum adsorbent mixture, and bentonite-limestone adsorbent mixture. Studies reveal that bentonite at a concentration of 400 mg/L at pH 3.7 results in 90% COD removal. The bentonite-zeolite adsorbent mixture at a ratio of 60:40 yields good results, with 83.33% COD removal at pH 3.7. The bentonite-alum adsorbent mixture at a ratio of 50:50 resulted in COD removal of 93.09% at pH 8, while the bentonite-limestone adsorbent mixture (60:40) resulted in COD removal of 76.20% at a pH range of 2 to 6. Researchers conclude that the results obtained using combinations of clay minerals are much better compared to those using bentonite alone [46].

Experimental investigations by Nandi et al. reveal [47] the efficiency of kaolin, with an average particle size of  $2.37 \mu\text{m}$  and a specific surface area of  $13.69 \text{ m}^2/\text{g}$ , as an adsorbent for brilliant-green dye. The characterized kaolin was used to remove brilliant-green dye by optimizing the treatment conditions such as pH, kaolin concentration, dye concentration, and temperature. Concentrations

of kaolin ranging from 1 to 4 g/L; dye concentrations from 10 to 40 mg/L; temperatures of 26°C, 40°C, and 50°C; and pH ranging from 2.85 to 10.32 were used in the study. The dye treated using the above parameters proves that at pH 7, with an increase in contact time, the adsorption increases and then remains constant, thereby adhering to Langmuir isotherm [47].

#### 4.7.3 Silica Gel

Suman et al. studied [48] the use of silica gel wastes in treating cationic surfactants present in textile wastewater, and solid wastes generated from a silica gel factory were used for the study. The collected wastes were characterized and found to have particle sizes in the range of 150–300 µm, with a surface area 264.6 m<sup>2</sup>/g. The effluent was treated with 0–20 g/L of adsorbent, and it was observed that nearly 87% of cationic surfactants can be removed using the adsorbent at concentrations as low as 10 g/L. Regeneration studies with 18% hydrochloric acid for 2 h show a loss in adsorbent efficiency to the extent of 4%–5% in the case of the first regeneration cycle and of around 9%–12% for the second regeneration cycle.

Gaikwad and Misal studied the sorption of silica gels to remove methylene blue from effluents [34]. Concentration of the adsorbent, time, temperature, and pH were considered as the prime factors in their study. Temperatures ranging from 35°C to 65°C; pH of 1, 3, 6, 8, and 10; adsorbent concentrations ranging from 1 to 7 g/L; and time of 1–10 min. were used to assess the adsorption capacity of silica gel. Researchers reported the maximum removal of methylene blue using 195 mg/L silica gel at pH 8–10 and a temperature of 35°C.

#### 4.7.4 Agricultural Waste

Kumar et al. studied the adsorption efficiency of cashew nut shells in the removal of Congo red from effluents [21]. The adsorbents were prepared by thoroughly washing and drying the shells and subsequently powdering and sieving them for characterization. An adsorbent dose of about 5–30 g/L, with contact duration of 90 and 120 min., and temperatures ranging between 30°C and 60°C were the parameters used for the treatment. It was found that the removal of Congo red increased from 56.3% to 99.3% with an increase in

the adsorbent concentration from 5 to 30 g/L. Other parameters influencing Congo red adsorption reveal that with an increase in the contact time to 90 min., Congo red removal increases and then remains constant.

Gong et al. studied the use of peanut hulls to produce biomass powders for the removal of anionic dyes from effluents [49]. The adsorbent powder was used to treat effluents by optimizing the pH ranging from 2 to 11. The adsorption capacity of the peanut hulls ranged from 14 to 15 mg of dye per gram of adsorbent, and the adsorption fitted both Langmuir and Freundlich isotherms. Reports suggest that peanut hull could be an efficient adsorbent to remove anionic dyes from textile effluents.

#### 4.7.5 Industrial Waste

Gupta et al. studied the use of carbon slurry as a low-cost adsorbent, obtained from the fertilizer industry wastes [36]. The adsorbent efficiency for hexavalent chromium was studied using influencing parameters like pH, contact time, concentration of the adsorbate, concentration of the adsorbent, and temperature. Raw materials collected from the industry were powdered and oxidized using hydrogen peroxide for 24 h, followed by drying and activation in a muffle furnace at approximately 850°C, followed by further treatment with 0.1 M HCl and drying. The prepared material was found to have a wide range of particle sizes, between 100–250 mesh. The researchers found the maximum adsorption capacity of prepared activated carbon slurry to be 15.4 mg/g of chromium with a slurry dose of 4 g/L at pH 2 in 70 min.

Kadirvelu et al. studied the use of activated carbon prepared from industrial solid wastes to remove rhodamine B, a highly carcinogenic dye, using sago wastes [50]. Sago wastes collected from the sago industry were activated using 50%  $H_2SO_4$  and 0.5%  $(NH_4)_2S_2O_8$ , followed by drying at 100°C for 12 h. The material was thoroughly washed and treated with 5%  $NaHCO_3$  for about 12 h, followed by washing and drying. The particle size was found to be 125–250  $\mu m$ . The activated sago wastes were found to have an adsorption capacity of 15.9 mg/g of rhodamine B. The adsorption percentage was found to increase to 78% with an increase in pH from 2 to 10.

## 4.8 Conclusion

A wide range of options is available for the treatment of industrial effluents, starting from the preliminary process to final tertiary treatments. Different oxidizing, microbial, and physical methods are employed by the industry to treat the effluents at different stages and to meet the norms for reuse or discharge. However, the removal of pollutants using adsorbents offers a cost-effective solution with reusable options using different regeneration methods. In many cases, the removal of toxic substances can be achieved to the extent of 80%–85% using activated carbon. Safe methods for the disposal of saturated adsorbents with less impact on the environment would make the adsorbents a highly accepted practice as a cheaper and better alternative with faster deployment possibilities.

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## **Chapter 5**

# **Ligninolytic Enzyme Production by Microbes and Their Role in Textile Dye Decolorization**

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Wastewaters from the textile industry can be considered as the most polluting among all industrial sectors, and their treatment is greatly challenging. Increasing discharge and improper management of liquid and solid industrial wastes have created a great concern among industrialists and the scientific community in terms of their economic treatment and safe disposal. The presence of very low concentrations of dyes in effluents is highly visible and undesirable. Synthetic dyes are important organopollutants contaminating the water environment, often due to the fact that massive amounts are released from the textile dyeing process into effluents. The white-rot basidiomycete fungi and bacteria have been recorded for the

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maximum degradation of synthetic dyes. This property is due to the adsorption and production of extracellular lignin-modifying enzymes—manganese peroxidases (MnP), lignin peroxidases (LiP), and laccases (Lac)—that are able to degrade a wide range of xenobiotic compounds, including dyes. In this chapter, we will try to cover the role of ligninolytic enzyme systems of white rot fungi and potential bacteria under different culture conditions for higher dyes' decolorization.

## 5.1 Introduction

Dyes can be said to be colored, ionizing, and aromatic organic compounds that show an affinity for the substrate to which they are being applied. Dyes are applied to numerous substrates, such as textiles, leather, plastic, and paper, in liquid form. Dyes are basically aromatic compounds; structurally, they have an aryl ring that has a delocalized electron system. These structures are said to be responsible for the absorption of electromagnetic radiations of varying wavelengths. Rather than making the dyes colored, chromophores make the dyes proficient in their ability to absorb radiations of varied wavelengths. Chromophores act by making energy changes in the delocalized electron clouds of the dyes.

Discharge of colored industrial effluents into water bodies results in reduced dissolved oxygen concentration, thus creating anoxic conditions that are hazardous for inhabiting living biota. The toxicity of the effluent is due to the presence of the dye or its degraded products, which are mutagenic or carcinogenic in nature [27]. Therefore, the treatment of industrial effluents contaminated with dyes becomes essential prior to their final discharge into the environment.

## 5.2 Alternative Technologies for Dye Decolorization

The presence of dyes in wastewaters presents a significant problem in wastewater treatment, mainly because of their complex and varied

chemical structures, along with other residual chemical reagents and impurities. Such wastewaters have high organic content and low biochemical oxygen demand/chemical oxygen demand (BOD/COD) ratios, in addition to the recalcitrant nature of dyes. In addition, the degradative products may be even more toxic. Accordingly, no universal method is in vogue for their treatment. The degradation of synthetic dyes present in waste streams can be performed with various technologies, which can be subdivided into four main types of processes: (i) physical, (ii) chemical and photochemical, (iii) electrochemical, and (iv) biological. Biological processes using fungi and bacteria for dye decolorization have been reported by several workers [23, 49]. Regulatory agencies, especially in developed countries, are more concerned with their impact on environment and public health. Consequently, the imposition of the stringent environmental legislations is increasingly putting pressure on the textile and dyestuff industry. The legislations and color standards for waste discharge vary in different states. In addition, there are several standard methods for determining the color standards, which make a comparison of different color degradation methods from various sources more complex [19, 49].

### 5.2.1 Physical Methods

Physical techniques involve the use of strictly physical phenomena, without any gross chemical or biological changes to improve or treat the effluent. Adsorption has gained favorable interest due to efficient pollutant removal, quality product, and economical feasibility. It is influenced by many physicochemical factors, such as dye-sorbent interaction, adsorbent surface area, particle size, temperature, pH, and contact time. Materials like activated carbon, peat, wood chips, fly ash and coal, silica gel, and microbial biomass and other inexpensive materials (natural clay, corn cobs, rice hulls) are used since they do not require regeneration. Sedimentation is a solid–liquid separation method. In the case of dye solutions, combinations with coagulation/precipitation or with some other chemical methods are generally used for dye removal or dye degradation products. The rate of

sedimentation of particles suspended in a fluid can be described by Stoke's law and is influenced by many physicochemical factors. The disadvantage of this process is high sludge production. On the other hand, flotation is a foam separation technique and generally performed by adding a surface-active ion of the opposite charge to the ion to be separated from the solution. The solid product, which appears on the gas–liquid surface, is levitated to the surface of the solution by inserting a gentle stream of fine gas bubbles. Coagulation can be induced by an electrolytic reaction at the electrode surface, by changing pH, or by adding coagulants [47]. Furthermore, membrane filtration can be used to remove dye molecules. The classification of membranes is done on the basis of their pore size, aimed to retain solutes of different molecular weights. The membrane parameter is called molecular weight cutoff (MWCO). In the case of dye separation, reverse osmosis ( $\text{MWCO} < 1000$ ), nanofiltration ( $500 < \text{MWCO} < 15,000$ ), and ultrafiltration ( $1000 < \text{MWCO} < 100,000$ ) membranes are used according to the characteristics of dyes. In addition to the dye solution filtration, membranes are used for the separation of particles after adsorption or coagulation/precipitation instead of sedimentation [19]. However, in the case of dye degradation, the radiation treatment of aqueous media leads to the formation of strong oxidizing species, such as OH radicals, which react with dye molecules, degrade them, and, consequently, enhance the degradation process. Therefore, radiation methods are included in the advanced oxidation processes (AOPs) for wastewater treatment [40]. During ultrasonic irradiation, the propagation of an ultrasound wave leads to the formation of cavitation bubbles, consequently leading to chemical degradation of the dye. In general, solid waste disposal is required after the physical methods of separation.

### **5.2.2 Chemical and Electrochemical Methods**

Chemical oxidation is the most commonly used method of decolorization, mainly due to its simplicity of application. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is the commonly used oxidizing agent; however, it needs to be activated before use. The way in which  $\text{H}_2\text{O}_2$  is activated decides the method of oxidation. It removes the dye from the effluent

by way of aromatic ring cleavage of the dye molecules. A well-known activator of  $\text{H}_2\text{O}_2$  is Fe (II) salt, known as Fenton's reagent. The result of sorption or bonding of dissolved dyes is sludge generation, which again needs disposal; this is therefore disadvantageous. Ozonization can also be used for the activation of  $\text{H}_2\text{O}_2$ . However, a major drawback of it is the short half-life of ozone in water and its cost, as it degrades in about 20 minutes and has to be applied continuously. Moreover, its stability is affected by the presence of dyes, salts, and pH and temperature of the effluents. Ultraviolet (UV) radiation can also be used for the activation of hydrogen peroxide. The major advantage of  $\text{H}_2\text{O}_2/\text{UV}$  treatment is the requirement of no other chemicals. The wet air oxidation (WAO) process presents a hydrothermal treatment of dissolved and suspended components in water, and it has been successfully used for several azo dyes [42]. Chlorination, using chlorine gas or sodium hypochloride, is an inexpensive and effective method. However, its use has become less frequent due to the generation of toxic and carcinogenic compounds. Moreover, the use of chemicals containing chlorine is restricted due to environmental reasons. As already mentioned, photochemical methods are based on the use of UV light, which activates the chemicals and, consequently, enhances the chemical reaction and makes the process more efficient. The principle of electrochemical methods is to charge the electric current through electrodes made of different materials (e.g., iron or aluminum), resulting in oxidation at the anode and reduction at the cathode with  $\text{H}_2$  production. The resulting processes are known as electrocoagulation, electroflootation, electro-oxidation, and electroreduction. The majority of the above-mentioned methods are AOPs and are essentially based on the generation of highly reactive radical species [19, 23].

### 5.2.3 Biological Methods

The process in which biological systems are used to remove pollutants is known as bioremediation [52]. A biological treatment presents a process of degradation of organic substances by a mixed microbial system or monoculture of microorganisms in aerobic or anaerobic conditions, and such treatments have been widely used

and researched [43]. The dyes are generally resistant to oxidative biodegradation. In addition, toxicity and acclimating ability are the drawbacks of using microbial cultures. It has been demonstrated that mixed bacterial cultures are capable of decolorizing textile dye solutions. Nevertheless, several studies have showed that little biodegradation actually occurs, while the primary mechanism is adsorption to the microbial biomass [27]. It has also been reported that a few species of algae are capable of degrading azo dyes and utilize them as a sole source of carbon. Some articles on dye decolorization with yeasts are also there in the literature [23]. Several fungal systems have been found to degrade various classes of dyes. More emphasis has been given to the white rot fungi and azo dyes, the largest class of commercial dyes. Fungal treatment of dyes is an economical and feasible alternative to the present treatment technologies based on biological methods [27, 49].

### **5.2.3.1 White rot fungi and role of their ligninolytic enzymes in dye decolorization**

Several studies have demonstrated that white rot fungi are capable of degrading a wide variety of structurally different dyes, such as azo, anthraquinone, heterocyclic, triphenylmethane, and polymeric dyes [2]. The dyes are degraded with the involvement of lignin-degrading enzymes, especially lignin peroxidase (LiP), manganese peroxidase (MnP), and laccase [54, 60, 53]. The ligninolytic system of *Pleurotus* species has been studied, and it appears to be an effective alternative for the bioremediation of recalcitrant pollutants. For the detoxification of textile effluents and their color removal, ligninolytic enzymes of fungi have played a significant role [64, 66]. Considering bioremediation as an environment-friendly and cost-competitive solution for dye wastewater treatment, researchers have focused upon microorganisms that are capable of degrading broad structure-based dyes. Ligninolytic fungi seem to be the most promising organisms, characterized by their degradative capabilities toward a broad spectrum of structurally different dyes and their highly oxidative and nonspecific enzyme systems [67]. A great deal of work has been carried out on assessing dye decolorization capabilities of ligninolytic fungi. However, it has remained restricted to a few species.

**Table 5.1.** Potential fungi and their role in decolorization of textile dyes

S. No.	Organisms	Enzyme activities	Types of dyes	Aerobic/ anaerobic	Refs.
1.	<i>Schizophyllum commune</i>	Laccase, MnP, LiP	Textile effluents, acid orange 7, acid red 18, and reactive black	Anaerobic	[41, 54]
2.	<i>Ceriporiopsis subvermispora</i>	Laccase, MnP	Reactive orange 16, Remazol brilliant blue R, copper (II) phthalocyanine	Anaerobic	[6]
3.	<i>Ischnoderra resinosum</i>	MnP, laccase	Reactive black 5, reactive blue 19, reactive red 22, reactive yellow 15	Anaerobic	[13, 28]
4.	<i>Phanerochaete chrysosporium</i> and <i>Coriolus versicolor</i>	Laccase	Direct red-80, malachite green, azure B, poly R-478, anthraquinone blue, Congo red, and xylylidine	Anaerobic	[12, 30, 45]
5.	<i>Lentinus edodes</i>	Crude enzymes	Different synthetic dyes	Anaerobic	[51]
6.	<i>Trametes versicolor</i>	Laccase, MnP	Different pollutants	Anaerobic	[57]
7.	<i>Funalia trogii</i>	Crude enzymes	Drimarene blue X3LR, Remazol brilliant blue R	Anaerobic	[37]
8.	<i>Irpex lacteus</i>	Laccase	Reactive orange 16 and Remazol brilliant blue R	Anaerobic	[59]
9.	<i>Trametes hirsuta</i>	Laccase	Acid red 97, acid green 26	Anaerobic	[11]
10.	<i>Pezizomyces</i> sp.	Laccase, MnP, LiP	Methyl violet 2B, rhodamine B	Anaerobic	[56]
11.	<i>Pleurotus sajor-caju</i>	Laccase, MnP, LiP	Methyl violet 2B	Anaerobic	[50, 55]
12.	<i>Ganoderma lucidum</i>	Laccase	Textile dyes industry wastewater	Anaerobic	[44]
13.	<i>Pleurotus sajor-caju</i> and <i>Pleurotus flabellatus</i>	Laccase, MnP, LiP	Azure B, methyl violet 2B, Chicago sky blue, orange II sodium salt, rhodamine B	Anaerobic	[53]

The most studied organism is the white rot fungus *Phanerochaete chrysosporium*, but other species, belonging to the genera *Pleurotus*, *Bjerkandera*, *Trametes*, *Polyporus*, and *Irpex*, have also been investigated [67]. Ligninolytic fungi, especially *Coriolus versicolor*, *Cerrena unicolor*, *Daedalea quercina*, *Funalia trogii*, *Irpex lacteus*, *Pleurotus pulmonarius*, *Schizophyllum commune*, and *Pleurotus ostreatus*, have been reported for laccase production and their role in decolorization of structurally different dyes [5, 32, 59]. Similarly, *Lentinula edodes*, *P chrysosporium*, *Pleurotus ostreatus*, *Schizophyllum commune*, *Trametes trogii*, *Trametes versicolor*, etc., have shown manganese peroxidase production and decolorization potential of structurally different dyes [5, 7, 37, 62]. Work carried out with other fungi has proved the synthetic dye decolorization capability of *P chrysosporium*. It has also been stressed upon that the decolorization potential of different fungi varies against chemically different dyes; hence the screening of fungi for ligninolytic enzyme activity and dye decolorization must be conducted under similar conditions [60, 56]. In one study conducted with *Lentinula edodes*, it has been noted that the fungal mycelial growth became visible after 24 hours of inoculation and the medium became completely decolorized within 6 days [6]. For decolorization of structurally different dyes using white rot fungi, temperature played an important role, and 30°C to 37°C has been recorded for the highest decolorization [6], while 25°C to 35°C was noted specifically for decolorization of methyl violet 2B by *Schizophyllum commune* [56].

### 5.2.3.2 Role of bacteria in dye decolorization

Efforts to isolate bacterial isolates capable of degrading azo dyes started in the 1970s with reports of *Bacillus subtilis*, then *Aeromonas hydrophila* [9, 36] and *Bacillus firmus*, followed by *Bacillus cereus* [35]. Thereafter, numerous bacteria capable of dye decolorization, in isolation or in consortia form, have been reported [39, 64]. In several earlier studies the role of various bacteria for azo dye decolorization, that is, *Pseudomonas fluorescens* for rhodamine B [3], *Bacillus fusiformis* for disperse blue 79 acid orange [29], *Pseudomonas aeruginosa* for Navitan fast blue [33], and *Bacillus* sp. for disperse dye, has been reported.

**Table 5.2** Bacteria and their potential role in decolorization of textile dyes

S. No.	Organisms	Enzyme activities	Types of dyes	Aerobic/ anaerobic	Refs.
1.	<i>Clostridium bifermentans</i>	Crude enzymes	Reactive red 3BA, reactive black 5, reactive yellow 3G-P	Anaerobic	[22]
2.	<i>Bacillus cereus</i>	Crude enzymes	Orange II	Anaerobic	[68]
3.	<i>Citrobacter</i> sp.	Crude enzyme	Reactive red 180	Anaerobic	[66]
4.	<i>Pseudomonas aeruginosa</i>	Crude enzyme	Navitan fast blue S5R	Anaerobic	[33]
5.	<i>Bacillus fusiformis</i>	Crude enzyme	Disperse blue 79, acid orange 10	Anaerobic	[29]
6.	<i>Pseudomonas desmolyticum</i>	LIP, laccase	Direct blue-6	Anaerobic	[24]
7.	<i>Bacillus firmus</i>	Crude enzyme	Acid red 249, acid red 151, acid red 299, direct red 80, direct red 89, reactive red 141	Anaerobic	[35]
8.	<i>Cerrena unicolor</i>	Laccase	Acid blue 62, acid blue 40, reactive blue 81, direct black 22, acid red 27	Anaerobic-aerobic	[32]
9.	<i>Paenibacillus</i>	Crude enzyme	Remazol brilliant orange 3R, Remazol black B, RB violet 5R	Anaerobic-aerobic	[58]
10.	<i>Escherichia coli</i> JM109	Crude enzyme	Direct blue 71	Anaerobic	[21]
11.	<i>Acinetobacter calcoaceticus</i>	Crude enzyme	Direct brown MR	Anaerobic	[16]
12.	<i>Alcaligenes faecalis</i> PMS-1	Veratryl alcohol oxidase, tyrosinase and NADH-DCIP reductase enzymes	Reactive orange 13	Anaerobic	[46]
13.	<i>Pseudomonas fluorescens</i>	Crude enzymes	Orange II sodium salt, Chicago sky blue, azure B	Anaerobic	[3]
14.	<i>Pseudomonas luteola</i>	Crude enzymes	Reactive red 22	Aerobic-anaerobic	[8]

### **5.2.3.3 Immobilization of fungi**

Immobilized forms of living microorganisms have been described to be more useful in biological wastewater treatment. It is widely known that immobilized cells offer many advantages, such as reusability of the biocatalyst, control of reactions, and noncontamination of products [15]. The immobilization of fungi on suitable solid supports has been studied by several workers, and they have reported that it helps them to grow well, ensuring higher enzyme production, dye decolorization, and pollutant degradation. Subsequently, Tavcart et al. [61] have also reported many more advantages of using immobilized forms of fungi in dye decolorization, like it helps in their long-time use, handling large volumes, and the possibility of refreshing cultures between different cycles and allowing persistence in competition with faster-growing species. The higher suitability of certain immobilizing media over others is attributed to their ability to support the growth of fungi and their ability to do so continuously.

### **5.2.4 Mechanism of Fungal Dye Degradation and Decolorization**

The mechanisms of fungal dye decolorization and degradation are listed in Fig. 5.1. The accumulation of chemicals with the microbial biomass is termed as “biosorption,” and it can take place on living or dead biomass. Waste and/or dead microbial biomass can be used as an efficient adsorbent, especially if it contains a natural polysaccharide chitin and its derivative chitosan in the cell walls. Chitosan, a cell wall component of many industrially useful fungi, has a unique molecular structure with a high affinity for many classes of dyes [23]. It is known that most of the white rot fungi produce at least two of the three highly nonspecific enzymes (LiP, MnP, and laccase), which enable the generation of free radicals [27, 38] (Fig. 5.1). The structure of a dye strongly influences its degradability by pure cultures and isolated enzymes. Plenty of data about biodegradation of various synthetic dyes with selected white rot fungi have been published. Nevertheless, limited data are available on systematic studies carried out on the relation between the structure and biodegradability of a dye, especially for commercial dyes with a complex structure. To understand the decolorization and degradation mechanism of azo dyes, detailed information is needed about the initial enzymatic

breakdown of azo linkages. Enzymatic processes are very promising for the decolorization of synthetic azo dyes. Previously, the pathways of azoreductase-, laccase-, peroxidase-, and polyphenol oxidase-mediated degradation of recalcitrant synthetic azo dyes have been taken into account. Azoreductases are a major group of enzymes expressed in azo dye-degrading bacteria for decolorization and degradation of these dyes. Azoreductases catalyze the reaction only in the presence of reducing agents like NADH, NADPH, and FADH<sub>2</sub>.

Fungal action rarely leads to the mineralization of dyes, and it depends on the chemical structure of the dye [31]. Higher mineralization occurs in dyes with substituted aromatic rings in their structures compared to those with unsubstituted rings. Better mineralization is observed also under nitrogen-limiting conditions. Some reports on the utilization of dyes as a carbon source have been published in the last decade. When a consortium of microorganisms is generally used for decolorization of textile dyes, certain bonds in the dye molecule are cleaved and utilized as a carbon source, while the chromophore remains affected [27, 49].

## 5.3 Factors Affecting Decolorization and Degradation of Dyes

The prevailing cultural conditions not only determine the level of growth of the target microorganisms used for dye decolorization but also determine the production and activities of the extracellular ligninolytic enzymes in the dye decolorization process. The fungal growth and enzyme production, dye decolorization, and degradation are influenced by numerous factors, such as media composition, pH value, agitation, aeration, temperature, and the initial dye concentration. Their effects are briefly presented and discussed below.

### 5.3.1 Media Composition

There is no doubt that the composition of the media has an enormous effect on fungal and bacterial growth and production of enzymes leading to decolorization of dyes. It must be noted that the composition of industrial effluents varies with location and time, not

to mention that they offer very complex composition with a lack of nutrients, unlike the well-defined media used in the research under submerged conditions. Therefore, the focus has to be on the supply of carbon and nitrogen sources, together with mineral nutrients and other additives [19, 27, 49]. The effect of the growing medium on the growth and activity of microorganisms is well known, and fungi are not an exception [57].

### 5.3.2 Effect of Carbon Sources on Dye Decolorization

A carbon source is necessary for fungal and bacterial growth and to provide oxidants the microbes require for decolorization. Glucose has been used in the majority of research studies. Alternatively, fructose, sucrose, maltose, xylose, glycerol, starch, and xylan have also been tried and found useful. All the carbon sources added at 1% level were found to stimulate microbial growth, especially fungus, and enhanced dye decolorization was noted in all replications. Addition of glucose and fructose enhanced the rate of dye decolorization as compared to control [54]. Effluents from dyeing or chemical/dye production usually do not contain usable carbon substrates, while those from distilling or paper pulping may have a range of carbohydrates, useful for certain white rot fungi. The need to add a carbon source depends on the organism used and the type of dye to be treated.

Addition of glucose to the dye decolorization medium provides an easily metabolizable energy source to the potential microorganisms and creates an environment to enhance the decolorization rate of dyes. The carbon sources are the primary source of energy for the growth of different microorganisms. However, their requirement varies from microbe to microbe and their growth conditions. The earlier studies have also proved that adding of an additional amount of glucose at 0.2%–2.0% enhances dye decolorization [4, 22]. Different studies have also shown higher decolorization in the presence of varied carbon sources, out of which glucose has been found to be effective at a lower concentration (0.50%) than other carbon sources (1.0%) [54]. This enhancement in dye decolorization or effluent decolorization is attributed to easy utilization of glucose by growing microorganisms, leading to shortening of their lag phase of growth.

### 5.3.3 Other Media Components

The role of growth factors in the degradation of textile dyes has been studied by many researchers. However, considering their cost, it is not economical to use them in the decolorization technologies. All microbes have specific requirements for minerals. For example, white rot fungi need ions of iron, copper, and manganese. They can be a part of the effluent and if not, then they must be added to the media. A variety of other compounds, like veratryl alcohol, tryptophan, and aromatics (phenol and aniline), can act as low-molecular-mass redox mediators of ligninolytic activities and therefore promote decolorization [27, 49]. It is interesting that some components available in wood and straw induce enzyme production in white rot fungi. For example, the enzyme activity ratio of laccase/MnP can be regulated using beechwood as the immobilization support and inducer, together with a combination of various concentrations of additional nitrogen and carbon sources in the liquid media, during the cultivation of *Ceriporiopsis subvermispora* [6]. Ligninolytic enzyme production in *Dichomitus squalens* can be substantially induced by adding beechwood and straw particles to the liquid growing media.

The roles of composition of cultural media and presence of dyes in media have also been studied earlier in *Pleurotus* species [14], and both of these have been reported to influence the decolorization process. The activities of laccase and manganese peroxidase were recorded higher in malt extract broth compared to Kirk medium. Literature supports our conviction that the composition of the media substantially influences the decolorization process in fungi; this opinion has also been shared by other authors [60].

### 5.3.4 Effect of pH on Dye Decolorization

The majority of the research studies on growth and enzyme production by fungi have been performed on batch cultures and usually without any control of pH during fungal cultivation. The role of buffering capacity of the medium is also required to be investigated for studying the influence of the initial pH. The majority of filamentous fungi, along with white rot fungi, grow optimally at acidic pH values. The change in pH during fungal growth depends upon the type of medium used for growth. The

growth on carbohydrate-rich media generally causes acidification of the media, which further depends on the available carbon source and the buffering capacity of the medium. Decolorization can be performed with a whole fermentation broth (mycelia and enzymes) or with isolated enzymes. Distinction has to be made between the optimum pH values for growth, enzyme production by the fungi, and action of isolated enzymes for dye degradation. Therefore, optimum pH depends on the growth medium, microbes and their enzyme systems, and the decolorization of dye under consideration. The majority of the researchers have suggested optimum pH in the range of 4 to 4.5 [27]. The pH of the medium plays an important role in decolorization of dyes using white rot fungi. White rot fungi have been reported to show highest growth and dye decolorization in the acidic pH range [5, 26].

Several researchers have studied the pH and temperature optima of the microorganisms of their interest and have reported a wide range of pH [22, 34, 38] and temperature (20°C to 40°C) for optimum decolorization by those microorganisms [22]. In literature, wide variation in pH requirement for decolorization of different dyes through different microorganisms has been cited and it varies from 10 in the case of *Clostridium bifermentans* SL186 for reactive dyes [22] to 7 in the case of *Citrobacter* sp. CK3 for reactive red [65] and 5 in the case of *Aspergillus niger* SA1 for acid red 151 [4].

### **5.3.5 Effect of Temperature on Dye Decolorization**

The role of temperature has to be considered from diverse angles: its influence on growth and enzyme production, the rate of enzymatic decolorization, and the temperature of the waste stream [48]. Most of the white rot fungi are mesophiles, with an optimal cultivation temperature of 27°C to 30°C. White rot fungi exhibit better growth under medium-temperature conditions compared to higher temperatures [62]. Temperatures in the range of 30°C to 37°C have also previously been reported previously [5, 7] for decolorization of chemically diverse dyestuffs using white rot fungi. The optimal temperatures for enzyme reactions are usually higher. However, enzyme instability and degradation has to be taken into account at such temperatures because various textile and dye effluents are produced at a temperature range of 50°C to 60°C. Thus the optimal temperature for decolorization for a particular process has

to be selected on a case-to-case basis according to the mentioned parameters [27, 49]

Again, for temperature, a specific temperature has been indicated for the decolorization of a specific dye through a specific microorganism [4, 65]. However, unlike the present study, the optimum decolorization of reactive red through *Citrobacter* sp. CK3 has been cited to be at 32°C, while that of acid red 151 through *Aspergillus niger* SA1 has been said to be at mesophilic temperature (25°C-45°C) and that of Remazol brilliant blue R through *Streptomyces psammoticus* is reported to be at 32°C [4].

### 5.3.6 Effect of Agitated and Stationary Conditions on Dye Decolorization

Ligninolytic fungi are obligate aerobes and thus need oxygen for their growth and vigor. In addition, the lignin degradation system requires oxygen, either for the mycelial generation of H<sub>2</sub>O<sub>2</sub> for peroxidases or for the direct action of oxidases. Oxygen can also act directly on lignin fragments, and oxygen demand depends on the fungus and its ligninolytic system. Oxygen supply to the culture media during fungal cultivation has remained an interesting research topic for decades and has been covered in numerous articles [8]. To satisfy the microbial oxygen requirements of fungi during their cultivation and to enhance the oxygen gas-liquid mass transfer, aeration and agitation are necessary. The availability of oxygen might affect the morphology of filamentous fungi and lead to a decreased rate of enzyme synthesis. As a result various bioreactor types, generally divided into static and agitated configurations, were invented. The choice of reactor depends on a particular system, although appropriate agitation gives as good a result as or even better results than those from static conditions. Studies specifically on the effect of agitation and aeration on the decolorization process are scanty [27].

However, in similar findings, Wesenberg et al. [67] reported higher decolorization efficiency under stationary (71.3%) conditions than with agitated cultures (57.2%), and the best decolorization efficiency (78%) was when the two conditions were combined. Singh et al. [55] attributed the higher decolorization in the presence of the pellet form of mushroom mycelia to the uniform suspension of these spherical pellets in the growing medium.

### **5.3.7 Effect of Initial Dye Concentration on Dye Decolorization**

It is important to optimize the initial dye concentration for complete color removal. Dyes are usually toxic to microorganisms, and the presence of even low concentrations of dyes in an effluent is highly visible and undesirable, reducing light penetration and potentially inhibiting photosynthesis [31], while the toxicity depends on the type of dye. Higher concentrations of dyes are always toxic. The range of initial dye concentrations studied in the literature has varied from 50 to 1000 mg/L, which depends on the microorganism investigated and the type of dye used [49, 68]. However, in a good number of cases where fungi have been used as decolorizing agents, higher decolorization has been recorded at a lower initial dye concentration [4, 65] and like the present study, this was more evident in studies with *Pleurotus florida* and *Pleurotus ostreatus* [34]. The lesser decolorization at a higher initial dye concentration in the case of *Schizophyllum commune* has been explained in the light of growth inhibitory activity of azo dyes [41].

### **5.3.8 Effect of Cofactors**

Earlier studies have also highlighted the role of veratryl alcohol and Mn<sup>2+</sup> in dye decolorization of different dyes and have reported that the addition of 0.4 mM veratryl alcohol to the medium considerably increased the decolorization rate. It has also been reported that the addition of veratryl alcohol to fungal cultures leads to higher lignin peroxidase activities and dye decolorization but has no significant effect on manganese peroxidase production [52]. Further, Couto et al. [12] have reported that veratryl alcohol stimulates and is necessary for lignin peroxidase secretion by white rot fungi. In another study, the optimal concentration of Mn<sup>2+</sup> and dosage of H<sub>2</sub>O<sub>2</sub> (the cofactors involved in the catalytic cycle of the manganese peroxidase enzyme and responsible for maximizing the efficiency of the degrading and/or decolorizing processes *in vitro*) have been reported to depend on the nature and concentration of the dyes to be used [10].

## 5.4 Kinetics of Dye Decolorization

The kinetic model offers a powerful tool to describe biological degradation processes and to elucidate the quantitative degradation behaviors. Furthermore, it provides useful information for the optimization of biodegradation processes. It is recognized that the order of kinetics for dye decolorization is determined by the rate-limiting step [63]. First-order kinetics, or the same-grade reaction, such as the Michaeli-Menten rate model, have been widely used for modeling the decolorization of azo dyes by mixed cultures, where the transfer of reducing equivalents presents a rate-limiting step. On the other hand zero-rate kinetics are frequently used for modeling pure cultures, where the production of reducing equivalents appears to be the rate-determining step [63]. Despite the substantial development in the simulation of the dye decolorization process, some important influencing factors have been underestimated. For example, azo dyes are adsorbed considerably by the anaerobic sludge. However, the kinetics of the dyes' degradation during decolorization is still not clear. This could lead to inaccurate modeling of the real decolorization process [17].

Information about the kinetics of decolorization and the environmental factors affecting the decolorization rates is relatively scarce. Monoazo dye decolorization has been reported by several workers [63] to follow first-order kinetics with respect to dye concentration, whereas a few others have reported zero-order [20] or even half-order kinetics. Furthermore, for diazo and polyazo dyes, only the first part of the decolorization profiles has been reported to follow first-order kinetics with respect to the dye concentration. The various experimental conditions used in the reported studies may have been responsible for these apparently contradictory kinetic results since the rate-limiting step of azo dye reduction is highly dependent on these conditions. For example, in pure cultures, the zero-order process of production of reducing equivalents is likely to be the rate-limiting step, whereas in aggregate sludge under anaerobic conditions, the transfer of reducing equivalents, rather than their production, is the probable rate-limiting step [63].

Studies of the degradation of environmental pollutants, especially a petroleum-contaminated site, with bacteria [1] have reported first-order kinetics for the degradation process. The use

of first-order kinetics has been reported to have many advantages, like ease of presenting and analyzing the data, simplicity of plotting the logarithm of the dye remaining versus the decolorization time as a straight line, and the ease of predicting concentrations [18]. While working with Reishi mushroom (*Ganoderma lucidum*) for decolorization of textile dye wastewater, Selvakumar et al. [44] have also reported first-order kinetics.

## 5.5 Extracellular Ligninolytic Enzymes

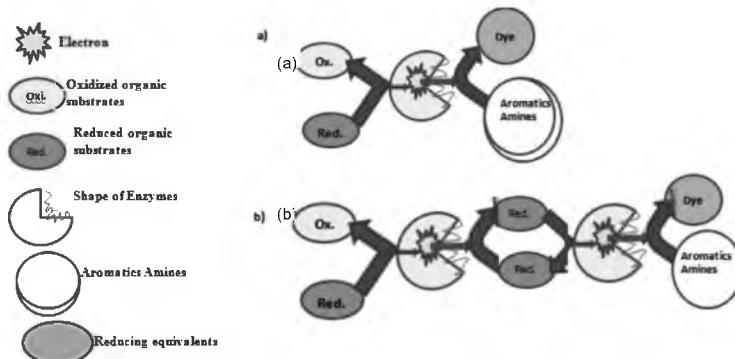
Extracellular ligninolytic enzymes (laccase, lignin peroxidase, and manganese peroxidase) play a crucial role in the complete biodegradation of the lignin present in the mushroom substrate, the mechanism of which is quite similar to that of dye degradation. Bacteria and fungi play an important role in dye decolorization with the involvement of their extracellular ligninolytic enzymes. Fungal ligninolytic enzymes are commercially in use in the textile industry and have potential for more industrial applications. One of the possible alternatives for the treatment of colored effluents, the use of white rot fungi is considered cost effective, efficient, and environment friendly. The decolorization by white rot fungi is mediated by their extracellular ligninolytic enzymes, such as LiP, MnP, and laccase, which can oxidize a wide spectrum of organic pollutants, including synthetic dyes [28, 38]. The activity of laccase and LiP was higher in fungi, while that of MnP was higher in bacteria. The role of ligninolytic enzymes produced by fungi and bacteria in dye decolorization is well documented in literature.

## 5.6 Anaerobic and Aerobic Degradation of Dyes

### 5.6.1 Anaerobic Degradation of Azo Dyes

Anaerobic conditions degrade azo dyes by reducing their highly electrophilic azo bonds with the help of nonspecific enzymes, which leads to reductive cleavage of azo linkage, leading to the generation of aromatic amines, which are usually colorless [25]. Therefore, the reduction is denoted as dye decolorization. Anaerobic degradation of azo dyes exhibits different mechanisms, which are categorized

into direct and indirect mechanisms. Direct enzymatic reduction of azo dyes and indirect reduction of azo dyes are catalyzed by enzymatically generated/regenerated redox-mediating compounds (Fig. 5.1). Anaerobic reduction is usually nonspecific, as various groups of azo dyes are decolorized by an assorted group of bacteria. Under static conditions, depletion of oxygen is effortlessly achieved, permitting obligate and facultative anaerobic bacteria azo dye reduction. Thus, anaerobic decolorization of azo dyes is a casual process, where the dye molecule probably serves as an electron acceptor for the electrons facilitated through the carriers of the electron transport chain. Contrastingly, dye decolorization may be accredited to nonspecific reactions occurring extracellularly among reduced compounds formed by anaerobic bacteria (Table 5.2).



**Figure 5.1** Proposed mechanism of (a) direct enzymatic reduction of azo dye and (b) indirect, biologically mediated azo dye reduction.

A characteristic of the textile processing industry is that a wide range of structurally diverse dyes is used within short periods in one and the same factory, and therefore, effluents from the textile industry are extremely variable in composition. The mixed bacterial consortia decolorize structurally different azo dyes, suggesting that anaerobic decolorization is not a specific process. It is clear that the majority of the color removal occurs in the anaerobic stage. On the other hand, the anaerobic phase of decolorization operations give low COD removal and most of the COD is removed in the subsequent aerobic phase, including the decolorized metabolites formed from anaerobic phases.

### 5.6.2 Aerobic Oxidation of Dyes

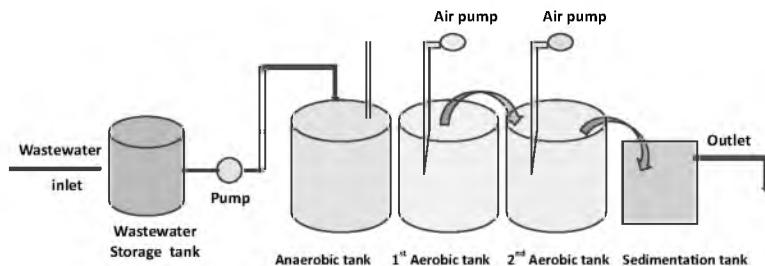
Most of the azo dyes are nondegradable under aerobic conditions. However, under anaerobic conditions, the bacteria can reduce azo linkages in the dye molecule to form colorless aromatic amines. Several bacteria, such as *Pseudomonas luteola* [8], *Pseudomonas aeruginosa* NBAR12, *Acetobacter liquefaciens* S-1, and *Pseudomonas desmolyticum* NCIM 2112 [24], have been reported to have azo dye degradation abilities. It is known that azoreductase-driven bacterial decolorization of azo dyes is normally inhibited by the presence of oxygen, primarily due to the competition in the oxidation of reduced electron carriers (e.g., NADH) with either oxygen or azo groups as the electron receptor [1]. Consequently, in the bioreactor design, the aeration and agitation that provide oxygen for cell growth and stimulate the contact of the cells with medium substrates should be properly regulated to attain optimal efficiency of decolorization. Even though azo dyes are usually resistant to bacterial degradation in aerobic conditions, a few selected aerobic bacterial strains with specialized azo dye-degrading enzymes were noticed to degrade azo dyes under absolutely aerobic conditions. Additionally, it is presumed that the initial step in the biodegradation of azo dyes is their reduction to the corresponding aromatic amines, a reaction catalyzed by the enzyme azoreductase. The aromatic amines generated are then further mineralized aerobically. Sulfonated aromatic amines, except simple sulfonated amino benzene and amino naphthalene compounds, are specifically challenging to degrade because of the hydrophilic nature of their sulfonate group, which hampers membrane transport. Yet another additional transformation that the aromatic amines, substituted with an *ortho*-hydroxy group, may undergo upon contact with oxygen is autoxidation. Several aromatic amines, like substituted anilines, amino benzidines, and naphthyl amines, initially get oxidized to oligomers and in due course to dark-colored polymers with reduced solubility and, therefore, are effortlessly removed from the aqueous phase [63].

### 5.6.3 Combined Anaerobic-Aerobic Degradation of Azo Dyes

It is generally presumed that most azo dyes can be reductively decolorized under anaerobic conditions (Tables 5.1 and 5.2),

while the biotransformation products produced during dye biodegradation, being insusceptible to anaerobic degradation, are readily metabolized under aerobic conditions (Fig. 5.2). Consequently, anaerobic degradation followed by aerobic treatment is usually recommended for treating the dye-containing effluent from textile processing and dye production industries. Two distinct strategies are usually detected: integrated treatment in a single reactor and sequential treatment in distinct reactors.

Sequential treatment of a dye-laden effluent can be done under anaerobic conditions and aerobic conditions (Fig. 5.2). Various investigators have studied this technique over the past few years and have pointed out that the anaerobic phase of the sequential system shows noticeable color, COD, and organic matter removal. Furthermore, it increases the biodegradability of azo dyes for subsequent aerobic treatment. However, evidence on complete biodegradation of azo dyes is not clearly available.



**Figure 5.2** Schematic layout of the sequential anaerobic-aerobic wastewater treatment process.

The ability of aerobic as well as anaerobic microorganisms to coexist symbiotically in a biofilm underlies the success of this technique. Providing oxygen to an oxygen-tolerant anaerobic consortium and exposing a biofilm to a low concentration of oxygen together with a cosubstrate are some of the ways to generate an integrated anaerobic-aerobic system. The integrated systems exhibit transient accumulation of aromatic amines, generated from the bioreduction of the azo dyes. These compounds are ultimately mineralized, probably with the support of facultative aerobic bacteria already existing in the anaerobic sludge or by subsequent addition of the aerobic enrichment culture to the anaerobic sludge. As

reported recently, the sequential anaerobic-aerobic system proved advantageous as compared to integrated system. Azo dye reduction was detected under sequential anaerobic-aerobic states due to utilization of the cosubstrate only for providing electrons for the reduction of dyes; however, in an integrated system, the cosubstrate is used partly for creating anaerobic microniches and partly for dye reduction. Additionally, aerobic degradation of the cosubstrate under integrated systems generally increases the unavailability of either oxygen or the cosubstrate, which ultimately is unfavorable for decolorization and degradation of dyes. These unfavorable effects certainly do not arise in the sequential anaerobic-aerobic conditions. The performance of sequential as well as integrated anaerobic-aerobic processes for the bioremediation of reactive black 5-laden synthetic wastewater was studied and compared. Both processes showed color removal to a significant extent during the anaerobic phase, while partial mineralization of the anaerobic dye metabolites, approximately to a similar degree, was achieved later during the aerobic stage. A combined anaerobic and aerobic biological system's anaerobic decolorization of dyes is inadequate with respect to mineralization of the degradation products. Moreover, aerobic decolorization of dyes is practically not feasible in wastewater treatment plants.

In recent years, notable achievements were made in the use of biotechnological applications in the area of wastewater treatment, not only for color removal, but also for the complete mineralization of dyes. Anaerobic digestions have been proved more successful than aerobic systems for the degradation and destruction of dye-containing wastewaters. Anaerobic reactors are truly accepted for the degradation and destruction of various dyes in wastewaters because of their low initial operational costs, smaller space requirements, high degradation efficiency, and low sludge production, combined with a net energy benefit through the production of biogas.

However, complete dye degradation in wastewater treatment plants only on the basis of aerobic processes is difficult to achieve since the main mechanism responsible for color removal is adsorption onto the sludges. Anaerobic treatment may be a feasible alternative to treating textile wastewaters with the optimization of their cultural parameters and in most of the cases, they are easily reduced under anaerobic conditions [63].

## 5.7 Conclusion

The preferential pH and temperature for achieving the highest level of decolorization with different fungi and bacteria are dye specific. However neutral pH and 25°C temperature are preferential to a pH level of 4 and 10 and temperatures of 15°C and 35°C. Different culture parameters (initial concentration of the dye, presence of additional amount of carbon and nitrogen sources in the medium, presence of enzyme cofactor/mediator, etc.) in the growing medium have been studied for their effect on decolorization of structurally different dyes and textile effluents. As reported by many earlier workers the initial concentration of the dye has a direct bearing on its decolorization (a lesser concentration of dye supports more microbial growth and consequently affects dye decolorization), and the same is true with the present study. The present study shows that an additional amount of carbon source in the growing medium promotes dye decolorization as this additional amount of carbon source acts as an easily available substrate for the growth of different types of microorganisms. The presence of a nitrogen source acts in a dual way, as in earlier studies a higher amount of nitrogen has been reported to decrease activities of several ligninolytic enzymes (LiP, MnP, laccase, etc.), which have been reported to have a role in dye decolorization, and that is why lower concentrations of these sources had supported more decolorization than their higher concentrations. Studies carried out on the role of enzyme mediators, cofactors, and stabilizers on dye decolorization, including veratryl alcohol and manganese ions, have clearly elucidated the role of these in dye decolorization. However, the presence of veratryl alcohol and manganese ions has supported higher decolorization only at lower concentrations during the initial stage of the experiment.

Because of potential applications in the textile industry effluent treatment, the use of microbes (bacteria and fungi) having ligninolytic enzymes opens up new possibilities for the development of green technology alternatives to existing chemical treatment. For further research work, there is a need to optimize the potential ligninolytic enzymes of novel microbes and in consortium form for an economical and ecofriendly tool to minimize the pollution by textile and leather industries to a significant extent.

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## Chapter 6

# Catalytic Ozonation Facilitated by Carbon Aerogel Materials for Textile Dyeing Wastewater Treatment and Reuse

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Wastewater treatment is a crucial issue in the textile industry, which generates plenty of polluting effluents containing significant residual dyes and dyeing auxiliaries. The most frequently adopted biological treatment may be ineffective in degrading dyes satisfactorily and is extremely time consuming. Therefore, some other approaches, which employ chemical oxidation to remove contaminants, have been developed. Among them, ozonation technology has been thought to be a promising approach due to merits of ozone. This chapter concentrates on the application of catalytic ozonation promoted

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by carbon aerogel (CA) materials for wastewater treatment and reuse. The catalytic performance of the catalysts in the degradation of the typical anthraquinone dye, C.I. reactive blue 19 (RB19), in simulated dyeing wastewater is discussed in detail in this chapter. In addition, considering the recent topic in wastewater treatment has been extended to advanced reclamation for reuse of waste effluents, catalytic ozonation with CA materials is introduced for the regeneration of the waste effluents from reactive dyeing, pursuing direct reuse in subsequent processes.

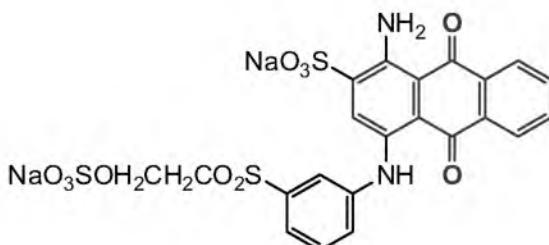
## 6.1 Introduction

### 6.1.1 Wastewater in the Textile Industry

The textile industry uses large quantities of water for pretreatment, dyeing, and finishing of fibers and fabrics and therefore consumes millions tons of fresh water annually. The generated wastewater is considered to be one of the most polluting wastewaters among those from various industrial sectors. Textile dyeing wastewater, which is collected from the textile dyeing or printing plants mainly, is often characterized by severe color and extremely high chemical oxygen demand (COD) load. Particularly in textile dyeing and printing, substantial quantities of unfixed dyes may be disposed of with the wastewater, which is eventually discharged into natural water bodies. If treated inappropriately or insufficiently before discharging, these color effluents would not only pollute the receiving water bodies in appearance but also cause potential hazards to human health because of the possible toxicity and carcinogenicity of the contaminants [1].

Commercial textile dyes are organic compounds for coloration of textile materials for aesthetic consideration. Among them, reactive dyes occupy the largest market share among all textile colorants worldwide [2]. It is long known that reactive dyes are an essential dye category for dyeing of cellulosic substrates due to numerous advantages, such as easy application, excellent color fastness, and brilliance in color. In terms of structural features a reactive dye molecule contains water-solubilizing groups, reactive sites, chromophores (i.e., azo or anthraquinone), and a bridge structure

connecting the whole molecule. Reactive dyes could form covalent bonds with cellulosic materials, such as cotton and rayon, through either nucleophilic addition or nucleophilic substitution. They are generally highly soluble in water and have good color fastness owing to the strong covalent bonds formed between dyes and fibers. The molecule structure of a typical anthraquinone reactive dye is shown in Fig 6.1. Anthraquinone dyes are of low biodegradability due to the more refractory nature of the chromophore group than that from azo dye molecules [3]. Up to now, though reactive dyes have been developed for decades and the majority of properties are improved to facilitate their wide application in cellulosic dyeing, a relatively low dye fixation rate is still the biggest concern. The fixation percentage may vary with the class of dyes used and the dyeing process involved. Because of the low affinity between dye molecules and fiber substrates, the exhaustion rate is generally not satisfactory. Plenty of dyes may remain in the dyeing bath but may not get fixed onto the fibers. In addition, during dye fixation a part of the adsorbed dyes would desorb from fibers and, shortly after, hydrolyze in the alkaline fixation bath. These unfixed reactive dyes are later discharged with waste dyeing effluents, which account for considerable color in the wastewater. Generally, these organic contaminants are chemically stable and poorly biodegradable in the environment. For example, the half-life time of RB19 after hydrolysis was estimated to be as long as 45 years at room temperature in neutral conditions [4].



**Figure 6.1** Typical anthraquinone dye: RB19

### 6.1.2 Conventional Wastewater Treatment

To minimize the adverse impacts of textile wastewater on the environment, appropriate treatment of the wastewater is critical.

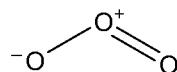
Industrial wastewater treatment is a combination of individual processes for specific purposes. Depending on the principles applied, it can be divided into physical, chemical, physicochemical, and biological processes. In a wastewater treatment plant, the treatment system can also consist of essential treatment units connected to one another. In addition, the effluent from one specific unit is often the influent for the connected unit.

Biological processes are the most widely applied efficient methods to remove dissolved contaminants from wastewater currently. During biological digestion, organics present in the aqueous phase are fed to microorganisms as food for their reproduction and metabolism. Depending on the oxygen demands, the microorganisms participating in wastewater treatment can be divided into aerobic, anaerobic, and facultative types. However, for textile wastewater, conventional biological methods are not always satisfactory. One of the shortcomings in biological treatment is the lengthy time required. Thus some cutting-edge methods have been developed on the basis of advanced oxidation processes (AOPs) that apply oxidation of organics with the in situ-generated hydroxyl radicals [5] to enhance treatment efficiency and reduce overall treatment time. Ozonation is one of the AOPs for potential application in wastewater treatment.

### 6.1.3 Ozonation Technology

#### 6.1.3.1 Overview of ozone

Molecular ozone consists of three oxygen atoms, two of which are attached to the central atom at equal distances (Fig. 6.2).



**Figure 6.2** The chemical structure of ozone.

Owing to the unique molecular structure, ozone can react with other reactants while complying with either the electrophilic principle or the nucleophilic principle. It possesses a higher redox potential compared to chlorine and oxygen, suggesting the oxidation capacity of ozone is even higher than chlorine.

### 6.1.3.2 Fundamental chemistry of ozonation

Because of the high reactivity of ozone, gaseous ozone is particularly unstable. To apply ozone as an oxidant, mass transfer of gaseous ozone into the liquid phase is required to create a contact opportunity between ozone and organic matters. The ozonation reaction in an aqueous solution is greatly complex. A great number of reactions occur in an aqueous solution simultaneously. Ozone molecules could react with organic matter directly or indirectly, depending on the effective oxidants involved. The direct reaction is the oxidation in which molecular ozone reacts with organic substances. For instance, ozone molecules would selectively attack the unsaturated double bonds of dye molecules in the ozonation of the dye solution process. The indirect reaction involves hydroxyl-free radicals, produced from the decomposition of molecular ozone through a chain reaction pathway, reacting with organic compounds. The indirect reaction can be initiated by hydroxyl ions or catalysts. Thus the solution pH could significantly affect ozone decomposition and, in turn, influence the entire reaction in water.

Both direct and indirect reactions occur in oxidative degradation of organics. The dominance of the reaction types and pathways is generally affected by factors such as concentration of resolved ozone, contaminants, temperature, and pH of the wastewater.

### 6.1.3.3 Catalytic ozonation

Ozonation is an effective technology for the degradation of organic matters in color removal. In addition no excess sludge is produced in the effluent tank after the treatment. What's more, the facilities of ozonation technology occupy a relatively smaller amount of space and are easy to install on-site. Unfortunately, ozone generation involves high operation costs currently. Besides, solo ozonation is selective in the degradation of contaminants; some refractory compounds accumulate in the solution but not much of these compounds is removed regardless of the ozonation time. Therefore ozonation technology has not been economically applicable in industrial wastewater treatment over the years. To tackle these problems, catalytic ozonation technology has been developed to enhance the ozonation efficiency and, in turn, reduce operation costs. Depending on the physical form of catalysts, catalytic ozonation can

be divided into two main categories, homogeneous catalysts and heterogeneous catalysis.

In homogeneous catalytic ozonation, the catalysts involved are generally metal ions, which are capable of promoting ozone decomposition. The widely used metal ions are transition metals, including  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cr}^{3+}$ . The catalytic degradation of contaminants complies with two mechanisms:

- Organic compounds are directly oxidized by free radicals produced from ozone decomposition that was catalyzed by metal ions [6].
- Organic compounds first form a complex with the catalyst and then the complex is oxidized by hydroxyl radicals eventually [7].

To summarize, catalytic ozonation can proceed through free radical reactions and/or molecular ozone oxidation with transition metal ions. According to some studies [8], the organic matter may form complexes with metal ions, which are then oxidized by ozone molecules or hydroxyl radicals.

For homogeneous catalytic ozonation, the metal ions should be removed after the reactions for elimination of secondary pollution and catalyst reuse. However, because the catalyst is resolved in solution in ionic form, it is difficult to separate and collect. Consequently these ionic catalysts are used much less than heterogeneous catalysts, which are in solid form and easy to separate from the liquid after catalytic ozonation.

Heterogeneous catalytic ozonation, which widely uses solid materials as catalysts, would be substantially influenced by both physical and chemical characteristics of the catalysts. For instance, density, chemical stability, surface area, and surface chemical groups contribute to the catalytic activity of the catalyst. Besides, as mentioned earlier, pH is considered to be the most important factor affecting ozonation because it could appreciably influence the kinetic reaction constant in ozone decomposition. A higher pH value will result in a higher kinetic decomposition constant of ozone. Furthermore, pH may affect the characteristics of the catalyst surface. For example, the net surface charges may be varied adversely by pH, which would seriously affect the adsorption affinity and capacity between catalysts and organic compounds in an aqueous solution.

Apart from that, temperature is also important as it could directly affect the stability and solubility of ozone molecules resolved in water.

Depending on the substrate nature of the materials, catalysts can be roughly classified into four groups. They are metal oxides or metal oxides on supports, metals on supports, minerals modified with metals/metal oxides, and nonmetal materials such as activated carbon. The mechanisms of heterogeneous catalytic ozonation propose that ozone decomposition could be provoked by:

- The redox state of metals on a solid support surface [9]
- The Lewis centers of metal oxides [10]
- Surface hydroxyl groups over metal oxides [10]
- The basic centers on the AC surface [11]

## 6.1.4 Carbon Aerogel

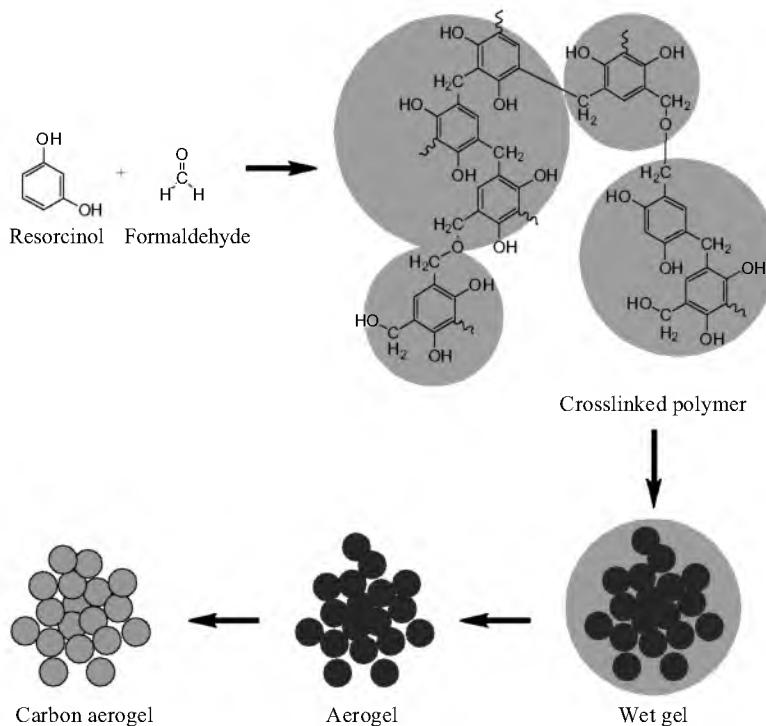
### 6.1.4.1 Overview

Aerogels, which were prepared in the early 1930s, are highly porous materials [12]. Through the sol-gel preparation process, both the pores and the solid skeleton are of a nanoscale. CA is one special category of aerogel materials obtained from high-temperature pyrolysis of organic precursors, which can be obtained by the aqueous polycondensation of resorcinol with formaldehyde via the sol-gel process [13].

CA can be prepared from several reactant combinations, including resorcinol and formaldehyde, melamine and formaldehyde [14], phenol and furfural [13], cresol and formaldehyde [15], phenol and melamine [16], and polymeric isocyanate [17] and polyvinyl chloride [18]. Among these systems, resorcinol and formaldehyde is the most frequently studied system, leading to a good understanding of preparation, characterization, and application. The typical synthesis process for CA is illustrated in Fig. 6.3.

In polymerization, resorcinol acts as a monomer that is capable of reacting with formaldehyde at its 2-, 4-, and 6-ring positions [19]. Nanometer-sized clusters are then produced in solution by condensation of the substituted resorcinol rings. At the end, clusters cross-link to form the gel through the surface group  $-\text{CH}_2\text{OH}$ . The major reactions that occur in the process are [14]:

- The formation of resorcinol derivatives having  $-\text{CH}_2\text{-OH}$  groups
- The formation of  $-\text{CH}_2-$  and  $-\text{CH}_2\text{OCH}_2-$  bridged compounds by the condensation of resorcinol derivatives
- The formation of  $-\text{CH}_2-$  bridges and formaldehyde by the disproportionation of  $-\text{CH}_2\text{OCH}_2-$  bridges.



**Figure 6.3** Preparation scheme of carbon aerogel.

The cross-linked polymer finally grows into discrete particles to further produce a wet gel, which can be transferred to the aerogel (organic precursor) in possession of three-dimensional networks after drying [20]. After calcination at a high temperature under argon or nitrogen gas flow, aerogel would be converted to CA eventually.

#### 6.1.4.2 Process control in preparation of CA

When the cross-linked gel is finally prepared, the removal of the solvent from the gel system is necessary. Different methods adopted

in the drying of the organic gel may lead to striking effects on the physical and chemical properties of the final prepared organic aerogel.

The most widely used drying method is supercritical drying, in which the solvent in gel products is exchanged with supercritical liquids [21]. The products dried from the carbon dioxide supercritical fluid may have less shrinking in the pore structure, high pore volumes, and high surface areas. But this process generally should be operated at a high pressure for a long period to ensure a thorough exchange of the solvent with supercritical fluids [22]. Alternatively, supercritical acetone may be used in the drying process, as the process with acetone could be operated at a relatively lower pressure with shortened drying duration [23]. However, this process generally is accompanied by side effects, for example, the already dried products thermally decompose during the drying process, which decreases the performance of the product [24].

Over the years, the capacity of the supercritical drying process is still unsatisfactory. Large-scale production of aerogel is inevitably limited by the drying process. Thus plenty of efforts have been made to substitute the supercritical technology so as to improve the productivity. In a study, it was found that the ambient-pressure drying of resorcinol-formaldehyde (RF) aerogels resulted in minimal shrinkage of organic gels if the resorcinol/catalyst ratio could be improved to more than 500 and the surface tension of liquids in the pores was decreased [25]. The ambient drying process drastically improved the productivity of aerogel products, which is beneficial to its wide application in industries.

After efficient drying to remove solvents from organic gel products, calcination at a high temperature is necessary for pyrolysis of the organic gels to form aerogel products. The pyrolysis process is commonly performed in a tube furnace, which is ventilated with inert gas flow in the ceramic tube for carbonization, at a high temperature. The tube loaded with organic gels is first ventilated with inert gas for some time to evacuate air in the furnace with inert gas at room temperature. Shortly after, the furnace temperature is raised gradually by the program, which integrates in the furnace.

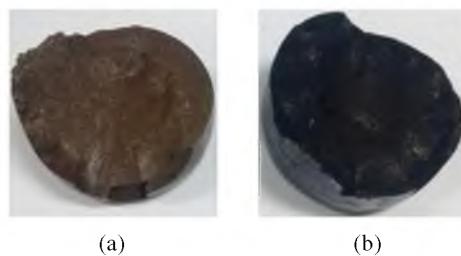
The pyrolysis conditions, corresponding to temperature and time, are responsible for the textural properties of the final aerogel. In general, increasing the calcination temperature may lead to reduced

surface area, porous volume, and oxygen contents of the products, and meanwhile it may also account for increased size distribution of macro- and micropores; while increasing the calcination time is capable of increasing surface area, pore size, and pore volume of the final products [21].

Weight loss during carbonization was found to predominantly occur when the temperature was no more than 750°C, after which the loss percentage remained at around 50% [26]. Weight loss could be divided into two stages. During the first, which began when the heating temperature was raised from ambient temperature to around 250°C, the release of adsorbed water corresponded to 3% mass loss. Thereafter, as the temperature was further raised, the mass loss could be attributed to volatilization of organic compounds from organic gels [27]. After these two stages, weight loss barely occurred, though organic groups within gel products were burned out continuously to form pores in the substrates.

#### 6.1.4.3 Structure

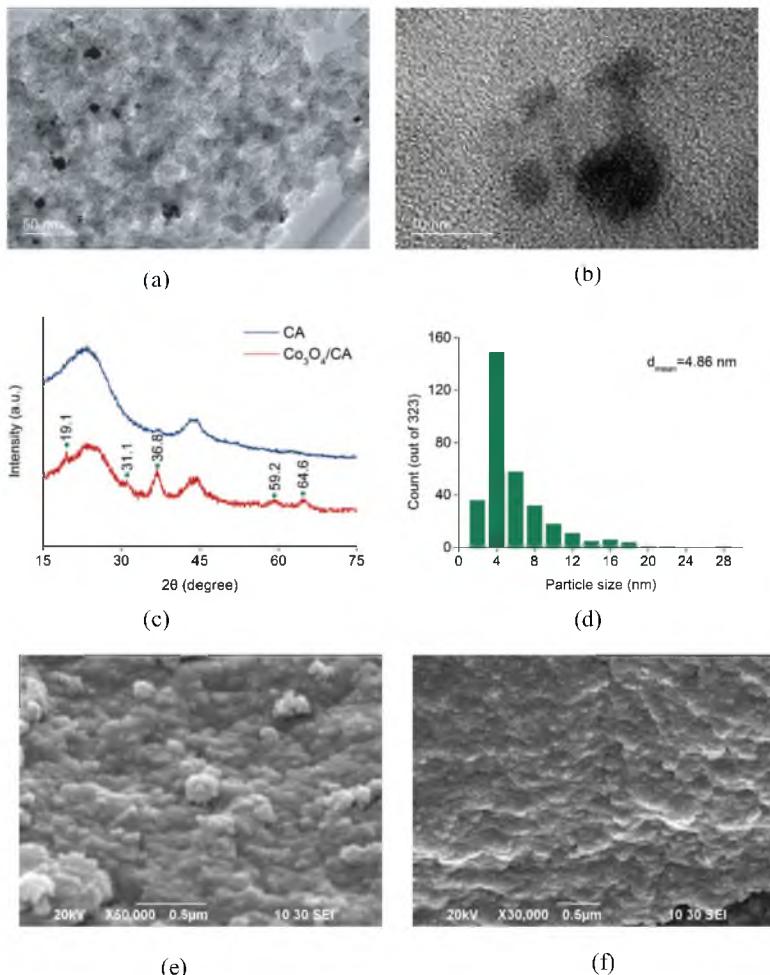
CA materials are black solid, which can be further crushed to appropriate sizes for the particular application. Figure 6.4 presents photos of CA gel and a CA product. It is clear that the color of the CA gel is dark red, which possibly stems from the generation of red oxidation products during polymerization. In addition, it can be observed that the CA product is much smaller in size compared to its gel precursor, which can be ascribed to mass loss and shrinking [18].



**Figure 6.4** CA gel product (a) and CA (b).

Figures 6.5a and 6.5b show a transmission electron microscopy (TEM) illustration of  $\text{Co}_3\text{O}_4/\text{CA}$ . Gray flakes and black spots are assigned to carbon particles and  $\text{Co}_3\text{O}_4$  particles, respectively, which are the main components of the composite. Carbon particles, ranging

from 20 to 30 nm, are interconnected to each other to form the three-dimensional structure, and meanwhile numerous mesopores have been generated among the agglomerated carbon nanoparticles [28, 29]. In addition, the even distribution of nano-size black spots on gray flakes demonstrates that  $\text{Co}_3\text{O}_4$  nanoparticles are well dispersed and embedded in the amorphous CA.



**Figure 6.5** Characterization of CA materials. (a, b) TEM image, (c) XRD pattern, (d) distribution of particle size of  $\text{Co}_3\text{O}_4$ , (e) SEM image of CA, and (f) SEM image of  $\text{Co}_3\text{O}_4/\text{CA}$ . Reprinted from Ref. [48], Copyright (2016), with permission from Elsevier.

X-ray diffraction (XRD) patterns of CA and  $\text{Co}_3\text{O}_4/\text{CA}$  are presented in Fig. 6.5c. For both of the samples, the broad peaks at around  $2\theta = 23^\circ$  can be associated to the (0 0 2) plane of amorphous carbon materials [30], which are similar to that of carbon nanofibers [31]. By comparing  $\text{Co}_3\text{O}_4/\text{CA}$  to pure CA, some new peaks are clearly observed. According to the JCPDS card no. 80-1541, characteristic peaks at  $19.1^\circ$ ,  $31.1^\circ$ ,  $36.8^\circ$ ,  $59.2^\circ$ , and  $64.6^\circ$  well match up to the (1 1 1), (2 2 0), (3 1 1), (5 1 1), and (4 4 0) planes of  $\text{Co}_3\text{O}_4$  in sequence, suggesting that  $\text{Co}_3\text{O}_4$  has a crystalline cubic structure [32, 33].

The diameter distribution of total 323 grains of  $\text{Co}_3\text{O}_4$  nanoparticles was statically analyzed, and the result can be found in Fig. 6.5d. It apparently has a nanoparticle diameter size, 4.86 nm on average (mainly 2 to 8 nm). The particle sizes of almost 50% of all nanoparticles are rather close to 4 nm, implying that the size distribution is of excellent monodispersity.

Figure 6.5e shows the scanning electron microscopy (SEM) images of CA. A rough surface is evident, which predominantly stems from agglomerated carbon particles. This is parallel to the TEM patterns in Fig. 6.5a. The surface morphology of  $\text{Co}_3\text{O}_4/\text{CA}$  is illustrated in Fig. 6.5f. It is hard to observe  $\text{Co}_3\text{O}_4$  nanoparticles clearly, which could be explained by the fact the size of the nanoparticles is too small to be noticed in the current SEM resolution. This is additional evidence to prove the particles are of nanoscale [30].

#### 6.1.4.4 Applications

Because of the versatile properties, such as high specific surface area, high micro- and mesoporosity, outstanding electrical conductivity, and high porosity, CA has been extensively applied on solid-liquid interfaces for heterogeneous reactions. Its final applications include double-layer capacitors [34], batteries [35], and storage of hydrogen [36]. Moreover, it is used as an adsorbent for the removal of hazardous contaminants from an aqueous solution physically [37].

In addition to physical removal of hazardous contaminants, it has also been adopted as a heterogeneous catalyst directly or modified as catalysts in many research studies for organic materials' degradation for environmental engineering, including catalytic ozonation for the degradation of dyes in simulated dyeing wastewater in the presence of CA materials.

## 6.2 Degradation of Anthraquinone Dye

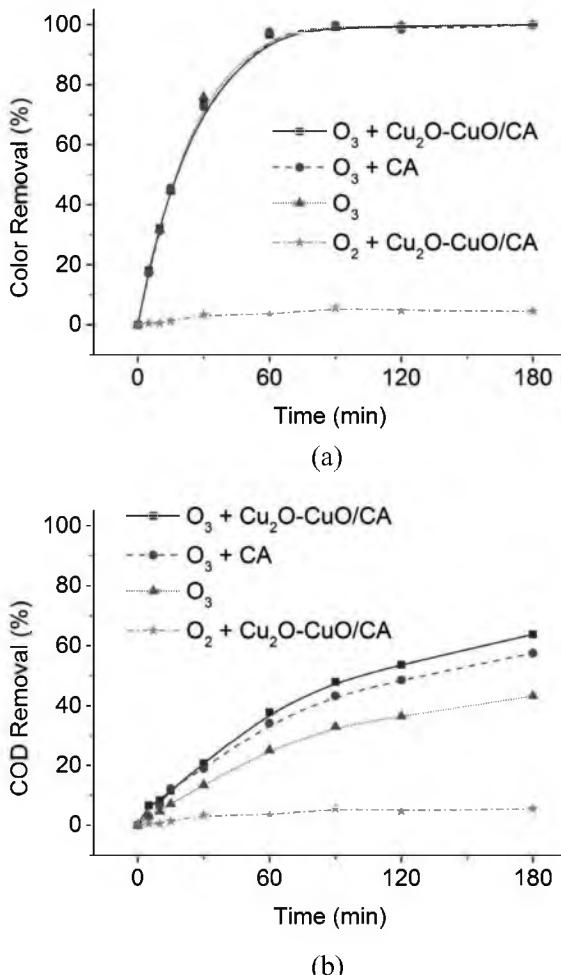
### 6.2.1 Performance of Catalysts

Due to the high specific area of  $\text{Cu}_2\text{O}-\text{CuO}/\text{CA}$ , it is capable of absorbing dye molecules and/or oxidized fragments from degradation of dyes, allowing color and COD removal by a physical approach. However, it is suggested that the absorption of dye onto the catalyst is negligible. The enhanced reduction of COD, as a result of the presence of catalysts, is the consequence of chemical degradation instead of the physical absorption effect.

In addition, higher removal rates were observed in the catalytic ozonation process, which could be attributed to the presence of the catalyst in the reaction system promoting the oxidation of dye molecules. In the ozonation process, a growing number of by-products were generated from degradation of the dyestuff by ozone. Some of these oxidation products would be refractory to ozone. As the treatment proceeded, these chemically inert substances were accumulated gradually. Consequently, ozonation without a catalyst could not effectively convert these organic matters into inorganic ones. However, when catalysts were added, the efficiency was elevated. The presence of catalysts in the dye solution promoted the decomposition of ozone into reactive species, such as hydroxyl radicals, of which the oxidation potential is even higher than that of molecular ozone [38]. Thus organics were more likely to be converted to smaller molecules. Ultimately, catalytic ozonation displayed more effectiveness in COD removal than pure ozonation. Moreover, CA loaded with copper oxides brought a slight enhancement in COD removal. This phenomenon was probably because the presence of  $\text{Cu}_2\text{O}-\text{CuO}/\text{CA}$  accelerated and promoted ozone decomposition, which led to enhanced generation of hydroxyl radicals exerting higher oxidation potential. A similar study has reported that copper can enhance the mineralization of pollutants rapidly, probably owing to the increased generation of oxidative radicals during the reaction [39].

In color removal, completed decolorization was achieved after about 90 min. of ozonation. The difference in color removal in the two catalytic experiments was unnoticeable. One probable reason

was that in specific conditions decolorization may predominantly involve oxidation between molecular ozone and molecular dyes, while catalysts rarely participate in the decolorization stage.



**Figure 6.6** Comparison of color (a) and COD (b) removal of RB19 (temperature, 303 K; pH, 5.64; ozone concentration, 5000 mg/L; gas flow, 0.5 L/min.; catalyst, 1 g; initial color, 800 mg/L; and initial COD, 722 mg/L). Reprinted from Ref. [48], Copyright (2016), with permission from Elsevier.

Color removal in both catalytic ozonation and ozonation alone was much higher than COD removal. This can be explained by the fact

that decolorization was the initial and primary oxidation step only involving cleavage of chromophore group(s) from dye molecules [40]. This was much easier to be implemented than advanced oxidations, which not only included decolorization but also involved additional multiple oxidation stages to convert organics to inorganics. The difference arose from the definition of color removal and COD removal. Decolorization only counted the completed chromophore groups in the solution, but COD removal was associated with the quantity of organic carbon. In the entire ozonation treatment, decolorization of dye molecules and further oxidation of decolorized dye molecular fragments may have happened simultaneously, which yielded both color and COD removal. However, at the very beginning, decolorization dominated the degradation reaction, in which the color of the dye solution was dismissed by the cleavage of the chromophore structures of RB19 into simpler fragments. As is shown in Fig. 6.6a, color removal reached almost 100% after 60 min. of ozonation, suggesting that no dye molecules with complete chromophore groups were present in the dye solution. On the other hand, dye intermediates produced from decolorization were then further oxidized by ozone molecules directly and/or by hydroxyl radicals generated from ozone decomposition, which contributed to COD removal but not color removal. This could be verified from Fig. 6.6b, in which further COD removal was observed after the first 60 min. of ozonation.

## 6.2.2 Effect of Treatment Parameter on Color and COD Removal

### 6.2.2.1 Catalyst amount

The influence of catalyst dosage in dye degradation cannot be ignored as it may determine the cost of the catalytic processes. In practice, catalyst amount rarely influences decolorization. One possible reason might be that decolorization may not rely on oxidation by radicals that were generated substantially after the introduction of the catalyst. However, COD removal is found to be significantly dependent on catalyst dosage. The possible reason may be that the contact surface area and availability of reactive sites of the catalyst were enhanced when the catalyst amount was increased. The enlarged

contact surface area hence facilitated reaction between ozone and the pollutants, and the growing number of reactive sites effectively promoted ozone decomposition to generate reactive radicals for dye degradation [41]. As a consequence, catalytic oxidation between dye molecules and radicals was enhanced remarkably and the reduction of COD was therefore promoted.

#### **6.2.2.2 Effect of ozone concentration**

Color and COD removal will be enhanced on increasing ozone concentration [42]. This is because the higher ozone concentration supplied indicates an improved mass transfer of ozone in the liquid phase, providing essential molecular ozone for degradation of dye molecules and their primary oxidation products via either direct or indirect oxidation.

#### **6.2.2.3 Effect of temperature**

Temperature control for ozonation treatment is critical, and it may account for two effects in general. On the one hand operational temperature is related to the solubility of ozone, which would influence mass transfer of ozone in the aqueous phase; on the other it influences the action rate for both oxidation of dye molecule and self-decomposition of ozone molecules to produce free radicals.

In general, good solubility of molecular ozone benefits mass transfer of ozone to the liquid phase. Nevertheless, in catalytic ozonation with CA, the removal of color and COD is enhanced with increased temperature. The most possible explanation may be that direct degradation via oxidation by molecular ozone or indirect degradation via oxidation by radicals from ozone decomposition is significantly accelerated in a warm solution, although the tendency of dissolution of ozone molecule declines simultaneously.

#### **6.2.2.4 Effect of pH**

Among all the parameters in catalytic ozonation, pH may be the most important factor that influences the degradation. Some research has reported that decomposition of ozone could be significantly affected by pH. It has been revealed that the decomposition rate of ozone in an aqueous solution would be remarkably increased when the solution is more alkaline [43, 44].

For catalytic ozonation with CA, pH exerts little effect on color removal, suggesting color removal is barely pH dependent. This is because decolorization probably mainly relies on molecular ozone rather than radicals produced from molecular ozone. The destruction of RB19 chromophore is mainly ascribed to direct attack from molecular ozone [45].

Nevertheless, pH plays an important role in COD removal, which is more prevailing in an alkaline condition. Since COD removal mainly relies on indirect reaction by oxidation from hydroxyl radicals, it is more productive in a basic solution [2, 46]. However, it is worth noting that during catalytic ozonation, the solution pH may decline due to the accumulation of acidic by-products from the oxidation of dye contaminants by ozone. System pH may drastically convert from alkaline to strong acidic as ozonation progresses.

### 6.2.3 Reusability

Either the catalysts of homogeneous catalytic ozonation for wastewater are difficult to reuse, or the recovery approaches are expensive. Nevertheless, heterogeneous catalysts are much easier to reuse. For batchwise treatment, it could be separated from the aqueous solution after treatments and reused for the next run if it is still effective; And for continuous treatment, it could be fixed in the liquid flow as fillings in the catalytic ozonation reactors. As a consequence, an ideal heterogeneous catalyst should not only be effective and stable during the first primary application(s) but also display excellent reusability in subsequent utilizations.

CA has excellent reusability in COD removal. There is only a slight drop of removal within the first four or five runs, and thereafter the efficiencies are maintained with minimum variations. The slightly decreased removal may be attributed to the oxidation of the catalyst surface [47]. The side oxidation of the catalyst surface in catalytic ozonation increases the acidic groups on the catalyst surface, and simultaneously the basic sites are decreased. Because basic groups participate in the decomposition of molecular ozone to free radicals, the reduction of basic groups leads to declined efficiency in the production of free radicals. As a result, the overall COD removal decreases. Another possible reason for the decreased degradation might be ascribed to the leaching of the metal oxides from the

catalyst substrate, which would result in the drop of degradation efficiency.

## 6.3 Reuse of Spent Textile Dyeing Effluent

Currently the environmental policy is getting increasingly more restricted. For instance, in Mainland China, the discharging standard of COD in wastewater was required to reduce from 80 mg/L to 60 mg/L from January 1, 2016, which was 100 mg/L before 2015 [48]. Thus more sustainable approaches are needed for cleaner production of textiles. Recent studies have been extended to carry out advanced treatments of dyeing effluents for reuse by suitable technologies, being directed toward sustainable development.

With this in mind, CA materials were used in catalytic ozonation with the aim of renovating the spent textile dyeing effluents for reuse. Dyeing effluents for catalytic ozonation were collected from the first/initial spent dyeing bath (known as the exhaustion and fixation bath), which is highly contaminated and full of residual hydrolyzed dyes, alkalis, and electrolytes. Fabrics which were dyed using freshwater (fresh dyeing) and those dyed using the treated/regenerated effluent (reuse dyeing) were compared in terms of color quality to assess the reusability of treated effluents.

### 6.3.1 Catalytic Ozonation of Dyeing Effluents

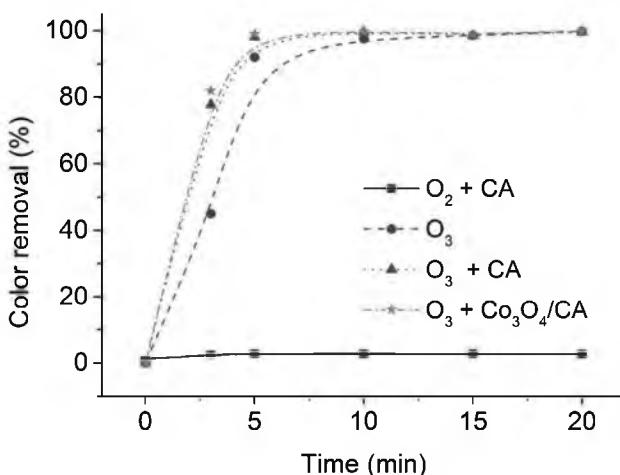
#### 6.3.1.1 Decolorization of dyeing effluents

Color quality, in terms of color tones, color depth, and color fastness, would be adversely affected if color removal is not conducted in the reused effluent, because the residual dyes in the reused dyeing bath may influence the subsequent dyeing procedure.

The decolorization behavior for the spent dyeing effluent is shown in Fig. 6.7. In cases involving ozonation, the decolorization percentage was rapidly enhanced with time on the whole. In addition, before reaching completed decolorization, color removal rates of catalytic ozonation were substantially larger than that in ozonation alone. This was a little different from that in decolorization of simulated wastewater, where the catalytic process is not advantageous in color removal. This may be ascribed to the different

concentrations of the probe contaminants in the aqueous solution. When dye concentration is low, the presence of catalysts, either CA or  $\text{Co}_3\text{O}_4/\text{CA}$ , might increase decolorization by the generation of hydroxyl radicals.

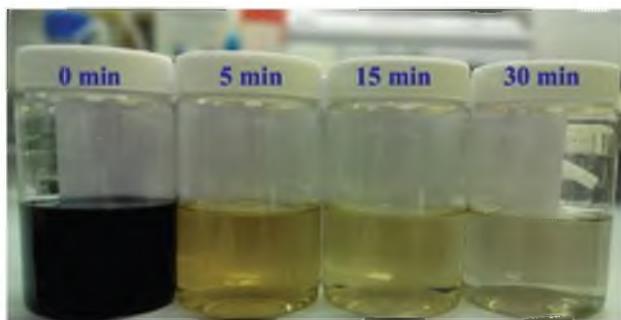
In addition to absorption, porous carbon materials can also help in the improvement of degradation efficiency in catalytic ozonation [49]. In the experiment by Wu et al. [49], the most possible mechanism was that porous carbon could increase the mass transfer of ozone into the aqueous phase and also help ozone to decompose into reactive species with a higher oxidation capacity than ozone itself. Due to the fact that dye decolorization was a result of oxidative cleavage of chromophoric group (anthraquinone group) in dye molecules, decolorization probably accelerated because of the resulting reactive species. Since nearly complete decolorization was reached after the first 5 min., it was assumed that catalysts only benefited at the very start of the decolorization process.



**Figure 6.7** Decolorization of RB19 dyeing effluent by catalytic ozonation (temperature = 24°C; ozone dosage, 2.5 mg/min.; and catalyst amount = 3 g). Reprinted from Ref. [48], Copyright (2016), with permission from Elsevier.

As is illustrated in Fig. 6.7, >99% decolorization rate was achieved in ozonation with CA after the beginning 5 min. But further providing ozone was improbable to obtain additional color removal, demonstrating total color removal had been realized. However, when

the appearance of catalytic ozonated effluents was visually examined in different time intervals, shades of these treated effluents were significantly distinct. It can be observed in Fig. 6.8 that the dark-navy effluent progressively changed to lighter yellow as the ozonation time proceeded. As a result, >99% decolorization only indicates that all dyes containing complete chromophoric groups, instead of other coloring substances, were decomposed. The inconsistency between the observed yellow shade and >99% decolorization of the effluent may suggest that 5 min. of ozonation is not sufficient to ensure the effluent can be reused directly.



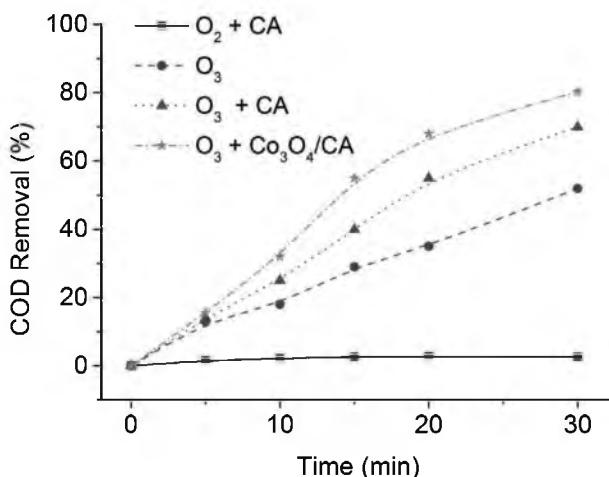
**Figure 6.8** RB19 dyeing effluents after catalytic ozonation. Reprinted from Ref. [48], Copyright (2016), with permission from Elsevier.

### 6.3.1.2 COD removal in catalytic ozonation

With respect to catalytic ozonation for wastewater treatment, in addition to decolorization, the investigation of the degradation of organic pollutants toward total mineralization by catalytic ozonation is considered to be a more vital objective. To assess the capability of the catalysts in mineralization enhancement, COD was evaluated to quantitatively measure the mass of organic pollutants in the solution indirectly, possibly containing residual dyes, dye intermediates from dye decomposition, and other products from advanced oxidation of the dye or its intermediates. This is because COD evaluates the total organic matters that can be chemically oxidized in solution.

According to Fig. 6.9, COD removal efficiency was dramatically improved by 20% in the ozonation with catalyst CA, when compared to solo ozonation. In addition to the contribution from absorption

(approximately 2.6%), CA could moderately enhance COD removal, indicating that dye degradation was accelerated through chemical oxidation by ozonation promoted by CA. Such enhancement is due to the capability of the carbon material to stimulate the decomposition of ozone into hydroxyl radicals ( $\text{HO}\cdot$ ). Besides, ozonation with catalyst  $\text{Co}_3\text{O}_4/\text{CA}$  was the most effective treatment. This can be explained by the fact that the polyvalent oxidation states of  $\text{Co}_3\text{O}_4$  enhanced interfacial transfer of electrons, which is essential in oxidation, leading to the promotion of catalytic activity of the catalyst.



**Figure 6.9** COD removal of RB19 dyeing effluents by catalytic ozonation (temperature, 24°C; ozone dosage, 2.5 mg/min.; and catalyst amount, 3 g). Reprinted from Ref. [48], Copyright (2016), with permission from Elsevier.

### 6.3.2 Color Reproducibility

As noted earlier, wastewater treatment has not been the only objective in chemical oxidation in recent years. Reuse of the treated wastewater has also become an essential issue. Hence, assessment is not limited only to the removal of color and COD. The more important aspect is to determine whether catalytic ozonation is feasible in the regeneration of dyeing effluents for reuse. Consequently, after 30 min. treatment time, effluents were used for cotton dyeing to study the reuse ability. The color quality of fabrics dyed with treated RB19

effluents is assessed by the three-dimensional CIELAB color system, including color difference  $\Delta E_{cmc(2:1)}$  and differences of lightness value  $\Delta L^*$  and chromaticity  $\Delta a^*$  and  $\Delta b^*$ .

As exhibited in Table 6.1, fabrics from reuse dyeing (fabric-R) had higher lightness than the control fabric from fresh dyeing (fabric-F), which revealed that fabric-R had a lighter shade than fabric-F. The chromaticity  $a^*$  and  $b^*$  represent the green-red axis value and the yellow-blue axis value, which refers to the location of specific color in the color space. These differences of the above color parameters were influenced by the by-product accumulation from dye degradation, which affected the dyeing procedure, in either exhaustion or fixation stages.

**Table 6.1** Color quality of fabrics dyed with fresh water and treated effluents

Catalyst	RB19			
	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E_{cmc(2:1)}$
/	1.62	-1.13	1.89	1.54
CA	0.38	-0.63	0.85	0.69
$Co_3O_4/CA$	0.20	-0.15	0.25	0.19

The color difference  $\Delta E_{cmc(2:1)}$ , which associates well with visual evaluation by the naked eye, is the most vital indicator to assess color reproducibility objectively. It can be observed that compared to the control fabric, the highest  $\Delta E_{cmc(2:1)}$  was obtained on the fabric dyed with effluent treated by solo ozonation. On the contrary, the lowest  $\Delta E_{cmc(2:1)}$  was obtained on the fabric dyed with effluent treated by catalytic ozonation with  $Co_3O_4/CA$ . It has been accepted that a larger  $\Delta E_{cmc(2:1)}$  means easier identification by the naked eye of the color difference between two fabrics. Thus, it can be summarized that a closer color performance in shade can be reproduced in the case of effluents treated with catalytic ozonation, suggesting that catalytic ozonation with a highly efficient catalyst based on CA materials could extensively remove by-products from the effluent by a noticeable mineralization effect.

Generally, the acceptable limit of  $\Delta E_{cmc(2:1)}$  for the assessment of color reproducibility is no more than 1.0 [50] because a color difference within this range can be barely perceived by the naked eye. Therefore, it can be concluded that solo ozonation in the present

conditions was not sufficient to effectively reclaim the RB19 effluent for reuse dyeing. By contrast, it can be verified that catalytic ozonation in the same conditions can successfully regenerate effluents for reuse, with color quality maintained within the tolerable limit.

## 6.4 Conclusion

Wastewater treatment and reuse are important for environmental protection and sustainability development in the textile industry. Very little research has been conducted concentrating on the application of CA materials in promoting catalytic ozonation of highly polluting dyeing effluents for reclamation. Catalyst materials have the potential to facilitate the degradation of contaminants in dyeing waste effluents. Color and COD removal was improved in the process with catalysts. The presence of the novel catalysts enabled the waste dyeing effluent to be successfully regenerated, making it ready for reuse in successive dyeing. Fabrics dyed with reused effluents have equivalent color quality, which could not be obtained in solo ozonation without catalysts under the same treatment conditions.

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## **Chapter 7**

# **Emerging Technologies for Source Reduction and End-of-Pipe Treatments of the Cotton-Based Textile Industry**

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There is an increasing demand to develop innovative textile products of high quality and with remarkable functionality in an environmentally friendly way, taking into account human, production, and disposal ecology. Utilization of the best available ecofriendly processing techniques and practices, especially in cotton-based textile wet processing, the main producer of contaminated textile wastewater in the whole production chain, would contribute to promotion and adoption of cleaner production strategies, smart use of resources, and reduction in waste generation and hence minimization of environmental impacts and burdens as well as production of ecofriendly textile materials to cope with the textile

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*Handbook of Textile Effluent Remediation*

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users' demands and requirements. This chapter gives an overview of textile fibers, textile chain, and conventional textile wet processes and their negative impacts, especially on textile effluents, with a special emphasis on the cotton-based textile industry. In addition, the emerging technologies, criteria to identify the best available techniques, and cleaner production opportunities to minimize resource consumption and pollutant generation are discussed. The positive impacts of utilizing proper emerging technologies for wastewater load abatement and remediation of textile effluents without adversely affecting the product quality are also covered. Finally, the chapter ends with the most recent developments and future trends in textile wastewater remediation.

## 7.1 Introduction

The textile industry is one of the main sources of severe water pollution problems worldwide and creates several environmental concerns. Wastewater generated from wet processes of cotton textiles is rich in color and contains a huge number of hazardous pollutants. Therefore implementation of an integrated pollution prevention strategy comprising pollution prevention followed by effluent treatment is a prerequisite for upgrading product quality/productivity and improving environmental, economic, and social performance.

The aim of this chapter is to discuss:

- The common wet processes of cotton textiles and their negative impacts, especially on water pollution
- Cleaner production opportunities to minimize both the volume and pollution load of textile effluents
- Current technologies available for effective end-of-pipe (EOP) treatments

The chapter then discusses the potential future applications of innovative technologies, as effective/economically alternatives, in effluent treatment to minimize pollution load for satisfactory recycling and reuse as well as their range of applicability.

## 7.2 Textile Fibers

Textiles can be classified into the following two classes by origin:

- Natural fibers, which are either of cellulosic origin, such as cotton, flax, and jute, or of animal origin, such as wool and silk
- Man-made fibers, which encompass regenerated fibers, like rayon, lyocell, and cellulose acetate, or full synthetic fibers, such as polyester and polyamide

Both classes of fibers can be used individually as well as in combination with each other for a wide range of applications, taking into consideration performance and quality demands in addition to durability and economic concerns [1–4].

### 7.2.1 Textile Chain

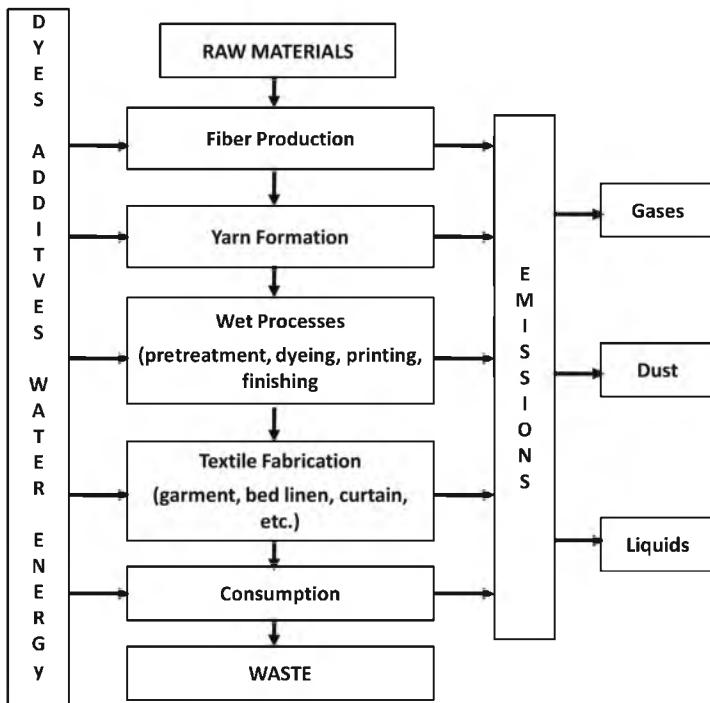
In general, the textile industry comprises the following stages of production:

1. Yarn formation
2. Fabric formation, for example, woven and knitted nonwoven
3. Wet processing, that is, pretreatments, coloration, and chemical finishing
4. Textile material fabrication

The textile chain is represented in Fig. 7.1.

With regard to emissions, particular attention is given to the negative impacts of conventional wet processing, pretreatment → coloration → finishing, on emission to water through often-untreated effluent disposal. Intensive use of clean water, a wide variety of processing chemicals (e.g., acids, salts, alkalis, textile auxiliaries, and dyestuffs), and energy results in highly contaminated textile industrial effluents with high chemical and biochemical oxygen demands (COD and BOD); containing large amounts of total dissolved and total suspended solids (TDS and TSS); having noticeable color, high temperature, and a broadly fluctuating pH; containing nonbiodegradable contaminants (e.g., synthetic dyes, pigment colorants, and textile auxiliaries); and in some cases containing heavy metals [5–8]. The variation in the aforementioned characteristics of textile effluents is governed by the type of

substrate, available techniques and equipment, the production chain, the sequence of treatments, processing chemicals used, as well as the demanded final products [9–13].



**Figure 7.1** Textile chain.

## 7.2.2 Conventional Wet Processing and Water Concerns

This part is intended to provide an overview of the conventional wet processing of cotton-based textiles, cotton being the most abundant and significant cellulosic fiber [14], which includes pretreatment, coloration, and chemical finishing stages (Fig. 7.2). Of all the nominated wet processing stages, the pretreatment processes (desizing, scouring, bleaching, and mercerization) constitute the most obvious source of water pollution. Also, around 100–150 m<sup>3</sup> of clean water is used for every ton of processed cloths. On the other hand, around 20%–25% of globally produced chemical compounds are utilized in the textile finishing industry worldwide [15–17].

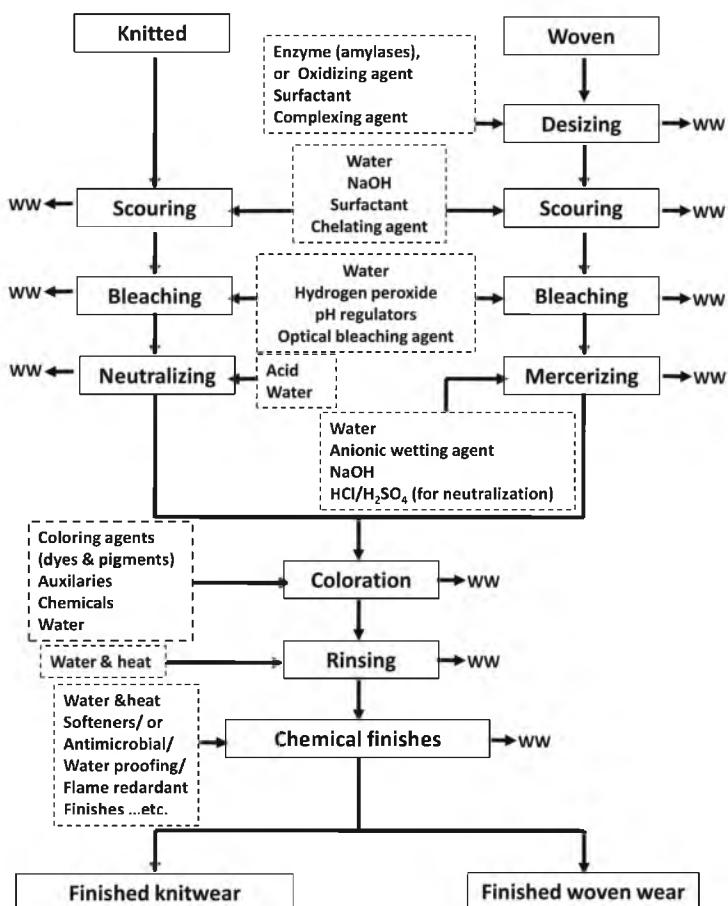


Figure 7.2 Wet processing of gray cotton fabrics. WW stands for wastewater.

### 7.2.3 Pretreatment of Cotton-Based Textiles

Pretreatment processes prepare the cotton-based textile substrates for the subsequent wet processing, for example, dyeing and/or printing and chemical finishing. Pretreatment conditions are governed by type of substrate, available production line, processing chemicals, production quantity, as well as quality required. The main tasks of pretreatment processes for successful subsequent coloration and/or finishing processing operations are [2–5, 18, 19]:

- Uniform removal of the inherent and added impurities, for example, the sizing agent, pectins, waxes, and seed husks
- Uniform hydrophilicity and absorbency of the pretreated textile materials
- Uniform degree of whiteness
- High color yield, better dimensional stability, and minimal impact on the treated fabric strength

Raw woven cotton fabrics contain around 15%–25% on weight of fabric (owf) of inherent noncellulosic impurities, for example, hemicellulose, pectins, waxes, proteins, ash, and pigments, along with up to 20% owf of sizing agent and sizing auxiliaries, which have to be completely removed in the pretreatment stage, usually carried out in several steps. On the other hand, around 60%–70% of defects that appear during subsequent coloration and subsequent finishing processes most probably are attributed to wrong, inefficient, and/or inadequate pretreatment processes. As far as the pretreatment processes are concerned, the steps, the used chemicals, the functions, and the final products as well as their negative impacts, especially on the discharged wastewater, are summarized in Table 7.1.

#### 7.2.4 Coloration of Cotton-Based Textiles

The most common classes of dyestuffs currently used for dyeing; the most important cellulosic fibers, cotton; as well as the mode of fixation, the dye-fiber bond, are listed in Table 7.2.

Dyeing or printing formulation, application method, coloration conditions, auxiliaries, extent of exhaustion and fixation, type of colorant-fiber bond, end uses, environmental impacts, effluent-treatment steps, and treatment costs depend on the used coloring agent, dye, or pigment [20–23].

As far as textile auxiliaries are concerned, several dyeing and printing methods; localized dyeing to obtain the desired pattern; and auxiliaries such as surface-active, sequestering, solubilizing, buffering, defoaming, reducing, oxidizing, binding, and thickening agents are utilized to enhance the extent of coloration and colorant fixation through physical and/or chemical bonds or via oxidation of the reduced leucoform of solubilized vat or sulfur dyes or via their entrapment in the cellulose structure [24, 25].

**Table 7.1** Pretreatment of cotton-based textiles and its environmental impacts on water pollution

Pretreatment steps	Inputs	Tasks	Output	Major environmental issues
1. Desizing: Desizing formulation depends on the type of sizing agent, e.g., based on modified starch, PVOH, polyacrylate, CMC, etc.; sizing auxiliaries; sized fabric; and available technique.	- Sized fabric - Enzymes for starch size - Oxidant for oxidative desizing - Mild alkali - Surfactants - Water and energy	- Breakdown of insoluble size - Removal of water-soluble warp size - Preswelling of cellulosic fabrics	Size-free	- BOD (from natural sizing agents) - COD (from synthetic sizing agents) - Biocides - Nonbiodegradable auxiliary contaminants
2. Scouring: Scouring formulation is governed by the type of substrate as well as the available equipment, e.g., open width or rope form.	- Desized or knitted fabric - Alkali, i.e., caustic soda and/or soda ash - Textile auxiliaries	- Uniform removal of various contaminants, such as noncellulosic hydrophobic impurities from the cellulosic substrate, residual size, and general soil and dust - Facilitation of postdyeing of dark shades - Swelling and solubilizing of the seed coats, thereby facilitating their removal during subsequent $H_2O_2$ bleaching	Clean fabric with uniform wettability	- High BOD - High pH - Fats, waxes, and detergent contaminants - High temperature

(continued)

**Table 7.1** (Continued)

Pretreatment steps	Inputs	Tasks	Output	Major environmental issues
3. Bleaching: Factors affecting the bleaching process are: - The type and source of substrate and its quality - Bleaching formulation - Available technique, e.g., continuous or batchwise - Demanded quality, e.g., full white or bright for pastel-shade dyeing or printing	- Scoured cotton fabric - Oxidizing bleaching agents, e.g., $H_2O_2$ , NaOCl, and NaClO <sub>2</sub> - Alkalis - Inorganic or organic stabilizers (especially for $H_2O_2$ ) - Surfactants - Chelating agents - Water and energy	- Removal of the seed husks - Oxidative decoloration of inherent natural colorants from the cellulosic fiber - Removal of residual size - Uniform absorbency for posttreatments - Creation of a full-white substrate - Creation of bright-shade dyed or printed fabrics	- Full-white goods - Pastel shades - Bright, full shades - Improved appearance due to the NaOCl bleaching agent removal of seed husks	- Low to moderate BOD - High pH and temperature - Adsorbable organic halogen (AOX) emissions, especially in the case of using NaOCl bleaching agent - Very high alkaline pH - TDS - NaOH - Some BOD products - High water and energy consumption
4. Mercerization: It is mainly carried out for attaining high-quality fashionable textile articles.	- Desized or scoured cotton fabric, i.e., before scouring or bleaching, respectively - Caustic soda (26–30 °Bé) - Wetting agent - Acid for neutralization	- Imparting of luster to the fabric surface (under tension) - Assurance of better dyeability and printability, i.e., improvement of dye uptake - Assurance of good dimensional stability	- High-quality and washable textile	

**Table 7.2** Different colorants and main constituents used in dyeing of cotton textiles

Class	Mode of fixation	Main constituents
(i) Water soluble		
Direct	Physical bonding (by hydrogen bonding and van der Waals forces)	Dye, salt, surfactant
Reactive	Covalent bonding (by nucleophilic and/or substitution addition)	Dye, alkali, salt, urea, surfactant
(ii) Water insoluble		
Vat	Reduction followed by oxidation/ in situ deposition	Dye, reducing and oxidizing agents,
Sulfur	Reduction followed by oxidation/ in situ deposition	alkali, surfactant, salt
(iii) Pigment	Binding using a proper binder	Pigment, binder, pH controller, other auxiliaries

The traditional textile coloration industry consumes large quantities of clean water and generates large volumes of heavily polluted and colored dye-house effluents, which often contain residual colorant, remnant processing auxiliaries, high concentrations of salts, heavy metals, and absorbable organic halogen (AOX), which especially increase on using chlorotriazine reactive dye type and contribute to the high BOD/COD pollution load.

Table 7.3 demonstrates the negative impacts of textile coloration processes on the discharged wastewater characteristics.

### 7.2.5 Finishing of Cotton-Based Textiles

Cotton-based textiles, which are the most widely preferred and used textiles, go through different finishing treatments that impart desired end-use properties, for example, the fact that they are easy to care for, antimicrobial, anti-UV, flame proof, water and oil repellent, and soft to touch [26–33]. The conventional finishing treatments consume huge numbers of textile processing chemicals and auxiliaries as well as enormous amounts of water and energy. Finishing treatments are often carried out as a separate operation

after full bleaching and/or after coloration. All conventional finishing processes contribute to water pollution as a direct consequence of using nonecofriendly and nonbiodegradable textile processing chemicals and auxiliaries, thereby causing major water pollution problems and posing a serious problem to aquatic life. This means that the main environmental concerns associated with traditional cotton finishing treatment arise from emissions to water.

**Table 7.3** Coloration processes of cotton-based textiles and their negative impacts on effluent characteristics

Coloration process	Inputs	Output	Major environmental issues
Dyeing	<ul style="list-style-type: none"> <li>- Pretreated cellulosic materials (woven and knitted fabrics, yarns)</li> <li>- Water and energy</li> <li>- Dyestuffs, e.g., direct, reactive, vat, sulfur, or pigment colorant</li> <li>- Auxiliaries, electrolytes, etc.</li> <li>- Reducing and oxidizing agents (for vat and sulfur dyeing)</li> <li>- Binders (for pigment dyeing)</li> <li>- Alkali</li> </ul>	<ul style="list-style-type: none"> <li>Dyed cellulosic materials</li> </ul>	<ul style="list-style-type: none"> <li>- Colored effluent</li> <li>- High pH</li> <li>- High salinity</li> <li>- High BOD and COD</li> <li>- AOX emissions (in case of using chlorotriazinre (reactive dyes))</li> <li>- Heavy metals Cu or Cr<sup>+6</sup> and Mn<sup>+6</sup> in the case of aftertreatment of direct dyeing and oxidation of sulfur dyes, respectively</li> <li>- H<sub>2</sub>S (sulfur dyeing)</li> <li>- High temperature</li> </ul>
Printing	<ul style="list-style-type: none"> <li>- Pretreated woven and knitted fabrics</li> <li>- Water and energy</li> <li>- Dyes or pigments</li> <li>- Thickeners and binder (for pigment printing)</li> <li>- Kerosene (for pigment printing)</li> <li>- Urea</li> <li>- Softeners, etc.</li> </ul>	<ul style="list-style-type: none"> <li>Printed cellulosic materials</li> </ul>	<ul style="list-style-type: none"> <li>- Colored effluent</li> <li>- Suspended solids</li> <li>- Urea</li> <li>- Solvents</li> <li>- BOD and COD</li> <li>- Metals</li> </ul>

*Note:* The extent of variation in the characteristics of untreated wastewater is governed by the type of chemicals used as well as the coloration processes involved.

Normally, continuous finishing treatments of cotton-based textiles using the pad-thermofixation technique do not require after-washing operations. On the other hand, the environmental concerns related to water emissions arising from the conventional finishing processes are restricted to system losses, for example, residual finishing liquor in the foulard chassis and excess liquor dumps in the pipes, at the end of each batch as well as draining of rinse water used for cleaning the equipment after finishing treatments.

Environmental concerns related to the finishing agents commonly used in conventional finishes of cotton textiles are attributed to the release of numerous pollutants into water, such as formaldehyde-containing finishing agents, poor biodegradable finishing additives, toxic biocides, emissions of fluorine-containing compounds, nonreadily biodegradable phosphorous-organic flame retardants, poor biodegradable polysiloxanes and fluorocarbon resins, and cationic softeners.

In general, wastewater generates from the conventional temporary and permanent finishing treatments are often rich in suspended solids, spent solvent, toxic substances, and materials with high BOD and COD, and their degree of contamination is greatly dependent on the type of finish, the kind and concentration of the used specialty chemicals/auxiliaries/chemicals, as well as the method of application, which in turn affects the amount of the released hazardous substances and the pollution load.

On the other hand, textile effluents generated from the aforementioned conventional wet processes, that is, preparation, coloration, and finishing processes, are mixed together and discharged from the final outlet of the production sit into receiving water bodies, without in-site separation, as a composite effluent, that is, heavily polluted/medium polluted/low- or zero-polluted effluent, thereby minimizing/hindering the efficiency of wastewater treatment processes to achieve the desired discharge requirements.

### 7.3 Integrated Pollution Prevention and Control

The release of very large volumes of contaminated wastewaters with large variation in composition and pollution load, especially

from textile wet processes, has given rise to search for an integrated pollution prevention and EOP treatment strategy for achieving a high level of environmental protection and performance taking into account the increased demands for high product quality under technically, economically, and social viable conditions [17, 34, 35]. Integration of waste minimization with end-of pipe solutions for cotton-based textiles industry is the road map to ensure efficient use of natural resources; to support sustainable production processes of ecofriendly textile products; to minimize water, chemical, and energy consumption, especially in textile wet processes; and to control and abate pollution load [9, 10, 36–38].

### **7.3.1 Cleaner Production**

Cleaner production, as a proactive environmental strategy, is a continuous application of an integrated prevention environmental win-win strategy to:

- Improve overall efficiency, profitability, and competitiveness
- Protect the environment and the health and safety of workers and consumers
- Reduce the negative impacts on the environment along with the entire life cycle of the fabric product

Cleaner production is an appropriate strategy to cope with the environmental and economic concerns, instead of resorting to EOP solutions alone [2, 34, 38].

Cleaner on-site production steps are shown in Fig. 7.3. Cleaner production activities comprise various measures, such as waste minimization, pollution prevention, source reduction, and ecofriendly approaches.

Sustainable reduction in chemical water and energy consumptions as well as reduction in the wastewater volume and pollution load released from the wet processes of cotton textile could be accomplished by implementing numerous cleaner production opportunities, as explained in Table 7.4.

Implementing a combination of the cleaner production opportunities mentioned in Table 7.4 has had significant positive impacts on production ecology, human ecology, and disposal ecology.

**Table 7.4** Opportunities for the implantation of a cleaner production strategy (pollution abatement and waste minimization)

Potential cleaner production opportunity	Some application scenarios	Positive impacts	Refs.
(i) Housekeeping	<ul style="list-style-type: none"> <li>- Proper storing and handling of textile materials and chemicals</li> <li>- Segregation of liquid wastes</li> <li>- Steam pipe insulation</li> <li>- Proper selection and maintenance of equipment</li> <li>- Improvement of process control</li> </ul>	<ul style="list-style-type: none"> <li>- No-cost/ low-cost options</li> <li>- Less water, chemical, and energy consumption</li> <li>- Reduced volume of and pollution load in wastewater discharge</li> </ul>	[39]
(ii) On-site recycling, reuse, and recovery	<ul style="list-style-type: none"> <li>- Recycling and reuse of wastewater according to its degree of contamination, e.g., recycling and reuse of cooling water and condensate and reusing of bleaching bath or rinses</li> <li>- Reuse of dyebath or rinses in another dyebath</li> <li>- In-process sequential recycling</li> <li>- Reuse of remnant printing pastes</li> <li>- Heat recovery</li> <li>- Soda recovery</li> <li>- Size recovery</li> <li>- Application of the countercurrent washing technique</li> </ul>	<ul style="list-style-type: none"> <li>- Medium-cost options</li> <li>- Less water consumption and chemical requirement minimization</li> <li>- Cost savings</li> <li>- Considerable reduction in freshwater use</li> <li>- Reduction of pollution load and effluent volume</li> <li>- Better use of resources</li> </ul>	[39]

(Continued)

**Table 7.4** (Continued)

Potential cleaner production opportunity	Some application scenarios	Positive impacts	Refs.
(iii) Processes optimization and modification	<ul style="list-style-type: none"> <li>- Rationalization, optimization, and modification of textile wet processes</li> <li>- Shortening of the process sequence and time, e.g., combined pretreatment processes, combined coloration and finishing, and one bath for multifunctional finishing</li> <li>- Substitution of overflow-washing/rinsing in favor of drain/fill methods</li> <li>- Low add-on techniques for conventional padding methods</li> <li>- Improvement of right first time (RFT) performance</li> </ul>	<ul style="list-style-type: none"> <li>- Low-to-medium-cost options</li> <li>- Remarkable resource reduction</li> <li>- Considerable reduction in wastewater volume and load</li> <li>- Minimized production cost</li> <li>- Improved process efficiency</li> <li>- Maximized productivity</li> </ul>	[40–61]
(iv) Input substitution	<ul style="list-style-type: none"> <li>- Use of recoverable synthetic sizes, e.g., PVOH, for starch based lubricant</li> <li>- Use of biodegradable lubricants for the conventional mineral oil-based lubricant</li> <li>- Use of biodegradable surfactants for nonbiodegradable ones</li> <li>- Use of formic acid for acetic acid</li> <li>- Use of <math>H_2O_2</math> for chlorine-based bleaching agents</li> <li>- Use of peracetic acid for Na-hypochlorite bleaching</li> <li>- Use of high-fixation/no- or low-salt reactive dyes instead of traditional ones</li> </ul>	<ul style="list-style-type: none"> <li>- Medium-cost options</li> <li>- Better use of resources</li> <li>- Improved quality and productivity</li> <li>- Significant reduction in effluent volume and pollution loads</li> <li>- Sustainable reduction in chemical composition</li> </ul>	[62–66]

Potential cleaner production opportunity	Some application scenarios	Positive impacts	Refs.
	<ul style="list-style-type: none"> <li>- Use of nonbenzidine dyestuffs for banned azo dyestuffs</li> <li>- Use of reducing sugars for sodium sulfide in sulfur dyeing</li> <li>- Use of peroxide as the preferred oxidant for <math>K_2Cr_2O_7</math> in sulfur dyeing</li> <li>- Use of cathodically regenerable reducing agents for nonregenerable reductants, e.g., <math>Na_2S_2O_4</math> in vat dyeing</li> <li>- Use of synthetic thickeners for kerosene in pigment printing</li> <li>- Selection of high-affinity dyes</li> <li>- Use of liquid ammonia for caustic soda mercerization</li> <li>- Use of salt-free reactive dyeing at lower liquor ratio baths</li> <li>- Maximization of fixation and wash-off, e.g., bifunctional for monofunctional reactive dyestuffs</li> <li>- Minimization of the quantity of the used auxiliaries and use of greener ones</li> <li>- Use of PEG for urea textile printing</li> <li>- Use of metal-free reactive dyes for metal-containing types</li> <li>- Use of natural dyes with ecofriendly mordants for synthetic dyes</li> </ul>		(Continued)

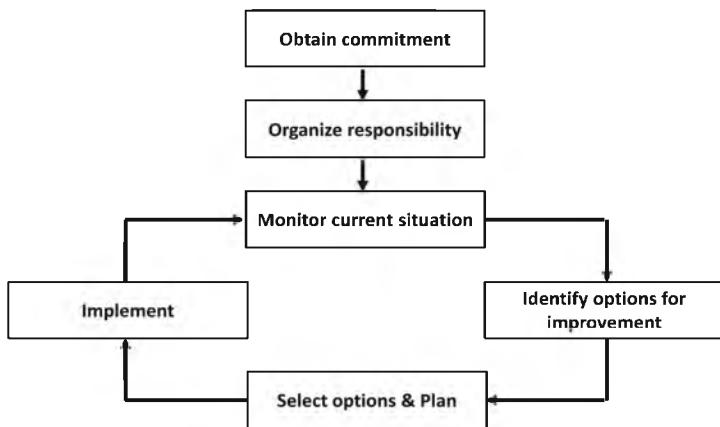
**Table 7.4** (*Continued*)

Potential cleaner production opportunity	Some application scenarios	Positive impacts	Refs.
(v) New technologies	<ul style="list-style-type: none"> <li>- Use of organic cotton for traditional cotton grown with toxic pesticides or chemical fertilizers</li> <li>- Use of biodegradable polymer for nonbiodegradable ones</li> <li>- Use of lyocell and tencel for traditional viscose</li> <li>- Use of greener finishing agents, e.g., formaldehyde-free finishes, nonhalogenated flame retardants, and ecofriendly bioactive materials</li> </ul>	<ul style="list-style-type: none"> <li>• Capital-intensive options but it can potentially improve profitability</li> <li>• Remarkable reduction in consumption as well as minimization of wastewater volume and pollution load</li> </ul>	[67-71]
	<ul style="list-style-type: none"> <li>- Biotechnology</li> <li>• Use of a thermal-stable <math>\alpha</math>-amylase enzyme for harsh chemicals in desizing of starch</li> <li>• Use of pectinase for replacing alkalis in cotton scouring</li> </ul>	<ul style="list-style-type: none"> <li>• Biodegradability</li> <li>• More sustainability</li> <li>• Remarkable decrease in pollution load and effluent volume</li> </ul>	

Potential cleaner production opportunity	Some application scenarios	Positive impacts	Refs.
	<ul style="list-style-type: none"> <li>• Use of catalase enzyme as <math>H_2O_2</math> killer for replacing <math>NaS_2O_4</math></li> <li>• Use of cellulases for washing of jeans articles and biofinishing</li> <li>• Use of lipase enzyme for complete removal of lubricating tallow-material in sizing formulation</li> <li>• Enzymatic bleaching using glucose oxidases for in situ generation of <math>H_2O_2</math></li> </ul>	<ul style="list-style-type: none"> <li>• A valuable alternative for harsh and hazardous chemicals</li> <li>• Production of more with less</li> <li>• Cost savings</li> <li>• Achievability in mild conditions</li> </ul>	[72–75]
	<ul style="list-style-type: none"> <li>-Nanotechnology</li> <li>• Use of nanomaterials for replacing hazardous chemicals in textile finishing to provide innovative and desirable properties</li> </ul>	<ul style="list-style-type: none"> <li>• Better affinity for cotton textiles</li> <li>• Remarkable decrease in chemical consumption to impart the desirable effect</li> <li>• Production of high-quality functional textile products</li> </ul>	
	<ul style="list-style-type: none"> <li>-Plasma technology</li> <li>• For surface modification and functionalization of cotton textiles, thereby avoiding and/or minimizing the conventional chemical wet processing negative impacts</li> </ul>	<ul style="list-style-type: none"> <li>• Water, materials, and energy savings</li> <li>• Shortening of the wet processing time</li> <li>• Reduced BOD/COD textile effluents</li> </ul>	[76–81]
			(Continued)

**Table 7.4** (Continued)

Potential cleaner production opportunity	Some application scenarios	Positive impacts	Refs.
(v) New product design	<ul style="list-style-type: none"> <li>- Laser technology           <ul style="list-style-type: none"> <li>• For denim processing</li> </ul> </li> <li>- Sustainable digital printing</li> </ul>	<ul style="list-style-type: none"> <li>• Chemical-free and water-free denim processing</li> <li>• Less water use and less waste production than the traditional technique</li> </ul>	[82]
	<ul style="list-style-type: none"> <li>- Supercritical carbon dioxide</li> <li>Through application of:           <ul style="list-style-type: none"> <li>• Green chemistry principles</li> <li>• Cleaner production aspects</li> <li>• A systematic ecoplan and assessment</li> <li>• Life cycle assessment (LCA) of the textile product that determines its environmental impact, i.e., cradle-to-grave analysis</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Water-less dyeing</li> <li>• High technology and investment requirements and positive impacts on both upstream and downstream sides of the product's life cycle</li> <li>• Potential reduction in natural resource consumption with minimal environmental risks</li> <li>• Materials and energy savings</li> </ul>	[84]



**Figure 7.3** Basic steps for cleaner on-site production assessment.

### 7.3.2 Current End-of-Pipe Management Practices in the Textile Sector

In general waste minimization by reduction at the source has great positive impacts on decreasing the pollution load as well as minimizing the production costs. From the environmental point of view, the discharge of textile wet process effluents, either batch or continuous process, with various harmful and toxic components, for example, chemicals, heavy metals, dyes, and auxiliaries, into the aquatic ecosystem results in the deterioration of water quality; constitutes a serious source of aesthetic pollution and eutrophication and perturbation in aquatic life; makes the receiving water bodies, for example, rivers, lakes, and streams, unsafe for reuse; and imposes significant negative impacts on public health. Textile wastewaters must be properly treated before being discharged through primary, secondary, and tertiary steps. An inefficient and improper EOP treatability technique results in large-scale negative impacts, especially on the ecological balance of the receiving water system. Therefore industrial textile wastewaters require efficient, ecofriendly, and economically feasible EOP treatment technologies to achieve a high level of environmental protection as well as to comply with the stringent environmental regulation [5, 17, 96, 97].

Physicochemical, biological, and advanced oxidation practices have been in use for management of EOP effluent. The high COD and the presence of nonbiodegradable contaminants along with the presence of heavy metals in the textile effluent require an integrated wastewater management system, more than a single treatment approach, to cope with the currently enforced environmental legislations, to achieve recovery of water and chemicals, as well as to minimize the cost directed toward EOP treatments [97–99].

### **7.3.2.1 Physicochemical methods**

Physicochemical practices comprise coagulation/flocculation, adsorption, biosorption, and ion exchange and membrane separation systems, like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [5, 100, 101]. A list of some physicochemical treatment technologies are given in Table 7.5.

To have a highly efficient performance and an economically feasible and environmentally sustainable wastewater treatment regime, many physicochemical methods need further modification and integration with other best available technologies to conserve water resources as well as to meet the strict regulations and legislative requirements concerning textile wastewater discharge.

### **7.3.2.2 Biological treatment methods**

Biological treatments have become attractive ecofriendly options for decolorization and decontamination of dye-house effluents. Biotreatment of contaminated wastewaters using living organism, like bacteria, fungi, algae, enzymes, and yeasts, can be carried out directly at the production site or at sewage treatment plants. Factors affecting the efficiency of biological treatments include the activity of the microorganism, the concentration of potentially toxic contaminants, nitrogen- and phosphorus-containing sources to maintain microorganism population, and proper pH and temperature, as well as the molecular size, chemical structure, and bioavailability of the target dye. The common treatment regime for textile effluent treatment is physicochemical flocculation followed by biological treatment [13, 124].

Bioremediation of azo dyes comprises the following two steps: (i) anaerobic reduction of the azo bond, producing two amines and (ii) aerobic digestion of the resultant aromatic amines by a mixed

**Table 7.5** Physicochemical techniques

Available techniques	Positive impacts	Remarks	Refs.
Coagulation/flocculation	<ul style="list-style-type: none"> <li>- It effectively eliminates insoluble dyestuffs and organic contaminants.</li> <li>- It is economically feasible.</li> <li>- Electrocoagulation results in less sludge and better performance than the conventional one.</li> </ul>	<ul style="list-style-type: none"> <li>- Soluble dyestuffs are not eliminated.</li> <li>- A large amount of sludge is generated.</li> <li>- Decolorization efficiency is low.</li> <li>- There are restrictions concerning sludge disposal.</li> </ul>	[102, 103]
Adsorption by using, e.g.:			
Clays	<ul style="list-style-type: none"> <li>- They enhance flocculation of organic contaminants.</li> </ul>		[104, 105]
Activated sludge	<ul style="list-style-type: none"> <li>- It is suitable for the removal of water-soluble anionic dyes and water-insoluble disperse dyes.</li> </ul>	<ul style="list-style-type: none"> <li>- It cannot cope with the modern discharge limits alone.</li> </ul>	[106]
Activated carbon	<ul style="list-style-type: none"> <li>- It is mainly effective in the elimination of nanoionic and cationic dyes.</li> </ul>	<ul style="list-style-type: none"> <li>- It is a very expensive technique.</li> <li>- It needs to be regenerated.</li> <li>- Fouling occurs by organic contaminants.</li> <li>- The extent of removal of different dye classes is governed by the pH.</li> </ul>	[107]

(Continued)

**Table 7.5** (Continued)

Available techniques	Positive impacts	Remarks	Refs.
Fly ash	<ul style="list-style-type: none"> <li>- Higher silicone oxide content facilitates the removal of reactive dyes.</li> <li>- They have the ability to form complexes with both cationic and anionic dyestuffs on the basis of their functional groups.</li> </ul>	<ul style="list-style-type: none"> <li>- They have poor hydrodynamic properties compared with activated carbon.</li> <li>- Further filtration is required to separate the formed flocs.</li> <li>- Only a few resins are proper for use in a wastewater treatment facility.</li> </ul>	[108]
Ion exchange resins	<ul style="list-style-type: none"> <li>- Ion exchange resins based on natural or synthetic products, e.g., chitosan, sugarcane bagasse, sawdust, bentonite, and cellulose, have remarkable pollutant removal efficiency.</li> </ul>	<ul style="list-style-type: none"> <li>- The choice of membrane processes like RO, NF, UF, and MF must be guided by the final product quality.</li> <li>- Production of concentrated sludge occurs.</li> </ul>	[109–114]
Membrane processes	<ul style="list-style-type: none"> <li>- They allow simultaneous reduction in coloration, BOD, and COD of the textile effluents.</li> </ul>	<ul style="list-style-type: none"> <li>- The choice of membrane processes like RO, NF, UF, and MF must be guided by the final product quality.</li> <li>- Production of concentrated sludge occurs.</li> </ul>	[115, 116]
RO	<ul style="list-style-type: none"> <li>- It permits the removal of the hydrolyzed reactive dye, chemical auxiliaries, and mineral salts in a single step.</li> <li>- There is recovery of both hot water and dyes in continuous dyeing.</li> </ul>	<ul style="list-style-type: none"> <li>- The higher the dissolved salts concentration, the greater is the required energy for the separation processes.</li> </ul>	[117]

Available techniques	Positive impacts	Remarks	Refs.
- NF	<ul style="list-style-type: none"> <li>- A combination of preadsorption followed by NF can be adopted for the treatment of dye-house effluents.</li> <li>- It is an efficient technique for the removal of COD, color, and nonbiodegradable contaminants.</li> </ul>	<ul style="list-style-type: none"> <li>- A major problem is the accumulation of dissolve solids, thereby hindering the discharge of the treated effluent into water streams.</li> <li>- It involves high energy consumption, high membrane cost, and short membrane life.</li> </ul>	[104, 118–121]
- UF	<ul style="list-style-type: none"> <li>- It is an efficient technique for the removal of all types of dyestuff and for PVA and indigo dye recovery.</li> </ul>	<ul style="list-style-type: none"> <li>- The quality of the treated effluent is not enough for reuse, especially in dyeing.</li> <li>- UF can be used only as a pretreatment for RO or in combination with a biological reactor.</li> <li>- Membrane pores are frequently clogged.</li> </ul>	[122]
- MF	<ul style="list-style-type: none"> <li>- It can be utilized for treating dye-house effluents containing pigments and for the subsequent treatment of rinsing baths.</li> </ul>	<ul style="list-style-type: none"> <li>- MF can also be used as a pretreatment for NF or RO.</li> <li>- Pore sizes are large.</li> </ul>	[123]

bacterial population, resulting in their complete mineralization [125–127]. Thus, successful decolorization of a wide range of azo dyes could be achieved via anaerobic, aerobic, and sequential anaerobic → aerobic treatment techniques [13, 97].

Aerated lagoons, trickling filters, as well as activated sludge systems are common aerobic biological treatments for attaining remarkable BOD removal efficacy >95%. The major disadvantages of these technique are (i) large space requirement and risk of bacterial contamination, as in the case of aerated lagoons, (ii) high capital cost and odor formation, as in the case of trickling filters, and (iii) the large amount of time required, as in the case of using an activated sludge system [126].

Anoxic decolorization condition of various classes of dyestuffs using mixed aerobic and facultative anaerobic microorganisms has also been reported [128]. On the other hand, various attempts have been made to decolorize textile effluents containing a mixture of dyes by using fungal and enzymatic treatment methods [97, 129, 130].

Laccases and peroxidases are the most important oxidative enzymes used in enzymatic dye degradation and may exhibit different substrate specificities. Laccases have the ability to decolorize a wide range of industrial dyes, with molecular oxygen as a cosubstrate, via sufficient aeration. Laccases have many potential applications, such as dye decolorization and degradation. Degradable dye fragments may have an enhancing effect on the extent of decolorization, most probably due to redox mediation. Laccases exhibit very broad substrate specificity in comparison with cellulases or lipases [130, 131]. Currently, large-scale utilization of enzymes in dye-house effluent treatment is not economically viable [130].

Moreover, several algae species have been successfully used in dye removal. Dye removal by algae is most probably attributable to the consumption of dye for algae growth, biodegradation of the dye structure to noncolored intermediates or CO<sub>2</sub> and H<sub>2</sub>O, and/or biosorption of dye chromophores on algae, leading to decolorization of dyes present in the textile effluent [18].

The biological processes have many benefits, compared to the physical oxidation treatment methods. For example, they are environmentally benign, form less sludge, consume less water, produce nonhazardous metabolites or full mineralization, and are cost competitive [132].

### 7.3.2.3 Common oxidation methods

The advantages and disadvantage of conventional oxidation processes like chlorine, Fenton's reagent ( $H_2O_2/FeSO_4$ ), electrochemical, and ozonation oxidation processes are shown in Table 7.6.

**Table 7.6** Common oxidation methods

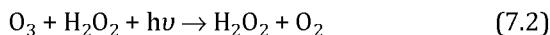
Oxidant type	Advantages	Limitations
NaOCl	<ul style="list-style-type: none"> <li>- It is cost effective.</li> <li>- Decolorization of water-soluble anionic dyes occurs.</li> <li>- Subsequent biological treatment results in significant reduction in COD.</li> </ul>	<ul style="list-style-type: none"> <li>- It is unsuitable for decolorization of vat and disperse dyes.</li> <li>- There is increase of AOX content.</li> <li>- Aromatic amines are released.</li> </ul>
Fenton's reagent ( $H_2O_2/FeSO_4$ )	<ul style="list-style-type: none"> <li>- Generated <math>\cdot OH</math> radicals render the dye colorless.</li> <li>- There is reduction of COD, TOC, and toxicity.</li> <li>- Decolorization of water-soluble anionic dyes occurs.</li> </ul>	<ul style="list-style-type: none"> <li>- Fenton sludge is generated.</li> <li>- It is unsuitable for decolorization of vat and disperse dyes.</li> <li>- Continuous treatment requires processing time.</li> </ul>
Electro-chemical destruction	<ul style="list-style-type: none"> <li>- It has a wide range of applications.</li> <li>- It enables the removal of recalcitrant pollutants.</li> <li>- It is an effective method for dye removal (especially acid dyes at acidic pH).</li> <li>- There is no or little chemical consumption.</li> </ul>	<ul style="list-style-type: none"> <li>- Iron hydroxide sludge is formed.</li> <li>- High flow rates cause direct decrease in dye removal.</li> <li>- Electricity costs are involved.</li> </ul>
Ozonation	<ul style="list-style-type: none"> <li>- Degradation of chlorinated hydrocarbons, phenols, aromatic hydrocarbons, etc., occurs.</li> <li>- There is decolorization and reduction in COD load.</li> <li>- It can be used alongside a physical method to avoid increased toxicity.</li> </ul>	<ul style="list-style-type: none"> <li>- The half-life is short.</li> <li>- Accelerated decomposition occurs in an alkaline medium.</li> <li>- It is a costly technique.</li> </ul>

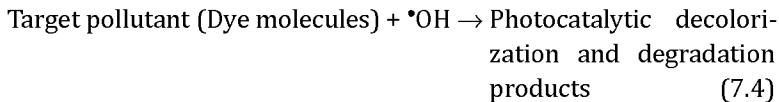
Sources: [5, 101, 133–137]

## 7.4 Emerging Techniques for End-of-Pipe Treatments

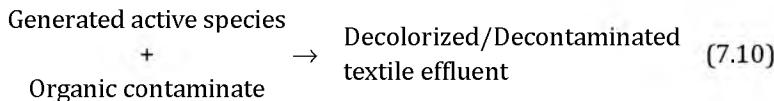
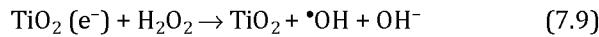
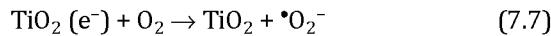
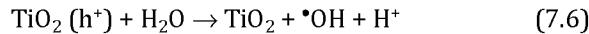
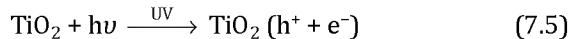
### 7.4.1 Advanced Oxidation Processes

Recently advanced oxidation processes (AOPs) have been widely used for decolorization of dye-house effluents and for the removal of recalcitrant organic contaminants via the generation of a very active and powerful oxidizing agent,  $\bullet\text{OH}$  radicals.  $\bullet\text{OH}$  radicals have the capability to attack and react with most dyes as well as to destroy a wide range of complex organic and inorganic contaminants in wastewaters. Utilization of combined  $\text{H}_2\text{O}_2/\text{UV}, \text{O}_3/\text{ultrasonic}, \text{O}_3/\text{TiO}_2/\text{H}_2\text{O}_2, \text{O}_3/\text{H}_2\text{O}_2, \text{O}_3/\text{UV}/\text{H}_2\text{O}_2, \text{O}_3/\text{TiO}_2/\text{electron beam irradiation},$  or  $\text{O}_3/\text{electron beam irradiation}$  accelerates the generation of  $\bullet\text{OH}$  radicals and enhances their extent of decolorization and decontamination of textile effluents [18, 126, 138]. AOPs show significant advantages over conventional remediation of textile effluents, such as their ability to remove mixed dyes and to eliminate nonbiodegradable organic contaminants without developing any chemical sludge [97, 126]. The decolorization efficiency is governed by the type of oxidant (follows the decreasing order  $\text{H}_2\text{O}_2/\text{UV} > \text{UV}$  and  $\text{TiO}_2/\text{UV} > \text{TiO}_2/\text{H}_2\text{O}_2$ ), the type and concentration of target pollutant, the extent of generation of  $\bullet\text{OH}$ , the concentration of the surrounding oxygen, treatment conditions, pH and temperature, as well as the presence and concentration of radical scavengers [126]. On the other hand, implementation of cavitation technology can result in the decrease of the toxicity levels of the effluent stream, minimizing the COD/TOC (total organic carbon) ratio, improving the biodegradable index ( $\text{BOD}_5/\text{COD}$  ratio), as well as reducing the color [139, 140]. Use of UV light along with other oxidants, like  $\text{H}_2\text{O}_2$  and  $\text{O}_3$ , in the hybrid AOP technologies to activate the  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  decomposition and generate  $\bullet\text{OH}$  radicals (Eqs. 7.1–7.3) results in significant decolorization of the treated effluent (Eq. 7.4). The application of the photocatalytic process was accompanied not only by color removal but also by COD reduction.



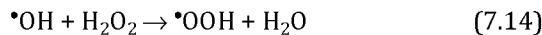
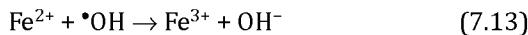
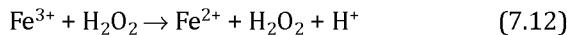
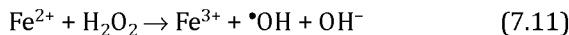


Moreover, photocatalytic degradation of the target pollutant, for example, the dye if using the  $\text{TiO}_2/\text{UV}$  system, is carried out according to the following equations [100, 126]:



#### 7.4.2 Combined Techniques for Textile Wastewater Treatments

Recent studies on adopting combined or sequential Fenton/biotreatment for textile wastewater treatment have investigated the efficient removal of pollutants from wastewater and meeting of more stringent discharging regulations. The generation of  $\cdot\text{OH}$  radicals that are capable of attacking and destroying the target pollutant in the Fenton process ( $\text{Fe}^{2+}$  as catalyst/ $\text{H}_2\text{O}_2$  as oxidant) is as follows:



On the other hand, biological treatment can remove the dissolved pollutants by organisms or extracellular enzymes. Additional research and development (R & D) efforts are needed to promote large-scale implementation of the nominated Fenton/biotreatment alternative technology for textile wastewater remediation while taking into account economic concerns [141].

- Combined electron beam irradiation followed by ozonation, for attaining a higher extent of dye mixture removal, was reported [142].
- A coagulation technique followed by adsorption was accompanied by full elimination of reactive dyes from synthetic water along with a remarkable reduction in COD, TOC, and AOX [143].
- Adsorption of textile dyes using sugarcane bagasse (SCB) pretreated with  $\text{CaCl}_2$  followed by biodegradation under solid-state fermentation (SSF) could be efficient, economical, and ecofriendly combined techniques for textile wastewater treatment [144].
- Moreover, application of a membrane bioreactor (MBR) as an emerging hybrid technology (biotreatment/membrane filtration) for textile mill effluent treatment with a view of its full-scale implementation could be an alternative technology for producing very high quality recyclable treated water [16].

On the other hand, efficient remediation of textile dyes and effluents using a plant-bacterial synergistic strategy was accomplished via degradation of the water contaminants into different nontoxic metabolites [145]. The developed consortium reactor demonstrated efficient removal of dyes, COD, BOD, and TOC from the pollutant textile effluents.

#### 7.4.3 Phytoremediation of Textile Dyes and Effluents

The phytoremediation approach has emerged as an efficient, ecofriendly, reasonably new, and cost-effective alternative approach to performing the removal of pollutants from textile effluents, compared with the available physicochemical and biological techniques. Synergistic action of living plant biomass and the plant's oxidoreductive enzymes, for example, peroxidases and laccases, has

been proposed to be more effective for adsorption, accumulation, and subsequent degradation of the textile dyes and other textile industry wastewater pollutants. The extent of phytoremediation of the textile dyes and effluent is governed by the growth form of the plant; the pollution load; the availability and accessibility of the dye; the availability of water, oxygen, and nutrients for a healthy state of the plant; the temperature, solar energy, and radiation; as well as the weathering process [146].

#### 7.4.4 Nanomaterials for Dye Removal from Aqueous Media

Several studies have investigated the application of carbon nanotubes (CNTs) as efficient adsorbents and dye scavengers for the removal of organic pollutants from aqueous media [147]. The adsorption capacity of CNTs is governed by physical properties of CNTs, nature of dye (adsorbate), premodification/functionalization of CNTs with acids or oxidizing agents, and whether using CNTs in composite form, for example, chitosan/CNT or activated carbon fabric (ACF)/CNT composites. On the other hand, factors affecting the adsorption process include the nature, size, and charge of the adsorbent and adsorbate as well as the pH and temperature of the solution. The adsorption of dyes onto CNTs is mainly achieved via hydrophobic interactions,  $\pi$ - $\pi$  interaction, hydrogen bond, and covalent as well as electrostatic interactions. Thermal and chemical regeneration methods are the most proper and applicable methods for regeneration of saturated CNTs. More R & D efforts for the development of CNT-based nanosorbents, taking into account cost, efficiency, as well as commercial application concerns, should be made [147].

Recently, use of nano zerovalent iron (nZVI) in environmental remediation as well as in the degradation of textile dyes has received great attention, most probably due to its high efficiency in the removal of pollutants, less toxicity, and cost-effectiveness. The extent of degradation of textile dyes using nZVI particles depends on the nZVI dose, the initial dye concentration, the dye volume, as well the pH of the reactive medium. Green supports are recommended to improve stability as well as integration with other treatment techniques, for example, UV, microwave, and ultrasonic, to upgrade the extent of dye

degradation. More bench-scale and pilot-scale studies are needed to ensure the efficiency of implementing this technique in treating real textile dyeing effluents [148].

#### **7.4.5 Gamma Radiation for Textile Wastewater Treatment**

The decolorization and degradation of coloring materials and organic pollutants in a textile waste stream by gamma irradiation for its safe recycling in textile processing of cotton knitted fabric have been investigated [149]. Generation of  $\cdot\text{OH}$  radicals during the radiolysis of water results in (i) decolorization of dye molecules when the  $\cdot\text{OH}$  radicals attack their chromophore groups, producing colorless smaller organic compounds, and (ii) degradation of organic and suspended solid materials, reducing the amount of total suspended solids (TSS), along with lowering both COD and  $\text{BOD}_5$  values of the irradiated water, without affecting the dissolved solids and electric conductivity of treated wastewater.

### **7.5 Future Prospects**

In the future, sustained multidisciplinary efforts will focus on the development, implementation, and commercialization of integrated pollution prevention and control (IPPC) routes to achieve a high level of environmental protection and economic performance of the textile finishing industry. The development of innovative technologies and their potential application in textile wet processing for source reduction and EOP remediation will have strong positive impacts on opening up new opportunities for textile products with novel and smart functions to face the rapid changes in the textile consumer's demand as well as on complying with the stricter regulation concerning wastewater discharge into the aquatic ecosystem. More efforts are required for further development of the best available cleaner production options and wastewater management techniques; for their full-scale implementation taking into consideration the final product quality and the increased public concerns about related environmental issues; as well as for minimizing effluent treatment and disposal costs. Smart, proper,

and cost-effective combinations of different treatment technologies will provide more efficient and powerful integrated systems for achieving minimum or zero water pollution. Additionally, future R & D activities should focus on phytoremediation (using developed transgenic plants), as a green/cost-effective trend, for decolorization and detoxification of heavily polluted textile effluents.

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## **Chapter 8**

# **Recent Trends and Future Prospects in Bioremediation of Synthetic Dyes: A Review**

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Bioremediation is one of the chief processes in the elimination of recalcitrants. Microorganisms having the capability to vitiate a wide range of effluents have been found to occur all over the ecosystem. A large amount of effluents contaminated with synthetic dyes and metal complex dyes is generated every day from various industries, including dyemaking industries. Ex situ and in situ remediation should be preferred for the degradation of effluents arbitrated by pure microbial strains or with mixed microbial consortia. Reductive processes are involved in the remediation of highly explosive and halogenated recalcitrants. Bioremediation involves mineralization and biotransformation of organic contaminants from toxic to less

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toxic metabolites. Biological remediation alone, or in combination with other clean-up technologies, has become recognized as a soil restoration technology. Three cases have been discussed in this chapter. Moreover, this chapter compares the efficiencies of these methods, which have been applied to remove dyes from wastewaters, and defines the advantages and disadvantages of these methods. Depending on the nature and toxicity of wastewater, selection of appropriate wastewater treatment technology is a major concern that may easy approach and produce environment friendly by-products.

## **8.1 Introduction**

Many synthetic dyes are employed daily for commercial uses, including textile printing, leather coloring, agricultural research, photoelectrochemical cells, and hair coloring. The annual world production of textiles is about 30 million tons, and these materials require 700,000 tons annually of different dyes [1]. The use of such dyes produces considerable environmental pollution [2]. The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes [3]. In the textile industry the process of dyeing results in the production of large amounts of wastewater exhibiting intense coloration, which has to be eliminated before the wastewater can be released into natural water streams, because these dyes are toxic and potentially hazardous; moreover, they can be a source of aesthetic problems [4]. Dye wastewater characteristics are variable; many methods are used for its treatment; which treatment is most effective depends upon the dye waste in the water [2]. Although many physicochemical techniques of decolorization have been developed over the last 20 years, few have been implemented by the textile industries due to their high cost, low efficiency, and inapplicability to a wide variety of dyes [5]. Biodegradation is nature's way of recycling wastes, which involves breaking down organic matter into nutrients that can be used and reused by other organisms. In this method, microorganisms, for example, bacteria and fungi, use organic matter of both synthetic and natural origins for their growth. These microorganisms need carbon (C), nitrogen

(N), phosphorous (P), and other elements as a source of energy for biosynthetic reactions. This pivotal, natural, biologically mediated process is the one that transforms hazardous toxic chemicals into nontoxic or less toxic substances [6]. The secondary metabolites, intermediary molecules, or any “waste products” from one organism become the food/nutrient sources for others, providing nourishment and energy while they are further working on/breaking down the so-called waste organic matter. Some organic materials will break down much faster than others, but all will eventually decay [7].

There are several reasons for which this process is better than chemical or physical processes. For example, this process directly degrades contaminants rather than merely transforming them from one form to the other; employs metabolic degradation pathways that can terminate with benign terminal products, like CO<sub>2</sub> and water [8]; derives energy directly from the contaminants themselves; and can be used *in situ* to minimize the disturbances usually associated with chemical treatment at the clean-up sites. Biological degradation of organic compounds may be considered an economical tool for remediating hazardous waste-contaminated environments [9]. While some environments may be too severely contaminated for initial *in situ* treatment to be effective, most contaminated media will use some form of biological degradation in the final treatment phase [10]. A literature survey shows sugars, organic acids, amino acids, etc., are the constituents of living microorganisms. Different organic compounds, like dyes, serve as the growth supplements for microbes because most of the dyes are composed of C, N, H, O, etc. [11].

## 8.2 Acclimation

The mineralization of many organic compounds that are introduced into treatment systems or into natural environments is often preceded by an acclimation period. The acclimation period is taken to mean the time interval during which biodegradation is not detected; hence it does not imply an explanation for the phenomenon or the way in which the biodegrading populations are growing or metabolizing during that period. Because no detectable mineralization occurs during the acclimation period, a compound

may pass through treatment systems and into natural environments during this time [12]. To minimize the environmental impact of these chemicals, it is important to understand the mechanisms involved in the acclimation of microbial communities. In our previous study, data were presented to show the existence of several mechanisms for acclimation before the onset of rapid biodegradation. The results of that investigation indicated that acclimation for the mineralization of 4-nitrophenol (PNP) in sewage and lake water resulted from the time needed for small populations to become sufficiently large to give detectable loss of the chemical [13]. The growth of the mineralizing organisms was affected by predation by protozoa and competition for inorganic nutrients. An acclimation period may also occur because of environmental conditions at the site where the chemical is discharged or because of the rarity in nature of microorganisms able to mineralize certain chemicals. Of particular importance in many municipal waste streams and in groundwaters adjacent to disposal sites for toxic wastes is the presence of compounds inhibiting microorganisms. Inhibitory compounds may influence the length of time before commencement of microbial decomposition, as indicated by the findings [14].

Indeed, evidence exists that the acclimation period is increased at high chemical concentrations. Researchers observed that the acclimation period for degradation in soil of the herbicide picloram increased as its concentration increased, and researchers reported that the acclimation period for decomposition of meco-prop by a five-member microbial consortium became longer with increasing concentrations of this herbicide [15]. Similarly, a report showed that the acclimation period for degradation of nitrilotriacetate in sewage treatment plants was longer at high concentrations of this chelating agent [16]. Other evidence exists that one compound may shorten the acclimation period needed before another is degraded [17]. Researchers showed that the mineralization of 2,4-dichlorophenoxyacetate in sewage could be stimulated by glucose and acclimation of the sewage microflora reduced the time before the first detectable mineralization of other monosubstituted aromatic hydrocarbons. The creation of a new genotype may also be an explanation for acclimation [18]. Researchers noted the appearance of a mutant during the acclimation of river water microbial communities for aniline mineralization [19].

### 8.3 Growth-Linked Biodegradation

Microorganisms are present in our surroundings. Many chemicals, like C, N, P, and S, and energy are essential for their growth. But carbon and energy are most important for the growth of fungi, bacteria, and microorganisms. Organic substrates are also very important for biosynthetic reactions. All microorganisms use a common procedure of organic compounds as the source of energy and C for their growth, which is called enrichment culture technique. Some species use these chemicals and increase their populations [20]. The agar medium is also very important for this purpose. The enrichment culture techniques are isolated for the pure culture of the fungi and bacteria that are to use a large number organic molecules and energy and C source. Microorganisms can also grow on a variety of other organic compounds. Sometimes the concentration of organic compounds may be too low or too high in the enrichment solution, so the microorganisms fail to grow and develop in this toxic medium. For the growth of microorganisms selective medium and selective components are required [21].

A large number of fungi and bacteria have been isolated that grow on one or more synthetic compounds. Sugar, amino acids, and organic acids are essential for their growth. Pesticides increase the growth of bacteria. As the concentration of energy and C decreases, the growth of bacteria and fungi also decreases. Mineralization of organic compounds is a characteristic of growth-linked biodegradation. In this process the organisms convert the substrate to CO<sub>2</sub> using a catabolic process. Some species of fungi and bacteria grow without C. When oxygen is present it reacts with the C and forms CO<sub>2</sub> [22]. A compound that is present in the environment may be the source of C and energy for the particular populations in that environment. This compound first reacts with the enzymes and converts to intermediates that characterize major metabolic sequences [23]. The intermediates, energy, and the C source start the biosynthetic process. In the initial phase of biodegradation intermediates are formed [24]. Aerobic and anaerobic both processes take place. Two categories for transformation exist: (a) bioaugmentation, in which microbes are added to supplement the existing microbial population, and (b) biodegradation, in which microbes use compounds to get C and energy to enhance growth, so this is called growth-linked

process. Several studies have demonstrated that the number of microbial cells acting on the chemical of interest increases as degradation proceeds. The cells use the energy and C source of their organic substrate to make new cells. During the process of growth, large amounts of energy are used [25].

## 8.4 Assimilation

There are two types of assimilation.

- Assimilation of carbon
- Assimilation of other elements

### 8.4.1 Assimilation of Carbon

The percentage of the C in many organic compounds is converted into the cells that are carrying out the biodegradation. So, in this process of biodegradation the substrates are converted into the biomass. This substrate is water soluble in nature. The anaerobic microbial degradation of the chemicals in soil, wastewater, sewage or sediments, and insoluble substances from enzymatic reactions is of increasing interesting currently [26]. Assimilation of C is estimated as

$$C_{\text{assimilated}} = C_{\text{substrate}} - C_{\text{mineralized}}$$

The carbon is further mineralized as the cell metabolizing the original substrate is consumed or decomposed. The pure cultures of microorganisms are called the growth yield. This yield is obtained by the biomass, and the biomass yield is obtained from the substrate. The values of the pure cultures may also be given as molar growth yield [27]. The carbon is mineralized in the fresh water as well as in the wastewater. The mineralization of the C is different in both cases. In metabolic pathways  $\text{CO}_2$  is formed as the result of C assimilation. For example, 93%–97.99% of phenol, aniline, benzoate, benzylamine, and 2,4-dichlorophenoxyacetic acid (2,4-D) added to the samples of lake water or sewage water at the levels of 300  $\mu\text{g/L}$  was converted to  $\text{CO}_2$  and direct measurement was taken of the C assimilation during the mineralization of 24 ng to 250  $\mu\text{g/L}$  of benzylamine [28]. Similarly, only 1.2% of the C of

2,4-D added to the stream water was converted to the particulate form. This lack of significant C assimilation may be the result of organisms trying to obtain C and energy for respiration in order for the cells to maintain their viability [29]. A high percentage of the C is present in some compounds. The growth of the bacteria may sometimes be in large numbers. The percentage of the substrate mineralized depends on the species carrying out the transformation. The percentage of the substrate affects many environmental factors, like substrate concentration and temperature. Increase or decrease in the concentration of the substrate is more important [30]. The effect of concentration on the percentage mineralized by some bacteria may not change over enormous ranges of the substrate concentration. The temperature can also affect the substrate C concentration [31]. The microbial community grows well via the decomposition of chemicals. The microbes use C of these chemicals as a source of energy [32]. In the environment, the cell grows on the decomposed chemicals. The concentration of the C reacted with the biomass of the natural community of the microorganisms. In soil and other environments, a small or large part of the substrate C is also converted into high-molecular-weight complexes that are resistant to rapid biodegradation [33].

#### 8.4.2 Assimilation of Other Elements

Synthetic molecules, like carbon, N, P, and S, and energy are used for the production of microorganisms. These molecules may be satisfactory for the degradation of compounds. In this process organic compounds may be converted into inorganic compounds [34]. For example, *Klebsiella pneumoniae* uses a N source, but it does not convert it into nitrile. This is assimilated [35]. For heterotrophic microorganisms in ecosystems, the carbon, N, P, and S elements are usually sufficient for the production of microorganisms. There are some other elements for the microbial demand [36]. The C is limited for the production of microorganisms. In addition, the microorganisms use the molecules as C or energy source. The biodegradative process usually will still lead to the mineralization of the other elements in the chemical [37].

## 8.5 Bioremediation Techniques

There are two techniques of bioremediation

- In situ bioremediation
- Ex situ remediation

### 8.5.1 In situ Bioremediation

#### 8.5.1.1 Introduction

During in situ bioremediation, spontaneous microbial processes are used to destroy or immobilize contaminants to relatively less toxic or nontoxic forms, specifically at the site of contamination. This technique is found to be fast, safe, and cheap as compared to other clean-up methods to get rid of environmental pollutants [38]. Plants are also used (phytoremediation) to get rid of contaminants by combined utilization of microbial processes, chemical engineering, and geological studies. Normally the contaminants in the topsoil are targeted more easily due to accessibility as compared to contaminants in the deep soil or groundwater, which pose a greater challenge and need specific strategies [39].

In aerobic conditions, the pollutants are converted to carbon dioxide and water and ultimately microbial biomass increases. In anaerobic conditions, with limited oxygen available, the contaminants are converted to methane and a very limited amount of hydrogen or carbon dioxide as the final electron acceptor is not molecular oxygen but other compounds, like nitrates, sulfates, or CO<sub>2</sub>. [40]. Relatively simple organic compounds are more effectively degraded by microorganisms, while complex or more stable pollutants, including polycyclic aromatic compounds or polychlorinated phenyls, are found to be resistant to microbial degradation. Aerobic biodegradation is thermodynamically more favorable; quick and complete degradation of organic compounds is achieved [41].

Immobilization of a contaminant or its conversion to a nontoxic or less toxic product in the environment is the major objective of in situ bioremediation. The physical state and microbial communities available of contaminants are the major factors that influence transformation or degradation. Indigenous microbes are particularly acclimatized to a specific environment and thus able to bring about

transformations more effectively [42]. However, bioremediation is found to be less optimal because the physiological and nutritional requirements of microbes are not fulfilled. By controlling the rate limiting steps or providing deficit nutrient/electron acceptors the rate of degradation can be enhanced. The use of genetically modified or exogenous microorganisms to optimize bioremediation, termed bioaugmentation, is found to be more effective for *ex situ* than in *situ* bioremediation [43].

### 8.5.1.2 Factors affecting *in situ* bioremediation

#### 8.5.1.2.1 *Types of contaminants*

Naturally occurring organic compounds are more effectively treated with bioremediation. More effective biodegradable compounds include petroleum compounds (ethylene, benzene, and toluene), volatile compounds (tri- and pentachloroethylenes), pesticides, creosotes, and various organic solvents. Many persistent contaminants are resistant to microbial degradations due to:

- Toxicity of the compound to microbes
- Preference of other compounds as the substrate by the microorganism
- Genetic inability of the microorganism to use the compound as energy or carbon source
- Environmental conditions not supporting the growth of appropriate microbial strain [44]

Propagation of microbial populations able to degrade particular contaminants could be achieved by modification of environmental conditions like oxygen, compound concentration, pH, and temperature. In cometabolism, a microorganism metabolizing one compound secretes enzymes to transform another compound/contaminant upon which the microorganism could not feed [5]. For example, methanotrophic bacteria produce enzymes to bring about oxidation of many other organic compounds. Inorganic contaminants cannot be effectively degraded by microorganisms, but their valance states or their adsorption, accumulation, and concentration in living systems can be modified, thereby either stimulating their solubility and thus elimination from a particular environment or decreasing their solubility, resulting in immobilization of the compound [45].

### 8.5.1.2.2 Environmental factors

Here are examples of environmental conditions that influence bioremediation:

- Concentration of the cocontaminant may increase to an extent to be toxic to the biodegrading species, thus reducing bioremediation.
- There may be very long acclimation periods.
- The number of individual microorganisms may be too small, or the microorganisms may be unable to colonize in a particular environment.
- Suitable pH may not be present.
- The microorganisms may be deficit of the necessary elements (P, N, S, K, or trace elements) required to utilize the contaminant as an energy source [44].
- Contaminants may have penetrated to deep soils or groundwater and thus may not be easily accessible.
- The concentration of water/moisture may not be suitable, the environment being either too dry or too wet.

In situ bioremediation strategies are developed according to site specificities, including both microbial and geological studies, combined with nature, physical state, and biochemical fate of the contaminant [46].

### 8.5.1.3 Advantages of in situ bioremediation

- Naturally occurring processes are utilized in in situ bioremediations.
- Partial or complete degradation of the contaminants occurs at the same environmental site rather than the contaminants transferring to other environments.
- No transportation of the waste after remediation is required.
- The chances of further spread of contaminants are reduced.
- Migration of contaminants is inhibited by decreased permeability of the soil due to increased microbial growth.
- Sorbed contaminants trapped in pores could also be treated by this method [47, 48].

#### 8.5.1.4 Limitations of in situ bioremediation

- In situ bioremediation in an unsaturated zone may fail due to the lack of an electron acceptor (usually oxygen) at the site.
- Indigenous microbes may not have the genetic makeup to support the biodegradation of the specific contaminant by producing the required enzymes.
- The toxic effects of contaminants may inhibit the growth of specific beneficial microbes.
- The hydrocarbons or the contaminants may be inaccessible to the particular microbe.

High concentrations of heavy metals, inorganic salts, or chlorinated hydrocarbons may have toxic effects on microbes [49–52].

#### 8.5.2 Ex situ Bioremediation

##### 8.5.2.1 Introduction

In the last two decades, attempts were made to remove pollutants from the environment in an ecofriendly way. For this purpose, advancements in the bioremediation technique were made and the old ones were modeled and developed. Due to the presence of different types of pollutants there are no techniques to solve the longstanding problem of a polluted environment. Aboriginal microorganisms play a key role in bioremediation of polluting substances [53]. Bioremediation is a process that relies on biological mechanisms to lower (degrade, detoxify, mineralize, or transform) the amounts of pollutants to an innocuous state. The process of bioremediation depends primarily on the nature of the pollutant, which may include agrochemicals, chlorinated compounds, dyes, greenhouse gases, heavy metals, hydrocarbons, nuclear waste, plastics, and sewage. Taking into consideration the site of application, bioremediation techniques can be categorized as ex situ and in situ [54]. Ex situ bioremediation involves physically extracting media from a contaminated site and moving it to another location for treatment. At an ex situ site, if the pollutant is present in soil, the soil is unearthed. If pollution has reached the groundwater, the water is

then pumped up and both the polluted soil and water are removed. Ex situ bioremediation techniques are based on:

- The cost of treatment
- Depth of pollution
- Degree of pollution and pollutant types
- Geographical location of the polluted site [55]

### **8.5.2.2 Techniques used in ex situ bioremediation**

#### **8.5.2.2.1 Biopile**

Biopile-mediated bioremediation involves above-ground piling of excavated polluted soil, followed by nutrient amendment and sometimes aeration to enhance bioremediation by basically increasing microbial activities [56]. The use of this particular ex situ technique is increasingly being considered due to its constructive features, including cost effectiveness, which enable effective biodegradation on the condition that nutrients, temperature, and aeration are adequately controlled [57].

#### **8.5.2.2.2 Windrows**

In windrows there is periodic turning of piled polluted soil, which increases bioremediation by enhancing degradation activities of indigenous and transient hydrocarbonoclastic bacteria present in the polluted soil [58]. The periodic turning of polluted soil, along with addition of water, increases the aeration, nutrients, and microbial degradative activities and uniformly distributes the pollutants, thus increasing the rate of bioremediation. Windrow treatment shows a higher rate of hydrocarbon removal as compared to biopile [59].

#### **8.5.2.2.3 Bioreactor**

A bioreactor is a vessel in which raw materials are converted to specific products through a series of biological reactions. There are different types of bioreactors; the choice of operating mode depends on market economy and capital expenditure. A bioreactor provides optimum growth conditions that support the natural processes of cells by maintaining their natural environment [60].

#### 8.5.2.2.4 *Land farming*

The simplest bioremediation technique is land farming because it is low cost and there is less equipment requirement for operation. In most cases, it is regarded as ex situ bioremediation, while in some cases, it is regarded as in situ bioremediation technique. This is due to the site of treatment. Pollutant depth plays an important role as to whether land farming can be carried out ex situ or in situ [9].

#### 8.5.2.3 Advantages of ex situ bioremediation

- Ex situ bioremediation techniques are preferred because they do not require extensive preliminary assessment of the polluted site prior to remediation; this makes the techniques short, less laborious, and less expensive.
- Due to excavation processes associated with ex situ bioremediation, the pollutant, in homogeneity as a result of depth, nonuniform concentration, and distribution, can easily be curbed by effectively optimizing temperature and pH.
- Ex situ bioremediation techniques allow modifications of biological, chemical, and physicochemical conditions and parameters necessary for effective and efficient bioremediation.
- Ex situ bioremediation techniques are faster and easier to control and can be used to treat a wide range of pollutants [55].

#### 8.5.2.4 Disadvantage of ex situ bioremediation

- The excavation features of ex situ bioremediation tend to disrupt soil structure; as a result, polluted and surrounding sites alike experience more disturbances.
- Ex situ bioremediation techniques require more workforce and capital to construct any of the techniques [61].

### 8.6 Anaerobic Biodegradation of Dyes

The efficiency of anaerobic technology in degrading dyes has been well demonstrated [62]. Experiments have shown that reduction by sulfide is partially responsible for degrading acid orange 7

anaerobically. A mathematical discussion of the experimental results clarified that autocatalysis played an effective role where 1-amino-2-naphthol causes the chemical reduction of azo bond [63]. Starch has been used to supplement and enhance the removal rate of dyes in industrial wastewater [64]. The synthetic dye tartrazine was found to be readily decolorized in an anaerobic baffled reactor. In another study, great differences occurred among the decomposition rates of various dyes in anoxic settled bottom sediments [65].

Many experimenters concluded that microorganisms could successively reduce azo dyes, anaerobically, finally causing cleavage of the aromatic ring [66]. The reduction of the azo bonds causes a remarkable reduction in the colors of dye-house effluents. However, some researchers have reported the resistance of many aromatic rings to reduction carried out by microbes. It is considered that reduction of dyes involves various mechanisms, like enzymatic [67], nonenzymatic [68], intracellular [69], and extracellular [70] or a combination of more than one mechanisms. Moreover, adsorption of the dye on the mycelia of fungi may also take place [71]. Great variations were observed among the degradation rates of different azo dyes [65]. The reactive azo dye reactive red 141 was decomposed under anaerobic conditions. The azo bonds were cleared by the microbes, which resulted in the liberation of 2-aminonaphthalene-1-disulfonic acid [70]. It was further demonstrated that the use of redox mediators enhances the rate of decomposition of azo dyes [63]. The presence of salts (nitrate and sulfate) greatly affects the decomposition rate of the azo dye reactive red 141 aerobically. The results indicated that nitrate delays the decomposition process while sulfate does not affect the biodegradation process considerably [72].

## **8.7 Aerobic Biodegradation of Dyes**

Under aerobic conditions, mono- and dioxygenase enzymes catalyze the incorporation of oxygen from  $O_2$  into the aromatic ring of organic compounds prior to ring fission. Some aerobic bacteria are able to reduce azo compounds with the help of oxygen-catalyzed azoreductases and produce aromatic amines. It was also reported that the aerobic azoreductases were able to use both NADH and NADPH as cofactors and reductively cleaved not only

the carboxylated growth substrates of the bacteria but also the sulfonated structural analogues [73]. There are only a few bacteria that are able to grow on azo compounds as the sole carbon source. These bacteria cleave azo bonds reductively and utilize amines as the source of carbon and energy for their growth. Such organisms are specific to their substrate, for example, *Xenophilus azvorans* and *Pigmentiphaga kullae*, which can grow aerobically carboxy orange I and carboxy orange II [74]. Only a few bacteria with specialized azo dye reducing enzymes have been found to degrade azo dyes under fully aerobic conditions [75, 76]. Aerobic degradation of naphthalene sulfonic acids by *Phanerochaete chrysosporium* was reported [8]. After desulfonation, the naphthalene compound was mineralized to carboxylic acids, CO<sub>2</sub>, H<sub>2</sub>O, and energy. Different microbial species are susceptible differently to azo dyes [73].

## 8.8 Microbiological Decomposition of Synthetic Dyes Using Mixed Cultures (Microorganism Consortiums)

From the perspective of the issues associated with physicochemical treatment methods, biological methods have aroused interest due to their cost-effectiveness, ability to produce less sludge, and environmental friendly nature [77]. These are considered to be the most effective means of removing wastes from wastewater enriched in organic constituents. Microorganisms play an important role in the mineralization of complex organic molecules and xenobiotic compounds. An advantage of biological treatment over physicochemical treatment methods is that more than 70% of the organic materials can be degraded easily [78]. Using microorganisms to biodegrade synthetic dyes is an attractive and simple operational method. However, biological degradation mechanisms can be complex. Many microbial species have been evaluated for their ability to either decolorize or mineralize various dyes. The use of microorganisms to treat industrial effluents that are contaminated with dyes offers two clear advantages: first, they are often capable of mineralizing the dyes, and second, the end products are either less toxic or nontoxic. Biological removal of dyes from textile and dye manufacturing industrial wastewaters can be broadly classified

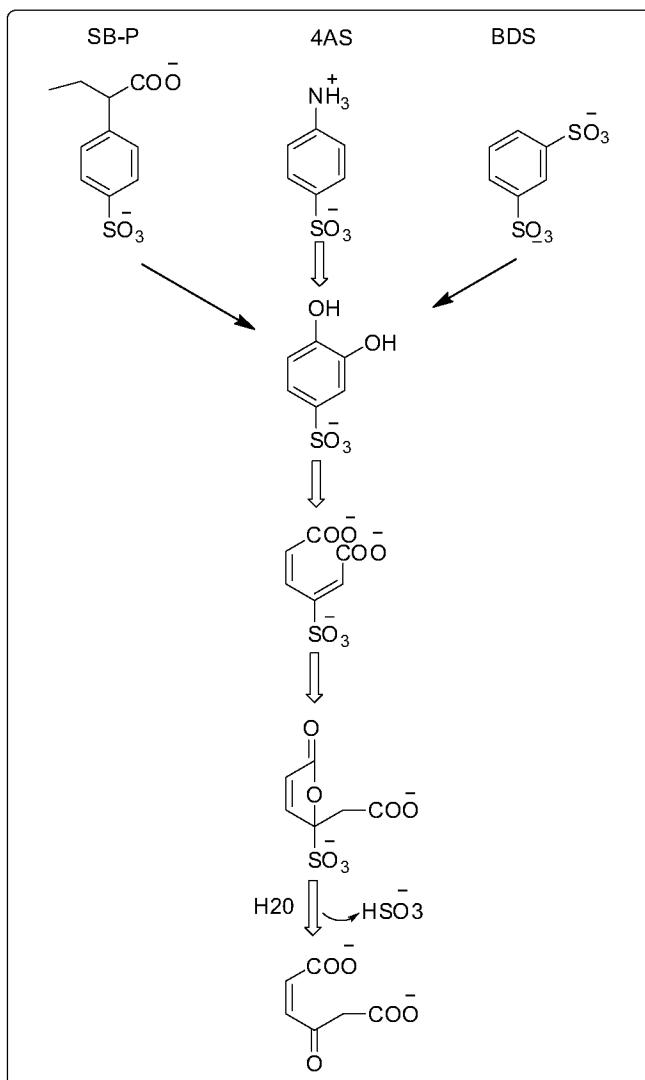
into three categories: aerobic treatment, anaerobic treatment, and combined aerobic-anaerobic treatment [79].

Researchers have reviewed various aspects of the microbial decomposition of synthetic dyes. In addition to traditional wastewater-cleaning technologies, other methods have been employed to degrade dyes [80]. For instance, an activated sludge process using microorganisms derived from cattle dung was developed for removing methyl violet and rhodamine B from dyestuff effluents [79]. A multistage rotating biological contractor was used to biodegrade azo dyes, in which an azo-dye-assimilating bacterium was immobilized in the system [81]. The use of mixed microbial cultures over pure ones has advantages in the decolorization of synthetic dyes. Individual microbial strains may attack the dye molecule at different structural sites or may use end products produced by another strain for further decomposition. The efficiency of decomposition largely depends on the chemical nature of the synthetic dye; hence, mixed biodegradation of mixed cultures is positioned to degrade a wider array of chemical structures [77]. What constitutes optimum conditions for microbial decomposition of dyes varies with application of both individual and mixed anaerobic-aerobic processes. For example, the aerobic process is more efficient in the degradation of dyes than the anaerobic process [80].

## 8.9 Role of White Rot Fungi and Their Enzymes in Biodegradation of Dyes

White rot fungi produce a wide variety of extracellular enzymes (laccase, lignin peroxidase, manganese peroxidase) responsible for decomposition of lignin, hemicellulose, cellulose, etc. Because of their high biodegradation capacity, they are of considerable interest and their use in the decolorization of industrial wastewaters has been extensively investigated [82]. Literature is available on decolorization of wastewater by fungi. Exact knowledge of the enzymatic processes involved in the decomposition of dyes is of great concern. Lignin peroxidase isoenzymes were isolated from *Polyporus chrysosporium* and purified by chromate focusing [83]. The activity of isoenzymes toward decolorization of dyes was

compared with that of a crude enzyme preparation. Optimum pH requirements were different in each case. The results indicated the marked difference among the decomposition capacities of crude enzymes and purified enzymes, although the structural variations



**Figure 8.1** Desulfonation after ring cleavage [87].

of dyes exerted a slight influence [84]. The degradation rate was highly dependent on pH [85]. Enzymes of white rot fungi showed different potentials toward the degradation of different dyes. Veratryl alcohol considerably enhanced the decomposition rate [86]. Similar findings proved that pure laccase was unable to degrade remazol brilliant blue R but the degradation rate was enhanced considerably in the presence of a mediator (violuric acid) [84]. Textile and pharmaceutical industries are the major consumers of sulfonated azo compounds and so are responsible mainly for the release of such compounds into wastewater streams. Desulfonation or mineralization of these compounds in the environment results in the release of sulfur-containing groups (Fig. 8.1).

Biodegradation of reactive azo dyes present in a textile effluent is a complicated one due to versatility in the structure of dyes. A number of other environmental factors, like the dye's chemical structure, the nature of substituent, the type of microorganisms, cell permittivity, pH of water, and concentration of the dye and other additives can affect biodegradation of dyes [88]. A literature study revealed the role of enzymes in the biodegradation of dyes (Table 8.1). Researchers studied the oxidation of Congo red at pH 4.0 in the presence of peroxidase [84]. The dyes undergo reduction by enzymatic action of microbes [89].

**Table 8.1** Biodegradative abilities of various strains of white rot fungi for different dyes

Mode of action	Effluent/dyestuff	Removal (%)	Fungus	Refs.
Ligninases catalyzed	Bagasse-based pulp effluent	80–90	<i>S. commune</i>	[90]
Biodegradation	Wastewater from alcoholic fermentation	80	<i>T. versicolor</i>	[91]
Biodegradation	RBBR	75	<i>P. chrysosporium</i>	[92]
Ligninases catalyzed	Reactive black	75	<i>T. versicolor</i>	[82]
Laccase, MnP	Congo red, direct blue	70	<i>P. chrysosporium</i>	[8]

Mode of action	Effluent/dyestuff	Removal (%)	Fungus	Refs.
Biodegradation	Orange II	99	<i>Polyporus ciliatus</i>	[5]
Biosorption	Drimanene red, blue	90	<i>T. versicolor</i>	[93]
Degradation/ laccase, MnP	Diazo, anthraquinone, azotriphenylmethane	70–80	<i>Pleurotus ostreatus</i>	[5]
Biodegradation	Disperse orange 3	99	<i>Pleurotus ostreatus</i>	[5]
Biodegradation	Solar golden yellow	80–100	<i>S. commune,</i> <i>G. lucidum</i>	[94]
Laccase	Levafix blue CA, Procion blue H-EXL	85	<i>L. sulphureus</i>	[95]
Laccase	Reactive blue, reactive black	86, 88	<i>Datronia sp.</i>	[96]

## 8.10 Advantages of Combined Anaerobic-Aerobic Treatment

A literature survey showed anaerobic reduction of azo dyes to be more satisfactory than aerobic one; the toxic products are degraded by an aerobic process into less toxic or even harmless products. A number of technologies have been developed for anaerobic-aerobic treatment of dye effluents. Decolorization rates were 20%, 72%, and 78% for acid yellow 17, basic blue 3, and basic red 2, respectively [97]. The combined method has been employed for the decomposition of anthraquinine-based reactive dyes [98], and results showed the dependence of decolorization rate on the molecular structure of reactive dyes. Dye effluents were also treated using a sequential system. Results showed that basic red was removed very efficiently anaerobically; however, no removal of the acid yellow 17 occurred [99, 100]. Anaerobic-aerobic treatment is suitable for the cleavage of the azo bond in various azo dyes [101]. The azo bonds of acid orange 8, acid orange 10, and acid red 14 were cleaved only under anaerobic conditions [102]. The efficiency of the removal of reactive diazo remazol black B dye by aerobic/anoxic treatment has been

studied. The results showed that a prolonged anoxic and anaerobic period enhanced decolorization [98]. The azo dye Procion red H-E7B has been decolorized in a combined anaerobic-aerobic process [103, 104]. A comparison of biodegradative properties of various organisms has been given in Table 8.2.

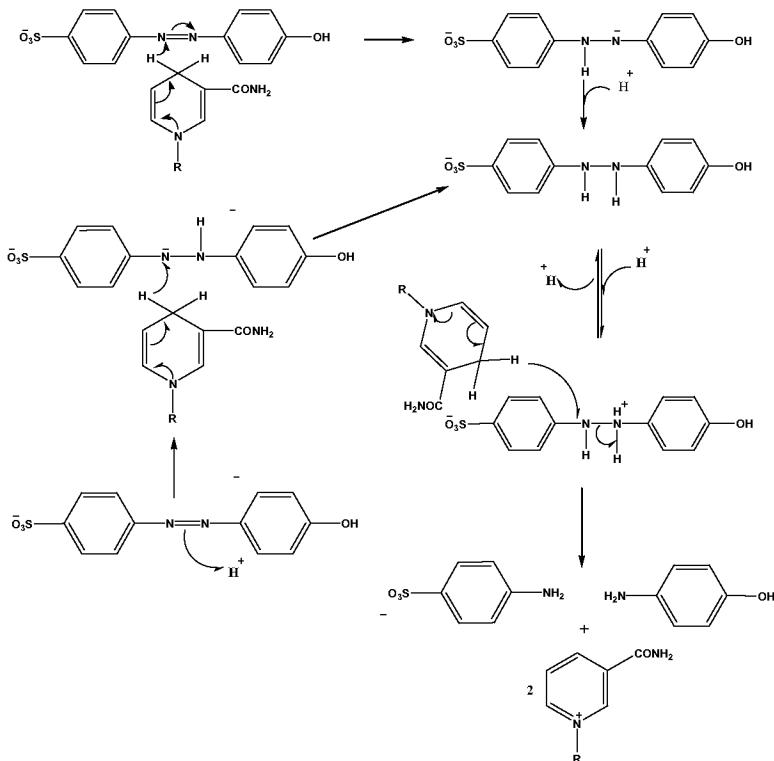
**Table 8.2** Comparison of biodegradative properties of various organisms [89]

S. No.	White rot fungi	Bacteria	Algae
1.	Environment friendly end product	Probably a more toxic end product	Less data available
2.	High adaptability	Poor adaptability	-----
3.	Wide range of application due to extracellular enzymes	Limited applicability due to intracellular enzymes	Limited applicability because $H_2O$ is required for survival
4.	High surface area due to presence of mycelia, by which they have greater contact with the environment	Single celled	A lot of time required for multiplication
5.	Light independence	Light independence	Light dependence

## 8.11 Identification and Mechanisms of Dye Degradation

In a report given by researchers, the enzymatic oxidation of Congo red by crude lignin peroxidase occurred at pH 4.5 [105]. Efficiency of the treatment system is dependent on the pH of wastewater or the dye solution used. The optimum pH varied depending upon the type of microorganisms and the structure of dyes [106]. Cell permeability is another very important factor not related with the structure of dye but having a major role in dye decolorization mechanism and extent. The chemical structure of azo dyes has a prominent effect on the biodegradation rate [71]. Depending on the position of the azo groups and their numbers, different dyes degrade differently; more

number of azo groups on a dye molecule would lead to a decrease in the rate of degradation as it would require more time to reduce more azo groups [66]. The production of toxic dye metabolites from dye molecules further suppresses dye degradation. Textile wastewater has a high concentration of salt and dispersing and solubilizing agents, which have adverse effects on biodegradation [107]. Reports showed that the degradation rates of dyes decreased due to production and accumulation of toxic products in the growth culture [108]. The effect of dye concentration on the rate of color removal by various fungal strains has been well reported. Higher concentrations of dyes might inhibit cell growth, leading to a decreased rate of decolorization [109–111]. Figure 8.2 shows the proposed mechanism of azo dye degradation.



**Figure 8.2** Proposed mechanism for the reduction of azo dye.

## 8.12 Conclusion

Bioremediation is an emerging green technology that facilitates the removal or degradation of the toxic chemicals in soils, sediments, groundwater, surface water, and air. Bioremediation mainly depends on microorganisms that enzymatically attack the pollutants in the presence of optimum environmental conditions and sufficient nutrients to breakdown contaminants. Both in situ (in place) and ex situ (removal and treatment in another place) remediation approaches are used. The successful implementation of a remediation regime requires a consideration of the indigenous biota, nutrient availability, as well as other environmental parameters necessary to achieve optimum results. The versatility of microbes in terms of degrading a vast array of pollutants makes bioremediation a technology that can be applied in the degradation/removal of pollutants. Though it can be inexpensive and in situ approaches can reduce disruptive engineering practices, bioremediation is still not a common practice. A combination of technologies regulated within stringent conditions and allowed enough time will prove tremendously important in returning contaminated soils/waters to fit-for-purpose states.

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## **Chapter 9**

# **Textile Effluent Remediation by Membrane-Based Techniques**

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The textile industries have always had a remarkable position in the world industrial arena because of their undisputed contributions to the basic needs of human satisfaction and to the global economy. Water, dyes, and toxic chemical are used in textile industries. The effluents released from each processing step contain significant quantities of unused resources. The discharged effluents are potential sources of pollution due to their many hurtful effects on the environment if they are released without any prior treatment. The treatment of textile effluents has raised the demand for the application of environment-friendly technologies with considerable water reformation potential. An effluent is treated by various modern membrane-based techniques. This chapter clarifies the share of membrane technology in textile effluent treatment and the recovery of unspent raw materials. In primary dye houses membrane-based

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techniques, such as ultrafiltration and nanofiltration, are explored, along with a techno-economic evaluation of these membrane-based textile wastewater treatment processes.

## 9.1 Introduction

These days the whole world stands as a witness to the overturning socioeconomic moves of assorted industries. Unfortunately, the commercial sector has whipped up many repercussions, leading to an inevitable trade-off between industrial progress and environmental degradation. Textile industries, for example, are one of the largest consumers of water, dyes, and various processing chemicals, which are used during the various stages of textile processing. Subsequently, substantial quantities of effluents are generated, mostly consisting of spent or unutilized resources, which are not suitable for further usage. These effluents are likely to cause environmental problems if discharged without prior treatment. The wastewater obtained from the textile industry is usually rich in color, chemical oxygen demand (COD), complex chemicals, inorganic salts, total dissolved solids (TDS), pH, temperature, turbidity, and salinity [1, 2]. Classification of textile waste is advised by the Environmental Protection Agency. Textile wastes are specifically diffused matter and are divided into four principal parts: high-volume wastes, hard-to-tear wastes, unsafe wastes, and toxic and hazardous wastes [3]. Between the assorted advanced constitutions present in textile wastewaters, the dyes are counted as the most dominating source of contamination. Freshwater bodies are adversely affected by the direct discharge of the colored textile effluent. The water bodies degrade the taste and odor, water transparency, and dissolved oxygen (DO) [4, 5]. Apart from these, dyes exhibit extremely advanced structures, high molecular weights, and low biodegradability [2, 6]. The effluents show a toxic effect on the flora and fauna present in the water bodies. At worst, these dyes also show mutagenic and carcinogenic effects [5].

The main concern in terms of textile effluents is water consumption, and this poses big danger to environmental sustainability

because it is responsible for the depletion of available freshwater resources. The main objective is to develop a wastewater treatment technique that is environmentally friendly and cost effective and treats textile effluents to permissible levels, which fulfills the current environmental needs. For sustainable development of the industrial sector of any country, the effluent treatment process should be equally adapted for regenerating the water used in textile processing [7].

Many treatment techniques are used to minimize the contamination caused by textile wastewater. Table 9.1 shows the full overview of the various conventional and new engineered treatment processes used for the treatment of textile effluents. Still, these processes suffer from serious undisputable drawbacks. For example, the otherwise ecofriendly biological processes, like the traditional activated sludge systems or anaerobic textile waste bioremediation processes, usually lack flexibility. Flexibility, individual efficiencies, and unit area are adversely plagued due to the biologically persistent constitution of pollutants present in textile waste. In addition, diurnal fluctuations within the surroundings in terms of variation in waste pH, temperature, and concentration of contaminants in textile waste are a major problem [8].

## 9.2 Different Processes Adopted for the Treatment of Textile Effluents

The various techniques employed in the various textile mills are generally classified as wet processes and dry processes, in conformity with the properties of the effluents generated in these processes [2]. Effluents generated in textile mills, particularly within the wet processing ones, vary greatly in composition and degree of toxicity, depending on the recipes of raw materials administered, specific processes operating, the present process stage in consideration, the machineries and instrumentality utilized, the standard of the water used for the process, and also the prevailing management concept applied to protect the use of water; on the other hand, dry process units usually generate solid wastes as fabric rejects [23].

**Table 9.1** Overview of the various conventional and new engineered treatment processes used for the treatment of textile effluents

Process name	Major effluents features
Photo-Fenton oxidation (solar and UV-C irradiation, zero-valent iron (ZVI) catalyst) [9]	Synthetic wastewater (azo dye C.I. reactive black 1)
Photodegradation ( $\text{TiO}_2/\text{H}_2\text{O}_2$ and sunlight) [10]	Real textile effluents
Photocatalyzed degradation (UV-C/ $\text{TiO}_2$ , UV-C/ $\text{H}_2\text{O}_2$ , and UV-C/ $\text{TiO}_2/\text{H}_2\text{O}_2$ ) [11]	Azo dye reactive orange 16
Ozonation (semibatch reactor) [12]	Remazol red RB, remazol turquoise, remazol black RL, and remazol golden yellow RNL
Ozonation (batch reactor) [13]	Persistent anthraquinone dye C.I. reactive blue 19
Coagulation/flocculation (CF)/microfiltration (MF), CF/ultrafiltration (UF), and CF/powdered activated carbon (PAC) [14]	Simple textile effluent (dyeing processes) and complex global effluents (dyeing, bleaching, and washing outlets)
Adsorption (activated carbon) [15]	Raw textile effluent obtained from a cotton textile mill
Adsorption (PES/PEI nanofibrous membrane) [16]	Anionic dyes sunset yellow FCF, fast green FCF, and amaranth
Catalytic degradation (biosynthesized silver nanocatalysts) [17]	Methyl orange, methylene blue, and eosin Y
Catalytic ozonation (activated carbon, ceria catalysts) [18]	One acid azo dye (C.I. acid blue 113) and two reactive dyes (C.I. reactive yellow 3 and C.I. reactive blue 5)
Biodegradation (facultative <i>Staphylococcus arlettae</i> bacterium) [19]	Textile azo dyes C.I. reactive yellow 107, C.I. reactive black 5, C.I. reactive red 198, and C.I. direct blue 71

Process name	Major effluents features
Electrolysis (anode materials: Ti/Ru <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub> ; Ti/Ir <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub> ; Ti/RuXSn <sub>1-X</sub> O <sub>2</sub> , with X ¼ 0.1, 0.2 or 0.3) [20]	Real textile effluent
Electrolysis (Ti/Ru <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub> DSA®- type electrode) [21]	Real textile effluent
Electro-Fenton process [22]	Synthetic textile wastewater (reactive blue 49 dye (RB49) and polyvinyl alcohol [PVA])

Water is generally used for scrubbing, flushing, desizing, scouring or kiering, bleaching, mercerizing, dyeing, washing, neutralization, and salt bath, which are process steps used in textile industries. The water consumption varies with each process in the case of temporary arrangement of wastewater removal, which is a comparatively less water intensive process. In a certain process, such as dyeing, print and postwashing are more water intensive than the other steps (US EPA, 1996). In addition, raw materials, such as wool, synthetic fibers, and felted fabrics consume water to fulfill their abrading needs. Furthermore, the water demand varies with different processing equipment requirements in accordance with the technological concerns. Machines, like Hank machines and dyeing winches, are the biggest water consumers. In dyeing machines, water consumption declined from 0.03 m<sup>3</sup>/kg to 0.006 m<sup>3</sup>/kg during the batch process. There are many factors responsible for textile effluent discharge and have complex compositions and various ecotoxicological effects [23].

### 9.2.1 Textile Industrial Wastewater

In the textile sector wastewater includes water from water processing, water cleaning, noncontact cooling water, and storm water. The major textile wastewater is created by the process stages, which are scouring, dyeing, printing, finishing, and washing. There are a number of factors responsible for the characteristic quality of processed fabric, such as chemical and physical characteristics of the applied dye, nature of finishing of the process, the equipment

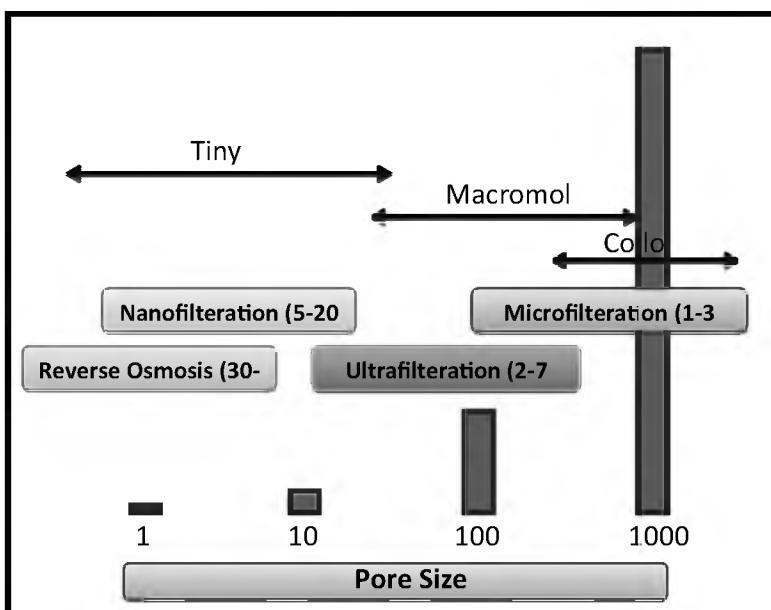
and principles used, and water formed. Large-volume wastes include wash water from preparation and continuous dyeing; alkaline wastewater resulting from fiber preparation; and batch dye wastewater containing large amounts of residual dye, salts, acids, alkalis, and other noxious additives in smaller amounts; also such operations as dyeing, printing, and finishing are usually liable for the injurious hike in biochemical oxygen demand (BOD), COD, TDS, and total suspended solids (TSS).

### **9.3 Membrane-Based Processes**

Membrane-based technology or membrane filtration involves the use of four different membrane groups, microfiltration, nanofiltration (NF), ultrafiltration, and reverse osmosis (RO), as per the rejection potential of the membrane [24]. Figure 9.1 shows the filtration spectrum of a membrane. A difference in pressure between the two sides of the membrane is the driving force for the separation of all mentioned membrane types [25]. Membrane-based technology is universally recognized due to the production of water of a respectable quality from surface water, seawater, well water, and brackish water. Membrane-based technology is used in industrial wastewater treatment and processes and also used in the area of treating secondary and tertiary municipal wastewater and oil field-produced water. Membrane-based technology has regressed as a viable alternative to conventional treatment processes of dye wastewater and water consumptions by water recycling [26–28]. Usually, this technique is used as a final treatment after biological and physical-chemical treatments [29, 30]. It has also been used in dye manufacturing to concentrate and purify the compounds [31, 32]. These techniques are only used at the start and in the middle of the process and not allow as end-of-pipe solutions to recovery and reuse of some reagents [27, 30, 33–35]. The schematic representation for filtration is shown in Fig. 9.1.

#### **9.3.1 Microfiltration Process**

Microfiltration has confined application in the treatment of textile wastewater due to its similarity to traditional raw filtration processes [36]. The pore sizes are generally in the range of 0.1–



**Figure 9.1** Filtration spectrum of membranes.

10 µm in microfiltration membranes; low pressure helps in the microfiltration separation usually at a differential within 2 bar [37]. These characteristics are restricted to its implementation in the textile industry. Microfiltration is generally used for the separation of colloidal dyes from the exhausted dye bath and discarded rinsing bath discharge and particles suspension; Microfiltration membranes still let the unconsumed auxiliary chemicals, dissolved organic pollutants, and other soluble contaminants escape with the permeate [38, 39]. Therefore, microfiltration is not often used as an unassisted autonomous treatment technique for remediation of complex industrial wastewater such as textile effluents. It is generally applied as a pretreatment step in mixed systems to fully complement the other consequent processes that normally target dyes and other soluble pollutants but fail to remove the suspended particulate matter present in wastewater. Textile wastewater treatment performances were compared by using coagulation/flocculation/NF and microfiltration/NF, and it was noticed that for the same volume reduction factor (VRF), of about 8, the NF permeate flux obtained for feed pretreated by microfiltration [34]

L/h m<sup>2</sup>) was high and the permeate flux is 14 L/h m<sup>2</sup> in feed effluent pretreated using coagulation/flocculation. Microfiltration is also used as a posttreatment step while treating industrial effluents [40]. A single reactor was designed by combining electro-oxidation using a boron-doped diamond (BDD)/Ti anode and ceramic membrane microfiltration to remove soluble organic matters and suspended particulate matters at the same time, comprising AY-36 azo dye and kaolin, respectively, of the model textile wastewater [38].

### 9.3.2 Ultrafiltration Process

Ultrafiltration is mostly used for the separation of macromolecules and colloids from a solution [36, 37]. Being immensely successful in dealing with contaminants present in wastewaters discharged from various chemical, food, and pharmaceutical industries [41, 42], the ultrafiltration membrane process has confined applications in the textile industry because the molecular weights of the dyes present in the colored textile discharge are much lower than the molecular weight cutoff (MWCO) of the ultrafiltration membranes [43]. Accordingly, the dye rejection from ultrafiltration alone generally does not exceed 90% [44], though higher percentages of dye retention and COD removal have been reported for hydrophobic ultrafiltration membranes, such as poly(ether sulfone) and poly(vinylidene fluoride) (PVDF) ultrafiltration membranes [45, 46]. Ultrafiltration is generally applied as a pretreatment step for systems demanding a high degree of process stream purification; it's followed by processes like NF and RO stages, which satisfy the demands of process water quality [47].

Many innovative measures are examined with the objective to enhance the performance exhibited by the ultrafiltration technique in treating textile wastewaters.

Different people have carried out different investigations. For example, Marcucci et al. [30] used flat ultrafiltration membranes, which operate under vacuum (engineered modules), and Koseoglu-Imer [48] used polysulfone (PS) membranes at different evaporation temperatures by the phase inversion process and examined the observed consequent variation in the properties and textile effluent

removal efficiencies of the as-fabricated membranes. Some other novel mechanisms are reported, such as polymer/polyelectrolyte-enhanced ultrafiltration (PEUF), which involves the complexation of dyes with high-molecular-weight polymers, followed by ultrafiltration [49, 50]. In an ultrafiltration pilot plant applied to the study of the effect of varying cross flow velocities on the performance of ceramic membranes (three commercial membranes) with MWCOs of 30, 50, and 150 kDa, respectively, the three commercial membranes successfully removed 99% of the turbidity and the retention percentage of the color components ranged between 84% and 98%. The observations of ultrafiltration ceramic membranes indicate that they can be executable pretreatment alternatives for textile wastewater management. The beneficial prospects of ceramic ultrafiltration membranes have actuated the participation of many researchers; a consequence of the extended experiments has been lately to formalize the suitableness of these membranes in treating of refractory effluents in textile wastewaters. Zuriaga-Agustí et al. examined the separation efficiency and fouling propensity of tubular ceramic ultrafiltration membranes utilized to treat imitated textile wastewater determined by a binary foulant system [51].

### 9.3.3 Nanofiltration Process

The NF process is placed between two processes, such as ultrafiltration and RO [37]. The popularity of the NF process has grown over the years because its effectiveness and simplified textile effluent treatment technology can be assigned many benefits in terms of environmental pollution suspension, reduction, recovery and recycling of textile dyes, divalent salts and other auxiliary chemicals, and recovery and recycling of saltwater. That being the case, the production quality permits the reuse of treated wastewaters in some major processes, such as dyeing and finishing [39]. The NF process runs at a comparatively low pressure (range 500 to 1000 kPa); it is capable of low retention of monovalent ions, which increases the range for low saltwater rejection and reuse while allowing almost 100% rejection of multivalent ions, hence showing high solute selectivity. Charge repulsion and steric hindrance are responsible

for the rejection of species in NF and also high solvent permeability, retention of dissolved uncharged solutes (such as organic molecules) with molecular weight greater than 150 Da, lack of the need for chemical cleaning, modular construction facilitating scale-up, and the ability of NF membranes to resist high temperatures (up to about 70°C), which reduces the energy consumed to heat fresh water [44, 52]. Many investigations have been examining the various options available for the improvement of the NF process performance in textile effluent treatment. Khouni et al. (2011) and Yu et al. (2012) analyzed the execution of submerged NF of an aqueous solution of anionic dye through sodium carboxymethyl cellulose/polypropylene (PP) thin-film composite hollow-fiber membranes [1, 52]. Barredo-Damas et al. [47] examined the execution the six different spirally wound NF membranes, namely TFC-SR2, ESNA, NF270, DS-5 DK, DS-5 DL, and Duraslick, for treating secondary textile effluents. The demeanor of all six NF membranes was studied around a broad scope of volume concentration factors (VCFs). It was found that commercially available NF membranes are negatively charged at normal operating conditions, with a low value pH isoelectric point [53].

Positively charged NF membrane and their potential applications have led to a revival of interest. In the field of color removal from dilute wastewater obtained from textile industries, positively charged NF membranes hold particular promise because of their prominent hydrophilicity and high retention capacity of multivalent cations, which eases the recovery of rejected dyes and reusable cationic macromolecules. For example, an unconventional self-assembled positively charged NF membrane (PA6DT-C), fabricated in the Swansea laboratory, was characterized and its performance evaluated on the basis of the extent of methylene blue (MB) retention and recovery from imitated dye house wastewater [54].

### **9.3.4 Reverse Osmosis**

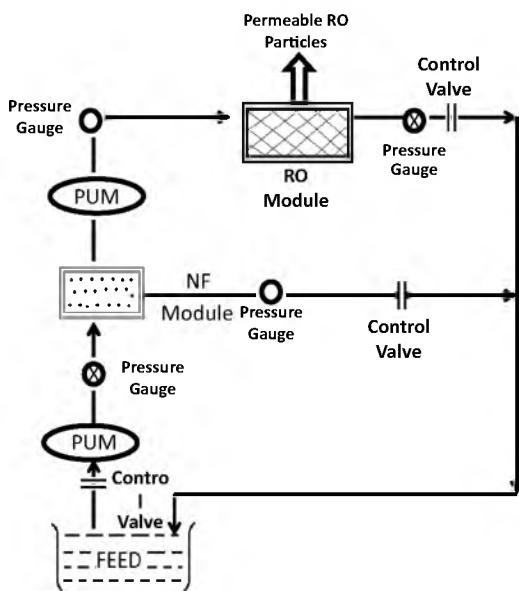
For the removal of macromolecules and ions from textile discharge RO is effectively used; the treated effluent obtained from textile

industries generally has low salinity and lack of color [39]. So far, the use of dense polymeric membranes and also the high osmotic pressure buildup because of the presence of high salt concentrations significantly define the pass-through flux, and occasionally serious fouling takes place that affects the membrane performance. Therefore, in RO, transmembrane pressures larger than 2000 kPa are necessary to keep up affordable percolate flux, which once more deals a severe blow to the economics of the method [44].

The effectiveness demonstrated by NF and RO in dealing with biologically remediated textile effluent is supported by analysis of the percolate quality obtained from each of the processes; the percolate was tested for percolate flux, COD and BOD removal, and salinity content. By using BW30 RO and NF90 NF flat-sheet membranes, cross flow filtration tests of the textile effluent were carried out over a wide range of concentration ratios and under different hydrodynamic conditions. Both treatment processes satisfied the reclamation criteria, and the reusable water quality was good. Therefore, the yield with each membrane is cost-economic in terms of washing, dyeing, water saving, and minimizing energy consumption [55].

The difference between NF and RO is based on the performance detail after carrying out a comparative study based on the rejection efficiency of the NF and RO modules. Therefore a pilot plant has been established to assess the strength of spiral-wound NF and RO modules. It covers a limited contaminated wastewater mixture of color and  $\text{Na}_2\text{SO}_4$  and salt rejection, over variable feed concentrations and feed pressures with methyl orange (MO) as the model dye compound. Figure 9.2 shows the schematic chart for NF and RO modules.

MO rejection obtained by RO (99.99%) was marginally higher than the rejection brought about by NF (99%); the marked fall in percolate flux can perhaps be assigned to concentration polarization and membrane fouling. Furthermore, in both NF and RO experiments the rates of conductivity, TDS removal, and sodium retention are similar in all content [56].



**Figure 9.2** Schematic diagrams of nanofiltration and a reverse osmosis pilot plant.

## 9.4 Conclusion

These days the textile industry is progressing toward advanced operations such as membrane-based treatments, which would play an important role in reclaimable textile effluents. The quality of the effluent is influenced by the selection of the appropriate membrane-based method, characteristics of the membrane, providing high-quality water, and the cost spectrum. To conclude:

- For separation, no phase change is required in the membrane process except in the evaporation of the colloidal solution. For this reason energy requirements for driving the permeating components across the membrane are low.
- Membrane processes separate at the molecular scale to a scale at which particles can be visualized; this means that a very large number of separation needs might really be met by membrane processes.

- Membrane processes produce premier-quality treated effluents that can be directly reused in the primary textile steps, such as dyeing, which demand clean and consistent supply of soft water.
- Membrane processes present basically single or hybrid treatment schemes. There are no moving parts (except for pumps or compressors), no complex control schemes, and little ancillary equipment compared to many other processes. As such, they can offer a simple, easy-to-operate, low-maintenance process option.
- Using a membrane-based technique requires the use of relatively simple and nonharmful materials, which is potentially better for the environment and the textile industry also.

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## **Chapter 10**

# **Green Materials from Plant Sources for the Remediation of Methylene Blue Dye: An Emerging Wastewater Treatment Technology**

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The global problem of water pollution is increasing with each coming day. The effluents discharged from industries, especially textile industries, act as a prominent source of pollution in developed and developing countries. The colored water discharge contains large quantities of dyes, which due to their complex structure are not biodegradable and are harmful to the environment as well as human health. Methylene blue, being one such cationic dye, has adverse effects on living organisms. This chapter discusses the use of untreated and treated plant materials as bioadsorbents for methylene blue dye remediation.

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## 10.1 Introduction

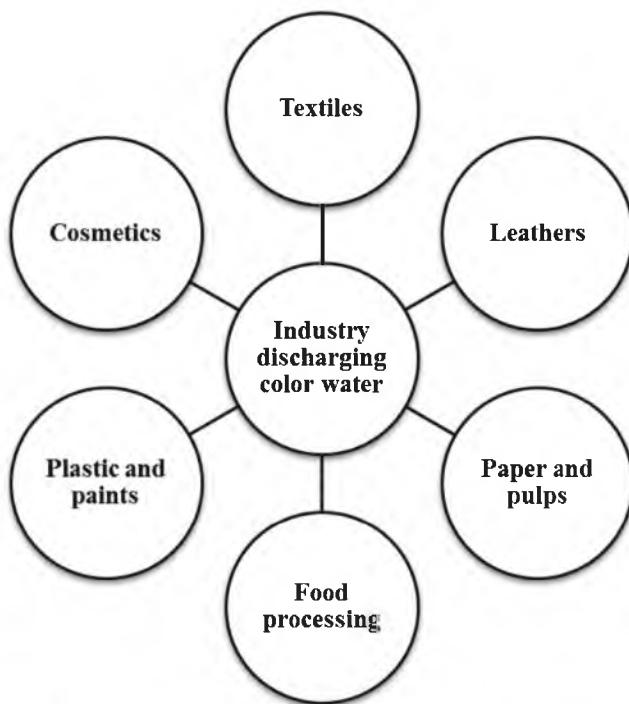
Almost 70% of the earth's surface is covered with water, but only a small percentage of it is fresh water, fit for human consumption, which equals only 3%. About two-thirds of the fresh water is present in the form of frozen glaciers and thus unavailable for human consumption. The remaining one-third is used by human beings in various ways [1]. However, increasing population, urbanization, agricultural activities, rapid growth of large-scale and small-scale industries, and other economic activities are imposing a huge demand on the freshwater supply, which is already limited. The imbalance between demand and supply has led to a great shortage of water resources, which is likely to become more critical in the coming time. Furthermore, industrial and domestic wastewater is being released into fresh water without proper treatment, which is causing contamination of fresh water and thus further limiting the quality and quantity of fresh water available for consumption [2].

## 10.2 Colored Water Discharge

Various industries discharge large quantities of colored pollutants annually into the water bodies and thus degrade water quality. Textiles, plastics, paper and pulp, leather, food, and cosmetics industries discharge colored wastewater (Fig. 10.1) into water bodies without adequate treatments. The discharged colored wastewater contains hazardous dyes, which create serious environmental problems and affect human health [3].

A dye can be understood as a substance that imparts color when applied to a substrate by a process that brings about modifications, even if not permanent, to the crystal structure of the coloring substances [4, 5]. Such substances, having considerable ability to color, are used widely in the pharmaceutical, paper, textile, cosmetics, plastics, photographic, and food industries [6, 7]. A dye consists of clusters of atoms called chromophores, which are responsible for providing the color of the dye. These centers containing chromophores have different functional groups

present, such as azo, carbonyl, methine, nitro, anthraquinone, and aryl methane. In addition to this, dyes have electron donating or withdrawing substituents that develop or intensify the color of the chromospheres and are called auxochromes. Some common auxochromes are hydroxyl, amine, sulphonate, and carboxyl [8, 9] (Table 10.1).



**Figure 10.1** Discharge of colored water from various industries.

Dyes generally possess aromatic molecular structures that are complex and thus are highly stable and are not easy to biodegrade. Also, many of these dyes have toxic effects on various microorganisms and thus cause inhibition or directly destroy their catalytic abilities [10]. They inhibit sunlight penetration into the stream of water, affecting the photosynthetic activities of algae and thus seriously affecting the food chain [11].

**Table 10.1** Identification of chromophores and auxochromes in various dyes

Dyes	Chromophore	Auxochrome	Structure
Methylene Blue		Amine $(\text{CH}_3)_2\text{N}-$	
Congo Red		Amine $(-\text{NH}_2)$ Sulfonate $(-\text{SO}_3^-)$	

Dyes	Chromophore	Auxochrome	Structure
Rhodamine B 	Amine [(CH <sub>3</sub> ) <sub>2</sub> N-] Carboxyl (-COOH)	Pyrilium	
Methyl Violet 	Aryl (C <sub>6</sub> H <sub>4</sub> ) <sup>2+</sup>		

Because of their structural layout, dyes have a high potential to resist any fading on being exposed to water and light. They are not aesthetically pleasing and affect the visibility and quality of water [12]. They can cause allergic reactions to skin, eyes, mucous membrane, etc. They are mutagenic, carcinogenic, and/or toxic to life [13].

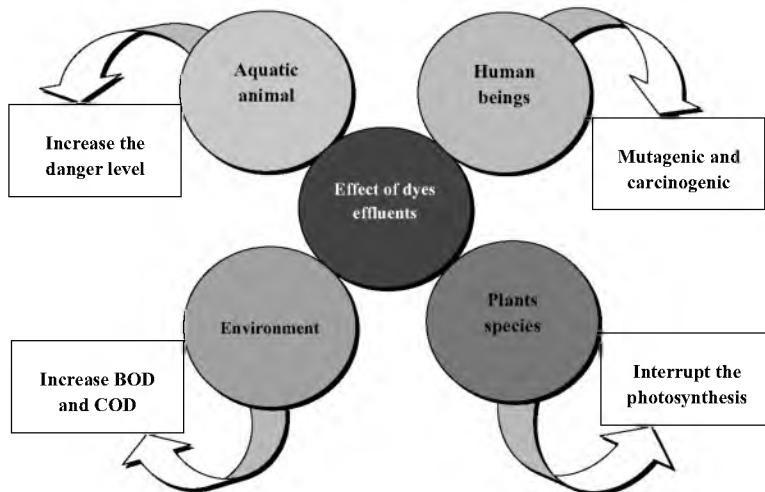
### **10.3 Effluents from the Textile Industry**

The textile industry uses pigments and dyes to color a material. There exist more than 10,000 dyes, which are easily available commercially, with more than  $7 \times 10^5$  tons of dyed stuff being produced annually [14]. Different dyes are being used in textile industries, which may be acidic, basic, direct, and reactive dyes [15].

The major operations performed in a textile processing industry are mercerizing, desizing, scouring, bleaching, finishing, dyeing, printing, and neutralizing [16]. In the textile industry, tons of dyes are lost as effluents each year, generated from the bleaching and washing of fibers and from the finishing and dyeing process, due to the inefficient industrial process [17]. The various dyes have high stability against temperature and light and also have high chemical complexity and diversity, and they are not properly treated in wastewater treatment plants [18]. Thus, unfortunately, many of the dyes easily escape the treatment steps and are retained in the surroundings [19]. Also, in the manufacture of textiles, antimicrobial agents are added to prevent their biological degradation, mainly for cotton and other natural fibers [20]. The complex aromatic structure and synthetic origin of dyes make them more stable toward biodegradation [21, 22].

The textile industries utilize a large amount of water resources in their various processes, mainly in the dyeing and finishing processes. The effluents generated from textile processes are one of the most highly polluting among the various industrial sectors, taking into consideration the large volume of the effluents generated and their composition [23, 24]. Also, there has been a huge increase in the demand for products from the textile industry and thus a proportional increase in their production and increase in the usage of synthetic dyes, which contributes to dye effluents being one of the main sources of severe pollution.

Textile wastewaters are characterized in terms of various parameters, like chemical oxygen demand (COD), biochemical oxygen demand (BOD), color, pH, and salinity. In textile wastewater, the presence of even little amounts of dyes (even less than 1 mg/L for certain dyes) in the water is clearly visible and affects the aesthetic quality and clarity of water bodies, such as rivers and lakes, leading to huge damage to aquatic surroundings [6, 25, 26].



**Figure 10.2** Effects of colored stuffs.

It has been calculated that during the dyeing process the colorants lost to the surroundings can reach 10%–50% of the used amount [27, 28]. Moreover, it should be noted that dyes reduce penetration of light and photosynthetic activity of underwater organisms, causing oxygen deficiency, whereas certain dyes are mutagenic and toxic and limit the uses downstream, like drinking water and water for irrigation (Fig. 10.2) [29].

The numerous studies undertaken to evaluate the negative impacts of colorants on the ecosystem can be listed as follows: (i) dyes can cause chronic and/or acute effects on organisms exposed to them depending on the concentration of the dyes and the exposure time; (ii) dyes are largely visible inherently, and slight discharge of effluents may cause coloration of surface water, which will seem abnormal; (iii) dyes have the ability to reflect/absorb sunlight reaching the water bodies, which has negative effects on bacterial

growth, altering their biological activity; (iv) dyes have complicated and different molecular structures, and thus it is problematic to treat them with general wastewater treatment operations; (v) dyes present in effluents undergo biological and chemical changes, taking up dissolved oxygen from the water bodies and harming the aquatic environment; (vi) dyes also have an ability to sequester metal ions, leading to microtoxicity to aquatic organisms; (vii) dyes have a tendency to increase the biological oxygen demand of water [30, 31]. Considering the harmful impacts the waste generated from textile industries and processes has received a great amount of attention in the last few years since it can lead to the generation of great volumes of effluents, which, if not properly treated prior to being discharged into water bodies, can be a great environmental problem, as mentioned above.

Effluents discharged from the textile sector are highly complex as they have many dyes and their derivatives might change per season, further increasing the challenge to find useful treatment methods. These industries generate wastewater that is colored with a high organic load that contributes greatly to the pollution of the surface water if treatment plants do not treat the discharge effectively before disposing of it into the water bodies [32]. The intake of water polluted with textile dyes by humans and other living creatures can lead to damage to their health due to its high toxicity and the mutagenicity of its components [33, 34]. Thus, treatments that are efficient and economical than the ones currently present are needed.

## **10.4 Specific Dye: Methylene Blue**

Methylene blue (MB), prepared for the first time by Heinrich Caro in 1876, also called methylthioninium chloride, is used as a dye in textile industries. It is a phenothiazine derivative having a heterocyclic aromatic structure. It is a cationic dye that appears as a solid, odorless, dark-green powder at room temperature and gives a blue solution on being dissolved in water. The hydrated form of MB has three molecules of water. MB is basic in nature and in water at 25°C has pH 3 [35].

MB is commonly used for dying wool, cotton, and silk. On being exposed to it, it can cause burns, which may lead to temporary or

permanent injury to the eyes of animals and human beings. On inhalation or through ingestion, it causes difficulty in breathing and can cause nausea, along with producing a burning sensation and leading to profuse sweating, vomiting, confusion in mental coordination, and methemoglobinemia. Exposure to acute quantities of MB causes increased heart rate, vomiting, Heinz body formation, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans. Hence, its removal from water is important for the safety of human beings and animal [36–38].

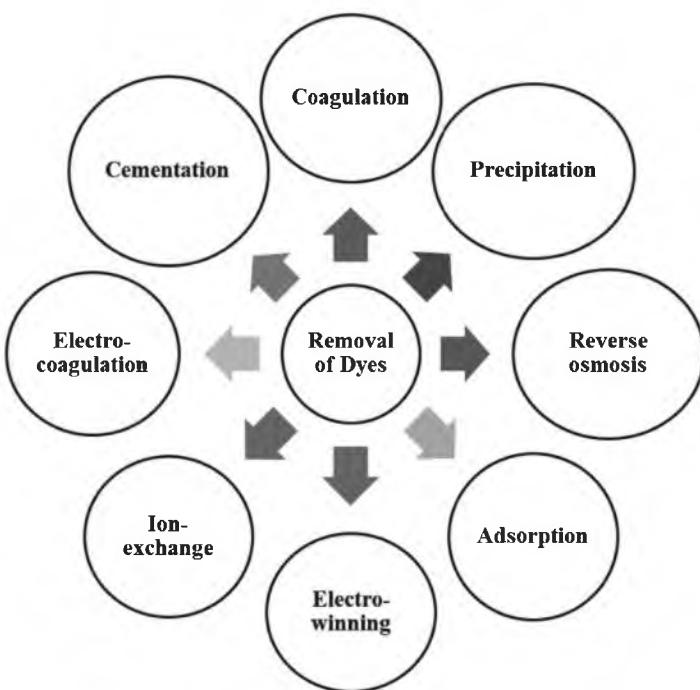
## 10.5 Dye Remediation

There are many conventional methods of dye removal, such as oxidation or ozonation, coagulation, flocculation, ion exchange, and membrane separation (Fig. 10.3) [39]. But most of these methods are not used much because of the high cost of installation and maintenance, making them economically unfavorable [40]. Moreover, coagulation and chemical and electrochemical oxidations are usually not feasible on a large scale. Thus, the various physical and chemical processes being used to treat dye-laden effluents or wastewater are costly and cannot effectively be applied to treat the wide range of dye effluents [41–43].

The most commonly used methods for dye removal or the removal of color from wastewater are biological and chemical precipitation. However, these processes are efficient and economical only when the concentration of the solute is relatively high [44–46].

## 10.6 Adsorption for Dye Remediation

On the other hand, the simple technique of adsorption is by far the most flexible and widely used. This is due to its cost effectiveness, simple design, abundance, highly efficient nature, ease of handling, biodegradability, and ability to treat dyes that are present in more concentrated forms [47, 48]. This has laid the path for researchers to look for adsorption that is inexpensive and efficient in the removal of dyes. The materials used as adsorbents include coal, fly ash, wood wastes, agricultural wastes, silica gel, and clays. These materials have been used with varying efficiency in dye removal [49].



**Figure 10.3** Various decolorization methods.

Not only does the adsorption capacity of the adsorbing material depend on the adsorbent's textual or porous structure, but it is also altered by the chemical nature of the surface of the adsorbent [50]. On the surface of the adsorbent, there may be saturated valences that are incomplete and/or certain functional groups and unpaired electrons that influence the attraction force of the surface and thus the adsorption capacity, especially when more and more amount of adsorbate is taken up onto the adsorbent surface via chemisorption [51]. Some of the commonly used adsorbent materials are metal hydroxides, alumina, silica, and activated carbons. It has been proved by researchers that usage of activated carbon for removal of dyes is effective and the first choice as adsorbent for the removal of all types of water pollutants. However, its generation and difficulties in regeneration make it expensive [52]. The use of carbon in the form of activated carbon or charcoal has been there since antiquity for many applications.

Activated carbon refers to carbon that is produced by carbonaceous materials, like coconut husk, nutshells, coal, wood, lignite, coir, peat, and petroleum pitch [53]. It can be prepared by physical and chemical activation of the above-mentioned source materials. It is prepared in such a way that it exhibits a high level of porosity and a surface area that is enhanced or enlarged [54]. The properties of the carbon material, such as pore and particle size, chemical nature of the surface, and surface area, influence the effectiveness of adsorption. The properties of the adsorbate are also of importance. Compounds that have low solubility in water have a higher likelihood to be adsorbed to the activated carbon. A second property is the tendency that a given adsorbate has with the surface of the carbon. This tendency depends on the charge present on an adsorbate and is greater for species having less charge. Thus, activated carbon is being used largely as an adsorbent because of its large surface area, high adsorption capacity, and microporous structure [55].

Furthermore, it is a largely used adsorbent for MB remediation since activated carbons have large specific surface area and large specific surface reactivity. Sadly, its use for dye remediation is limited because of its cost ineffectiveness [56]. Also, it has a high cost of maintenance. Also for a given adsorbate a specific source material must be used for the formation of activated carbon to have high efficiency of adsorption.

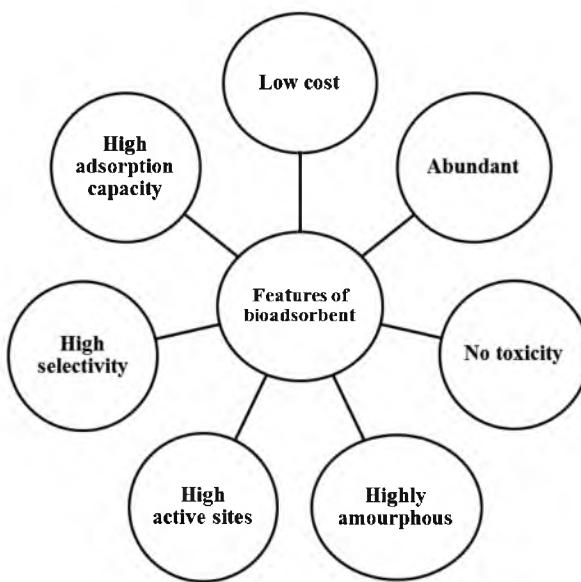
To move toward sustainability of dye treatment technology, finding adsorbents that are sustainable is necessary. Varieties of sustainable adsorbents have been developed where bioadsorbents have a striking potential for dye remediation [57]. Biosorbents have carboxyl, carbonyl, sulfhydryl, sulfonate, phosphonate, and hydroxyl groups present on their surfaces, which bind contaminants through these groups in the adsorption process [58].

## 10.7 Bioadsorbents

The accumulation and concentration of dyes on the surface of an adsorbent from an aqueous solution using biological substances is termed as bioadsorption. Often, bioadsorbents are more selective in their action than traditional ion-exchange resins and commercially

available activated carbon and can limit dye concentration to low parts per billion (ppb) levels. Bioadsorption is an economic, ecofriendly approach that is even effective in the presence of competitive ions (Fig. 10.4).

Biomass as a method for water treatment was first introduced by Arden and Lockett in the 1900s, in which they made use of cultured bacteria to recover nitrogen and phosphorus from raw sewage [59]. The environmental pollutant cleanup methodology, which makes use of living organism, is referred to as bioaccumulation, which in the 1970s was termed as biosorption when researchers discovered dead biomass as a tool for water treatment [60].



**Figure 10.4** Features of bioadsorbents.

Attention of researchers went to the abundantly found plants as an alternative for expensive material that adsorbs the dyes present in wastewater. Plant biomass, plant waste, and chemically modified plant materials have a variety of advantages over other adsorbents, including low cost, wide availability, and high sorption capacity with no toxicity.

A lot of research has been done on biosorption but less on the treatment of dyes. Researchers have found that bioadsorption of dyes

onto the cellulosic surface of plants is an economical process [61]. Untreated aquatic plant species, such as *Eichornia* species, *Pistia stratiotes*, *Lemna* species, and *Salvinia* species, could be utilized for the treatment of water [62]. A variety of discarded wastes have been utilized for water treatments [63]. Ronbanchob and Prasert have reported that bioadsorbents may also be derived from nonliving biomass, algal biomass, and microbial biomass [64]. However, the development of sustainable adsorbents based on plant has become a great concern for researchers. Biosorption, by utilization of a green adsorbent based on plant material, has emerged as an ecofriendly and sustainable water treatment technology, particularly suitable for dyes and considered as an alternative pathway for expensive and nonecofriendly water treatment technology.

## 10.8 Biosorption of Methylene Blue

Biosorption is a physiochemical process in which natural plants permit MB to accumulate onto their cellular structures. Plant materials, having a cellulosic surface, attract MB strongly from water.

In 2006, Hamdaoui [65] used cedar sawdust and crushed brick for the liquid-phase adsorption of MB by batch study. Adsorption isotherm and kinetic data were determined at 20°C, and the conclusion drawn showed that Langmuir isotherm equation with maximum adsorption capacity were 142.36 and 96.61 mg/g for cedar sawdust and crushed brick, respectively. Both film diffusion and particle diffusion kinetics fitted well with the given adsorption data.

Similarly, leaves of the phoenix tree have been used as an adsorbent for MB dye remediation. The leaves of this tree contain large amounts of floristic fiber, protein, and functional groups (like carboxyl, hydroxyl, and amidogen), which makes biosorption process possible. On increasing the temperature, its biosorption capacity increased from 80.90 to 83.80 and then to 90.70 mg/g at temperatures 295, 305, and 323 K, respectively [66].

Hameed and Hakimi [67] investigated jackfruit peel as bioadsorbents for MB remediation. They found that the percentage of dye removal was dependent on the amount of adsorbent used. On increasing the amount of adsorbent, the percentage of dye removal increased. The optimum pH value for effective dye adsorption was

found to be 4. The sorption capacity of MB on jackfruit peel was calculated to be 281.713 mg/g. The equilibrium biosorption data were analyzed, and it was observed that Langmuir model fitted better. Also, a low concentration of MB favored high adsorption.

Wang et al. [68] reported the usage of by-products of rice bran and wheat bran for determining the capacity and mechanism of adsorption of MB. It was observed and recorded that adsorption is a pH-dependent process for basic dyes. The dye, being basic in nature, on dissociation releases colored dye cation. The surface charge on the surface of the adsorbent influences the adsorption of these positively charged dye groups onto the adsorbent. On increasing the pH higher cation removal was observed. Four kinetic equations—pseudo-first-order, pseudo-second-order, external diffusion, and intraparticle diffusion equations—were used to analyze kinetic experimental data. The experimental data fitted a little better to Langmuir isotherm than to Freundlich isotherm for MB adsorption. It was also observed that the capacity of adsorption decreased with an increase in the concentration of the adsorbent. This is due to intraparticle interaction and the reason that some of the adsorbent sites remained unsaturated during the adsorption process.

Agricultural wastes of various crops have been utilized for the removal of MB [69, 70]. Hameed and Ahmad [70] investigated adsorption capacity of garlic peel for MB remediation from an aqueous solution. The experimental data were fitted to and analyzed for Langmuir, Freundlich, and Temkin isotherms. The maximum values of monolayer adsorption capacities were found to be 82.64, 123.45, and 142.36 mg/g at 303, 313, and 323 K, respectively. It has been observed that for MB, the adsorption capacity was higher due to the presence of functional groups that were polar.

Zhou et al. [71] used the natural peach gum (PG) as an adsorbent for the removal of MB and methyl violet (MV) from aqueous solutions. Within 5 min., 98% of the MB and MV were removed from the aqueous solution using PG. The pseudo-second-order kinetic model explained well the kinetics of the reaction. The Langmuir isotherm model explained well the maximum adsorption capacity. PG was regenerated in the acidic solution and was utilized for five continuous cycles of desorption-adsorption.

Similarly, Bouaziz et al. [72] performed the batch experiment using almond gum as an alternative adsorbent to remove MB

dye from an aqueous solution under various conditions, such as different doses of almond gum (0.05–2.0 g), contact times (up to 240 min.), pH solutions (3–10) and initial concentrations (20–200 mg/L), temperatures (303.16 K, 313.16 K, and 323.16 K), and rates of agitation of the sample (up to 250 rpm). The adsorbent was characterized using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) techniques. The isothermal data for the experiment fitted well with the Freundlich isotherm ( $R^2 = 0.99$ ), with adsorption capacities 250, 333.33, and 500 mg/g as the maximum values at temperatures of 303.16, 313.16, and 323.16 K, respectively. The kinetics of MB onto almond gum followed closely the pseudo-second-order kinetic model. The thermodynamic results showed that the process was endothermic and spontaneous.

Tanzim and Abedin [73] utilized the low-cost pomelo peels for the removal of MB from aqueous solution. For pomelo peels, maximum removal of 93.5%–94.8% was recorded at adsorbent mass of 10 g/L at pH 6.5 and contact time of 180 min. Similarly, *Cedrela odorata* seed chaff (COSC) was utilized for the removal of four different dyes, MB, MV, Congo red (CR), and methyl orange (MO), from aqueous solutions [74]. The adsorption experimental data obtained from a batch experiment were well fitted to the Fritz-Schlunder four-parameter isotherm model and the fractal-like pseudo-second-order (three-parameter) kinetic equation. The maximum value of monolayer adsorption capacities for MB, CR, MV, and MO were increased from 88.32 to 111.88, 79.46 to 128.84, 75.11 to 121.23, and 57.35 to 68.23 mg/g, respectively, as the temperature was increased from 298 to 318 K.

## 10.9 Modified Bioadsorbents

The use of plant materials or untreated plants as bioadsorbents have shown good results for the adsorption of MB from wastewater. However, the major problem with untreated plants is that they may increase the biological oxygen demand, the COD, and the total organic carbon (TOC) of water, which causes reduction of the oxygen content in water and deteriorates its quality by releasing water-soluble natural compounds found in plant material [75]. To overcome this, treated or modified plant materials or biomass and wastes have been investigated as green adsorbents for dye removal [75].

In 2012, tartaric acid-modified Swede rape straw (SRSTA), *Brassica napus* L., was also used to remove MB from an aqueous solution at different operational conditions, such as different initial concentrations of MB, adsorbent doses, temperatures, and pH values [76]. The equilibrium data fitted well to the Langmuir isotherm model, and the value of the maximum monolayer adsorption capacity of SRSTA was 246.4 mg/g. Similarly, oxalic acid-modified Swede rape straws (*Brassica napus* L.) have been used for MB removal from water [77]. The maximum adsorption capacity, 432 mg/g, was calculated by the Langmuir model.

The effectiveness and mechanism of bamboo charcoal (BC) and microwave-modified BC (BC-MW) for remediation by adsorption of MB and acid orange 7 (AO7) from aqueous solutions were also studied. Bioadsorbents BC and BC-MW have shown excellent adsorption of both dyes, MB and AO7 [78]. Chen et al. [79] utilized the activated carbon obtained from NaOH-pretreated rice husks, having an extremely high surface area of  $2028\text{ m}^2\text{ g}^{-1}$  and integrated properties. The morphology and chemistry of the surface of activated carbons were characterized using FTIR,  $\text{N}_2$  sorption, a transmission electron microscopy (TEM), an X-ray photoelectron spectroscopy (XPS), a SEM, etc. A batch experiment was performed to investigate their adsorption capacities toward MB. The adsorption experimental data were explained well by the Langmuir isotherm model and the pseudo-second-order kinetic model, where the maximum monolayer capacity was 578 mg/g.

Recently, Abdolalia et al. [80] incorporated various literatures on modified and nonmodified waste for MB remediation in their review paper. Treated and untreated *Phragmites australis* was utilized as a bioadsorbent for MB [81]. The adsorption process was conducted in a batch manner under the influence of various parameters, like initial pH, initial concentration of dye, and contact time. The maximum monolayer adsorption capacities of the raw and modified *Phragmites australis* were found to be 22.7 and 46.8 mg/g at an initial concentration of MB of 250 ppm, a biosorbent dosage 0.25 g, and an initial dye solution of pH 6.5, respectively. The kinetics data

of adsorption for the experiment followed the pseudo-second-order kinetic model. Both raw and modified biomass showed that the adsorption process of MB was a favorable and spontaneous process.

Raw *Salvia mitiorriza* Bge (SM) and citric acid- and  $\text{Na}_2\text{CO}_3$ -modified *Salvia mitiorriza* Bge (SM) were used as biosorbents for MB from polluted water [82]. A batch experiment was carried out, and the obtained experimental data were well described by Langmuir isotherm and the pseudo-second-order kinetic model. The citric acid- and  $\text{Na}_2\text{CO}_3$ -modified *Salvia mitiorriza* Bge (SM) have shown 161.29 and 178.57 mg/g of monolayer maximum adsorption capacity, respectively, while raw *Salvia mitiorriza* Bge (SM) has shown the maximum removal capacity of 100 mg/g.

Recently, a sesame straw (*Sesamum indicum* L.) was functionalized through treatment with carboxylic acid (SSCA) and utilized for dye remediation [83]. Adsorption experimental data obtained from the batch experiment were fitted to the Langmuir model. The maximum monolayer adsorption capacity of SSCA was 650 mg/g for MB. The excellent dye adsorption capacity of SSCA was because of the introduction of ester groups during citric acid modification and the tubelike structures.

*Cortaderia selloana* flower spikes (FSs) and *Cortaderia selloana* FS-derived carbon fibers (CFs) are applied to batch experiment for MB remediation from wastewater [84]. CF material was developed by the calcination method of *Cortaderia selloana* FSs. The *Cortaderia selloana* FS-derived CFs have shown enhanced MB removal performance, with maximum adsorption capacity of 114.3 mg/g, which was almost three times higher than that of *Cortaderia selloana* FSs. The reaction was well defined by the Langmuir model and the pseudo-second-order model. The reaction was spontaneous and endothermic in nature. These are the recently used bioadsorbents that could potentially remove various dyes, particularly MB, from wastewater and aqueous solutions. The uniqueness of these is their low cost, abundance in nature, and environmental soundness. A comparative study of used bioadsorbents for MB is given in Table 10.2.

**Table 10.2** Various tested plant materials (2006–2017) for MB remediation from water

S. No.	Year	Adsorbent	Modification	Efficiency (mg/g)	Refs.
1.	2017	<i>Cortaderia selloana</i> flower spikes	Raw	40	[85]
2.	2017	Sesame straw	Carboxylic acid	650	[83]
			$\text{Na}_2\text{CO}_3$	178.57	
3.	2016	<i>Phragmites australis</i>	Raw	22.7	[81]
			Chemically treated	46.8	
4.	2016	<i>Cedrela odorata</i> seed chaff	Raw	111.88	[74]
5.	2015	Almond gum	Raw	500	[72]
6.	2014	Waste tea	Citric acid	212.77	[80]
7.	2013	Swede rape straw	Oxalic acid	432	[79]
8.	2013	Rice husk	NaOH	478	[78]
9.	2012	Swede rape straw	Tartaric acid	246.4	[76]
10.	2009	Garlic peel	Raw	142.36	[70]
11.	2008	Jackfruit peel	Raw	281.71	[67]
12.	2007	Phoenix tree leaf	Raw	83.80	[66]
13.	2006	Cedar sawdust	Raw	142.36	[65]
14.	2006	Crushed brick	Raw	96.61	[65]

## 10.10 Conclusion

In a nutshell, the limited freshwater resources present on the earth's surface for human consumption are degrading in quality as well as quantity due to the ever-increasing industrial effluents being discharged in water. The effluents from textile industries have large quantities of dyes in them, which are harmful. Various methods have been used for dye remediation but are not found suitable due

to various reasons, like high cost and complex instrumentation. The method of adsorption is found to be quite effective in MB dye remediation. The chapter discusses the use of various treated and untreated plant materials that act as bioabsorbents for better MB dye remediation. These are easily available, low cost, and ecofriendly in nature. Thus, the chapter provided an insight into the capability of green adsorbents or bioadsorbents for MB dye remediation.

## 10.11 Future Prospects

The experimental conditions and results for the treated and untreated plant material used as bioadsorbents for MB dye remediation provide a path for further research and development of bioadsorbents with higher adsorption capacity for MB and various other dyes to reduce the amount of effluents discharged from various industries, especially textile industries.

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## **Chapter 11**

# **Graphene Oxide Nanocomposites for Azo Dye Removal from Wastewater**

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Azo dyes appear in almost all streams of wastewater and are considered as primary pollutants for their mutagenic and carcinogenic properties and biorecalcitrant nature. Recent studies have proved adsorption to be a powerful technique for wastewater treatment as it is inexpensive, easy to perform, and inert to toxic substances. Graphene oxide (GO) is one such example of a new, cost-effective, easy-to-use, and highly efficient adsorbent. The oxygenated groups present on GO surfaces impart it a strong hydrophilic nature, thereby facilitating its exfoliation in both water and other polar organic solvents for the formation of stable suspensions. Previous studies have reported the utilization of these oxygen-bearing groups of GO as nucleation sites of metals or polymers for the synthesis of

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different GO composites. In this chapter, the authors have compiled recent studies addressing the synthesis of different GO composites and their role in azo dye adsorption and established the same as an environmentally benign approach for effluent treatment. Moreover, a detailed discussion of adsorbent characterization, underlying mechanisms, process optimization, environmental implications, and future prospects has also been provided.

## 11.1 Introduction

Dyes have been extensively used for ages in many industries, such as textile, printing, and leather. An inefficient dyeing procedure often results in 10%–15% of the dyes used in industries being wasted and discharged into wastewater [1]. Dye hydrolysis is a major reason for wastage, which takes place when the dye molecule, instead of reacting with the hydroxyl groups of the cellulose, reacts with water. The characteristic lipophilic nature of the dyes enhances these problems. Other factors affecting the wastage of dyes are the type of dye, the procedure of application, and the intensity of the shade desired [2]. The poor biodegradability and water-soluble nature of most of the dyes make them persistent pollutants [3]. Dyes have multiple components and are harmful to the environment in various ways. Dyes consume dissolved oxygen from water and affect aquatic life. Some dyes have also been found to possess toxic or carcinogenic property and can harm human health [4]. In rivers, dyes can cause a significant fall in the quality of water due to their color, which reduces the availability of solar light, affecting the photosynthetic ability of aquatic organisms in turn [5]. Animal and human health can also be adversely affected by the persistence of dyes in water for a long time as they may often contaminate existing food chains.

Dyes have an aromatic molecular structure, which possibly comes from coal tar-based hydrocarbons, such as benzene, anthracene, toluene, naphthalene, and xylene [6]. The color of water can greatly influence public perception, as the existence of unwanted colors is unpleasant and usually related to contamination [7]. Textile dying industries are often found to expel a significant percentage of color

into wastewater. In a previous study, it was reported that up to 1.56 mg dm<sup>3</sup> of dyes can be perceived in watercourses, although in clear water dye concentrations as low as 0.005 mg dm<sup>3</sup> are visible [8].

Since September 1997, environmental policy in the UK has ordered zero synthetic chemicals to be released into the environment [9]. Since then, a considerable amount of concern has been raised in favor of the removal of dye pollutants from wastewater [10]. The Environment Agency, the current regulator of water quality and enforcer of government standards for proper utilization of water resources, assesses the need for color standards and imposes consents where necessary. Standards have been set using a range of colored sewage effluent samples, considering the fact that the human eye has the capacity to detect 1 part per million (ppm) of color [2].

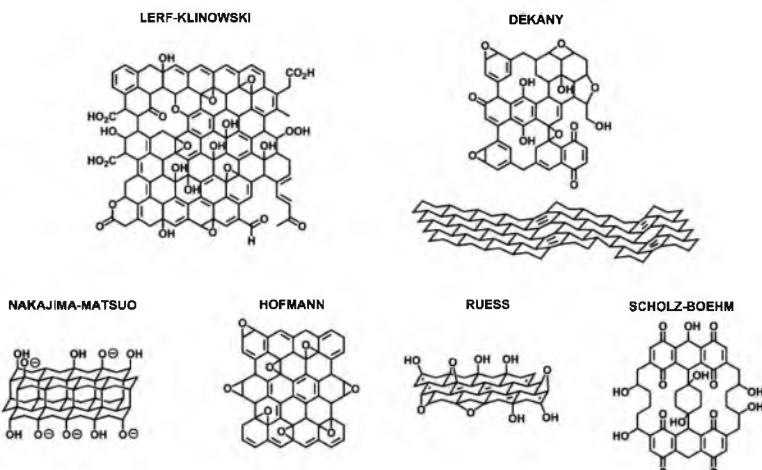
Previous studies have reported many methods, such as biodegradation [11], oxidation [12], ultrafiltration [13], photocatalytic degradation [14], and adsorption [15], for wastewater treatment. Of all other technologies proposed so far, adsorption has been globally recognized as the most promising method for wastewater treatment because of its versatility, wide applicability, and economic feasibility [16, 17]. Usually, the effectiveness of any adsorption process largely depends on the physicochemical properties of the used adsorbent [18]. Hence, it is very important and meaningful to seek new adsorbents with large specific surface areas, high adsorption capacities, fast adsorption rates, and special surface reactivity [19]. There are a lot of reports about the adsorption of some dyes on various adsorbents, such as fly ash [20], sand [21], rejected tea [22], polymers [23], waste pea shells [24], chir pine sawdust [25], water chestnut peel [26], bamboo sawdust [27], mango leaf powder [28], kaolinite [29], and activated carbon with modifications [30–34]. However, in comparison to other adsorbents reported so far, carbonaceous materials have received significant importance due to their nonhazardous and cost-effective synthesis, well-defined and uniform structures, and high mechanical stability [35].

Amidst all other carbonaceous adsorbents reported so far, graphene has received substantial global attention owing to its

2D structure and atomic thickness [36]. Graphene oxide (GO), an oxidized precursor of graphene [37], is decorated with hydroxyl and epoxy groups along its basal plane and carboxyl groups on the edges [38]. Its hydrophilic nature, along with a very high negative surface charge (occurring due to its oxygenated functional groups [39]), has rendered GO highly suitable for adsorption of environmental pollutants. Besides, it has been reported that GO is able to form a monolayer in solution and intercalate water molecules [39]. This layered structure of GO and its oxygenated functional groups were considered highly appropriate for application in adsorption-based water treatment processes.

## 11.2 Structural Models of GO

Various studies have investigated the structural details of GO. Figure 11.1 shows the different structures suggested till date. Of all the GO models shown in Fig. 11.1, the Lerf-Klinowski model has been most commonly accepted though a huge amount of disagreement is still prevailing amidst the scientific community [40]. The multiple structures of GO have arisen from the multiple routes of GO synthesis described by Dreyer et al. [40]. The structure of GO has also been found to depend on conditions of oxidation and the parent precursor employed [40]. In an investigation by Lou et al., graphite used as a precursor substrate was pretreated using potassium peroxodisulfate ( $K_2S_2O_8$ ) and phosphorus pentoxide ( $P_2O_5$ ) [41]. In a separate study, GO was prepared using cokes originating from petroleum and coal [42] and biochar obtained from rice straw biomass [43] as precursors. Hence, GO may be considered as a combination of materials rather than a single compound and should be investigated in terms of parameters like carbon-to-oxygen ratio, conductivity, particle size, spectroscopic features, etc. [40]. Sufficient characterization and nomenclature are also required in order to ensure reproducibility and synthesis-dependent variations [40]. The oxygen functionality of GO is also dependent upon its precursor substrate, conditions of oxidation, and synthesis processes [40]. Hence, identification and quantification of the functional groups coveting GO has been truly challenging.



**Figure 11.1** Proposed structural models of GO. Reproduced from Ref. [40] with permission from The Royal Society of Chemistry.

The most widely accepted Lerf–Klinowski model of GO has two distinct regions, one comprised of lightly functionalized, mostly  $\text{sp}^2$ -hybridized carbon atoms and the other of highly oxygenated, predominately  $\text{sp}^3$ -hybridized carbon atoms [40]. According to this model, the hydroxyl and epoxide functional groups are localized in the basal planes and are clustered as islands amidst lightly functionalized, graphene-like domains while the pH-sensitive carboxylic groups are arranged along the edges of the sheets [40]. The strong oxidizing conditions created for treatment of graphite/any other precursor substrate render the resultant GO both oxidizing and acidic, which promotes the applicability of GO as a catalyst in diverse chemical reactions [40]. A detailed comparative analysis of different synthetic oxidation processes has been provided in a recent report [44].

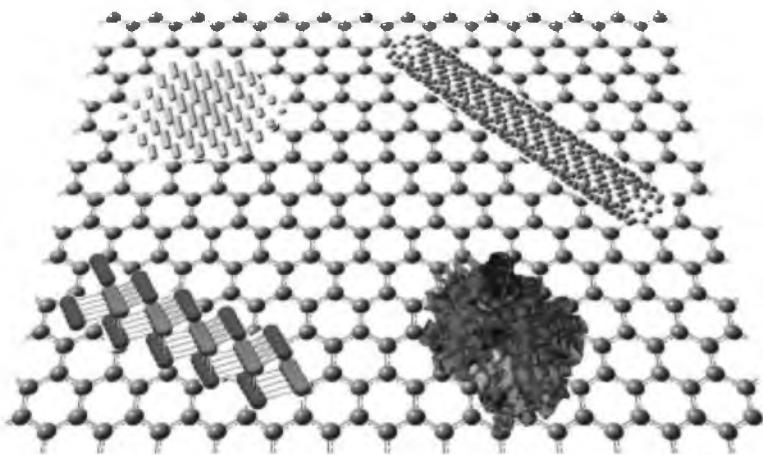
Some of the methods reported for GO synthesis (especially the Hummers and Tour methods) involve sulfur-bearing reagents, like  $\text{H}_2\text{SO}_4$  [40]. Eigler et al. [45], in their study, had reported the effect of sulfur moieties on the structure and physicochemical properties of GO. This study was also the first report of azide functionalization of the GO surface for stabilization of the thermally unstable groups of GO using sodium azide [45]. The reactivity of GO with water was also found to influence GO's stability under ambient condition and time-

dependent changes in GO structure as well [40]. The organic media used as an alternative to the conventional aqueous media used for the purification of GO (also referred to as “pristine GO”) prepared was found to alter both spectroscopic and morphological properties of GO. It also influenced the color of the GO so formed to make it off-white or tan in contrast to the usual brown or black obtained. The significantly reduced water content of pristine GO led to its degeneration when subjected to higher temperatures [40]. However, aqueous-treated GO was resistant to such decomposition [40]. Such reactivity of the functional groups introduced on oxidation of graphite may be considered responsible for controlling the catalytic activities and composite formation behavior of GO so prepared [40].

### **11.3 Synthesis and Functionalization of Graphene Oxide Nanocomposites**

The efficiency of graphene-based nanomaterials as adsorbents is strongly dependent on their ability to be homogenously dispersed in the aqueous phase and their affinity for different pollutants [16]. However, graphene in aqueous suspensions tends to agglomerate and revert to its graphitic structure by restacking [46]. Besides, GO weakly binds to anionic compounds owing to strong electrostatic repulsions operating between them [16]. Additionally, both graphene and GO are not easily separated from treated water and thereby lead to severe recontamination of the same [16].

Chemical functionalization of GO reportedly facilitates dispersion and stabilization of the same by resisting aggregation of GO sheets in suspension [47] and also enhances interactions between GO and various organic and inorganic contaminants [16]. Chemical functionalization of GO may be carried out with metal/metal oxide nanoparticles, organic polymers [16], and even nanoclays [48]. Previous investigations have reported that various polymers and nanoparticles may be directly deposited on graphene sheets without cross-linkers [16], bridged using cross-linkers [48], or inserted amidst adjacent sheets for achieving both higher adsorptive surface area and prevention of sheet aggregation [48, 49]. A schematic representation of functionalization of a graphene sheet with molecule, nano-object, and polymer has been shown in Fig. 11.2.



**Figure 11.2** Schematic representation of a graphene sheet functionalized with a molecule, a nano-object, and a polymer. Reproduced from Ref. [52] with permission from The Royal Society of Chemistry.

The resulting nanocomposite widely differs from its parent components, with totally novel functionalities and properties [16]. These incorporated materials have been reported to increase the distance separating adjacent GO sheets, widen interlamellar capillaries, and ensure higher fluid percolation, rendering the nanocomposite highly efficient for adsorption purposes [48, 50]. Depending on its structure, size, and crystalline nature, the inserted substrate is also found to facilitate high selectivity and stronger bond formation with the target pollutants [16]. The primary objective is the maximum utilization of the combined advantages offered by all components of the nanocomposite for improved adsorption efficiency [16]. The different strategies for synthesis of different graphene-based nanocomposites have been reviewed in detail by Huang et al. [51].

### 11.3.1 Nanocomposite Fabrication Methods

Fabrication of GO nanocomposites has been performed by various methods, including noncovalent and covalent interactions; physical, chemical, photochemical, electrochemical, and electrophoretic deposition; and hydrothermal and solvothermal growth and mixing [52]. Each method has both advantages and limitations, but the

synthesis of specific nanocomposites can be achieved by selecting the most appropriate method of preparation [52]. Different routes of GO nanocomposite fabrication, functionalization, and application have been reviewed by Chang and Wu [52].

Graphene nanocomposites are most frequently synthesized by noncovalent interactions between organic species and graphene [52]. Small molecules (like polymers) interact with graphene surfaces by participating in  $\pi$ - $\pi$  stacking and electrostatic or hydrophobic interactions, thereby resulting in the successful formation of graphene nanocomposites [52]. Another method applied for convenient fabrication of a graphene nanocomposite is a covalent reaction. GO reportedly establishes covalent bonding with polymers and nanoparticles [52]. Many studies have also reported chemical electroless deposition of Pt, Au, Ag, Cu, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, SnO<sub>2</sub>, and CdS nanoparticles, nanorods, and nanosheets on the GO surface for nanocomposite formation *in situ* [53–63].

Hydrothermal and solvothermal growth are another method employed for the fabrication of graphene nanocomposites [52]. High pressure applied in these processes leads to a close contact of graphene and deposited materials and may also result in covalent association between both [52]. Previous studies have reported successful and controlled growth of metal/alloy nano-objects like Ag and PtRu; oxides of metals like Ti, Sn, V, and Mn; chalcogenides like SnS, ZnS, and MoS<sub>2</sub>; as well as complex compounds like LiFePO<sub>4</sub> on graphene surfaces using hydrothermal or solvothermal routes of synthesis [52].

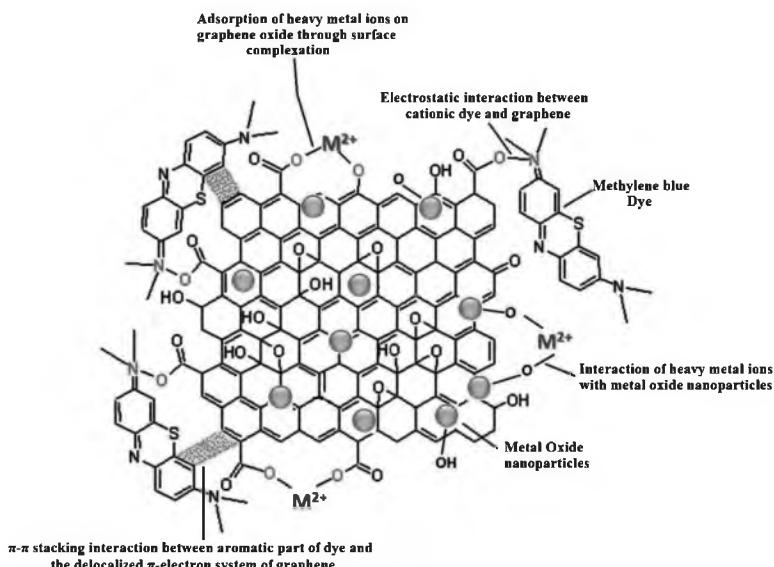
Nanoparticles of metals and metallic compounds have also been deposited on graphene surfaces by electrochemical reduction [52]. Even semiconductors like CdSe have been reported to be electrochemically deposited on graphene for the formation of nanocomposites [52]. Nanocomposites are also prepared through photochemical reactions on exposure to irradiated light [52]. Physical vapor deposition or atomic layer depositions have also been employed for nanocomposite formation of graphene with a high- $k$  dielectric metal oxide like Al<sub>2</sub>O<sub>3</sub> [64–66]. Chemical vapor deposition has also been applied for the synthesis of graphene nanocomposites, whereby graphene heterostructures are formed

besides other materials [52]. Previous studies have reported successful simultaneous growth of carbon nanotubes (CNTs) and metal oxide on graphene surfaces [52, 67].

Coupling the functionalities of nanoparticles/polymers/clays with the outstanding electronic, photonic, mechanical, and thermal properties of graphene reportedly results in the formation of nanocomposites with significantly improved performance.

### 11.3.2 GO-Metal Nanoparticle Composites for Dye Removal

Incorporation of metal oxide nanoparticles in a GO matrix reportedly results in increased mechanical strength of the composite and higher adsorbent robustness [68]. Different interactions between GO–metal oxide composites and various pollutants have been schematically represented in Fig. 11.3.



**Figure 11.3** Schematic representation of different interactions occurring between metal oxide/graphene oxide composites and pollutants during adsorption. Reproduced from Ref. [68] with permission from The Royal Society of Chemistry.

Nanomaterials have a greater surface-to-volume ratio, and hence their composites with GO potentially acquire a higher surface area, resulting in increased adsorption efficiency of the nanocomposites [68]. Different GO–metal oxide composites used as dye adsorbents have been listed in Table 11.1.

**Table 11.1** Different GO–metal oxide composites used as dye adsorbents

Composite	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Targeted adsorbate	Adsorption capacity (mg g <sup>-1</sup> )	Refs.
Titanate/GO	350.00	Methylene blue	83.26	[69]
ZnO/GO	-	Rhodamine B	32.60	[70]
Fe <sub>3</sub> O <sub>4</sub> /GO	-	Methylene blue and orange G	64.23 and 20.85	[71]
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /GO	-	Methylene blue	111.10	[72]
Fe <sub>3</sub> O <sub>4</sub> /GO		Reactive black 5	425.00	[73]
Fe <sub>3</sub> O <sub>4</sub> /GO	-	Methylene blue and neutral red	167.20 and 171.30	[74]
Fe <sub>3</sub> O <sub>4</sub> /GO		Reactive black 5	188.00	[75]

Retrieval of the nanocomposites from treated water still poses a challenge. Incorporation of magnetic nanoparticles in a GO matrix facilitates its convenient separation from treated waters using an external magnet and therefore reduces the risk of cross contamination [68]. Besides rapid adsorption rates, an efficient adsorbent should also support total desorption of adsorbed contaminants during regeneration, thereby facilitating reuse of the nanocomposites. For organic contaminants, like dyes, adsorbents may be regenerated by a simple washing with acids/solvents or heat treatment (for thermally stable adsorbents).

### 11.3.3 GO-Polymer Composites for Dye Removal

Graphene-polymer composites are broadly classified as polymers with graphene fillers, layered films, and polymer functionalized nanocomposites [76]. Polymer composites with graphene fillers are generally prepared by addition of solvents, melt blending, or

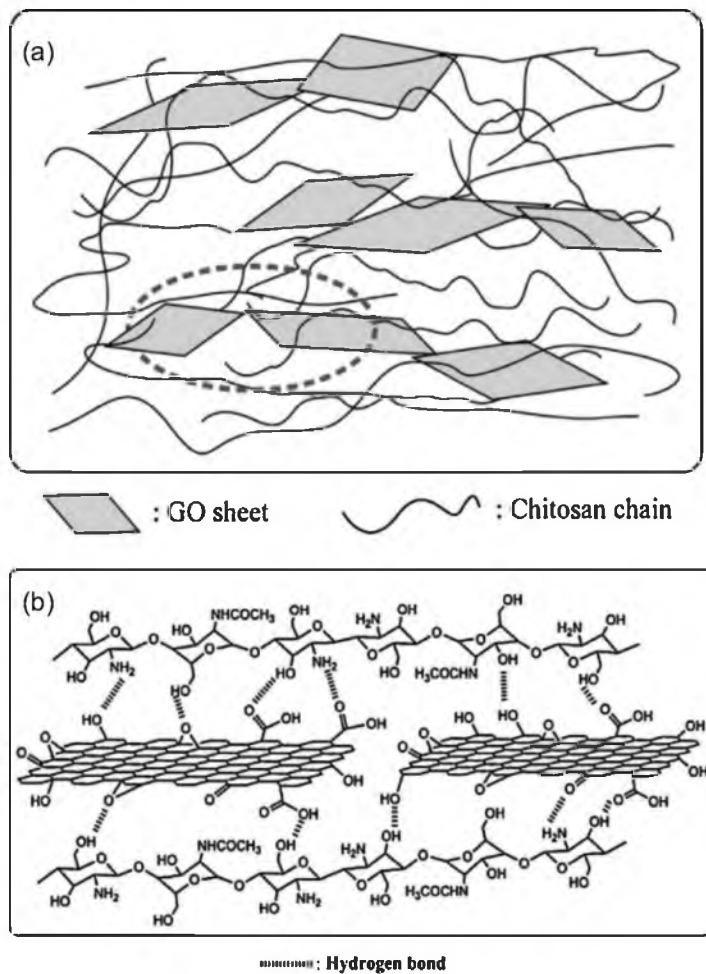
in situ polymerization [76]. Proper dispersion of the filler in the polymer is dependent upon the compatibility of both with the selected solvent. Owing to its oxygen-bearing functional groups, GO is able to combine directly with polymers soluble in water [76]. Pan et al. [77], in a recent study, have reported a green method where GO-chitosan nanocomposites were prepared by suspending GO in aqueous solutions of chitosan. The schematic representation of the interaction between GO sheets and chitosan moieties has been shown in Fig. 11.4. A similar study by Banerjee et al. [78] has reported the use of ultrasound irradiation at different stages of GO-chitosan composite preparation and its application for simultaneous removal of acid yellow 36 and acid blue 74 from their aqueous solution. According to this study, exposure to ultrasonic waves had facilitated better dispersion of GO in the chitosan matrix and resulted in improved adsorption efficiency of the GO-chitosan nanocomposite so prepared.

Nevertheless, in the case of nonpolar solvents, ultrasonic irradiation is applied to expedite the synthesis of GO-polymer composites [76]. GO-polymer composites have also been prepared by high-speed shearing followed by ice cooling [79]. However, in both processes, restacking, aggregation, and folding of the graphene-based nanosheets are often encountered, which in turn leads to a significant reduction in the specific surface area of the composites [76].

Both elevated shear forces and temperature are required for melt compounding of filler and matrix constituents [76]. Hence, fabrication of GO-polymer composites by melt compounding is independent of a common solvent [76]. In situ polymerization is another method applied for the synthesis of GO-polymer composites and has been applied successfully for the insertion of graphene fillers in polymers like epoxy, polyaniline, silicone, polystyrene (PS), and polyvinyl (chloride/acetate) copolymers [76]. Different GO-polymer composites used as dye adsorbents have been listed in Table 11.2. All these studies established successful nanocomposite formation using GO and different polymers and discussed their efficiencies for dye removal from solutions.

**Table 11.2** Different GO-polymer composites used as dye adsorbents

Composite	Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Targeted adsorbate	Adsorption capacity ( $\text{mg g}^{-1}$ )	Refs.
Chitosan-graphene mesostructures	603.20	Reactive black 5	-	[46]
GO-chitosan	511.80	Acid yellow 36, acid blue 74	55.55, 52.63	[78]
Magnetic chitosan-GO (MCGO)	392.50	Methylene blue, methyl blue	180.83, 95.20	[80]
Polyethersulfone-GO	25.67	Methylene blue	62.50	[81]
Polystyrene- $\text{Fe}_3\text{O}_4$ -GO	-	Rhodamine B	13.80	[82]
MCGO	-	Methyl blue	95.31	[83]
MCGO	-	Methylene blue	180.83	[84]
Magnetic $\beta$ -cyclodextrin-chitosan-GO	402.10	Methylene blue	84.32	[85]
GO-calcium alginate	-	Methylene blue	181.81	[86]
GO-sodium alginate (SA)-polyacrylamide	-	Brilliant green, methyl orange, Bordeaux red, rhodamine 6G, calcein, malachite green, methylene blue, rose Bengal sodium salt	5.61, 1.24, 2.43, 3.71, 4.76, 2.24, 2.62, 6.23	[87]
GO-encapsulating SA beads	31.30	Acridine orange	0.21 min. <sup>-1</sup>	[88]
GO-konjac glucomannan hydrogel cross-linked by CaO	-	Methyl orange, methyl blue	51.60, 92.30	[89]
Poly(acrylic acid)/GO	68.43	Methyl violet	1600.00	[90]
Polydopamine/GO	280.00	Methyl orange	89.00	[91]
Poly(diallyldimethylammonium chloride)/GO	25.8	Trypan blue	46.00	[92]

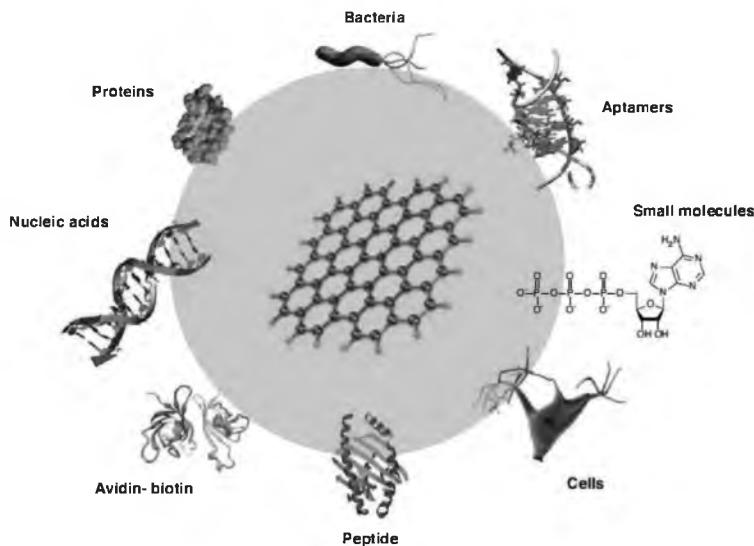


**Figure 11.4** Schematic representation of interactions between GO and chitosan moieties. (a) Possible microstructures present in GO-chitosan nanocomposites; (b) formation of hydrogen bonds between GO sheets and chitosan chains. Reprinted from Ref. [77], Copyright (2011), with permission from Elsevier.

#### 11.3.4 GO Biocomposite for Dye Removal

With parallel progress in nanotechnology and biotechnology, biofunctionalization of nanomaterials has received significant

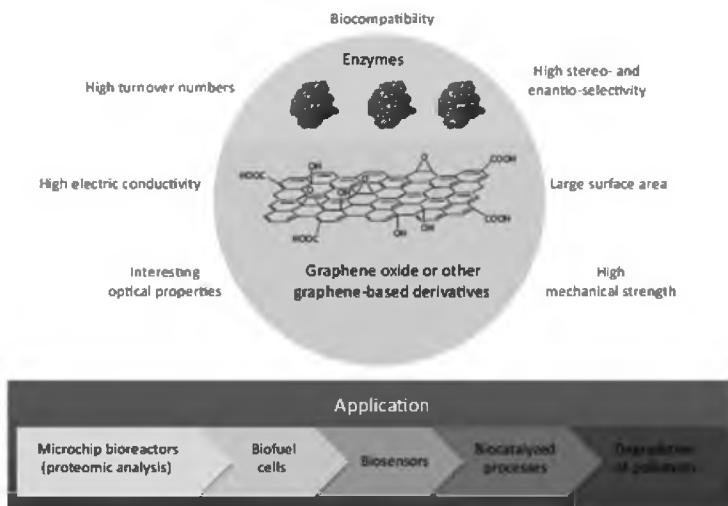
attention for the development of biodevices, biosensors, and biotechnological processes for pollutant degradation [93]. Graphene and its derivatives have been investigated as a substrate for functionalization with different biomolecules (like avidin-biotin, peptides, *N*-acryloyloxysuccinimides, proteins, aptamers, small molecules, bacteria, and cells) through physical adsorption or chemical conjugation, as schematically represented in Fig. 11.5. Functionalization of graphene derivatives with biomolecules has resulted in improved biocompatibility, solubility, and selectivity of these GO biocomposites [93].



**Figure 11.5** Schematic representation of functionalization of graphene and its derivatives with different biomolecules (like avidin-biotin, peptides, NAs, proteins, aptamers, small molecules, bacteria, and cells) through physical adsorption or chemical conjugation for the fabrication of biological platforms, biosensors, and biodevices. Reprinted from Ref. [93], Copyright (2011), with permission from Elsevier.

Of all other biomolecules investigated so far, functionalization of graphene-based composites with enzymes for development of robust nanobiocatalysts has received significant importance [94]. Enzyme immobilization facilitates enhanced stability, convenient separation from reaction substrate, and better reuse potential,

rendering the biocatalysts appropriate for application in commercial processes [94]. Different advantages and applications of enzyme immobilization on graphene and its derivatives have been shown in Fig. 11.6.



**Figure 11.6** Schematic representation of enzyme immobilization onto graphene-based nanomaterials, along with its advantages and applications. Reprinted from Ref. [94], Copyright (2014), with permission from Elsevier.

Functionalization of GO takes place at its chemically reactive sites, which include the carboxylic acid groups bordering the edges, the epoxy and hydroxyl groups arranged on the basal planes, and the  $\pi$ -conjugated system [37]. This functionalization may occur from covalent attachment of nucleophiles (such as amine or hydroxyl groups) to carboxylic acid groups or epoxy groups (via ring opening reactions of amines) present on graphene sheets, noncovalent attachments like van der Waals interactions (with polymers, surfactants, and other small molecules) or  $\pi$ - $\pi$  stacking (with polycyclic aromatic hydrocarbon derivatives), and/or cycloaddition and diazonium reactions of reduced GO [37]. These different routes of functionalization have been schematically represented in Fig. 11.7.

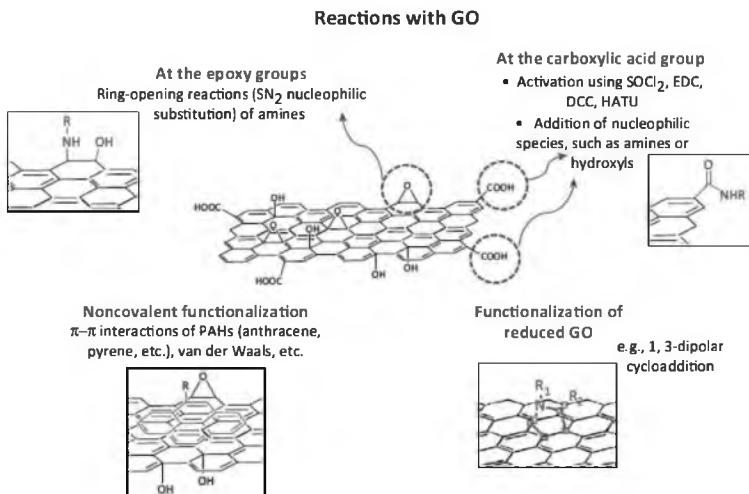
Graphene and graphene derivative-based nanobiocatalytic systems have been assessed for diverse applications, like biocatalytic conversions, pollutant degradation, and wastewater treatment, as

well as for designing of biofuel cells and microchip bioreactors [94]. Li et al. [95] have recently reported the fabrication of GO-enzyme hybrid nanoflowers and their successive application for the efficient removal of water-soluble dyes. In this study, the authors have reported efficient immobilization of laccase on copper phosphate/CNTs/GO-based hybrid nanocomposite and its successive implementation for crystal violet and neutral red removal from their aqueous solutions [95]. The nanocomposite demonstrated outstanding laccase-loading ability and also exhibited higher laccase activity (by almost 15%) and longer shelf life in comparison to free laccase [95]. In another study, dye decolorization was obtained by laccase immobilized on magnetic GO [96]. In this study, 94.7%, 95.6%, and 91.4% decolorization was recorded in the case of crystal violet, malachite green, and brilliant green, respectively, on treatment with magnetic GO-laccase biocomposite [96]. The biocomposite was found to retain 59.80% of its activity after the tenth cycle of reuse [96]. Patila et al. [97] have also demonstrated laccase-functionalized GO assemblies for decolorization of pinacyanol chloride (an industrial dye). In all studies, immobilized enzymes exhibited better reusability, longer storage stability, and higher thermostability in comparison to free enzymes, thereby establishing the potential of these GO biocomposites for applications in the treatment of dye-rich wastewaters.

GO biocomposites for wastewater treatment have also been prepared by immobilization of bacterial strains on GO. Zhou et al. [98] have reported polyvinyl alcohol-modified GO as the ideal carrier for halotolerant bacterial species and application of this biocomposite for highly saline wastewaters. In a similar study, Banerjee et al. [99] reported the immobilization of *Pseudomonas mendocina* on GO and its subsequent application for direct red 21 removal from aqueous solutions. Akhavan et al. [100] have also reported successful encapsulation of *Escherichia coli* using GO nanosheets for application in various biotechnological applications.

Advantages of biofunctionalization of GO were found to be resistance to mass transfer, high surface area, and reduction in diffusional problems [101]. However, applications of the GO biocomposites discussed in this study are limited to the treatment of synthetic solutions and their performance in real-time wastewater treatment is yet to be analyzed. Besides, GO biocomposite-based

wastewater treatment also has certain disadvantages, like cost-incurring fabrication processes and technology, for its wide-scale application [101]. Hence, GO biocomposites require in-depth investigation by the scientific community for application in industrial processes.



**Figure 11.7** Schematic representation of different methods for the functionalization of GO. DCC, *N,N'*-dicyclohexylcarbodiimide; EDC, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide; GO, graphene oxide; HATU, 2-(7-aza-1-H-benzotriazole-1-yl)-1,3,3-tetramethyluronium hexafluoro-phosphate; PAHs, polycyclic aromatic hydrocarbons;  $SOCl_2$ , thionyl chloride. Reprinted from Ref. [94], Copyright (2014), with permission from Elsevier.

## 11.4 Characterization of GO-Based Nanocomposites

Characterization of GO composites has been done mostly for understanding the physical characteristics (morphology, particle size and porosity, surface area, lattice defects, stacking behavior, etc.) and chemical behavior of the same [37]. The morphological parameters have been usually analyzed by electron microscopy—scanning electron microscopy (SEM) and transmission electron microscopy (TEM)—and atomic force microscopy (AFM). The atomic

and molecular structure of the composites has been investigated by X-ray diffraction (XRD) analysis. Specific surface area, pore size, and sample porosity have been estimated by isothermal nitrogen sorption via Brunauer–Emmett–Teller (BET) theory. Particle size and surface charge have been determined by dynamic light scattering (DLS). The magnitude of defects existing in the lattice and the number of layers in the stacked structure of GO may be determined by Raman spectroscopy. Chemical behavior of GO composites has been explained qualitatively and quantitatively by Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and solid-state nuclear magnetic resonance (NMR) spectroscopy.

### 11.4.1 Characterization of Physical Parameters

#### 11.4.1.1 Electron microscopy

Advantages of imaging a sample with SEM include large field depth, high resolution (50–100 nm), and a more controlled degree of magnification (20X to approximately 30,000X). These advantages facilitate fracture characterization, microstructure studies, thin film evaluation, surface contamination examination, and failure analysis of GO composites [102]. In comparison to conventional SEM, field emission scanning electron microscopy (FESEM) yields clearer, less electrostatically distorted images with spatial resolution <2 nm (three to six times better than SEM) and magnification of approximately 300,000X. Samples (powder/drop cast) for SEM analysis are attached to an aluminum stub with a sticky carbon tape. The sample surfaces are rendered conductive by metal (Au/Pt) coating. Nevertheless, environmental scanning electron microscopy (ESEM) can be used to image an uncoated nonconducting biofunctionalized sample by placing the sample in a high-pressure/vacuum chamber where the working distance between the electron gun and the sample is reduced. The prepared sample is then imaged with a variety of magnifications.

In TEM analysis, a high-energy beam of electrons is shone through a very thin sample and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure, like dislocations and grain

boundaries. Chemical analysis can also be performed. TEM can be used to study the growth of layers and their composition and defects in samples. High resolution can be used to analyze the quality, shape, size, and density of samples. Thus, TEMs can reveal the finest details of internal structure—in some cases as small as individual atoms. A TEM sample must be thin enough to transmit sufficient electrons to form an image with minimum energy loss. Therefore, specimen preparation is an important aspect of TEM analysis. For most electronic materials, the usual sequence of preparation techniques is ultrasonic disk cutting followed by dimpling and finally ion milling. In this process, charged argon ions are accelerated to the specimen surface by the application of high voltage. The ion charging upon the sample surface removes material as a result of momentum transfer. Samples for TEM analysis are mostly drop cast on commercially available carbon-coated copper grids of different mesh sizes depending on requirement.

#### **11.4.1.2 Atomic force microscopy**

AFM is used for determination of sample morphology, height, and surface roughness. AFM reconstructs the surface image of samples by scanning in x/y or x/y/z directions from diverse viewpoints [102]. Also, sample preparation for AFM analysis does not require any extra surface treatment, like metal or carbon coating [102]. Samples for AFM analysis are drop cast on freshly cleaved mica sheets. Images are mostly obtained in tapping mode in different phases (topography, amplitude, height, etc.), with a constant raster speed under ambient environmental conditions.

#### **11.4.1.3 X-ray diffraction analysis**

In XRD analysis, atoms of the sample cause diffraction of a beam of X-rays in a number of specific directions and thereby produce a 3D representation of the electron density within the sample particle. The physical properties, chemical compositions, and crystal structures of samples may be deciphered from this map of electron density so obtained [102]. A sample is loaded on to a plate and placed in the XRD chamber for analysis. XRD analysis reveals the physical state (crystalline or amorphous) of the sample. Interlayer spacing of GO composites is also often determined using XRD analysis [37].

#### **11.4.1.4 Specific surface area, pore size, and sample porosity**

BET theory (proposed by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller in 1938) explained the physical adsorption of gaseous molecules on a solid surface, thereby establishing the basis of an analysis technique for the measurement of specific surface area and pore size distribution of a sample [37]. Conceptualized as an extension of Langmuir theory, BET theory was based on the assumptions that physisorption of ideal gas molecules occurred on a solid in infinite layers; adjacent adsorption layers were noninteractive, with Langmuir theory being applicable for each layer; and both adsorbate and adsorbent were inert in nature. Nitrogen has been used as a conventional adsorbate for analysis. The volume of gas adsorbed by the sample surface is determined at the boiling point of nitrogen ( $-196^{\circ}\text{C}$ ). The total surface area (including pores in the surface) estimated in this method is expressed as  $\text{m}^2 \text{ g}^{-1}$  or  $\text{m}^2 \text{ cm}^{-3}$ . Gas adsorption also allows the determination of size and volume distribution of pores present on the sample surface.

#### **11.4.1.5 Particle size and surface charge analysis**

DLS (also known as photon correlation spectroscopy) is an analytical technique to determine the size distribution of macromolecular solutions. The technique relies on determination of the rate of fluctuations of laser light intensity that is scattered by particles. This is performed by measuring the second-order autocorrelation function of the intensity trace. At longer times, the autocorrelation function decays exponentially. The exponential function is related to the translational diffusion coefficient and hence to the motion of the particles. The instrument is equipped with zeta potential experiments that aid in the determination of surface charge of samples.

#### **11.4.1.6 Raman spectroscopy**

Characterization of features such as thickness, defects, and the degree of orderliness of GO composites is performed by a nondestructive tool called Raman spectroscopy [102]. Raman spectroscopy is one of the vibrational spectroscopic techniques used to provide information on molecular vibrations and crystal structures. It is also used for investigation of elementary excitation in GO composites [102].

## 11.4.2 Characterization of Chemical Behavior

### 11.4.2.1 Fourier transform infrared spectroscopy

FTIR detects the vibration characteristics of chemical functional groups present in a sample by recording its infrared absorption spectrum in the range of 4–14,000 cm<sup>-1</sup>. On exposure to infrared light, chemical bonds in a sample undergo stretching, contraction, and/or bending, thereby producing a molecular fingerprint of the same. The chemical functional groups present in the sample tend to absorb infrared radiations of specific wavenumbers irrespective of its molecular structure, rendering infrared spectroscopy applicable for different types of analysis [102]. Samples may be scanned for percentage transparency using a single-reflection horizontal attenuated total reflection accessory or cast into pellets using KBr prior to FTIR analysis.

### 11.4.2.2 X-ray photoelectron spectroscopy

Analysis of elemental composition, empirical formulas, and chemical and electronic state of elements existing in a sample is determined by XPS technique [102]. Electrostatic interactions between adsorbate and adsorbent moieties are also explained by this technique.

### 11.4.2.3 Solid-state nuclear magnetic resonance spectroscopy

The magnetic properties of certain atomic nuclei are analyzed using NMR spectroscopy, thereby determining the physical and chemical properties of constituent atoms or molecules. NMR can quantitatively analyze mixtures containing known compounds. For unknown compounds, NMR can be used either to match against spectral libraries or to infer the basic structure directly. Once the basic structure is known, NMR can be used to determine molecular conformation in solution as well as to study physical properties at the molecular level, such as conformational exchange, phase changes, solubility, and diffusion.

## 11.5 Factors Affecting Dye Adsorption

Significant factors affecting dye adsorption are solution pH, temperature, initial dye concentration, and adsorbent dosage. Effects of these factors on dye adsorption are discussed next.

### 11.5.1 Effect of Solution pH

Solution pH strongly influences the efficiency of an adsorption process by causing variations in adsorbate ionization and the adsorbent surface properties [103]. The adsorbate-adsorbent interaction is guided by the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) [103]. The  $\text{pH}_{\text{pzc}}$  of an adsorbent determines the electrokinetic behavior of its surface [103]. Values of pH represent pzc for systems where  $\text{H}^+$ /  $\text{OH}^-$  serve as the potential-determining ions. Hence, adsorption of cationic dyes is favored at  $\text{pH} > \text{pH}_{\text{pzc}}$ , where the adsorbent surface gathers negative charge, while adsorption of anionic dyes is favored at  $\text{pH} < \text{pH}_{\text{pzc}}$ , where the adsorbent surface acquires positive charge [103].

### 11.5.2 Effect of Temperature

A rise or fall in adsorption efficiency of an adsorbent with a corresponding increase in ambient temperature indicates that the process is endothermic or exothermic in nature, respectively [103]. An increase in temperature often leads to higher mobility of dye moieties and a larger number of active adsorption sites on the adsorbent surface, thereby facilitating better dye uptake. On the other hand, a decrease in dye adsorption efficiency of the adsorbent at lower temperatures may occur due to diminished adsorptive forces between dye species and the adsorbent active sites [103].

### 11.5.3 Effect of Initial Dye Concentration

Usually, an increase in initial dye concentration causes saturation of active adsorption sites on the adsorbent surface, resulting in a reduction in the rate of dye adsorption by the adsorbent [103]. In other cases, a rise in the initial dye concentration may increase the uptake capacity of an adsorbent by causing a gradient-based mass

transfer and result in removal of higher percentages of dye from the solution [103].

#### 11.5.4 Effect of Adsorbent Dosage

Generally, a higher adsorbent dosage provides a larger number of active sorption sites, resulting in an increase in the percentage dye removal [103]. Assessment of dye removal with different adsorbent dosages helps determine the minimum dosage of adsorbent required for effective dye removal and judge the economic feasibility of wide-scale application of the adsorbent [103].

### 11.6 Investigation of Process Mechanism

Process isotherms and kinetics may be determined over a range of different experimental variables, like solution pH, adsorbent dosage, and temperature. Process thermodynamics are calculated over a range of ambient temperatures. Highest values of correlation coefficient indicate best fit to one or more specific isotherm/kinetic model tested for.

#### 11.6.1 Process Isotherms

Fitting the experimentally obtained data to different isotherm models explains the interaction between adsorbent and adsorbate (adsorption mechanism) and provides an idea of adsorption capacity [103]. Several isotherm models have been described in previous reports. Of all isotherm models reported so far, the most widely investigated ones have been described and explained in Table 11.3.

#### 11.6.2 Process Kinetics

Mechanisms guiding adsorption processes (like chemical reactions, diffusion control, or coefficients of mass transfer) are guided by kinetic models, which in turn indicate the optimum operating conditions for an efficient full-scale batch process [103]. Elucidation of adsorption kinetics reveals the rate of adsorption and time taken to reach equilibrium. Hence, previous studies have reported

**Table 11.3** Different isotherm parameters for modeling dye adsorption

<b>Models and equations</b>	<b>Parameters</b>	<b>Unit</b>	<b>Description</b>	<b>Implication</b>
Langmuir	$C_e$ $q_e = \frac{C_e}{Q^0 b} + \frac{C_e}{Q^0}$	mg L <sup>-1</sup> mg g <sup>-1</sup>	Equilibrium dye concentration in solution Theoretical maximum adsorption capacity	<ul style="list-style-type: none"> <li>Adsorption takes place at specific homogeneous sites within the adsorbent.</li> </ul>
	$Q_0$	mg g <sup>-1</sup>	Maximum monolayer coverage capacity calculated from the slope of the $C_e/q_e$ vs. $C_e$ plot	<ul style="list-style-type: none"> <li>It has been used successfully for many adsorption processes of monolayer adsorption [78].</li> </ul>
	$b$	L mg <sup>-1</sup>	Langmuir coefficient of energy of adsorption calculated from the intercept of the $C_e/q_e$ vs. $C_e$ plot	
Freundlich	$n_f$		Adsorption intensity calculated from the slope of the $\ln q_e$ vs. $\ln C_e$ plot	<ul style="list-style-type: none"> <li>This isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption [78].</li> </ul>
$\ln q_e = \frac{1}{n_f} \ln C_e + \ln K_f$	$K_f$	mg g <sup>-1</sup>	Freundlich coefficient of adsorption capacity calculated from the intercept of the $\ln q_e$ vs. $\ln C_e$ plot	
Temkin	$B_T$	J mol <sup>-1</sup>	Coefficients of heat of adsorption calculated from the slope of the $q_e$ vs. $\ln C_e$ plot at operational temperature $T$ (K)	<ul style="list-style-type: none"> <li>This isotherm model provides information related to heat of the adsorption,</li> </ul>
$q_e = B_T \ln C_e + B_T \ln K_T$	$K_T$	L g <sup>-1</sup>	Temkin equilibrium binding constant calculated from the intercept of the $q_e$ vs. $\ln C_e$ plot at operational temperature $T$ (K)	<ul style="list-style-type: none"> <li>This explains adsorbate-adsorbent interactions [78].</li> </ul>

Models and equations	Parameters	Unit	Description	Implication
Dubinin–Radushkevich	B	mole <sup>2</sup> KJ <sup>-2</sup>	Dubinin–Radushkevich constant calculated from the slope of the $\ln q_e$ vs. $\varepsilon^2$ plot	• This isotherm model describes the porosity, free energy, as well as the adsorption properties of adsorbents [78].
$\ln q_e = \ln Q_s - B\varepsilon^2$	$Q_s$	mg g <sup>-1</sup>	Theoretical isotherm saturation capacity calculated from the intercept of the $\ln q_e$ vs. $\varepsilon^2$ plot	
	$\varepsilon$		Polanyi potential	

**Table 11.4** Different kinetic parameters for modeling dye adsorption

Models	Parameters	Units	Description	Implication
Pseudo first order	$k_1$	min. <sup>-1</sup>	Pseudo-first-order rate constant obtained from linear plots of $\log (q_e - q_t)$ vs. $t$	• The conc. of one relative reactant remains constant because it is supplied in great excess.
$\log(q_e - q_t) = \left[ \log q_e - \frac{k_1}{2.303} t \right]$	$q_e$ (cal)	mg g <sup>-1</sup>	Quantity of dye adsorbed at equilibrium	• The adsorption of the reactant in excess depends on its own conc. only.

Models	Parameters	Units	Description	Implication
Pseudo second order	$k_2$	mg g <sup>-1</sup> min. <sup>-1</sup>	Pseudo-second-order rate constant determined from the plot of $t/q_t$ vs. $t$	• The chemical reaction seems significant in the rate-controlling step.
$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}$	$q_e$	mg g <sup>-1</sup>	Quantity of dye adsorbed at equilibrium	• The kinetics of sorption correspond to a reversible second-order reaction at low sorbate/sorbent ratios (first order at very low ratios) and two competitive reversible second-order reactions at higher sorbate/sorbent ratios.

(Continued)

**Table 11.4** (Continued)

Models	Parameters	Units	Description	Implication
Intraparticle diffusion $q_t = K_{\text{diff}} t^{1/2} + C$	$K_{\text{diff}}$	$\text{mg g}^{-1}$ $\text{min.}^{-1/2}$	Intraparticle diffusion rate constant calculated from the slope of the regression plot of $q_t$ vs. $t^{1/2}$ , where $t$ is time (min.)	<ul style="list-style-type: none"> <li>The adsorption proceeds in several steps, involving transport of solute molecules from the bulk aqueous phase to the surface of the adsorbent particles, followed by transport of molecules into the interior of the solid pores [103].</li> </ul>
	$C$	$\text{mg g}^{-1}$	Constant calculated from the intercept of the regression plot of $q_t$ vs. $t^{1/2}$ , where $t$ is time (min.)	
Elovich	$\alpha$	$\text{mg g}^{-1}$ min.	Initial adsorption rate calculated from the intercept of the liner plot of $q_t$ vs. $\ln t$	<ul style="list-style-type: none"> <li>This is satisfactory in terms of chemical adsorption processes and is suitable for systems with heterogeneous adsorbing surfaces [104].</li> </ul>
$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	$\beta$	$\text{mg g}^{-1}$	Initial desorption rate calculated from the slope <sup>-1</sup> of the liner plot of $q_t$ vs. $\ln t$	<ul style="list-style-type: none"> <li>It also describes the kinetic behavior of many adsorption systems with a mildly rising tendency.</li> </ul>

different kinetic models for dye adsorption. The widely used models have been described in Table 11.4. The activation energy ( $E_a$ ) is calculated from the slope of the Arrhenius plot of  $\ln k$  vs.  $T^{-1/2}$ , governed by the equation  $\left[ \ln k = \ln A - \frac{E_a}{RT} \right]$ , where  $k$  indicates the kinetic constant,  $A$  represents the pre-exponential factor,  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) denotes the ideal gas constant, and  $T$  (K) is the absolute experimental temperature [43]. A value of  $E_a > 40$  kJ mol<sup>-1</sup> renders a process chemisorptive in nature while a value  $< 40$  kJ mol<sup>-1</sup> suggests that the same may be physisorptive in behavior [43].

### 11.6.3 Process Thermodynamics

The thermodynamic nature of an adsorption process is indicated by changes in Gibbs free energy ( $\Delta G^\circ$ ; kJ mol<sup>-1</sup>), enthalpy ( $\Delta H^\circ$ ; kJ mol<sup>-1</sup>), and entropy ( $\Delta S^\circ$ ; J mol<sup>-1</sup> K<sup>-1</sup>) [43]. Negative values recorded for  $\Delta G^\circ$  indicate that the process had occurred spontaneously throughout the specified thermal gradient [43]. Positive enthalpy values suggest that a process had occurred by utilization of energy from the concerned system, rendering the process as endothermic in nature [43]. The chemisorptive nature of the process is established when the heat of adsorption is found to exceed 200 kJ mol<sup>-1</sup>. Positive values of entropy denote a rise in randomness at the adsorbate-adsorbent interface [43].

## 11.7 Process Optimization

The best results may be obtained from a concerned process if it is carried out under optimized conditions. Previous studies have mostly reported effect of individual experimental parameters as it is tiresome, time taking, and intricate to execute the enormous number of experiments necessary for determining their combined effects on a concerned process [105]. Hence, recent studies have reported diverse statistical analogies for process optimization and elucidation of interparameter interactions using a highly reduced number of experiments with reduced time and cost requirements [105]. Optimization of the various experimental parameters influencing adsorption processes may be obtained using two mathematical- and

statistical-based tools, response surface methodology (RSM) and artificial neural network (ANN), discussed below.

### **11.7.1 Response Surface Methodology**

RSM is a collection of mathematical and statistical techniques applied for the optimization of a number of independent variables (experimental factors) through a series of experiments, called runs, for obtaining a desired response (in this case, dye removal) [106]. A range of variable parameters is selected as input during these experiments for determination of the reasons for changes in the desired response [106]. Application of RSM eliminates chances of repetitive analysis and helps in the reduction of the associated numerical noise. The desired response is represented either graphically in the 3D space or as contour plots. RSM can be implemented for the optimization of both experimental and numerical responses. The appropriate model for the optimization of the concerned process is signified by analysis of variance (ANOVA) [105]. Optimum experimental conditions are determined by Derringer's desirability function, whereby the applied goals present in the menu are chosen to remain within range and maximum for experimental factors and process responses, respectively [105].

### **11.7.2 Artificial Neural Networks**

An ANN, also denoted as neurocomputing, connectionism, or parallel distributed processing (PDP), is alternatively applied to problems where algorithmic and symbolic solutions are inappropriate [106]. ANN designs are derived from available knowledge of biological nervous systems, though they vary in almost every detail. An ANN model consists of parallelly distributed interconnected processing units and is implemented to assess whether the output of a designed process is in keeping with theoretically determined predictions [106]. Neural models usually consist of an input, a hidden, and an output layer [105]. Various functions, like poslin, tansig, satlin, logsig, and purelin, are selected as transfer functions for the hidden and output layers [105]. Experimental data used are normalized prior to optimization with different algorithms, like Levenberg–Marquardt

(Trainlm), resilient (Trainrp), scaled conjugate gradient (Trainscg), and gradient descent, with momentum and adaptive learning rate (Traingdx), etc. [105]. The highest coefficient of determination ( $R^2$ ) signifies the best fit of algorithm to the experimental data. Training of the neural networks strongly depends upon the number of neurons present in the hidden layer. While a higher number of neurons usually facilitate better applicability of the designed model for the concerned process, an excessive number of neurons may result in overfitting [105]. Appropriate numbers of neuron for the hidden layer are optimized by trial and error. The best output of the designed ANN model is ensured by keeping the performance target and ramp constant [105].

### 11.7.3 Comparing RSM and ANN for Better Applicability

The performance of each model is statistically assessed by parameters like coefficient of determination ( $R^2$ ), root mean squared error (RMSE), mean absolute error (MAE), and absolute average deviation (AAD), as described by Banerjee et al. [105].  $R^2$  is determined by least-squares regression and should have a value close to 1. AAD signifies the measure of deviation between predicted and experimental responses, and its value ought to be as low as attainable [105]. On the contrary, lower values of RMSE and MAE also denote applicability of the technique being assessed.

## 11.8 Conclusion

This review was aimed at compiling the recent investigations in GO nanocomposites for the removal of dyes from their aqueous solutions. Besides a detailed discussion on most of the GO composites reported so far, this review has also covered characterization techniques presently being applied for a better understanding of the mechanism of dye adsorption; the experimental factors significantly affecting dye adsorption; elucidation of process parameters like isotherms, kinetics, and thermodynamics; as well as optimization of adsorption processes. However, there are several other aspects that need to be considered in future research and development, including assessment of antimicrobial potential of these nanocomposites,

adsorption efficiency of GO nanocomposites in the simultaneous presence of multicomponent pollutants, mechanistic modeling for proper elucidation of adsorption mechanisms, estimation of adsorption efficiency of GO nanocomposites with real industrial effluents, recovery of pollutants for reuse, regeneration of adsorbents and recycling potential, and development of wide-scale and cost-effective separation technologies using these nanocomposites. For facilitating practical applications of GO nanocomposites for wastewater treatment and reuse, health impacts of these nanocomposites and their treated waters should be evaluated by toxicity and biocompatibility studies carried out both *in vitro* and *in vivo*.

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## Chapter 12

# Insights into Dye Confiscation by Low-Cost Adsorbents for Textile Effluent Remediation: A Review

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Today, effluents from the action of several industries, such as textile, leather, paper, and plastic, are a major environmental risk due to the presence of many stable dyes having adverse/toxic responses to many forms of life. The discharge of dyes into the environment is a matter of concern for both toxicological as well as aesthetic reasons because of the presence of a large number of contaminants, like acids, bases, dissolved solids, and colors. Therefore, dye removal from wastewater is a pressing requirement. In this regard, adsorption techniques are widely used to remove certain classes

of pollutants from industrial effluents, especially those that are not easily biodegradable. This chapter focuses on the effectiveness of adsorption and low-cost adsorbents for dye confiscation from effluents.

## 12.1 Adsorption

A phenomenon in which a substance from gaseous and liquid surroundings is accumulated on the surface of a solid body is referred to as adsorption [1]. From a bulk solution, the transfer of molecules to the surface of the solid occurs on the basis of different concentration values. The molecules of gases or liquids concentrate on the surface of the solid when they come in contact [2]. Adsorption can be done through continuous, batch, and semibatch processes. The batch process is mostly carried out for the treatment of less quantity of effluent. In this process the equilibrium distribution is influenced by the contact time [3]. Adsorbate (which adsorbs on the surface of the adsorbent) and adsorbent have some forces of attraction that bind them, and these can be of two types: weak forces, that is, van der Waals forces, and strong forces due to chemical bonding.

Adsorption based on the attraction force involved between adsorbent and adsorbate is of two kinds: physical adsorption and chemical adsorption.

### 12.1.1 Physical Adsorption

If the attraction forces between adsorbent and adsorbate are van der Waals forces then the process is called physical adsorption, also known as physisorption. This is a reversible process of adsorption. The enthalpy of adsorption of this process is processed between 20 and 40 kJ/mol. Physisorption decreases as the temperature increases; that is why it occurs at a temperature less than the boiling point of the adsorbate [4].

### 12.1.2 Chemical Adsorption

If attraction forces between the adsorbate and adsorbent are of a chemical type then the process of adsorption is chemisorption or

chemical adsorption because it occurs via chemical bonds. The enthalpy of adsorption of chemisorption is processed between 200 and 400 kJ/mol. With an increase in temperature this phenomenon firstly increases and then decreases [5]. Due to the higher strength of chemical bonding, it is difficult to remove chemisorbed species from the solid surface [4].

Table 12.1 shows a comparison of both types of adsorption on the basis of their action, appearance, and properties.

**Table 12.1** Comparison types of adsorption on the basis of their action, appearance, and properties

Factors	Physisorption (van der Waals adsorption)	Chemisorption (Langmuir adsorption)
Heat of adsorption	Low (usually in the range of 20–40 kJ/mol)	High (in the range of 200–400 kJ/mol)
Attraction forces	Van der Waals force	Chemical bonds
Type of reaction	Reversible	Irreversible
Temperature	Low temperature favorable; decreases on increasing temperature	High temperature more favorable
Layer type	Forms multimolecular layer	Forms monomolecular layer
Activation energy	No activation energy required	Requires high activation energy
Specificity	Not very specific	Highly specific
Example	Liquefiable gases, like NH <sub>3</sub> and HCl, adsorbed by physisorption	H <sub>2</sub> adsorption on metal surface an example of chemisorption

Source: [5–7]

## 12.2 Adsorbent Types

Any solid substance is capable of attaching or adsorbing other chemical species to its surface without any covalent bonding. An adsorbent has the ability to remove various substances from gases, liquids, and solids by attaching them to its surface.

The well-known adsorbents are:

- Activated carbon
- Silica gel
- Alumina
- Zeolites

### 12.2.1 Activated Carbon

The most common of known adsorbents is activated carbon. Lignite, coal, coconut shell, and timber are usually used for the preparation of activated carbon. To form long-short activated carbon, a physical preparation method is used. The chemical preparation method is to add chemical reagents to carbonized materials [8, 9]. Two forms of activated carbon are used for contaminants' removal from wastewater, granular activated carbon and powder activated carbon (GAC and PAC) [10].

### 12.2.2 Silica Gel

It is present in the form of porous and noncrystalline granules having different sizes and can be formed by the coalescence of  $\text{H}_4\text{O}_4\text{Si}$  (silicic acid) in colloidal form. It has a higher surface area than alumina, ranging 250 to 900  $\text{m}^2/\text{g}$  [4].

### 12.2.3 Alumina

It is a synthetic crystalline porous material, usually gel, and it exists in the form of different-sized granular types having surface areas between 200 and 300  $\text{m}^2/\text{g}$ . A naturally occurring crystalline porous form of alumina is bauxite, which is coupled with oxides of iron and kaolinite clay, having surface areas between 25 and 250  $\text{m}^2/\text{g}$  [11–13].

### 12.2.4 Zeolites

These are natural or synthetic microporous adsorbents. These show ion exchange activity [14] and molecular adsorption [15] and so are considered as selective adsorbents. Many zeolites are used to remove dyes [16–18] and also for other types of pollutants. Furthermore,

these substances have also the ability to exchange the cation/anion at their surface. These substances include polystyrene phosphonate, sulfonated phenolic resin, phenolic resin, amino-polystyrene, polystyrene-based trimethyl benzyl ammonium, polystyrene amidoxime, polystyrene sulfonate, and epoxy-polyamine, which are used as cationic/anionic exchange adsorbents to remove dyes from wastewater [19, 20].

### 12.3 Applications of Adsorbents

Adsorption is a commercially used technique for the treatment of wastewater. Adsorbents are porous materials and used in two forms, powder and granules, and these pores allow the contaminants to attach or adsorb on the surface. In this way contaminants are adsorbed and removed from wastewater. Some adsorbents commonly used are activated carbon, alumina, zeolites, and silica gel [21]. For heavy metal ion removal, alumina remains a frequently used active adsorbent. Alumina has the ability to remove various contaminants, including arsenic (As), excessive fluoride (F), and selenium (Se) [22]. Alumina has also been used for dye removal [13]. Zahra explored Pb(II) removal from water using alumina ( $\text{Al}_2\text{O}_3$ ) as an adsorbent [23].

Silica gels are used as adsorbents in several applications, for example, for the removal of impurities through adsorption and chromatographic separations. Silica gel is also studied for adsorption of different basic dyes. Investigation shows that the dye adsorption ability of silica is high [24, 25]. For surfactant and cationic dye removal by adsorption from organic water silica is mostly used [26].

The most important and common low-cost adsorbents include natural zeolites for the treatment of drinking water and wastewater. Natural zeolites are cation exchangers, and that is why these show a great ability to adsorb cations like ammonium ion and heavy metals in aqueous solutions. However, these do not show good adsorption of organics and anionic ions. To make them good adsorbents for anionic materials, surface modification can be done by changing the surface charge of zeolites [27].

Due to the high efficiency of activated carbon, adsorption has been considered a most suitable technique for the removal of

contaminants from wastewater [21]. Natural organic compounds, synthetic organic chemicals, and taste and odor compounds can be removed by this treatment from drinking and wastewater. Active charcoal carbon is used as a filter because it acts as an adsorbent; it is used to remove chlorine, volatile organic compounds (VOCs), sediment, and taste and odor compounds from wastewater [28]. It can also be used for the removal of heavy metal ions, like Pb [29].

Activated carbons are used not only to remove various dyes [30] but also to remove organic and inorganic contaminants, for instance, metal ions [31], pesticides, chlorinated hydrocarbons, humic substances, polychlorinated biphenyls (PCBs), detergents [32], organic chemicals that produce odor and taste, phenols [33], and many other compounds and organisms [34]. It is well known that for the removal of color and other contaminants from textile and dye wastewater, sorption by activated carbon is the most effective and easily available method [35]. Hence the overall view is that these adsorbents work by both processes and are working well in remediating textile effluents.

## 12.4 Mineralized Materials

A crystalline chemical compound that is biogenic, has a definite chemical composition, and is procured from natural sources is known as a mineral [36]. Its study is known as mineralogy. Some minerals act as adsorbents; that is why these are used in industries for water treatment. There are many mineralized materials that are used to treat wastewater, but here we will discuss only two mineralized materials:

- Clay
- Zeolites

### 12.4.1 Clay

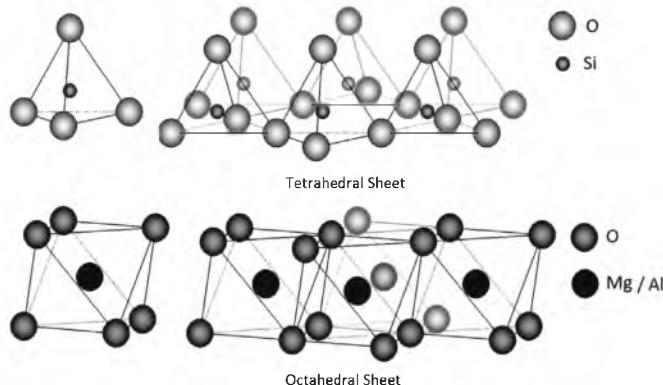
Clay is a natural mineral composed of fine-grained materials, is plastic in nature having appropriate water amounts, and it will harden if it is dried [37]. Clay mostly comprises phyllosilicates; it can consist of different materials that add plasticity. Hydrous aluminosilicates are minerals of clay with a specific particle size; two main building

blocks are involved in the formation of clay minerals: silicon-oxygen tetrahedron ( $\text{Si}_2\text{O}_5$ )<sup>2-</sup> and gibbsite sheet [38]. Different tetrahedrons that share every three out of four oxygens make tetrahedral sheets. Octahedral sheets are made up of specific octahedrons that share boundaries, which contain hydroxyl and oxygen anion groups typically working as the coordinating cation ( $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Mg}^{2+}$ ). These octahedral sheets are organized in a hexagonal pattern [39]. Thus clay material exists in various crystalline forms and acts upon the effluent load to treat.

#### 12.4.1.1 Kinds of clay materials

Clays are of different types due to different particle sizes and mineralogy. The basic building block of silica minerals is the  $\text{SiO}_4^{4-}$  units arranged in a tetrahedral or octahedral manner (Fig. 12.1). In clay minerals the tetrahedral sheet is always combined with an octahedral sheet. A cation ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , etc.) is surrounded by six neighbors, like oxygens or hydroxyls. Also, between two layers some water molecules are present along with  $\text{K}^+$  or  $\text{Na}^+$  ions, which are exchangeable. Some different types of clays are:

- Bentonite
- Kaolinite
- Montmorillonite and smectites
- Sepiolite and palygorskite



**Figure 12.1** Schematic representation of tetrahedral and octahedral sheets in clay minerals.

#### 12.4.1.1.1 *Bentonite*

Bentonite is an impure clay having montmorillonite, and it can act as an absorbent of aluminum phyllosilicate nature. Bentonite clay is of different types depending on whether the main element is calcium (Ca), aluminum (Al), potassium (K), or sodium (Na). Bentonite is mostly formed in the presence of water from weathering of volcanic ash [38]. Bentonite clay has excellent adsorbing capacity and is effectively used to shelter nutraceutical, diagnostic, and pharmaceutical products from degradation by moisture. Bentonite desiccants have a higher adsorption ability than silica gel desiccants [40].

#### 12.4.1.1.2 *Kaolinite*

It is another example of clay adsorbents. Kaolinite contains trioctahedral minerals (chamosite, antigorite, cronstedite, and chrysotile) and dioctahedral minerals (kaolinite, nacrite, dickite, and halloysite), having the formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  [41]. Kaolin is a soft clay and consists of kaolinite. The general composition of kaolinite is  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  (hydrated aluminum silicate) [42, 43]. The kaolinite structure is formed of sheets of silicate ( $\text{Si}_2\text{O}_5$ ) attached to gibbsite layers (aluminum oxide or aluminum hydroxide layers,  $\text{Al}_2(\text{OH})_4$ ). These layers are formed by silicate mineral linkage to a tetrahedral sheet that is further linked by atoms of oxygen to another octahedral sheet of alumina. In trioctahedral minerals, the octahedral spots are filled with iron and magnesium, but these spots are filled with aluminum (Al) in dioctahedral minerals. Single-layer structures include kaolinite and halloysite, but kaolinite, nacrite, and dickite are present as plates [44]. Halloysite occurs in a tubular structure in which a single layer of water is present between sheets, while nonswelling clay is kaolinite [45]. All these are forms of kaolinite that act in different ways.

It is found that a heterogeneous surface charge is present on kaolinite. Its basal surface has a constant charge, in which  $\text{Si}^{4+}$  is substituted by  $\text{Al}^{3+}$ . On the boundaries, the charge is due to protonation or deprotonation of surface hydroxyl groups so it depends on the pH of the solution [38]. Adsorption can take place on the exterior parts of the sheets of alumina and silica. Kaolin is an

environment-friendly material having no harmful effects on health as long as its fine particle dust is under control [46].

#### **12.4.1.1.3 Montmorillonite and smectites**

A soft phyllosilicate mineral that normally makes crystals that are microscopic in nature is montmorillonite. It is part of the family of smectites, having an expanding crystal lattice in a 2:1 ratio. The smectite family includes nonmetallic clays mainly made up of hydrated calcium aluminum sodium silicate, which is a group of monoclinic clay-like material [47]. It includes the salt of  $(\text{Na}, \text{Ca}, \text{H})(\text{Al}, \text{Zn}, \text{Fe}, \text{Mg})_2(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  having hydrated calcium, sodium, magnesium, aluminum, silicate hydroxide, that is,  $(\text{Ca}, \text{Na})_x(\text{Mg}, \text{Al})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$ . Iron (Fe), potassium, and other cations are substituents, and depending on the source, the cation ratio differs. A layer containing a central alumina octahedral sheet and two tetrahedral sheets is the structural unit of montmorillonite [42].

These are continuous in directions of width and length. There is weak bonding among layers, and thus they have a brilliant ability to cleave. So water molecules and other compounds can enter these layers and can cause enlargement. Different forms of smectite are made by isomorphic substitution of smectite. The charge on the structure is balanced with different cations, which allows the water to move in between the crystal lattice layers, causing reactions that are reversible; in this way it shows plastic-like properties. The volume of montmorillonite greatly depends upon the water content; as adsorption increases, the volume also increases [45].

#### **12.4.1.1.4 Sepiolite and palygorskite**

Natural clay minerals containing magnesium hydrosilicate, which is a group of silicates, are sepiolite and palygorskite. These clay minerals are silicates of magnesium, but palygorskite shows more structural variety than sepiolite and it contains more Al and a lesser amount of Mg. The general formula of sepiolite is  $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O}) \cdot 48\text{H}_2\text{O}$  and of palygorskite is  $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O}) \cdot 44\text{H}_2\text{O}$ . These are fibrous clay minerals, and their structures are formed by the storage of layers of octahedral and tetrahedral oxide that contain canal holes [48]. Both minerals have the same structure and tetrahedral layers going in a single direction that form ribbons in the ratio 2:1.

These ribbons then elongate toward the *a* axis, and the width of the *b* axis on average in sepiolite is three linked tetrahedral chains and in palygorskite is two linked tetrahedral chains [49]. These crystals are nonswelling and inert and may produce a random crystal lattice in water and can show liquid trapping, gelling, and thickening properties [50].

### 12.4.2 Zeolites

Zeolites are defined as crystalline aluminosilicates with channels of 3D molecular and porous structures [51–53]. There are many framework topologies that can be used for the synthesis of zeolites with different chemical structures, and almost 170 such topologies have been reported [54–56]. Usually zeolites act as adsorbents and catalysts due to their adsorption, as well as ion-exchange properties and molecular reactions in their cage structures [57–59].

#### 12.4.2.1 Adsorption phenomenon in zeolites

The adsorption phenomenon can be illustrated by the simple example of acetone's adsorption into the supercages of zeolite Y. Such adsorption will result in a mass change, and this capacity of the zeolite to adsorb gas molecules has been exploited in developing gas sensors [60] with zeolite Y (cage 13.2 Å, window 7.4 Å).

#### 12.4.2.2 Some natural zeolites

Various naturally occurring zeolites are known and available since the past few decades. The most common types are chabazite, stilbite, phillipsite, mordenite, laumontite, clinoptilolite, and analcime; but paulingite, offretite, mazzite, and barrerite are rarely found [51]. Clinoptilolite is the most commonly and extensively used all over the world because it is the most abundant of all zeolites. In terms of the structure of zeolite, three parts are commonly present: an aluminosilicate framework, zeolitic water, and exchangeable cations [52].  $M_{x/n}[Al_xSi_yO_{2(x+y)}]\cdot pH_2O$  is the formula of zeolite, where M is (Li, Na, K) or (Ba, Sr, Mg, Ca), *n* is the charge on the cation, and *p/x* = 1–4 and *y/x* = 1–6. The formulas of some common zeolites are given in Table 12.2.

**Table 12.2** Chemical formulas of some common zeolites

<b>Zeolite</b>	<b>Chemical formula</b>
Ferrierite	$(\text{Na}_2, \text{K}_2, \text{Ca}, \text{Mg})_3\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 20\text{H}_2\text{O}$
Erionite	$(\text{Na}_2\text{K}_2\text{MgCa}_{1.5})_4\text{Al}_8\text{Si}_{28}\text{O}_{72} \cdot 28\text{H}_2\text{O}$
Chabazite	$(\text{Ca}, \text{Na}_2, \text{K}_2)_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$
Laumontite	$\text{Ca}_4\text{Al}_8\text{S}_{16}\text{O}_{48} \cdot 16\text{H}_2\text{O}$
Phillipsite	$\text{K}_2(\text{Ca}, \text{Na}_2)_2\text{Al}_8\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$
Analcime	$\text{Na}_{16}\text{Al}_{16}\text{Si}_{32}\text{O}_{96} \cdot 16\text{H}_2\text{O}$
Clinoptilolite	$(\text{K}_2, \text{Na}_2, \text{Ca})_3\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 21\text{H}_2\text{O}$
Stilbite	$\text{Na}_2\text{Ca}_4\text{Al}_{10}\text{Si}_{26}\text{O}_{72} \cdot 30\text{H}_2\text{O}$
Scolecite	$\text{Ca}_4\text{Al}_8\text{Si}_{12}\text{O}_{40} \cdot 12\text{H}_2\text{O}$
Mordenite	$(\text{Na}_2, \text{Ca})_4\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 28\text{H}_2\text{O}$

## 12.5 Application of Mineralized Materials for Water Treatment

Industrial or household wastewater, surface water, and ground water contains several contaminants. These contaminants contain organic and inorganic components that are harmful to human beings, plants, and animals. Recent applications for the removal of different harmful pollutants from wastewater by using natural zeolites and clay materials are discussed next.

### 12.5.1 Applications of Clay Material in Water Treatment

All types of natural clays are used as adsorbents and show good results in the removal of different kinds of dyes, organic contaminants, and metals [37, 39]. Due to the sorption and complexation abilities, clay minerals have been widely studied [53]. Clay minerals having properties like high surface area, more availability and low cost [54], ion exchange potential, and nontoxicity [55] are replacing commercially existing adsorbents in recent years [56, 57]. The most common type of clay mineral (bentonite clay) is used for the removal of many chemical compounds, such as organic pigments ( $\beta$ -carotene), amines, cations (Zn and Ni), ketones and phenol,

phosphates, chlorophyll, pesticides, and nonionic compounds [48]. It has been proved to be the most important economic clay mineral to remove dyes due to its availability and abundance [58]. It can efficiently remove methylene blue [59], acid green 25 [60], reactive red 120 [61], Congo red [62], Evans blue [63], amido black 10B [64], and acid blue 12 [65] with different modified forms. It is also used for heavy metal ions' removal from water, like zinc  $Zn^{+2}$  [59], lead Pb(II) [66], nickel Ni(II), and cadmium Cd(II) [67]. Montmorillonite has been used for the removal of heavy metals Cu(II) [68], Cr(VI) [69], Co(II) [70], Hg(II) [71], As(III), and As(V) [72]. It is also used for the adsorption of VOCs like benzene, *n*-hexane [73], *p*-xylene [74], toluene, ethyl acetate, ethanethiol [75], and acetone [76]. Adsorption of biocides and other organic pollutants, like *p*-nitrophenol [77], phenol [78], catechol [79], triclosan [80], and 2-naphthol [81], also takes place on montmorillonite. Na-montmorillonite has the capacity to remove dyes like methyl orange [82].

In the present scenario, researchers have investigated the property of adsorption of a dye (Congo red) on montmorillonite clay fixed through the chitosan-making nanocomposite biopolymer chitosan-montmorillonite [83]. Consequently, kaolinite can remove Coomassie brilliant blue R 250 [84], malachite green [85], and 4-nitrophenol [86]. A bacterial biofilm (*Bacillus* sp.) that is kaolin supported was used for the removal of heavy metals like Cr(III) [87]. Rhodamine B dye adsorption on montmorillonite and kaolinite was also studied [88]. Pb(II) removal from aqueous solution by adsorption on kaolinitic was investigated by Zahra et al. [23]. Some compounds, like 4,40-bipyridyl; benzidine, tetrahydropyran, ammonium, and ammonia; 1,4-dioxan; methylene blue; and tetrahydrofuran, are removed through adsorption on sepiolite [38]. Ozdemir et al. (2004) tested modified sepiolite for azo-reactive dye adsorption [89]. It was found that adsorption abilities may be enhanced by some modifications with quaternary amines on surfaces [90].

### 12.5.2 Applications of Natural Zeolites in Wastewater Treatment

Natural zeolites have been extensively studied for the treatment of wastewater and proved to be an efficient method for environmental cleaning. Natural zeolites with ion exchange have been used to remove

ammonium and heavy metal ions in past decades. Clinoptilolite, a natural Australian zeolite, was studied for ammonium ion removal from water. It showed the highest ammonium removal efficiency [91]. Three cationic exchangers—a gel resin (Dowex50wx8), a macronet resin (Purolite MN-500), and natural clinoptilolite—were studied for ammonia removal from wastewater. The results revealed that all cationic exchangers show variable effects on removal of ammonium ion [92]. Natural Chinese clinoptilolites were also used to remove ammonia and showed more ammonium ion uptake with an adsorption capacity of 1.74 mg NH<sub>4</sub>-N/g [93].

A Bulgarian zeolite and its different forms were used to remove various heavy metal ions, like Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Ni<sup>2+</sup> [94], and Fe [95]. Synthetic zeolites NaP1 and natural clinoptilolite were studied to remove heavy metals from wastewater. The results revealed that NaP1 zeolite shows around 10 times more adsorption capacity than the natural ones. The adsorption capacities of clinoptilolite are 0.041 mmol/g for Cd, 0.034 mmol/g for Ni, 0.079 mmol/g for Cr, 0.093 mmol/g for Cu, and 0.053 mmol/g for Zn [96]. Modified adsorbents (clinoptilolite, cationic exchange resin, and manganese greensand) are used to remove arsenic from wastewater. Zeolites were chemically modified by saturation with Fe<sup>3+</sup> ions and then used for arsenic removal from water. The adsorption capacity of Fe<sup>3+</sup> saturated was found to be 36.4 g/g for As(V) and 55.3 g/g for As(III) [97].

Zeolites are also used for dye removal from textile wastewater. Natural clinoptilolite was studied for the removal two basic dyes, MG-400 and MG-300, having components (2-[[4-methoxyphenyl] methylhydrazone]methyl]-1,3,3-trimethylindolium methosulfate) and 2-[[4-[ethyl(2-hydroxyethyl) amino]phenyl]azo]-6- methoxy-3-methylbenzothiazoliumchloride, respectively. The adsorption capacity of clinoptilolite for the adsorption of these dyes was 14.9 and 55.9 mg/g, respectively [98]. Other toxic components, like toluene, naphthalene, and o-xylene, can also be adsorbed on the surface of chlorosilane-modified natural diatomite and zeolite materials [99]. Tert-butyldimethylchlorosilane (TBDMSCI), trimethylchlorosilane (TMSCI), diphenyldichlorosilane (DPDSCI), and dimethyloctadecylchlorosilane (DMODSCI) were used. DPDSCI-modified clinoptilolite showed the maximum power to adsorb aromatic compounds. The removal capacity of toluene, o-xylene, and

naphthalene from an aqueous solution of 10 mg/L was 30%, 16%, and 51%, respectively [100].

## 12.6 Biosorption

Biosorption is actually a biological adsorption process in which pollutants such as metal or metalloid species and chemical compounds are removed from water by using biological materials [101, 102]. Sources of biosorbents can be the nonliving biomass, including shrimp, bark, squid, crab shell, and lignin, and the living biomass, such as algal and microbial biomass, including bacteria, fungi, algae, and yeast [103]. Bacteria, fungi, algae, and yeast are biosorbents for the removal of heavy metals from wastewater. The biosorption process has significant advantages as compared to other methods, such as a reasonable cost, no additional requirement of nutrient, possibility of removal of metals with high efficiency, regeneration of biosorbents, and minimization of chemical and biological sludge [104–108]. Numerous studies have explored the use of biosorbents for the removal of dyes [109–113] and heavy metals [114–116]. Biosorption mechanisms can be single or a combination of complexation, electrostatic interaction, microprecipitation adsorption, ion exchange, coordination, and chelation [117–119].

### 12.6.1 Biosorption Mechanism

Biosorption mechanisms are commonly divided into two types on the basis of cells' metabolism dependence, and these are nonmetabolism dependent and metabolism dependent. It can also be classified into three types by the site of the cell where the metal is adsorbed from the solution: cell surface sorption/precipitation, extracellular accumulation/precipitation, and intracellular accumulation. Two phases are involved in the biosorption process: a liquid phase, which is a solvent having dissolved compounds (metal ions) to be adsorbed, and a solid phase, which is a biosorbent. There are many ways for metal uptake by the cell of microorganisms. But the biosorption mechanism is a complicated process [120].

### 12.6.2 Factors Influencing Biosorption

It is proved by literatures that some important factors affect biosorption, and these are solution pH, biomass concentration, presence of other metal ions, and temperature [121, 122].

**Solution pH:** The most important factor in the biosorption process is the pH due to its effect on the functional group's activity in the biomass and the metallic ions' competition [5].

**Biomass concentration:** The specific uptake of compounds depends upon the biomass concentration. It increases with decrease in the biomass concentration [123, 124].

**Temperature:** The normal range of temperature 20°C–35°C does not affect the biosorption capacity [125].

**Presence of other metal ions:** In some cases, biosorption is selective. Biosorption is commonly used to remove heavy metals from wastewater, and this removal is affected by the existence of other metallic ions. If  $Zn^{2+}$  and  $Fe^{2+}$  are present, the thorium adsorption capacity of *Rhizopus arrhizus* is not affected but the uranium adsorption capacity of *Rhizopus arrhizus* is affected [126].

### 12.6.3 Functional Groups in Biomass Related to Biosorption

Classes of compounds and functional groups in biomass have been shown in Table 12.3. According to researchers, the R represents the residue and its location specifies that what is attached at this site differs from one compound to another [127].

### 12.6.4 Biosorbents Types

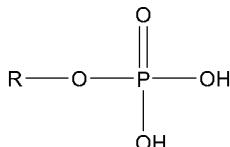
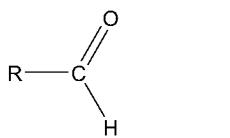
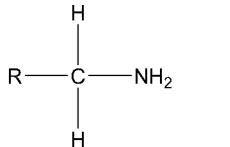
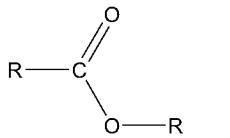
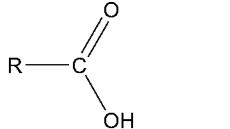
Living and nonliving biomass and cellular products can be used as biosorbents. Some of them have been briefly described here:

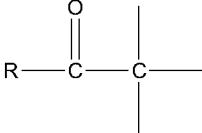
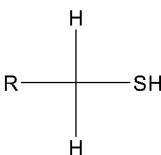
- Bacterial biosorbents
- Fungal biosorbents
- Marine algae as biosorbents

### 12.6.4.1 Bacterial biosorbents

The most versatile and abundant of all microorganisms are bacteria, and they represent a major fraction ( $\sim 1018$  g) of the total living native biomass. Bacteria are important biosorbents because of their small size, their ubiquity, their resilience against a wide range of environmental conditions and their capability to grow in controlled environments.

**Table 12.3** Classes of organic components in biomass and representative functional groups

Functional groups	Corresponding names	Class of compounds
	Phosphate	DNA, ATP, RNA
	Carbonyl terminal end	Aldehydes, polysaccharides
	Amino	Nucleic acids, proteins
	Ester	Lipids
	Carboxyl	Proteins, fatty acids, organic acids

Functional groups	Corresponding names	Class of compounds
	Carbonyl internal	Polysaccharides, ketones
R—O—H	Hydroxyl	Alcohols, carbohydrates
	sulfhydryl	Cysteine (amino acid)- proteins

The following bacteria species have been studied [70] for the removal of metals or organics:

- *Bacillus*
- *Pseudomonas*
- *Streptomyces*
- *Escherichia*
- *Micrococcus*

Bacteria have the ability to biosorb many elements [126].

#### 12.6.4.2 Fungal biosorbents

Fungi are a diverse and large group of eukaryotic microorganisms. Three types of fungi are most important and useful:

- Molds
- Yeasts
- Mushrooms

Filamentous fungi and yeasts are used in many orders to bind metals. These are naturally abundant in the environment and have significant importance in industrialized methods. In terms of morphology, there are unicellular yeasts, filamentous fungi, and polymorphic yeasts. Fungi act as decay organisms of synthetic and natural materials, such as paint, food, leather, fabrics, and wood,

and as decomposers of organic materials [128]. Yeast and fungi are used to adsorb and remove heavy metals, but their metabolism and fermentation processes are affected by the presence of different heavy metals. Many studies have been done to reveal the behavior of yeast and fungi in the presence of metals [129]. The results have led to the idea of using yeasts and fungi for the removal of toxic metals (cadmium and lead) from wastewater and recapture of precious metals (silver and gold) from processed water [130]. Both living and nonliving fungal cells have the ability to uptake precious and toxic metals [131].

#### **12.6.4.3 Marine algae as biosorbents**

Algae are used as biosorbents because of their ready availability and high adsorption capacity [132]. Comparative studies of algae with other types (bacteria and fungi) have been done for their biosorption. A statistic review has shown that as a biosorbent material the use of algae is less than that of other types of biomass, particularly bacteria and fungi (84.69% and 15.31%, respectively) [133]. Literatures show that brown algae are better biosorbents than green and red algae because they show a higher uptake ability than and red algae [134].

#### **12.6.4.4 Applications**

Bioaccumulation and biosorption have significant importance for wastewater treatment. In biological methods for water purification, microorganisms such as bacteria, plant material, fungi, and materials of biological origin, for example, chitosan are used [126]. It is the best alternative process for removal of toxic heavy metals from wastewater of other processes [106]. It is a cost-effective process because biosorbents are more easily available and have a relatively lower price than other adsorbents, like activated carbon (such as chitin, chitosan, etc.) [113].

*Pseudomonas luorescens* and *Bacillus mycoides* species were studied for the removal of heavy metals (Ni, Cu, Pb, Cr, Zn, Cd, and Co) at different levels. The result showed that bacterial species *Pseudomonas luorescens* ATCC 13525 was the most successful in the accumulation of zinc, cadmium, and chromium whereas *Pseudomonas luorescens* 2 was successful in the accumulation of

cadmium, chromium, and copper [135]. The three elements were also the most readily accumulated by the bacteria *Bacillus mycoides*. Metals such as Zn, Cu, Cr, and Cd were adsorbed by all examined bacterial species at about 100 µg/g [136]. The remaining three metals, Co, Pb, and Ni, were removed in less amounts than 100 µg/g [126].

Various workers have studied fungal species' capability of decolorizing triphenylmethane and azo dyes [137, 138]. *Phanerochaete chrysosporium* has been extensively studied for the ability to decolorize various dyes [139]. Fungal species like *Cyathus bulleri* [140], *Rhyzopus oryzae* [141], *Coriolus versicolor* [142], *Trametes versicolor* [143], *Laetiporus sulphureus* [144], *Streptomyces* sp. [145], and *Funalia trogii* [146] and other microorganisms have also been used for dye decolorization [147]. *Aspergillus niger* has the capability to remove dyes from wastewater. Carboxyl, phosphate, and amino are three major functional groups of *Aspergillus niger* that play a significant role in dye biosorption [148]. Khalaf investigated that *Aspergillus niger* is used as a biosorbent for the reactive dye syn-azol's removal from wastewater and matched it with *Spirogyra* sp. (a green algae) [149]. The results showed that the dried biomass of *Spirogyra* sp. and *Aspergillus niger* performs the maximum dye removal [149].

Some marine macro- and micro-algal species have been used as biosorbents for heavy metal ion removal [134]. It was reported that these algae are able to adsorb heavy metals, such as K, Cu, Mg, Mn, Ca, Fe, V, Co, Cd, As, Sr, Se, Pb, Mo, Al, Ni, and Zn, from wastewater efficiently [150]. Chojnacka et al. described the biosorption of Cr<sup>3+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> ions by *Spirulina* sp. (blue-green algae) [151]. In another study, researchers studied the removal of toxic heavy metals and radionuclides by using three genera of algae from different taxonomic groups [152].

## 12.7 Conclusion and Future Prospects

In the last few years, removal of dye contents from textile effluents has been the target of great attention, not only because of its potential toxicity, but also due to its visibility problems. Numerous approaches have been undertaken in this regard. Adsorption is

found to be one of the most eminent techniques. In this chapter, low-cost adsorbents with significant effectiveness were discussed. The use of natural biomaterials is a promising alternative due to their relative abundance, effectiveness, and low commercial value. Many nonconventional low-cost adsorbents have been proposed by several scientists, including natural materials, biosorbents, and waste materials from industry and agriculture, for example, clay materials (bentonite and kaolinite), zeolites, siliceous material (silica beads, alunite, and perlite), agricultural wastes (bagasse pith, maize cob, rice husk, and coconut shell), industrial waste products (waste carbon slurries and metal hydroxide sludge), biosorbents (chitosan, peat, and biomass) and others (starch, cyclodextrin, and cotton). There is a large scope for future research in utilization of low-cost adsorbents in textile effluent treatment processes. As biomass produced by various human activities can be suitably utilized for dye contents from effluents, all future research might be accompanied by adsorption/desorption and/or adsorption/readsorption processes so that there is no net sludge generation and, if any, it is minimum. In spite of the scarcity of consistent cost information, the widespread use of low-cost adsorbents in industries for wastewater treatment applications would fulfill the goal of zero waste, which is a pressing demand of the environment.

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## **Chapter 13**

# **Microorganisms for Textile Effluent Remediation**

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This chapter on microorganisms for textile effluent remediation deals with an introduction to the threat posed by industrial effluents from various textile industries. The emphasis is on various microorganisms, including bacteria and fungi, found growing in these textile effluents. Comprehensive information on the potential microorganisms and their microbial consortia studies addressed by various researchers across the globe is investigated. In addition, the effects of various parameters on the treatment of textile effluents by microorganisms are detailed. The growth and degradation kinetics of various microorganisms to aid the remediation processes are elaborately discussed. To conclude, a brief study on the metabolic products identified during the assimilation of different dyes by the individual microorganisms is presented to understand the end products and intermediates of microbial dye degradation.

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### 13.1 Introduction to Textile Effluents

The textile industry is the largest industry in the world, utilizing various forms of natural fibers, including cotton, silk, wool, and synthetic fibers. Different structures of synthetic dyes lead to the formation of effluents with a markedly variable chemical composition and different toxic substances. Over  $8 \times 10^5$  tons and approximately 15,000 different types of dyes and pigments are produced worldwide annually [1]. Dyeing is the process of applying color to a piece of cloth to improve and enhance its aesthetic value. Reactive, vat, naphthal, acid, basic, and natural dyes are the various types of dyes used in the textile industry [1, 2]. These dyes are applied to the fabrics in the textile dyeing process with the aid of various methods, like desizing, scouring, bleaching, washing, dyeing, fixing, washing, finishing, and drying of dyed fabric. The bleaching and dyeing processes are found to generate a huge amount of textile effluents. The major pollutants released in the process are composed of huge amounts of suspended solids, heat, color, and acidity. Effluent generation during the dyeing process is between 40 and 160 L/kg.

The effluents released in textile industries from various processes have varying characteristics. The effluents released from the desizing process, including polyvinyl alcohol (PVA), carboxymethyl cellulose (CMC), and starch, have a high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels. The possible pollutants in the scouring process are waxes, surfactants, and caustic soda. This part of the effluent has a high pH, a high COD, and a high BOD. The bleaching effluent has high amounts of caustic soda, chlorine, and hydrogen peroxide and a high pH and BOD. The dyeing wastewater also discharges volatile organic compounds into the atmosphere. It contains high amounts of surfactants, metals, salt, cationic ions, sulfide, and spent solvents. The textile wastewater is brownish to black in color, with alkaline pH of 8.5, total suspended solids at 270 mg/L, total dissolved solids at 2300 mg/L, BOD of 350 mg/L, and COD of 770 mg/L [3]. The dyes undergo photochemical degradation in aquatic environments and release carcinogenic amines, which are harmful to all living organisms. Aquatic organisms require light, but the light scattering is affected due to the color in the dye wastewater.

Low amounts of dyes in water cause hemorrhage, nausea, and ulceration of skin and mucous membranes. Damage to kidneys, liver, brain, the reproductive system, and the central nervous system is the most common effect of dyes.  $\text{Cr}^{6+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  are the most common metal ions found in textile effluents. All these together are causative agents for toxicity in textile dyes. In addition, textile effluents affect plant growth; development of roots; and the amount of photosynthetic pigment, responsible for the color of leaves, in plant species [2]. The pollution control boards of different countries have formulated norms for the discharge of effluents into the environment, and many have directed that, henceforth, textile wastewater must be treated before being discharged into the environment.

## 13.2 Potential Microorganisms and Consortium

Various microorganisms have the potential to grow in textile effluents. Literatures have reported several microbial species in the process of dye degradation. They include some species of bacteria, including *Aeromonas hydrophila*, *Escherichia*, *Citrobacter*, *Pseudomonas*, *Sphingomonas*, *Bacillus*, *Clostridium*, *Nocardia*, *Paenibacillus*, and *Streptomyces*. *Pseudomonas* strains have the potential to degrade certain azo dyes aerobically; nevertheless the intermediates formed are found to disrupt the metabolic pathways, leading to the nonmineralization of dyes [3]. *Bacillus subtilis* was found to have the potential to break down a specific azo dye, p-aminoazobenzene. *Pleurotus* species have been reported to be robust and more tolerant to high concentrations of polluting chemicals than bacteria due to the extracellular ligninolytic enzymes produced by them, with the capacity to degrade textile dyes.

A bacterial community composed of mixed cultures SB4 composed of six bacterial strains, namely *Bacillus* sp. V1DMK, *Lysinibacillus* sp. V3DMK, *Bacillus* sp. V5DMK, *Bacillus* sp. V7DMK, *Ochrobacterium* sp. V10DMK, and *Bacillus* sp. V12DMK, decolorized 200 mg/L of the azo dye reactive violet 5R (RV5) within 18 h under static conditions. *Proteus vulgaris* was found to have the potential to effectively decolorize azo dyes. *Aeromonas hydrophila* reportedly has

the potential to decolorize 90% of a deep-red azo dye solution (red RBN) within 8 days at a dye concentration of 3000 mg/L. *Pseudomonas putida* was found to aerobically degrade a mixture of textile azo dyes and individual azo dyes at alkaline pH (9–10) and salinity (0.9–3.8 g/L) at ambient temperatures. *Streptococcus faecalis* and *Escherichia coli* were found to have the ability to degrade tartrazine and quinoline yellow. *Paenibacillus polymyxa*, *Micrococcus luteus*, and *Micrococcus* sp. reportedly have the ability to decolorize RV5 within 36 h. The facultative bacterial isolates *Enterobacter* sp., *Serratia* sp., *Yersinia* sp., and *Erwinia* sp. degraded C.I. reactive red 195 in solid and liquid dye mediums. *Pseudomonas luteola* was found to have the potential to degrade reactive red 141.

*Klebsiella* sp. isolated from the activated sludge process of the textile industry reportedly degraded azo dyes. *Klebsiella pneumoniae* was found to be the best decolorizer of viscose orange-A, with a decolorization capacity of 98.44%. *Bacillus subtilis* is reportedly a good decolorizer of direct green-PLS, with a decolorization ability of 99.05%. *Klebsiella pneumoniae* decolorized direct violet-BL with 87.3% decolorization. *Escherichia coli* was found to be the finest decolorizer of direct sky blue-FF, with 61.56% decolorization. Direct black-E was decolorized by *Klebsiella pneumoniae* by upto 92.03%. *Pseudomonas cepacia*, *Pseudomonas aeruginosa*, *Pseudomonas oleovorans*, and *Pseudomonas putida* exhibited a good dye degradation capacity for acid orange 7. *Pseudomonas desmolyticum* NCIM 2112 was able to degrade 100 mg/L of the carcinogenic dye direct blue-6 within 72 h of incubation, with 88.95% reduction in COD under a static anoxic condition [4]. A consortium made up of *Aeromonas hydrophila*, *Pseudomonas putida*, *Pseudomonas plecoglossicida*, *Lysinibacillus fusiformis*, and *Pseudomonas monteilii* isolated and identified from the dyestuff industrial area was effective in the degradation of methyl orange, acid orange, malachite green, methylene blue, and rhodamine B. The highest decolorization, of 91%, was found for the dye malachite green by *Pseudomonas putida* after 5 days of incubation. *Comamonas testosterone* was found to decolorize 85% of methyl orange after 7 days of incubation. *Pseudomonas putida* was also found to decolorize 85% and 69% of acid orange II and methylene blue, respectively, after 7 days of

incubation. After 3 days of incubation, 56% of rhodamine B was decolorized by *Pseudomonas monteili*. *Trichoderma harzianum* was effective in degrading the dyes acid red, basic blue, bromophenol blue, Congo red, and direct green. A bacterial consortium consisting of *Providencia rettgeri* strain HSL1 and *Pseudomonas* sp. SUK1 successfully degraded and detoxified structurally varying azo dyes, including reactive black 5 (RB 5), reactive orange 16 (RO 16), disperse red 78 (DR 78), and direct red 81 (DR 81), within 12 to 30 h at 100 mg/L concentration at  $30^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$  with 98%–99% decolorization. *Pseudomonas aeruginosa*, *Bacillus cereus*, *Bacillus subtilis*, *Pseudomonas fluorescens*, and *Escherichia coli* were found to have a similar potential to degrade and decolorize textile dye effluents. *Phanerochaete chrysosporium*, a white rot fungus, and *Trametes (Coriolus) versicolor*, *Bjerkandera adusta*, *Aspergillus ochraceus*, species of *Pleurotus*, and *Phlebia* reportedly have the potential to degrade dyes. Ascomycetes yeast species *Candida tropicalis*, *Debaryomyces polymorphus*, *Candida zeylanoides*, and *Issatchenkia occidentalis* were able to enzymatically biodegrade and decolorize azo dyes. Recently, *Saccharomyces cerevisiae* MTCC-463 was reported to have a role in the decolorization of malachite green and methyl red. *Saccharomyces cerevisiae* has also shown bioaccumulation of some reactive textile dyes, including remazol blue, remazol black B, and remazol red RB, during its growth in molasses. *Galactomyces geotrichum* MTCC 1360 was able to decolorize triphenylmethane, azo, and reactive high textile dyes. *Trichosporon beigelii* NCIM-3326 was able to decolorize navy blue HER. *Chlorella* and *Oscillatoria* are capable of degrading azo dyes to their aromatic amines. More than 30 azo compounds were biodegraded and decolorized by *Chlorella pyrenoidosa*, *Chlorella vulgaris*, and *Oscillateria tenuis*, with the azo dyes decomposed into simpler aromatic amines [5].

The consortium containing *Bacillus subtilis*, *Stenotrophomonas* sp., *Pseudomonas stutzeri*, and *Pseudomonas aeruginosa* showed decolorization in the range of 90%–97% for reactive orange M2R, remazol brilliant red 5, reactive red 195, red HE8B, and reactive blue 59. *Trametes villosa* and *Pycnoporus sanguineus* were able to decolorize drimaren brilliant blue dye in a liquid synthetic medium. *Pleurotus platypus* could tolerate the reactive dye effluents

and degrade them. Microbial strains such as *Sphingomonas* spp., *Pseudomonas luteola*, *Streptococcus faecalis*, *Klebsiella pneumoniae*, *Penicillium* spp., and *Aspergillus* spp. are reportedly capable of reducing azo dyes. Genetically engineered bacteria have been in the limelight for the past few decades, and the genetically engineered bacteria pGEX-AZR/*E. coli* JM-109 possess the ability to degrade azo dyes [3].

### 13.3 Mechanism of Textile Dye Degradation

The mechanism of dye degradation is critical during the treatment of textile effluents. Biosorption is the initiator of dye degradation. Biosorption indicates the metabolism-independent processes, including physical adsorption, chemical adsorption, complexation, ion exchange, and chelation, taking place basically at the cell wall. It contributes to the process of degradation by means of concentrating the pollutants on the surface of the biological matrix. The sorbent is mostly of biological origin [6]. It contributes to decolorization by two mechanisms, adsorption onto the biological organism and ion exchange. These mechanisms are influenced by many physical-chemical factors, like initial dye concentration, pH, temperature, and the nature of the dye present in the solution.

Chemistry of a particular dye and the specific chemistry of the microbial biomass decide the interactions of microorganisms with the textile dyes. The challenge is to uncover microorganisms that thrive in the presence of salts and other harsh conditions of textile effluents. For this reason, it is important to isolate appealing microorganisms in the most diverse natural environments. Most of the dyes do not degrade easily in anaerobic conditions. Azo compounds are susceptible to biological degradation under both aerobic and anaerobic conditions.

Decolorization of azo dyes under anaerobic conditions is a relatively straightforward and imprecise process. Aerobic treatment of azo dyes with bacteria is usually not efficient due to the fact that oxygen is a more efficient electron acceptor than azo dyes [7]. Microorganisms that can degrade azo dyes are necessary for efficient treatment of textile wastewater. The azo dyes are changed by organic

and inorganic reactions into aromatic amines. The aromatic amines are responsible for the increase in the toxicity of effluents.

Enzymes with azoreductase activity have been found in many types of aerobic and anaerobic microorganisms, including bacteria, fungi, and algae. The azoreductase enzyme is thermostable and remains active upto 60°C over short periods of time. The most interesting oxidases are found in microorganisms that thrive in aerobic conditions. Aerobic microorganisms have oxidative enzymes that break down the aromatic amines released during anaerobic color removal. The remaining degradation products are found to be carboxylic acids and other small organics. Under aerobic conditions, the aromatic amines may also undergo autoxidation and turn back into colored molecules.

Decolorization under anaerobic conditions cannot completely mineralize azo dyes. Aerobic bacteria are capable of reducing azo compounds with the help of oxygen-catalyzed azoreductases and produce aromatic amines. Thus, to obtain aromatic amines as decolorized products, susceptibility to an oxygenase attack is critical. Thus, bacterial mineralization of azo dyes generally takes place in two steps: (1) anaerobic degradation to the corresponding colorless aromatic amines, which are carcinogenic and toxic, and (2) entire mineralization of the aromatic amines under aerobic conditions. Microbial degradation of azo dyes takes place by the following strategy. It involves the reductive cleavage of azo bonds with the help of an azoreductase enzyme, and this takes place under anaerobic conditions and involves the transfer of four electrons. This then advances in the course of two stages at the azo linkage, and at each stage, two electrons are transferred to the azo dye, which acts as a final electron acceptor [8]. These mechanisms result in dye decolorization and the formation of a colorless solution. The resulting intermediate metabolites, which are the aromatic amines, are then further degraded. The efficacy of various anaerobic treatment applications for the degradation of a wide variety of synthetic dyes has been demonstrated by various researchers. It has been reported that the low redox potential formation in anaerobic conditions causes effective decolorization of azo dyes. The presence of oxygen usually inhibits the azo bond reduction activity since aerobic respiration may dominate the utilization of NADH, thus

hampering the electron transfer from NADH to azo bonds. The azo dye might act as an electron acceptor supplied by the carriers of the electron transport chain. On the other hand, decolorization might be attributed to the nonspecific extracellular reactions occurring between reduced compounds generated by the anaerobic biomass.

Under aerobic conditions mono-oxygenase and dioxygenase enzymes catalyze the incorporation of oxygen into aromatic rings of organic compounds prior to ring fission. Aerobic azoreductases are able to use both NAD(P)H and NADH as cofactors and reductively cleave the carboxylated growth substrates of the bacteria and the sulfonated structural analogues. This type of azoreductase activity was found in *Pseudomonas* species strains K22 and KF46, and their enzyme system was flavin-free. Some bacteria are able to grow on azo compounds as the sole carbon source. These bacteria cleave –N<sub>55</sub>N– bonds as they are the chief hub of an oxidizing radical attack and thereby utilizing the amines as the carbon and energy source for their augmentation. Only a few bacteria with specialized azo dye reducing enzymes have been found to degrade azo dyes under fully aerobic conditions [6]. Azoreductases and oxidases are the most important enzymes for cleaving azo bonds and making the aromatic amines more accessible and for further breakdown of the previously released aromatic amines. Synergistic metabolic activities of a mixed microbial consortium lead to the complete mineralization of azo dyes. The mechanism of microbial degradation of azo dyes involves the reductive cleavage of azo bonds (–N=N–) with the help of azoreductase under anaerobic conditions and results in the formation of colorless solutions. Reduction to the anion radical occurs by a fast one-electron transfer reaction, followed by a second, slower electron transfer to generate the stable dianion. Thus the functional group of the azo dye with a higher electron density is unfavorable to this second electron transfer to form the dianion, leading to less ability for decolorization. The sulfonated reactive group of azo dyes is more recalcitrant than carboxylated azo dyes.

### 13.4 Parameter Optimization

Factors affecting bacterial decolorization should be optimized during the biodegradation of textile dyes. In biological treatment processes,

various physicochemical operational parameters, such as the pH, dye structure, agitation, oxygen, temperature, dye concentration, supplementation of different carbon and nitrogen sources, electron donor, and redox mediator, are responsible for influencing the bacterial decolorization performance of azo dyes. Thus, to make the process of biodegradation more efficient and practically applicable, prior determination of the effect of each factor on the bacterial decolorization of azo dyes is indispensable.

Decolorization of azo dyes occurs under strictly anaerobic, facultative anaerobic, and aerobic conditions by different groups of bacteria. Decolorization of azo dyes has been found to be far superior under strictly anaerobic conditions and partly under semianaerobic ones. Under anaerobic conditions reductive enzyme activities are higher and a small amount of oxygen is also required for the oxidative enzymes [9]. During bacterial degradation of azo dyes both oxidative and reductive enzymes play a role. Hence, for efficient color removal, aeration and agitation are critical since they increase the concentration of oxygen in the solution. The effect of oxygen on azoreduction is irreversible and the simple aromatic compounds formed during the azo dye reduction reaction are degraded via hydroxylation and ring opening in the presence of oxygen. The aerobic condition is required for the complete mineralization of the azo dye molecule.

Most of the azo dyes are deficient in carbon sources, and the biodegradation of dyes is complicated without any supplement of carbon or nitrogen sources. Azo dye decolorization by mixed as well as pure cultures generally requires complex organic sources and carbohydrates. During decolorization of azo dyes via reduction of azo bonds, the reducing equivalents from various carbon sources are relocated to the dye. In anaerobic consortia, acidogenic bacteria change the carbohydrates to acetic acid and methanol, and they are the competitive substrates for methanogenic, sulfate reducing, and acetogenic bacteria [6]. Addition of carbon sources was reportedly less effective in promoting decolorization due to the preference of cells in assimilating the extra carbon sources instead of using the dye compound as the carbon source. On the other hand, the addition of organic nitrogen sources regenerated NADH, which acted as an electron donor for the reduction of azo dyes by microorganisms.

A microbial cell has the inherent potential to respond to temperature changes by biochemical and enzymatic mechanisms. Temperature is of dominant importance for all processes associated with microbial vitality. Temperature changes lead to a sudden alteration in the activation energy. Moreover, effects of temperature on the growth rate, biomass yield, and reaction mechanism show that the decolorization rate of azo dyes increases up to the optimal temperature, followed by an insignificant reduction in the decolorization activity at higher temperatures due to a loss in cell viability and denaturation of the enzyme azoreductase.

Decolorization is highly dependent on the medium pH, and the optimal pH for color removal is often between 6 and 10. In most cases, the rate of color removal is higher at the optimum pH and decreases rapidly at strongly acid or strongly alkaline pH. It is related to the transport of dye molecules across the cell membrane, which is considered as the rate-limiting step for decolorization. Biological reduction of the azo bond results in an increase in the pH due to the formation of aromatic amine metabolites. The pH tolerance of decolorizing bacteria is very important, as it makes them suitable for practical biotreatment of dyeing industry effluents.

Increasing the dye concentration decreases the decolorization rate. This may be due to the toxic effect of dyes with regard to the individual bacteria and/or inadequate biomass concentration (or improper cell-to-dye ratio), as well as blockage of active sites of azoreductase by dye molecules with different structures [9]. Reactive group azo dyes with sulfonic acid ( $\text{SO}_3\text{H}$ ) groups on their aromatic rings greatly inhibited the growth of microorganisms at higher dye concentrations. Some of the nonenzymatic reduction mechanisms controlled by processes are independent of the dye concentration.

The diverse structures in the synthetic azo dyes, and changes in the chemical structures, significantly affect the decolorization capability in the form of biodegradability and reduction. Dyes with simple structures and low molecular weights exhibit higher rates of color removal, whereas the removal rate is lower in the case of dyes with substitution of electron-withdrawing groups in the para position of the phenyl ring, relative to the azo bond and high-molecular-weight dyes. The color removal rate is faster in

the case of monoazo dyes compared to diazo and triazo ones [10]. The production of azoreductase is related to dye structures. Azo compounds with hydroxyl or amino groups are more likely to be degraded than those with methyl, methoxy, sulpho, or nitro groups. For the terminal nonenzymatic reduction mechanism, reduction rates are influenced by changes in the electron density causing an increase in the reduction rate.

The sulfonated reactive groups of azo dyes are normally considered to be more recalcitrant than carboxylated azo dyes. The electron-dense hydrogen bonds have a significant effect on the reduction rate due to the influence of hydrogen bonds on the azo hydrazone tautomerism of hydroxyl azo compounds. It is necessary to have an electron donor to enhance the anaerobic decolorization performance. Some of the electron donors are sodium succinate, sodium acetate, sodium citrate, sodium formate, and sodium pyruvate. Electron donors such as glucose and acetate ions induce the reductive cleavage of azo bonds [5, 8]. The bacterial anaerobic azoreduction oxidizes the electron donors and transfers the electrons to the acceptors through a multicomponent system related to the electron transport chain. Dehydrogenases, cytochromes, and menaquinones act as essential electron transport components of the azoreduction mechanism. Various electron-donating half-reactions are different due to the influence of the specific types of electron donors. Formates acts as a very successful electron donor for the anaerobically induced electron transfer pathway due to the involvement of the formate dehydrogenase enzyme. Methanol is extensively used as a cost-effective electron donor for the biological treatment of textile effluent. The products of cell lysate residue are found to contribute as electron donors for anaerobic azo dye reduction. The electron donors are not only responsible for the reduction mechanism but also fuel the enzymatic scheme accountable for the reduction process. Thiomersal and p-chloromercuribenzoate are found to inhibit alcohol dehydrogenase of the NADH-generating systems required for dye reduction.

The transfer of reducing equivalents from a primary electron donor to a terminal electron acceptor acts as the rate-limiting step in the anaerobic reduction process. The supplementation of redox

mediators accelerates the transfer of reducing equivalents to the terminal electron acceptor and minimizes the steric hindrance of the dye molecule. Flavin adenine dinucleotide (FAD); flavin mononucleotide (FMN); and quinone-based compounds such as anthraquinone-2,6-disulfonate (AQDS), anthraquinone-2-sulfonate (AQS), riboflavin (vitamin B<sub>2</sub>), cyanocobalamin (vitamin B<sub>12</sub>), and lawsone (2-hydroxy-1,4-naphthoquinone) are some of the redox mediators; and these are required only in small concentrations.

The redox potential is critical in this scenario since it measures the ease with which a molecule will accept electrons and could be possibly reduced. The color removal rate is higher when the redox potential of the system is at its most negative. It was also reported that quinoid redox mediators, lawsone, AQS, and AQDS utilize cytoplasmic or membrane-bound quinone reductase and shuttle reducing equivalents from bacteria to azo dyes.

### 13.5 Growth and Degradation Kinetics

Microbial growth was measured by the intensity of turbidity in the medium. The nutrient medium is responsible for supporting the maximum growth rate. Enhancement in cell production is due to the presence of carbon sources and nutrients necessary for higher decolorization. Significant exposure of these organisms to a myriad of chemicals in the textile effluent affects their growth kinetics. Reports, however, indicate that though several microorganisms may seem to have a potential for dye degradation, very few strains can withstand the conditions of dyeing effluents and thus the effluent-adapted strains may be better candidates for potential bioremediative uses [3]. However, the result does not indicate the involvement of extra-chromosomal genes in the degradative activity of the isolates. Anaerobic degradation kinetics of a reactive dye with different carbon sources indicate that decolorization processes undergo first-order kinetics with some carbon sources and have a zero-order kinetic relationship with others. The decolorization rates increase with a decrease in dye concentrations.

Although general considerations concerning the kinetics of azo dye metabolism indicate that an accumulation of intermediate amines is not very likely, this possibility cannot be excluded under all

conditions. In addition, the longer growth cycle and complexity of the textile effluents, which are extremely variable in their composition, limit the performance of these fungi. The nitrifying bacteria are chemoautotrophs, and their growth rate is very low compared to heterotrophic bacteria. The energy obtained by the nitrification process is also not very high. In addition, the nitrifying bacteria have a larger generation time. All these factors mean that the nitrifying bacteria can appear in the reactor only when most of the organic matter is degraded. The heterotrophic bacteria while degrading the organic matter produce ammonia. This ammonia, which gets dissolved in water, is then used up by the nitrifying bacteria. To ensure that the microorganisms grow, they must be allowed to remain in the system long enough to reproduce. This period depends on their growth rate, which is related directly to the rate at which they metabolize or utilize the waste. If the environmental conditions are controlled properly, the growth rate of the microorganisms can ensure effective waste stabilization.

Experimentally it has been found that the effect of a limiting substrate or nutrient can often be defined adequately by the Monod model. Since bacterial decolorization is a reductive process, the presence of molecular oxygen in a medium may diminish its reduction potential [4]. During this process it was observed that while having relatively faster growth and higher cell density in an oxygen-rich environment as compared to a static condition, decolorization was much less due to the presence of oxygen. During dye decolorization in an aerobic environment electrons released by the oxidation of electron donors rather than azo dyes are preferentially utilized to reduce free oxygen. During decolorization in a microaerophilic environment, the demand for oxygen is very less, which will save a great deal of kinetic energy required in an aeration system and will reduce the operational cost. It was observed that organic nitrogen sources do not support appreciable decolorization, whereas combined with inorganic nitrogen, an increasing effect both on growth and decolorization was observed. Monod and Contois equations are mostly used by researchers to study degradation kinetics. Results suggest second-order kinetics with regard to dye concentration. Moreover, the effects of temperature on the growth rate, biomass yield, and reaction mechanism have also been reported. It was observed that the decolorization rate of azo dyes

increases up to the optimal temperature, and afterward there is a marginal reduction in the decolorization activity. This decline at higher temperatures can be attributed to the loss of cell viability or the denaturation of an azoreductase enzyme [7]. However, it has been shown that with certain whole bacterial cell preparations the azoreductase enzyme is relatively thermostable and can remain active up to temperatures of 60°C over short periods of time. It was also observed that reactive group azo dyes with sulfonic acid ( $\text{SO}_3\text{H}$ ) groups on their aromatic rings greatly inhibit the growth of microorganisms at higher dye concentrations.

However, the increasing concentration effect was reduced when a bacterial coculture was used instead of pure culture, and this might be due to the synergistic effect of both microorganisms. The rate of chemical reaction is the direct function of temperature. Bacteria require optimum temperature for growth. Since dye decolorization is a metabolic process a shift in the temperature from the optimum results in a decrease in dye decolorization because a high temperature causes thermal inactivation of proteins and possibly of cell structures such as membrane. This could be due to a greater production of enzymes and optimal growth conditions of the isolates [8].

## 13.6 Metabolite Identification

The decolorization of the dye remazol orange 3R by *Aster amellus* and *Gaillardia pulchella* was investigated. *Aster amellus* showed initiation in the activities of enzymes veratryl alcohol oxidase and DCIP reductase after degradation of the dye, while *Gaillardia pulchella* showed stimulation of laccase and tyrosinase, indicating their involvement in the dye metabolism. *Aster amellus* degraded the dye into acetamide, benzene, naphthalene, and 3-diazenylnaphthalene-2-sulfonic acid; and *Gaillardia pulchella* degraded the dye into acetamide, 3-diazenyl-4-hydroxynaphthalene-2-sulfonic acid, naphthalen-1-ol, and (ethylsulfonyl)benzene. The consortium of *Aster amellus* and *Gaillardia pulchella* resulted in the formation of 2-(phenylsulfonyl)ethanol and *N*-(naphthalen-2-yl)acetamide as the degradation products. The metabolites of the green HE4B dye metabolism were identified as 1-(4-methylphenyl)-

2-(7-[(Z)-phenyldiazenyl] naphthalen-2-yl)diazene; 7,8-diamino-2-(phenyldiazenyl) naphthalen-1-ol; and (Z)-1,1'-naphthalene-2,7-diylbis(phenyldiazenyl).

The initial reduction of benzidine-based azo dyes was the result of azoreductase activity, and the metabolites of direct black 38 were identified as benzidine, 4-aminobiphenyl, monoacetylbenzidine, and acetylaminobiphenyl. Nitroanilines formed by the reductive cleavage of the azo bonds ( $-N=N-$ ) are generated during the biodegradation of azo dyes under anaerobic conditions [6, 7]. Most of the aromatic amine metabolites are considered to be nonbiodegradable and result in a wide range of toxic effects on aquatic life and higher organisms. *Fusobacterium* reportedly has the potential to convert trypan blue into a mutagenic product, O-toluidine (3,3'-dimethylbenzidine), which has carcinogenic and teratogenic properties. The activity of benzopurpurine 4B and chlorazol violet N is attributed to the benzidine metabolite O-toluidine. The metabolites of disperse yellow 3, an azo dye widely used in the textile industry, were found to be 4-aminoacetanilide and 2-amino-*p*-cresol. 2-amino-*p*-cresol was a stronger allergen in this and in contrast, 4-aminoacetanilide was a weak sensitizer. Consortial degradation of scarlet RR in the presence of laccase or veratryl alcohol oxidase on scarlet RR led to the formation of the same intermediate as in the degradation pathway of scarlet RR by individual organisms, which is (ethyl[(4-oxo-3,4-dihydroquinolin-2-yl)methyl]amino)acetaldehyde, and further disintegration of (ethyl[(4-oxo-3,4-dihydroquinolin-2-yl)methyl]amino)acetaldehyde gave the final product 3,4-dihydroquinoline [9]. Formation of 1-3-chlorinin-2-amine was also observed by the removal of the nitro group from the unidentified intermediate species. Biodegradation of disperse azo dye rubine GFL resulted in an intermediate *N*-ethyl-4-[(2-methyl-4-nitrophenyl) diazenyl] aniline.

Veratryl alcohol oxidase brings about asymmetric cleavage of azo dyes, and further oxidative cleavage of the intermediate by laccase gives 4-[(2-methyl-4-nitrophenyl) diazenyl] phenol, which undergoes dehydroxylation to form 1-(2-methyl-4-nitrophenyl)-2-phenyl diazene. Furthermore, asymmetric cleavage of the intermediate by veratryl alcohol enzyme leads to the formation

of (2-methyl-4-nitrophenyl) diazene, which undergoes azo bond cleavage by azoreductase to form 2-methyl 4-nitroaniline, which is further oxidized by laccase to give 2-methyl-4-nitrophenol as the final metabolite. A consortium consisting of *Proteus vulgaris* NCIM-2027 and *Micrococcus glutamicus* NCIM-2168 degraded scarlet R and presented a very little amount of 1,4-benzenediamine in the decolorized solution. The consortium formed by *Bacillus odysseyi* SUK3, *Morganella morganii* SUK5, and *Proteus* sp. SUK7 degraded red HE3B, and the metabolites formed after the degradation were identified as 2,5-diaminobenzene 6-aminotriazine, aniline 2-sulfate, aniline 3-sulfate, 2-amino 5-chlorotriazine, and naphthalene. Sulfophthalimide is a major metabolite formed from sulfonated phthalocyanine dyes by *Bjerkandera adusta*. The degraded metabolites of Congo red dye by a novel marine bacterium *Dietzia* sp. were found to be closely matching with 4-amino-3-naphthol-1-sulfonate, which is comparatively less toxic than the Congo red dye. Biodegradation of reactive red 35 by *Pseudomonas aeruginosa* ARSKS20 in microaerophilic conditions by reductive symmetric cleavage of azo bonds carried out by an azoreductase enzyme resulted in the formation of two intermediates, 1-Amino-2-methoxy-5-(1-sulfonyl-2-sulfo-oxyethane) benzene (intermediate A) and 2-Amino-8-(acetyl amino)-1-hydroxy 3-6 naphthalene disulfonic acid (intermediate B). Degradation of reactive orange HE2R resulted in two metabolites, 2-amino butane 4-sulpho aniline and sulphoaniline [10].

Anaerobic biodegradation of azo dyes most commonly resulted in 2-methylphenol, 3-methylphenol, indole, 1,4-dione-2,5-cyclohexadiene, and butylated hydroxytoluene, whereas aerobic biodegradation resulted in 2-methylphenol, 3-methyl-benzonitrile, benzeneacetonitrile, and indole. The phthalocyanine dyes remazol turquoise blue G133, everzol turquoise blue, and heligon blue S4 are found to be biosorbed by *P chrysosporium* and metabolized by the ligninolytic extracellular enzyme laccase, resulting in organic metabolites with phthalocyanine ring breakdown. Manganese peroxidase releases the Cu<sup>2+</sup> from the phthalocyanine structure to give a non-copper-containing phthalocyanine metabolite. The phthalocyanine ring structure is further broken by desulphonation

and oxidation to give phthalimide and some unidentified electroactive metabolite. A consortium of *Portulaca grandiflora* and *Pseudomonas putida* showed complete decolorization of a sulfonated diazo dye direct red 5B. *Portulaca grandiflora* resulted in the formation of metabolites 1-(4-diazenylphenyl)-2-phenyldiazene, 7-(benzylamino) naphthalene-2-sulfonic acid, 7-aminonaphthalene-2-sulfonic acid, and methylbenzene. *Pseudomonas putida* degraded direct red 5B to give 4-hydroxybenzenesulfonic acid, 4-hydroxynaphthalene-2-sulfonic acid, and benzamide as metabolites.

The degradation of reactive orange 16 by *Bacillus* sp. resulted in the formation of 6-nitroso naphthol and dihydroperoxy benzene. The degradation of reactive red 2 by *Pseudomonas* sp. SUK1 resulted in the formation of 2-naphthol. Reactive green 19A by *Micrococcus glutamicus* NCIM 2168 resulted in the formation of naphthalene. *Bacillus* sp. degraded navy blue 2GL, resulting in the formation of 4-amino-3-(2-bromo-4,6-dinitro-phenylazo)-phenol and acetic acid 2-(*-*acetoxy-ethylamino)-ethyl ester. Direct brown MR degradation by *Acinetobacter calcoaceticus* resulted in the metabolites biphenyl amine, 3-amino 6-hydroxybenzoic acid, and naphthalene. The reactive dyes RP2B, V2RP, and Red 22 were degraded by *Pseudomonas luteola*, resulting in sulfonic acid. Direct black 22 degradation by the bacterial consortium resulted in the formation of 1-naphthol. *Vibrio logei* and *Pseudomonas nitroreducens* were able to degrade methyl red to produce metabolites 2 amino benzoic acid and *N,N*-dimethyl 1-4-phenylenediamine. Acid red 88 degradation by *Stenotrophomonas* sp., *Pseudomonas* sp., and *Bacillus* sp. formed 6 amino naphthalene sulfonic acid. Reactive red 22 degradation by *Pseudomonas luteola* formed 3-amino-4-methoxyphenyl-sulfone and sulfonic acid.

### 13.7 Conclusions

Microorganisms found growing in textile effluents adapt themselves to the harsh environments, and they are potential degraders of dyes used in the textile dyeing process. This fact is revealed by the significant information provided about the salient

microorganisms in this chapter. Comprehensive information on the possible microorganisms and the microbial consortia formed are investigated. The most important parameters required for the treatment of textile effluents by the microorganisms are discussed. The growth and degradation kinetics of various microorganisms to aid the remediation process are elaborated. The possible metabolic products and intermediates of microbial dye degradation are detailed.

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## Chapter 14

# Carbon Aerogel Materials for Real Textile Dyeing Wastewater Treatment via Catalytic Ozonation: An Industrial Trial Report

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Wastewater treatment is a crucial issue in the textile industry. Numerous novel technologies and processes have been developed to improve the efficiency and effectiveness of wastewater reclamation in wastewater treatment plants. The present chapter focuses on catalytic ozonation facilitated by carbon aerogel materials for on-site real textile dyeing wastewater treatment rather than a bench-scale study. A primary industrial trial in a dyeing wastewater treatment plant is reported to have validated the effectiveness and efficiency of catalytic ozonation technology in the reclamation of real textile

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wastewater. The industrial trial was carried out in an integrated treatment system comprising a catalytic ozonation reactor, a 3D electrolysis reactor, a membrane bioreactor, and a reverse osmosis unit for the comprehensive treatment of real wastewater. The water quality of effluents from each treatment unit was monitored and compared to industrial criteria for the reuse of wastewater.

## 14.1 Introduction

In Chapter 6, though it was said that carbon aerogel (CA) materials are capable of increasing the overall treatment efficiency compared to solo ozonation, its application potential for real textile wastewater is still not clear. This is because all the investigations on catalytic ozonation have only concentrated on simulated dyeing wastewater rather than real effluents from textile dyeing plants. So, in this chapter real wastewater was collected to evaluate the catalytic performance of novel catalysts. The present report includes two aspects:

- Bench-scale catalytic ozonation of wastewater samples collected from a textile dyeing wastewater treatment plant
- On-site catalytic ozonation of real wastewater with an integrated treatment system developed on the basis of catalytic ozonation technologies

In the bench-scale study, operational variations will be evaluated to confirm their influence on the degradation efficiency. In the on-site catalytic ozonation of real wastewater for industrial trial, the treatment efficiency of the main modules of the treatment system would be evaluated first. Later on, continuous treatment would be conducted with the integrated treatment system under the treatment conditions that were deduced from the results obtained in the individual treatment units.

## 14.2 Methodology

### 14.2.1 Sample Collection

For the bench-scale study, real wastewater samples were collected from a wastewater treatment plant maintained by a textile dyeing

plant located in Guangdong, China. The main contaminants in the wastewater were residual reactive dyes. The effluents from the raw wastewater tank, the primary sedimentation tank, and the secondary sedimentation tank were collected for characterization of the wastewater. Among them, the effluent from raw wastewater was selected for bench-scale catalytic ozonation. To remove the suspended contaminants, the original sample was left standing for 3 h to allow the suspended particles to settle down after neutralization. The supernatant liquor was then filtered through filtration paper ( $0.45\text{ }\mu\text{m}$ ) to form the target water sample for ozonation. The other chemicals involved, such as NaOH and HCl, were of analytical grade.

For on-site treatment of real wastewater from the raw wastewater tank, neutralization was performed first and later on the original sample was left standing overnight to allow the suspended particles to settle. The supernatant liquor was then pumped to a 1.5-ton water tank for subsequent ozonation investigation.

#### 14.2.2 Treatment System for Real Wastewater

An integrated treatment system was installed in the wastewater treatment plant for on-site treatment of real dyeing wastewater. Figure 14.1 presents the treatment system, which comprises a catalytic ozonation tank, a three-dimensional (3D) electrolysis reactor, and a membrane bioreactor (MBR). Before continuous catalytic ozonation of real wastewater for the industrial trial, primary trials were conducted on the specific individual treatment units first.



**Figure 14.1** Integrated treatment system.

### **14.2.3 Determination of Water Quality of Real Effluents**

#### **14.2.3.1 Color (multiple dilution method)**

Color determination of real wastewater after on-site treatment was determined by the multiple dilution method, which is universally adopted in China. The procedure is as follows: dilute the wastewater to certain folds and compare the diluted water with distilled water (or other color-free blank water sample) against a white background. Increase the dilution fold until the sample displays no difference from the distilled water. Record the dilution fold as the dilution factor (DF) to indicate the water color.

#### **14.2.3.2 COD**

The chemical oxygen demand (COD) was determined by Hach Method 8000: Oxygen Demand, Chemical [1]. In brief, 2 mL of a water sample was firstly transferred into a digesting vial that was filled with 2 mL of a reagent mixture. Inversion of the vial may be required for thorough mixing. Thereafter, the vial containing the water sample and digesting reagent was inserted into the slot in the COD digestion block (Model DRB 200, HACH, USA) and heated at 150°C for 2 h. After the sample was completely cooled down, the COD was determined by a COD colorimeter (Model DR 900, HACH, USA), where the COD could be directly read on the meter screen.

#### **14.2.3.3 Ferric ion**

The concentration of ferric ion in the treated effluent was measured by a rapid testing method with the Quantofix® Total Iron 100 testing strip (Macherey-Nagel, Germany). The testing procedure is interpreted as follows:

To begin with, acidize the effluent to around pH 3–5; then dip the testing strip into the sample for 1 s. After shaking off the excess liquid, wait for 1 min. and compare the strip color with the reference color scale. Thereafter, read the closest color scale as the concentration grade of the ferric ion in effluents. The strip should be blue if ferric ion is present in the sample.

#### 14.2.3.4 Manganese ion

The concentration of manganese ion in the treated effluent was determined by a rapid testing method with the Visocolor® ECO Manganese test kit (Macherey-Nagel, Germany), which measures total manganese with formaldoxime. The procedure is described as follows according to the official product instructions:

To begin with, pour 5 mL of a water sample with a syringe into both sample tubes and place one (Tube A) of the tubes on position A in the comparator. And then add 5 drops of Mn-1 reagent in the other tube (Tube B) and mix, followed by the addition 7 drops of Mn-2 reagent. After 1 min., add 1 level measuring spoonful of Mn-3 reagent in Tube B and shake gently but thoroughly. During the addition of reagents, ensure you seal the vial before mixing or shaking, to eliminate spilling. Five minutes later, remove the tube lid and place it on position B in the comparator. Slide the comparator until the colors match in the inspection hole on top. Check the measurement reading in the recess on the comparator. Tube A should be the original color of the effluent, and Tube B should be red if manganese ions are present in the sample. A higher concentration accounts for a dark-red color of the mixture in Tube B.

#### 14.2.3.5 Suspended solids

The total suspended solids in the effluent were evaluated by the weighting method, which adopted 934-AH™ RTU Glass Microfiber Filters (Whatman, General Electric) as filter paper to hold back the solid from the liquid. Every filter is sold with an aluminum pan, which clearly notes the exact filter weight. The operation procedure is as follows:

First, place the filter paper on a vacuum filtration funnel and prewet the funnel with a small volume of water by washing the bottle. Then filter 1000 mL of the effluent sample, followed by washing the filter with 10 mL of deionized water. Thereafter, dry the wet filter in the aluminum weigh pan to a constant weight at 103°C to 105°C. The suspended solid can be calculated as follows:

$$\text{Suspended solid} = \frac{(A-B) \times 10^6}{V}, \quad (14.1)$$

where  $A$  (g) is the final weight sum of dried filter and aluminum pan,  $B$  (g) is the initial weight sum of original filter and aluminum pan, and  $V$  (mL) is the volume of the effluent sample.

#### 14.2.3.6 Hardness ( $\text{CaCO}_3$ )

The hardness of the treated effluent was tested by a rapid testing method with the Quantofix® carbonate hardness testing strip (Macherey-Nagel, Germany). To begin with, dip the testing strip into the sample for 5 s. After shaking off the excess liquid, wait for 30 s and compare the strip color with the reference color scale. Thereafter, read the closest color scale as the concentration grade of hardness in the effluent. The strip should turn to blue if the hardness is high, while it would be bright green if the hardness is low in the sample.

### 14.3 Results and Discussion

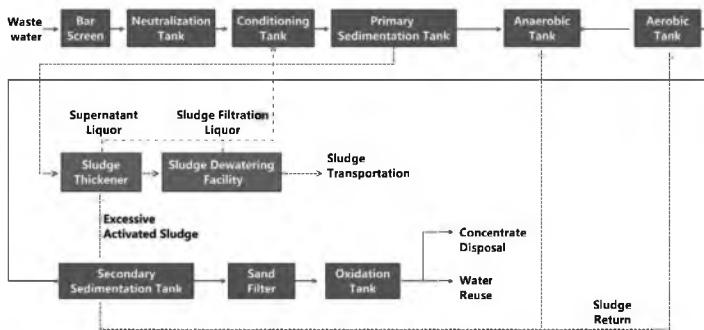
#### 14.3.1 Bench-Scale Investigation

##### 14.3.1.1 Characterization of water samples

The flowchart of the wastewater treatment process in the textile dyeing plant located in Guangdong, China, is illustrated in Fig. 14.2. The wastewater samples collected for the bench-scale study included effluents from (i) a raw wastewater tank (conditioning tank), (ii) the primary sedimentation tank, and (iii) the secondary sedimentation tank.

Only these effluents were collected because they could typically show the evolution of water quality of the wastewater, in terms of the COD and color, during the entire industrial wastewater treatment. The relevant water quality is listed in Table 14.1. A raw wastewater tank is used for the temporary storage of waste effluents from different processes. Depending on the business scope of the textile plant, it may contain effluents from the pretreatment process, dyeing process, and finishing process for the functionalization of fabrics. The COD and color of the raw wastewater were as high as 1115 mg/L and 211, respectively. This was because in reactive dyeing, the residual dye concentration in dyeing effluents was very

high, which contributed to a high COD and color density. After the wastewater was left standing, the COD decreased while the color was maintained. This can be explained as follows: when the wastewater was left standing, only suspended solid contaminants, which only contributed to the COD, settled down but the soluble color pollutants were more stable in solution and could not be isolated by gravity settling. The pH of raw wastewater was higher than the value for reactive dyeing pH (10–11), suggesting the plant may involve mercerization, which is generally applied in a strong basic bath.



**Figure 14.2** Process flow of wastewater treatment in a dyeing plant.

**Table 14.1** Water quality of effluents from textile wastewater treatment

Effluent sample	COD (mg/L)	Color (DF)	pH
Raw wastewater tank	1115	$2^{11}$	12.12
Raw wastewater tank*	985	$2^{11}$	12.12
Primary sedimentation tank	581	$2^7$	7.57
Primary sedimentation tank*	501	$2^7$	7.57
Secondary sedimentation tank	74	$2^4$	7.56

\*Effluent sample after (3 h) it was left standing

Primary treatment is used to remove gross, suspended solids and partially soluble impurities in the raw wastewater, including a screening process to separate large solid objects and sedimentation to isolate suspended solids by gravity. According to Table 14.1, after

primary sedimentation, around 50% of the impurities in terms of the COD in raw wastewater were removed by gravity. In industrial wastewater treatment, the suspended solid in effluents after primary sedimentation is very little because the solid would settle down and concentrate at the bottom of a sedimentation tank, whereas the effluents generally overflow to an anaerobic tank at the top of the tank. Thus the removal of almost 14% of COD after the wastewater is left standing could be ascribed to the attachment of the suspended solid to the tank wall during sampling.

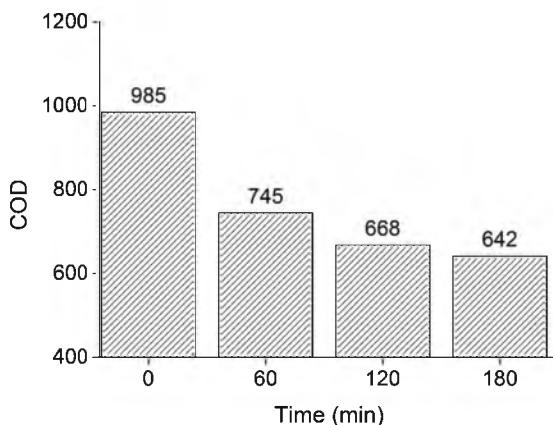
To enhance sedimentation effectiveness, chemical flocculants and coagulants are often dosed in the tank to improve the removal. The color density of the effluents was reportedly reduced drastically after primary sedimentation because the flocs formed adsorbed substantial amounts of soluble residual dyes, yielding considerable color removal. In addition, pH at this stage was neutralized to weak alkaline, which was the suitable pH for the biological digestion of the effluents by organisms in the anaerobic tank.

As illustrated in Table 14.1, biological processes, including anaerobic and aerobic digestion, as well as secondary sedimentation, are the main processes to reduce the soluble organic contents to an acceptable discharging requirement, mainly in terms of the COD and color. During biological digestion, residual dyes or other organic contaminants with relative larger molecular structures are cleaved into smaller contaminants by organisms in the anaerobic tank, which is sealed without oxygen supply; later on, the smaller organic contaminants are digested by aerobic organisms in the aerobic tank, which is aerated with air to supply oxygen. The secondary sedimentation is used to separate organisms from the effluent flow. After the biological process, both COD and color are in accordance with the discharging standard in China (before 2015).

#### **14.3.1.2 COD removal of a water sample from a textile dyeing plant**

In principle, the main difference between the water sample from a raw wastewater tank and a primary sedimentation tank is the concentration of the suspended solid in effluents. However, in the plant for collection of wastewater samples, the primary sedimentation tank has been dosed with  $\text{Fe}^{2+}$ , which may consume extra ozone in the aqueous solution. Therefore, in this section only

raw wastewater after it was left standing for a while was adopted to evaluate the degradation efficiency in terms of COD removal in catalytic ozonation. COD reduction in the specific condition is depicted in Fig. 14.3. Similar to catalytic ozonation of simulated wastewater, COD reduced with treatment time, but the efficiency at each treatment time was much lower. The 3 h treatment efficiency was about 35%. This may be attributed to the different initial COD of the wastewater sample, as a low dye concentration led to improved removal efficiency under the same treatment condition [2]. Another possible reason may be that the raw wastewater contained some organic pollutants from bleaching, such as starch, that are refractory to ozonation.

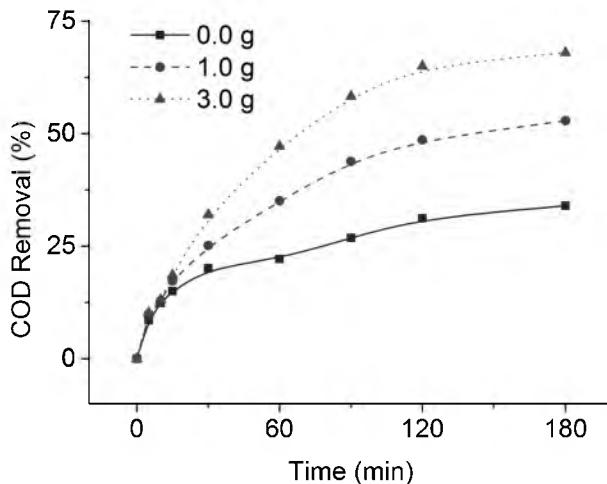


**Figure 14.3** COD in wastewater from the dyeing plant ( $60^{\circ}\text{C}$ , 2.5 mg/L ozone, pH = 7.1, 1 g of  $\text{Cu}_2\text{O}-\text{CuO}/\text{CA}$ , and 400 mL of dye solution).

#### 14.3.1.3 The effect of catalyst dosage on COD removal

To assess the effect of the catalyst amount on the degradation of pollutants in real wastewater, catalytic ozonation of water samples with different catalyst dosages under the same condition was conducted for comparison. As can be seen in Fig. 14.4, similar to what happened in catalytic ozonation of synthetic dyeing wastewater, the catalyst was able to improve the degradation due to the improved contact surface area and availability of reactive sites of the catalyst [3]. It was observed that COD removal was almost doubled after

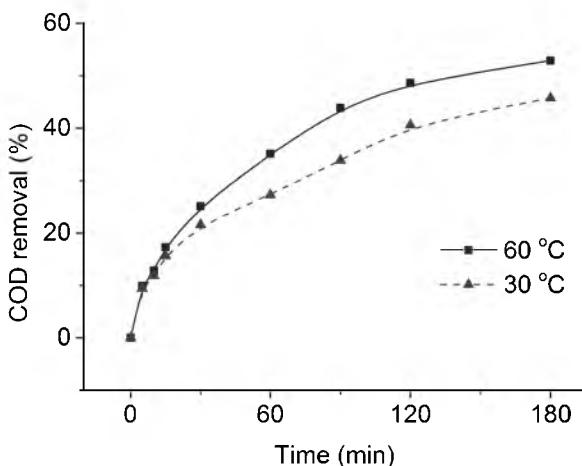
180 min. of treatment with 3 g of the catalyst, suggesting that the presence of the catalyst brought significant improvement in dye degradation.



**Figure 14.4** Effect of amount of catalyst on COD removal ( $60^{\circ}\text{C}$ ,  $\text{COD}_{\text{initial}} = 985 \text{ mg/L}$ , 2.5 mg/L ozone, pH = 7.1, and 400 mL of dye solution).

#### 14.3.1.4 Effect of temperature

Temperature effect on catalytic ozonation was also studied. Figure 14.5 demonstrates COD removal with time at  $30^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ . It was noticed that a temperature increase could benefit dye degradation as the reduction of COD was strengthened. COD removal increased from 35% to 50% after 2 h of catalytic ozonation when the treatment temperature increased from  $30^{\circ}\text{C}$  to  $60^{\circ}\text{C}$ . This variation trend was in line with catalytic ozonation of simulated wastewater. Notwithstanding the fact that a lower temperature is advantageous for the mass transfer of molecular ozone to the aqueous solution [4], the overall result suggested that a higher temperature was more favorable for dye degradation, which may be ascribed to an accelerated oxidation kinetic constant [5]. Considering the dye degradation efficiency, this may suggest that in real treatment, there is no need to cool down the warm effluent, even though sometimes it is inevitable for facilitating operations.



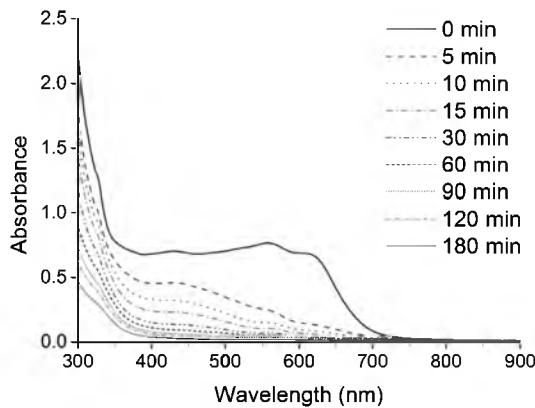
**Figure 14.5** Effect of temperature on COD removal ( $\text{COD}_{\text{initial}} = 985 \text{ mg/L}$ , 2.5 mg/L ozone, pH = 7.1, 1 g of  $\text{Cu}_2\text{O}-\text{CuO}/\text{CA}$ , and 400 mL of dye solution).

#### 14.3.1.5 Color removal

Color removal from real wastewater is quite different from color removal from simulated wastewater since the composition of real wastewater is much more complicated. In normal circumstances, real wastewater is a mixture of different dyestuffs with different colors. The UV-Vis absorbance of the wastewater could vary drastically since the absorbance peak could be within a wide range of wavelengths depending on the color that took up the largest proportion. Generally, the color of industrial wastewater is measured by the DF with the multiple dilution method. However, the UV-Vis spectrum photometer method was still used in the present case to examine the evolution of the absorbance. Figure 14.6 represents the absorbance of the effluent after catalytic ozonation for a certain amount of time. It was clear that there was no obvious peak observed in the range of visible light, corresponding to 400–800 nm. The visual color of the raw wastewater was dark navy, but it then converted to pale yellow after several hours' treatment. As long as the ozonation treatment lasted, the visual color got increasingly paler, suggesting the color matters in wastewater were degraded gradually.

According to Fig. 14.6, all the absorbance curves were similar except the initial one without catalytic ozonation. This may point to

the likelihood that during the first 5 min. decolorization dominated the degradation process [6], suggesting that ozonation was advantageous in color removal.



**Figure 14.6** UV-Vis absorbance of raw wastewater during catalytic ozonation ( $60^{\circ}\text{C}$ , 2.5 mg/L ozone, pH = 7.1, 1 g of  $\text{Cu}_2\text{O}-\text{CuO}/\text{CA}$ , and 400 mL of dye solution).



**Figure 14.7** Catalytic ozonation tank.

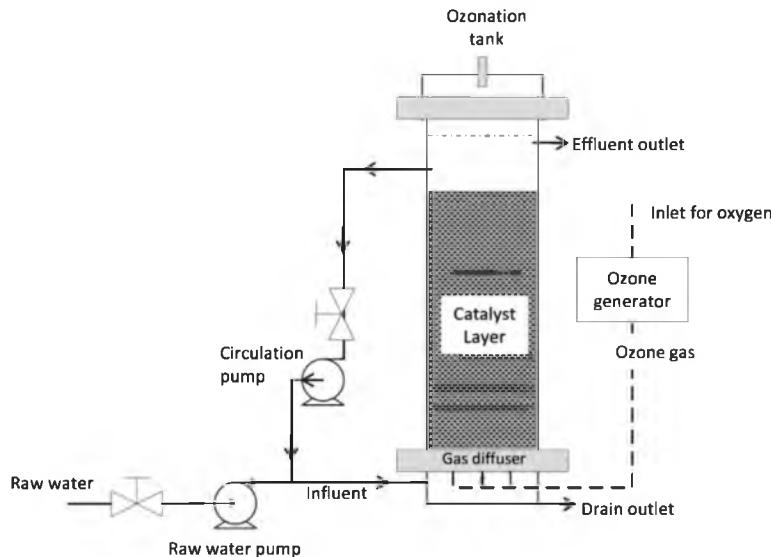
## 14.3.2 On-Site Industrial Trial

After preliminary bench-scale catalytic ozonation of real wastewater, it was planned that an industrial trial will be carried out for the on-site treatment of wastewater from a textile wastewater treatment plant. The main treatment units comprising the treatment system are a catalytic ozonation tank (Fig. 14.7), an electrolysis reactor, and an MBR. Before continuous catalytic ozonation of real wastewater for industrial trial, primary trials were conducted on the individual treatment units first.

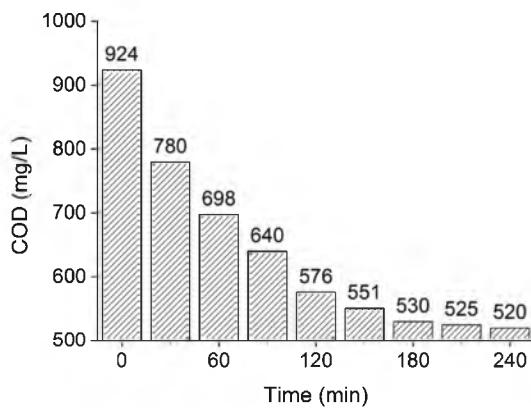
### 14.3.2.1 Catalytic ozonation of raw wastewater

In this section, raw wastewater was first pumped into a cubic plastic container, which was left standing overnight so the suspended solids in the wastewater could settle down. Afterward, the naturally settled wastewater was introduced into the reactor by a peristaltic pump for catalytic ozonation. The schematic of the ozonation tank is depicted in Fig. 14.8. During the treatment, the peristaltic pump induced the wastewater to flow to the column through a pipe allocated at the bottom; ozone gas was injected at the same time through a gas diffuser, which is also allocated at the bottom of the tank. Ozone gas and liquid flow came into contact dramatically at the bottom of the tank and then the gas-liquid mixture flowed through/over the catalyst layer, which was filled with 5 kg of CuO-Cu<sub>2</sub>O/CA particles over a porous plate within the column. A circulation pump was set beside the column to induce the superficial solution to the bottom of the tank again through a bypass pipe for a thorough contact of liquid flow and ozone gas, and to increase the retention time of liquid flow in the tank. The effluent eventually flowed over to the connected electrolysis reactor via the ozonation tank outlet, which was set on the top-right side of the column. During the treatment, ozone concentration was adjusted within the range of 10–16 mg/min. and the oxygen gas was supplied at a constant flow rate of 4–5 L/min. The wastewater was previously neutralized to pH 6.9 and maintained at room temperature during the treatment. COD removal of the effluent as a function of treatment time is shown in Fig. 14.9. It can be noticed that the COD reduced with treatment time but the reduction rate was not constant. It was found that the reduction was much more obvious in the first 2 h but declined significantly after

3 h, which could be ascribed to the fact that some retardant oxidation products from dye decomposition during ozonation gradually accumulated in water, which depressed the ozonation efficiency [7].



**Figure 14.8** Schematic of a catalytic ozonation tank.



**Figure 14.9** COD removal by catalytic ozonation.

Considering the moderate decrease in ozonation efficiency, in the subsequent trial in an integrated treatment system comprising an

ozonation tank, a 3D electrolysis reactor, and an MBR, the ozonation time was set as 3 h for better utilization of ozone and energy saving.

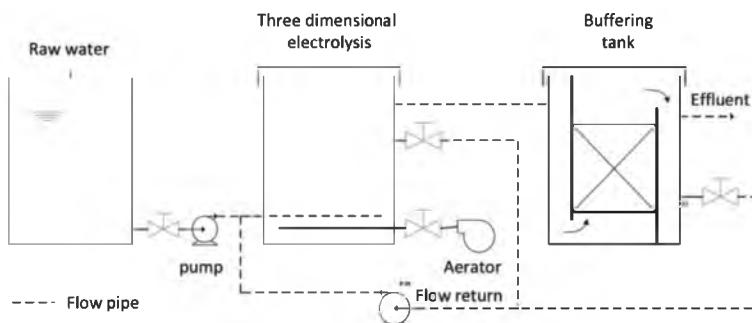
#### 14.3.2.2 3D electrolysis of raw wastewater

In recent years, the method of electrolysis with a 3D electrode (Fig. 14.10) has been developed for the treatment of wastewater from various sources, including landfill leachate, simulated phenol wastewater, dye wastewater, and paper mill wastewater [8].



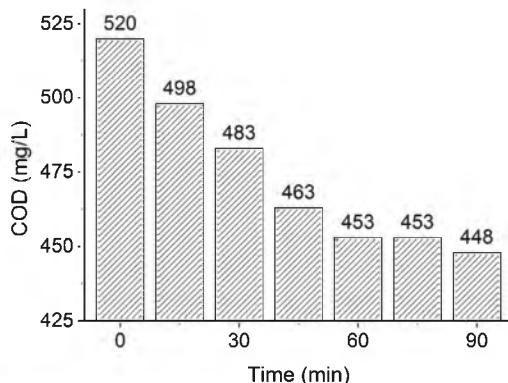
**Figure 14.10** 3D electrolysis reactor.

It was developed on the basis of the conventional two-dimensional (2D) electrochemical process, in which the third electrode is introduced in the electrolysis reactor. Granular or fragmental materials are filled between two counter electrodes as the third electrode, which is polarized to create a large quantity of charged microelectrodes at an appropriate voltage [9]. Figure 14.11 shows the schematic of a 3D electrolysis reactor. Similar to the catalytic ozonation tank, wastewater flow was also pumped to the 3D electrolysis system through the bottom until it overflowed. The difference was that an extra buffering tank for storing of the wastewater was put in the 3D electrolysis reactor. A bypass pipe was also installed for external/internal circulation of liquid flow in the electrolysis reactor. Besides, an aerator was mounted to supply air to aid the electrolysis reaction.



**Figure 14.11** Schematic of a 3D electrolysis reactor.

In this section, after the above 3 h of catalytic ozonation, the ozonated wastewater from the ozonation tank then overflowed to the 3D electrolysis reactor for further degradation of dye contaminants. The time factor was the only variation to examine the degradation efficiency. During the treatment, the electrolysis voltage and current were constantly set at 36 V and 20–25 mA, respectively. The solution pH was adjusted to pH 4.3. The treatment result is demonstrated in Fig. 14.12.



**Figure 14.12** COD removal by 3D electrolysis.

It was evident that in the first 1 h of the electrochemical process, the COD decreased almost linearly. It dropped from 520 to 453 mg/L after 60 min. of electrolysis. However, further treatment could not additionally remove the pollutants in terms of the COD, which may be because electrolysis-resistant substances from the degradation

of the dye or its intermediates were generated in the reaction tank. As a consequence, COD reduction since then was independent with electrolysis time. It remained at around 450 mg/L from 60 min. to 90 min. As electrolysis is an energy-consuming process, in the integrated treatment system the hydraulic retention time was fixed to 60 min. for energy conservation.

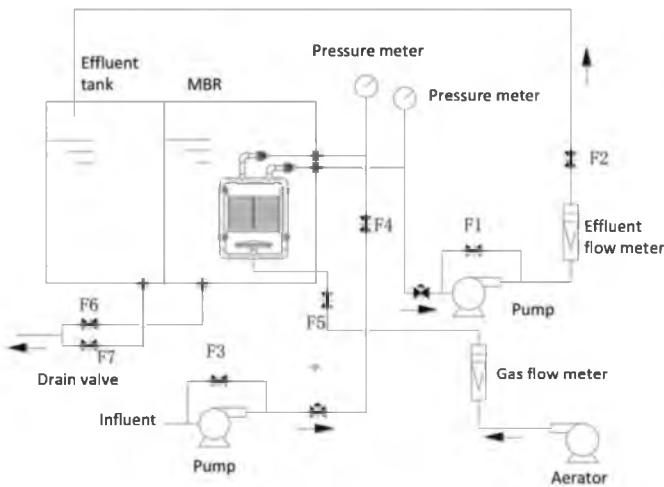
#### 14.3.2.3 Aerobic digestion of raw wastewater

MBR technology is a well-accepted alternative to the conventional activated sludge process (CASP). The MBR acts as a biological treatment processor, and the membrane is used as a filter in the filtration process. The advantages of the MBR include operation at higher mixed liquor suspended solids (MLSSs) concentrations, reduced sludge production, independent control of solid and hydraulic retention time (SRT and HRT), compact and modular system requirements (i.e., small plant footprint), and excellent performance and effluent quality [1]. Since the MBR unit (Fig. 14.13) can be operated under longer SRTs, nitrification could be more effective and complete due to low growth of nitrifying bacteria. Long SRTs applied to the MBR prevent the wash-out of nitrifying bacteria and other slow-growing microorganisms from the bioreactor and increase the biodiversity of the microorganisms in the activated sludge [2]. Simultaneous nitrification and denitrification (SND) could also occur in an MBR as a consequence of dissolved oxygen (DO) concentration gradients within microbial flocs or biofilm [3, 4]. Anoxic microenvironments develop inside the flocs/biofilm, whereas an aerobic condition prevails at the outer surface layer [5]. Moreover, it is highly efficient in removing carbonaceous organic matters, and COD removal could be as high as 90% [6, 7]. Due to these advantages, MBR technology has a great potential in many applications, including industrial textile wastewater treatment [8–12]. The schematic of MBR used in the present study is demonstrated in Fig. 14.14.

In this part, effluents from the electrolysis reactor were further treated by the MBR. The operation was performed at room temperature, and air was supplied at a flow rate of 1.5 L/min. The effluent was neutralized in a buffering tank before being induced to the MBR. The COD of effluents versus the retention time is illustrated in Fig. 14.15.



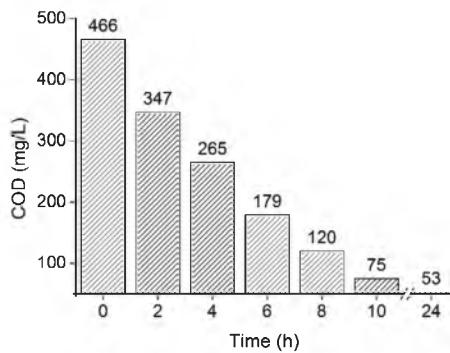
**Figure 14.13** Membrane bioreactor.



**Figure 14.14** Schematic of membrane bioreactor.

It was observed that the effluent COD decreased as the aerobic digestion time increased. After 10 h of digestion, the effluent COD was below 80 mg/L, which meets the discharging criterion for textile wastewater before 2015. When it was treated for 14 h, the COD declined to 53 mg/L. In biodegradation, contaminants that have been pretreated by ozonation and electrolysis acted as food

for bacteria in the MBR, for their metabolism and reproduction [12]. As the retention was prolonged, organic pollutants were gradually digested by organisms, leading to declined COD in the MBR effluent. In the first 10 h the COD reduced almost linearly; the 10 h treatment led to a removal rate as high as 84%. Yet in the subsequent 14 h COD removal improvement was minimal, which may be attributed to the fact that residual contaminants with low biodegradability were resistant to aerobic organisms in the MBR and could not be converted to inorganic substances.



**Figure 14.15** COD removal by membrane bioreactor.

#### 14.3.2.4 Integrated treatment system

On the basis of the above trials, a semicontinuous treatment trial, which involved an ozonation tank, an electrolysis reactor, and an MBR, was conducted for raw wastewater treatment. The flowchart for the on-site treatment is illustrated in Fig. 14.16.



**Figure 14.16** Flowchart of on-site trial with the integrated treatment system.

The color removal is shown in Fig. 14.17. The first 3 h of treatment enabled the effluents to reach to their discharging requirement for color, which is 50 (DF), suggesting that ozonation displayed excellent decolorization capacity (Fig. 14.18).

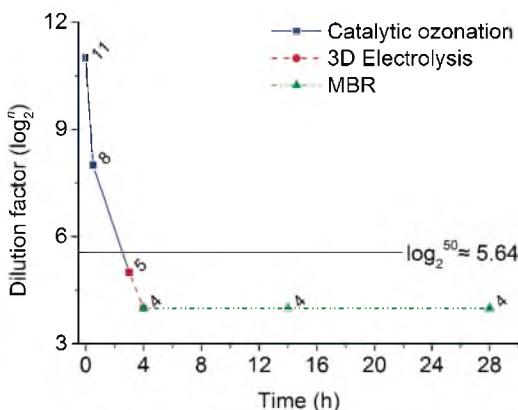


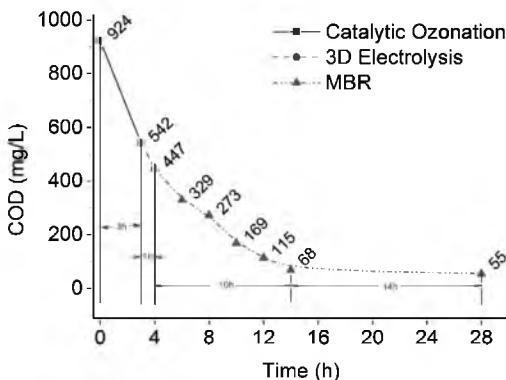
Figure 14.17 Color removal in the integrated treatment system.



Figure 14.18 Wastewater samples. #1, raw wastewater; #2, effluent from ozonation tank (2 h); #3, effluent from ozonation tank (3 h); #4, effluent from 3D electrolysis reactor (1 h); #5, effluent from MBR (10 h); #6, effluent from reverse osmosis.

COD removal is illustrated in Fig. 14.19. It reduced from 924 to 542 mg/L, corresponding to a removal of 41.3%. Further treatment by 3D electrolysis reactor and an MBR reduced the COD to 68 mg/L, which was in accordance with the COD standard for effluents discharged into the environment in China before 2016. The entire treatment time for the present process was 14 h, which was adequate to achieve the discharging standard for COD of wastewater, while the subtotal treatment for biological treatment in the wastewater treatment plant is around 34 h, including 16 h of anaerobic and 18 h of aerobic digestion processes. This suggested that the present process could shorten the entire treatment time by at least 58%.

$100\% - 14/(16 + 18) \times 100\%$ , excluding the sedimentation time in the primary and secondary tanks.



**Figure 14.19** COD removal in the integrated treatment system.

The effluent of the MBR, which had complied with the discharging criteria already, was then further purified by reverse osmosis toward reuse. The specifications of the final treated wastewater are shown in Table 14.2.

**Table 14.2** Water quality of reclaimed wastewater

Specification	Actual value	Criteria <sup>a</sup>	Criteria <sup>b</sup>	Criteria <sup>c</sup>
Reuse rate	62.3%	-	-	-
Color	2	=<25	=<25	25
COD	6	<20 mg/L	=<50	=<50
Transparency	>35	>=30 cm	>=30 cm	>=30 cm
pH	7-8	6-9	6-10	6-9
Ferric ion	<0.05 mg/L	0.2-0.3 mg/L	=<0.3 mg/L	0.2-0.3 mg/L
Manganese ion	<0.1 mg/L	<0.2 mg/L	=<0.2 mg/L	<0.2 mg/L
Suspended solid	2.4 mg/L	<30 mg/L	<30 mg/L	<30 mg/L
Hardness	17.5 mg/L	<400 mg/L	<450 mg/L	<450 mg/L

<sup>a</sup>Recommended by the China Dyeing and Printing Association.

<sup>b</sup>Quality standards of reusing water for dyeing and finishing of the textile industry (draft).

<sup>c</sup>Wastewater treatment project technical specifications for dyeing and finishing of the textile industry, China HJ 471 - 2009.

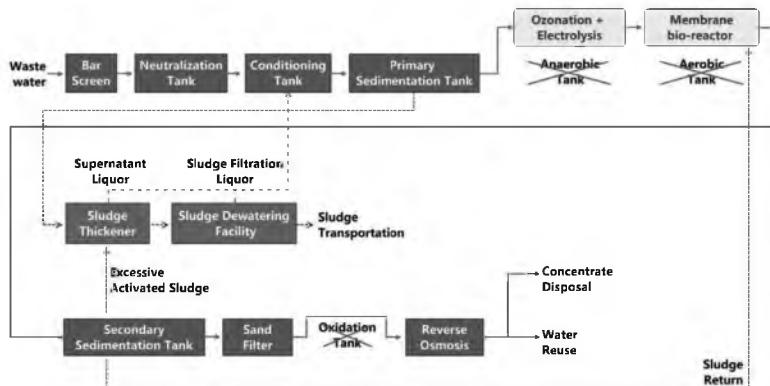
According to Table 14.2, the water quality of the treated effluent was better than the suggested criteria. The overall reuse rate could be 62.3% by backflow of the saline water (the concentrate) to the influent flow of reverse osmosis. Currently in China, there are no mandatory executive standards enforced for reuse of textile dyeing wastewater. One most probable reason for this is that the water quality required for the wet processing of textile materials is quite different. For instance, the quality of water for rinsing after reactive dyeing, especially in the foremost few instances of cold rinsing, is generally much lower than that for reactive dyeing. The existing criteria for wastewater reuse are more like references instead of enforced standards.

#### **14.4 Conclusion**

Wastewater treatment is important in textile processing. Currently, numerous technologies have been reported in the literatures, but few have focused on the treatment of real effluents from textile dyeing plant. The bench-scale studies only show the potential but not the applicability. In this chapter, on-site treatment of the wastewater from a textile dyeing plant was carried out. An integrated treatment system was installed in the wastewater treatment plant for continuous application. CuO-Cu<sub>2</sub>O/CA was filled into the catalytic ozonation tank to form the catalyst bed to strengthen dye degradation. In addition, 3D electrolysis and an MBR were coupled with an ozonation tank to assist in dye degradation in effluents. The results from the industrial trial suggested that the on-site treatment system on the basis of catalytic ozonation has shortened the overall treatment time by more than 50% of conventional processes to comply with the discharging standard for COD and color. By utilization of reverse osmosis, the water quality of the effluent could be further reclaimed. The water quality in all instances was better than the criteria recommended, suggesting the effluents could be reused in plenty of processes in textile dyeing plants.

If this technology could be disseminated in the future, the treatment flow could be modified as that depicted in Fig. 14.20. The new process would be more compacting, efficient, and rapid than conventional technologies. Up to now, the only difficulty was the

capital cost. Nevertheless, it still can be forecast that the technology would be more practical and applicable as the cost for ozone production would be reduced gradually in the future.



**Figure 14.20** Proposed water treatment process adopting ozonation technology.

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