

Chapter 2

Eco-friendly Production Methods in Textile Wet Processes



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Abstract Sustainable, 'economical', and 'eco-friendly' production has recently become important issues in textile manufacturing processes. In the world, textile conventional production industry is one of the major industries which cause environmental pollutions. During textile wet process, great deals of wastes are leaved in air, soil and, especially water. Due to these wastes, all species in the ecosystem are negatively affected. In order to manufacture a ton of textile, approximately 230–270 tons water is used. After the textile production, the water is undertaken with heavy chemicals and this waste water is leaved in environment. In textile production industry, there are two efficient methods to decrease the environmental pollution. Constructed of large and highly effective effluent treatment plants is a method to reduce the amount of wastes. The other method is the use of natural raw materials and ecological production methods. Recently, researchers have been seeking for ecological, sustainable, and biodegradable natural raw materials alternatively synthetic raw materials. Especially, natural textile raw materials have been begun to use acceleratingly in comparison with synthetic raw materials in textile industry. Furthermore, new natural fibers have been obtained from different source and the use of these fibers has searched in textile industry. In textile wet process, especially, waste water with heavy chemicals load is a major problem. In order to eliminate the negative effect of waste water, researchers have been searching for solutions. In literature, coating, microencapsulation, plasma applications, using of ultrasonic and microwave energy, using of supercritical carbon dioxide and ozone treatment are described as some of the eco-friendly process in textile wet industry. In this study, some eco-friendly production methods in textile wet industry were investigated, separately. Furthermore, the advantages of new production methods were searched.

Keywords Textile wet process · Eco-friendly production · Waste water

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1 Introduction

In human history, the most important equipment has been cloth after the nutritional requirement. For this reason, the history of textile fibers dates to B.C. 9000. Throughout these years, flax harvested in Mesopotamia, cotton cultivated in the region of Indus River, silk obtained from domesticated silk worm in North China and wool originated from West Asia have been used. The natural based textile fibers played a significant role due to their widespread use in nature and technical appropriateness for many centuries. In recent years, textile fibers have been used commonly in the areas of technical textiles because of low price, lightness, high strength properties, low thermal conductivity, accessibility, etc.

Starch derivatives can be used as alternatives to starch for desizing. These are carboxymethyl cellulose, heteropolysaccharides, polyvinylalcohol and polyacrilate. Chemical oxygen demand (COD) in starch is substantially lower than that of the other desizing materials however starch is the desizing material polluting waste waters the most due to utilization of excessive amount of starch desizing during desizing process. In case excessive loading of waste water by starch desizing material is desired, the simplest precaution would be the collection of desizing removal floaters with starch waste in a special sedimentation pool by a separate canalization. Since the majority of these starch wastes will sediment, COD and biological oxygen demand (BOD) values of water overflowing at the outlet will drop substantially.

Due to increasing industrialization, environmental pollution has arisen as a global issue. In literature, it is registered that more than 700,000 tons of dyes are manufactured. However, 280,000 tons of dyes are wasted due to adverse environmental impacts. Thus, textile industry is one of the industries that damages the environment with toxic wastewater. According to the World Bank, 17–20% of industrial water pollution is caused by industrial water pollution [1–3].

Clean production approach considers all possibilities that will alleviate the current pollution problem in textile wet treatment and will save water or energy. The things to be done are grouped under 4 main headings:

1. Process optimization: Less water consumption in every possible area, less chemical use, working in lower temperatures and less time loss.
2. All chemicals are environmentally friendly (use of environmentally friendly chemicals).
3. Reuse of water: By purification.
4. New technologies (transfer printing, enzymatic processes, plasma and ozone technologies, dyeing in CO₂-containing environment).

There are many conventional methods for the purity of textile wastewater such as chemical coagulation (using ferrous, and polyelectrolytes), biological treatment followed by activated carbon adsorption. However, conventional methods have a number of disadvantages, including the generation of a huge volume of sludge. In order to meet the demands of environmental standards, researchers have investigated new methods for the complete and successful disposal of textile wastewater [4].

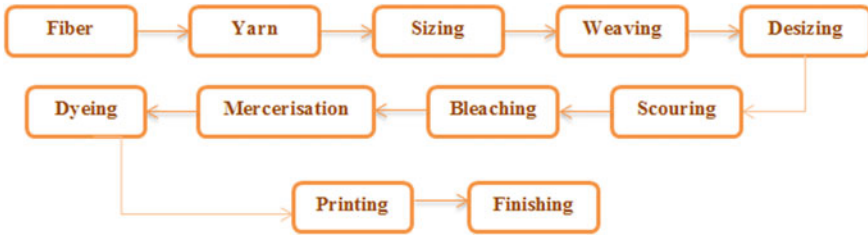


Fig. 1 Textile operations

In this study, eco-friendly production methods in textile wet industry such as ozonation, plasma applications and enzymatic treatments were investigated, separately. Furthermore, membrane filtration which is used to clean textile waste water was investigated. The advantages of new production methods were searched.

2 Textile Operations

Textile raw materials, called as fibers, are transformed to yarns, which are then turned to fabrics. These fabrics are exposed to several textile wet processes. Textile operations are shown in Fig. 1 along with some summaries of textile processes [5].

2.1 Sizing and Desizing

In textile industry, sizing process is known as a weaving preparatory process which is applied to warp yarns. The essential of the sizing is identified as reduction of yarn breakage and disposing the weaving machine stops. The most used sizing agents are starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC). In textile process, desizing process has been used to remove sizing agents that have been applied to warp yarns during a weaving process.

Enzymatic or oxidation process transforms starch to simple water-soluble products. Desizing waste has more biological oxygen demand in the range of 300–450 ppm and pH 4–5. In degradation of starch, hydrogen peroxide can be used to convert starch into CO_2 and H_2O . Furthermore, enzymatic process can be eased by converting starch into ethanol. After the distillation of ethanol, it can be used as a fuel [5].

2.2 Bleaching

Natural color substance causes the fabric to seem like cream. In order to obtain white fabric, the natural color matter should be removed from the fabric with bleaching. In the past, hypochlorite was the most used agent but recently H_2O_2 has taken its place [5].

2.3 Mercerization

Mercerization is a chemical treatment carried out on cotton fibers to gain shine and improve dye uptake. Furthermore, mercerization increases tensile strength of cotton fibers. Basically, cotton fibers are treated with a high concentration (almost 18–24% by weight) of sodium hydroxide for usually less than 4 min. Cotton fibers are then treated with water or acid for 1–3 min under stress to neutralize the sodium hydroxide. The material later gains easy dye uptake and its absorbency increases. In order to recycle sodium hydroxide in the wash water, membrane techniques or multiple effect evaporators can be used [5].

2.4 Dyeing and Printing

Dyeing is the treatment to color textile fibers, yarns and fabrics. Being responsible to gain color, these groups can be listed as azo ($-N=N-$), carbonyl ($-C=O$), nitro ($-N=O$), quinoid groups and auxochrome groups like amine, carboxyl, sulphonate and hydroxyl. Among these groups, azo and anthraquinone groups are the most significant ones. Furthermore, these groups are responsible from coloring of textile waste water and contamination. Figure 2 shows the type of dyes used for different types of fibers [5].

Printing is a regional color process of textile materials. In dyeing, dye is treated in a solution form whereas dye is applied in a thick paste form in printing. Wastes of dyeing and printing have quite similar compounds.

2.5 Finishing Process

Finishing processes are called as the whole set of operations performed to improve the handle, usage properties and appearance. At the present time, finishing processes are classified as chemical finishing process and mechanical finishing process. Finishing processes are listed in Figs. 3 and 4.

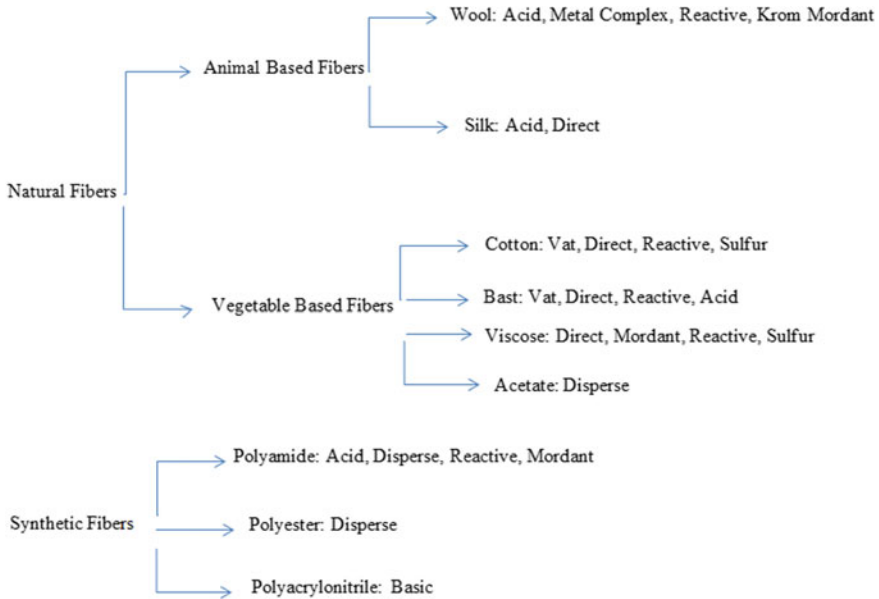


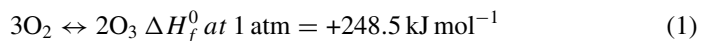
Fig. 2 The type of dyes used for different types of fibers

After the textile operations, textile wastewater is loaded with harmful chemical. In desizing process, textile wastewater is embarked with sizes, enzymes, starch and waxes. After the scouring process, scouring wastewater contains NaOH, surfactants, soaps, fats, pectin, oils, sizes and waxes. Considering the bleaching process, the wastewater includes H_2O_2 , sodium silicate, organic stabilizer and alkalis. Dyeing and printing wastewater comprises dyes, color pigments, metals, salts, surfactants, alkalis, acids, ureas, formaldehyde and solvents. After the finishing process, softeners, solvents, resins and waxes appear in finishing process wastewater [5].

3 Ozonation Technology

3.1 Properties of Ozone Gas

Ozone gas was first discovered by German chemist Christian Friedrich Schönbein based upon its distinctive smell after thunderbolt. In 1839, he named this smell “ozone” which stands for the verb “smell” in Greek. In 1856, Thomas Andrews stated that ozone comprised of oxygen and then Soret discovered the relation between oxygen and ozone as shown in Formula (1) [6].



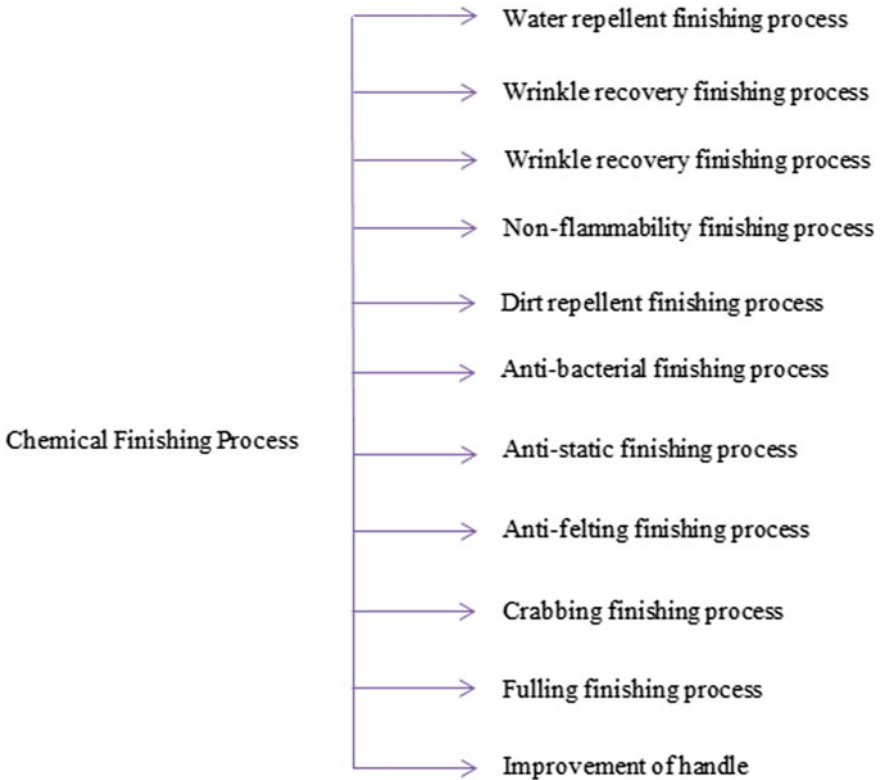


Fig. 3 Chemical finishing processes

Ozone molecule consists of three oxygen atoms which occurred at the end of the oxidation process of oxygen molecule. Ozone has high activation energy due to having a free bond. Ozone is colorless in gas form and blue in liquid form. The physical and chemical properties of ozone were given in Table 1.

Ozone is an organic molecule including three different oxygen atomic rings two of which are breathed. Oxygen is transformed to ozone because of exposure to ultraviolet rays in upper-layer of atmosphere. Due to the high weight of ozone, it comes down to the earth.

Ozone is a gas which is non-heat resistant, corrosive and is transformed to oxygen. Because of these properties, ozone is not stored or transferred and it should be produced in the environment in which it is used.

Ozone gas is used in a wide variety of industries, including iron-steel and metal, textile, chemistry, food, automotive, medical, agriculture and stockbreeding, odor and color removal in mine industry, storage, heating and cooling systems, purification of water and air, sterilization and protection of food materials.

Ozone is a powerful oxidizing agent used in some applications in swimming pools, industrial waters consisting of phenols and drinking water [7].

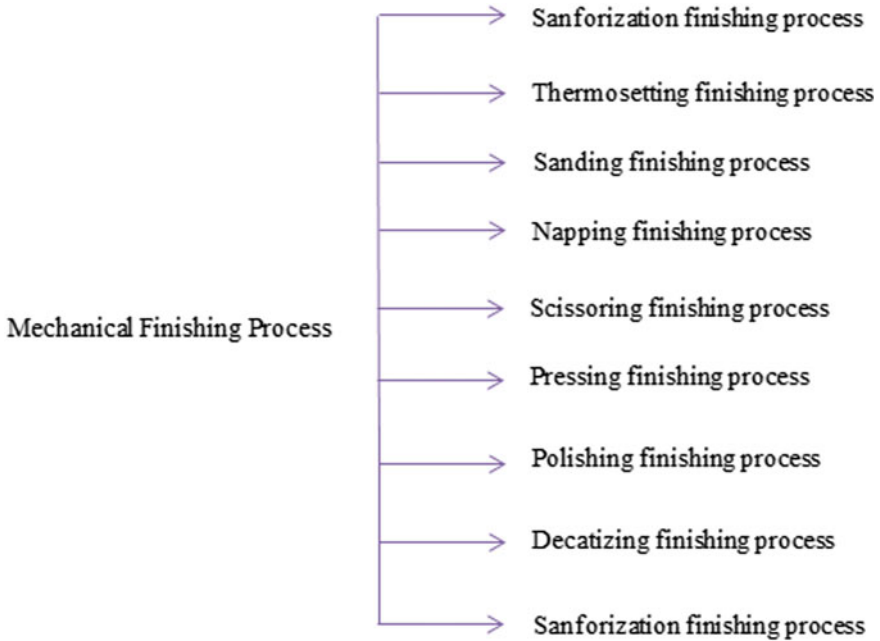
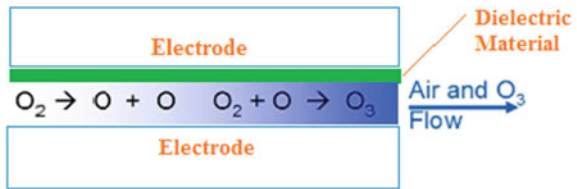


Fig. 4 Mechanical finishing processes

Fig. 5 Corona discharge ozone generator [9]



3.2 Production of Ozone Gas

Ozone gas can be produced in two different industrial methods. The first method is the use of UV at 185 nm and the second method is the use of Corona discharge. Corona discharge can be defined as an electrical discharge which is generated by the ionization of a gas surrounding a conductor that is electrically charged [8]. Production of ozone gas with Corona discharge is given in Fig. 5.

In this method, ozone is produced by supplying air or oxygen gas into the generator. In the ozone generator, oxygen or air is converted into ozone by the discharge of electric. First, primary components in air are separated into reactive atoms or radicals with the intense electric field. Then, these reactive atoms can react among themselves.

Table 1 The physical and chemical properties of ozone

Properties	Value
Molecular formula	O ₃
Molecular weight	48.0 g/mol
Boiling temperature	-111.9 °C
Melting point	-192.7 °C
Critical temperature	-12.1 °C
Critical pressure	5.53 MPa
Density in gas form	2144 kg m ⁻³
Redox potential	2.07 V
Density in liquid form (-112 °C)	1358 kg m ⁻³
Viscosity of liquid (-183 °C)	1.57 × 10 ⁻³ Pa s
Heat capacity of liquid form (-183 °C to -145 °C)	1884
Heat capacity of gas form	818 J kg ⁻¹ K ⁻¹
Heat of evaporation	15.2 kJ mol ⁻¹



3.3 The Usage of Ozone Gas in Textile Industry

3.3.1 The Use of Ozone Gas in Pre-treatment Process

Due to the many advantages of ozone gas, it is utilized in numerous fields of textile industry. Since ozone gas is an oxidative material, it is an alternative to hypochlorite, chlorite and hydrogen peroxide in bleaching process. Compared with other bleaching agents, it does not generate waste, with less damages to textile fabrics and no harm to environment as well as human health. In textile bleaching and washing, ozone gas provides energy and water saving, reducing the use of washing chemicals and decreasing the duration of process. Furthermore, as a new, dry, inexpensive and eco-friendly surface treatment for solid surfaces, ozone gas combined with UV-radiation is utilized in surface modification of textile fibers. Because of high oxidative properties of ozone gas with UV-radiation, surface adhesion can be improved, resulting in the production of high quality products. Ozone and UV-radiation has also etching effect which influences the surface wetting properties [10].

Recently, researchers have investigated the use of ozone in bleaching process of textile materials because of its high oxidizing capacity and opportunities. Perincek

et al. studied the use of ozone gas in bleaching cotton fabrics. According to the results, cotton fabric can be bleached in a short time with ozonation treatment [11].

Kan et al. investigated the effect of plasma-induced ozone treatment on the color fading of reactive dyed cotton fabric. In this context, cotton fabric was dyed with yellow reactive dye and then the dyed samples were treated with plasma-induced ozone under different conditions. The fading behaviors of samples were tested with spectrophotometer. The results showed that the plasma-induced ozone treatment reduced the processing steps and cost in comparison to conventional process [12].

In other study, jean fabric was treated with ozone injected water combined with ultrasound and hydrogen peroxide. A combined process effect on dye degradation was tested with electron paramagnetic resonance spectroscopy. According to the results, ozone was more effective with respect to bleaching of the jean samples than the hydroxyl radicals when combined with ultrasonic energy. The ultrasonic cavitations improved the diffusion of ozone through the fabric, resulting in the degradation of indigo dye. Furthermore, the use of moderate concentration of ozone caused no damage to cotton fibers [13].

Perincek et al. investigated the effects of ozonation on dyeing and bleaching properties of Angora rabbit fibers. The results showed that ozonation causes to improve the degree of whiteness and dyeability of Angora rabbit fibers [14].

In another study, cotton fabric samples were treated with ozone and ultrasound combination instead of conventional methods. After the pre-treatment, samples were dyed with different plant-based natural dyes. The use of ozone and ultrasound combination in pre-treatment caused not to use mordant agents. Furthermore, the fastness properties of dyed samples are good and sufficient for the use [15].

Prabaharan et al. researched the bleaching of grey cotton fabric with ozone/oxygen gas mixture and effects of ozone concentration and treatment time on the properties of bleached fabric. After the bleaching process, whiteness index, strength, elongation, extent of impurities removed, degree of chemical modification and reactive dye uptake were investigated. According to the results, the whiteness index of samples is found to be an acceptable value, with the acceptable results obtained via ozonation in a very short time. Ozone bleaching is ecofriendly since it is not harmful, requiring low quantities of water along with quite short durations of process [16].

3.3.2 The Use of Ozone in Color Remove of Textile Waste Water

In textile industry, among the hardest challenges are the improvements of wastewater after dyeing of textile materials and the amount of water used. In order to produce 1 kg of ready textile, nearly 200 L water is utilized, resulting in a high amount of chemicals. Throughout the world, it is estimated that textile wastewater is loaded with 280,000 t of textile dyes which have aromatic molecular structure. Furthermore, the biodegradation process of these compounds is highly difficult. In addition to these compounds, textile wastewater is charged with other organic and inorganic compounds having toxic effects on the ecosystem. In order to clarify and reuse textile wastewaters, various methods have been investigated. Physical methods can be

listed as filtration, coagulation/flocculation, precipitation, flotation and adsorption. Biological processes are aerobic, anaerobic and combination of them. Physical and biological processes are slower, requiring large storage areas and displaying low efficiencies when it comes to color removal. Chemical processes such as ozonation are generally simpler in application [17].

In the world, textile industry is one of the largest sectors which monopolize 8% of the world trade in manufactured goods. A major problem of textile production is wastewater [18]. The textile industry has adversely affected the environment due to its notorious water consumption and wastewater production. The water demand of the textile industry is estimated as 80–100 m³ Mg⁻¹ [19]. The wastewater of the textile industry includes high amounts of organic and inorganic compounds such as dyes, toxic heavy metals, pentachlorophenol, halogen carriers, carcinogenic amines, free formaldehyde, salts and softeners [20]. Owing to all these mentioned facts, the decontamination of textile wastewater becomes crucial. To this end, ozone technology is one of the eco-friendliest techniques among the available techniques.

Textile wastewaters are loaded with different types and concentrations of harmful compounds resulting from textile production steps. Textile wastewaters are indeed charged with highly colored and non-biodegradable colored dyes, surfactants and toxic chemicals. As these wastewaters are very harmful for the ecosystem, new methods have been investigated to meet the quality criteria of water [21]. Biological treatment methods for textile wastewaters are insufficient to meet biological oxygen demand (BOD) and chemical oxygen demand (COD) [22]. Thus, researchers have investigated methods alternative to biological treatment such as adsorption, membrane process and ozonation [22, 23].

Ozone gas is used to remove color from dyed textile wastewaters. During the ozonation process, ozone attacks unsaturated bonds of chromophores which leads to the elimination of color. Furthermore, ozone can degrade complex organic molecules to organic acids, aldehydes and ketones, resulting in the likely removal of color molecules. However, due to some difficulties arising from the high cost of ozone production and low ozone solubility and stability in water, an advanced oxidation process is required. Some significant oxidation processes can be listed as those being used with ozone as well as UV radiation and some chemicals [23].

In literature, the use of ozone gas was investigated with respect to textile wastewaters. Pazdzior et al. investigated the acute toxicity of textile wastewaters before and after chemical and biological treatments separately as well as a combination of chemical-biological treatments. According to the results, biodegradation followed by ozonation led to the highest toxicity reduction [24].

Bilińska et al. studied ozonation of textile wastewater discharged with Reactive Yellow 145, Reactive Red 195 and Reactive Blue 221. In this study, the effects of four ozonation process were investigated such as O₃, O₃/H₂O₂, O₃/UV and O₃/UV/H₂O₂. According to the results, it can be concluded that ozonation resulted in fast decolorization followed by further decomposition of by-products [25].

Reactive dyeing of cotton fibers brings about colored wastewater including residual dyes, electrolyte, alkali and other auxiliaries. Hu et al. investigated the reuse of reactive dyeing bath through catalytic ozonation with novel catalysts. In order

for degradation, two novel ozonation catalysts, mesoporous carbon aerogel and supported cobalt oxide nanoparticles were produced. Degradation efficiency was obtained with decolorization and chemical oxygen demand. According to the results, novel ozonation catalysts improved the decolorization and oxygen demand removal [26].

Recently, the use of ozonation as a pre-treatment before biological process has been largely studied in relation to the purification of textile wastewaters. Punzi et al. studied the use of an aerobic biofilm reactor followed by ozonation of real textile wastewater including azo dyes. Acute toxicity tests were carried out before and after ozonation. According to the results, the combination of anaerobic-ozonation processes caused to remove more than 99% of color, 85–90% of chemical oxygen demand and toxicity [27].

Cardoso et al. developed a bubbling annular reactor which provides to test the efficiency of photolysis, photocatalysis, photoelectrocatalysis and ozonation using oxygen or ozone gas flow. After bubbling of ozone, the results showed that 90% of color was removed [28].

3.3.3 The Use of Ozone in Sizing

In the textile industry, before the weaving, natural based warp yarns are treated to sizing process to stabilize the high-speeds of weaving. In order to obtain acceptable sizing properties for warp yarns, polyvinyl alcohol (PVA) has been widely used for decades. Though many advantages of PVA sizing, decomposition of PVA wastewater is difficult in nature with the high level chemical oxygen demand (COD). Because of these difficulties, researchers have sought for green sizing recipes and environmental production methods.

Sun et al. used phosphate-modified starch (PM-starch) and glycerol to sizing cotton yarns. According to the results, glycerol caused to decrease sizing pick-up, yarn breaking strength and breaking elongation [29].

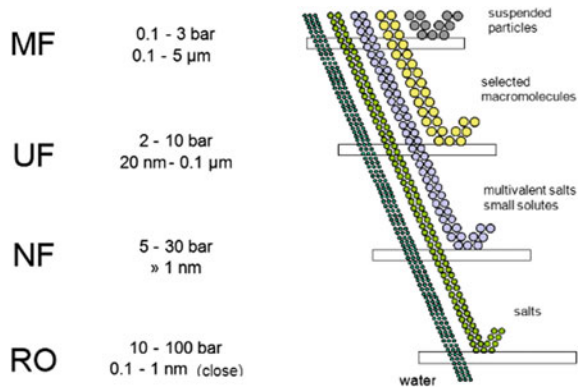
Recently, plasma treatment is a clean, dry and green technique to modify surface properties of textile materials.

4 Membrane Filtration Technology

Membrane filtration can be accepted as a very efficient and economical method to separate components dissolved in a liquid. The membrane can be described as a physical barrier which permits compounds to transfer with regards their chemical and physical behaviors. Commonly, membranes include a porous support layer on top of the actual membrane [30].

Membrane filters are selective barriers produced from several materials. Membrane filters are used in various areas in order to separate the compounds smaller than 10 μm from liquor. The flow on the membrane surface occurs in two directions which

Fig. 6 The filtration actions with regard to the pore size [31]



are parallel to the membrane axis and in a radial direction (cross-flow). Particles are bigger than the membrane pores are removed on the surface of the membrane and these particles have parallel flow. Particles are smaller than the membrane pores pass through the membrane with the cross-flow. Finally, the molecules in the liquor are separated physically according to their molecular dimensions [30].

In the industry, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are commonly used filtration processes to separate the compounds in the liquor. Figure 6 shows the filtration actions with regard to the pore size [30].

4.1 Types of Membrane Process

4.1.1 Ultrafiltration

Ultrafiltration is a type of filtration method that provides separating extremely small particles and dissolved molecules from fluids. In filtration processes, the most important factor affecting filtration is molecular size. However, in almost all of filtration processes, chemical and physical properties of samples can affect the permeability of filter. In ultrafiltration process, molecules of similar sizes cannot be separated. It means that ultrafiltration can separate molecules having different molecular sizes. Materials having 1–1000 K molecular weights are filtered by ultrafiltration membranes and salt molecules can pass through. Furthermore, materials larger than the membrane pore size pass through the filter, resulting in separation of the contaminants with high molecular weight from the fluid. Sugars, proteins and bacteria can be simply separated with ultrafiltration [30].

Ultrafiltration processes utilized in these fields are as the following;

- Purification of water in laboratory,
- Refine of wastewater,

- Refine of drinking water,
- Recovery of waste dyestuff in the textile and automotive industry,
- Juice and wine industry,
- Pre-treatment for reverse osmosis [32].

Ultrafiltration has been presumed as a practical industrial process due to purification or dewatering of solution. Recently, ultrafiltration process has been used in many industries because of its economic attractiveness and usefulness [33].

4.1.2 Microfiltration

Microfiltration is utilized in order to remove particles having particle size 0.025–10.0 μm from fluids by transferring through a microporous medium. Furthermore, microfiltration process can be used for final filtration or prefiltration [30].

Microfiltration membranes lead all bacteria to move away. However, viruses are not removed with microfiltration membrane as they are of smaller sizes than the pores of a microfiltration membrane. Microfiltration can be implemented in a lot of different treatment processes [30].

Microfiltration process utilized in these fields are as the following;

- Cold sterilization of pharmaceuticals,
- Purification of fruit juice and wines,
- Biological wastewater treatment,
- Separation of oil/water emulsions,
- Pre-treatment of water for nano filtration or Reverse Osmosis,
- Petroleum refining [34].

4.1.3 Reverse Osmosis

Reverse osmosis is described as the finest separation membrane process with pore sizes ranging from 0.0001 to 0.001 μm . Reverse osmosis can remove nearly all molecules without water. Compared with microfiltration, osmotic pressure of reverse osmosis is higher. In reverse osmosis process, osmotic pressure causes to occur chemical potential differences of the solvent [30].

Reverse osmosis filters salts and small molecules from solutions at high pressures using membranes. Reverse osmosis membranes are successfully used to purify water that distilled water quality [30].

Reverse osmosis process utilized in these fields are as the following;

- Removing ions, molecules and larger particles from drinking water,
- Removing bacteria,
- Concentration of fruit juice,
- Syrup production,
- Hydrogen production [30].

4.2 *Studies Concerning Membrane Use*

Membrane techniques are promising in terms of cleaning textile wastewaters, since dyes stuffs and auxiliary chemicals used for dyeing can be removed with these techniques. Indeed, membrane techniques can be utilized to purify complex wastewaters. In literature, there have been many researches treated to textile wastewaters due to purification. Aouni et al. investigated the reactive dyes' molecular weight and the effects of the membrane types on purification of textile dyeing wastewater. It was obtained that high chemical oxygen demand retention and color retention rates (>90%) were carried out with using ultrafiltration and nanofiltration [35].

In another study, biological treated wastewater was applied to nanofiltration in two ways, direct nanofiltration treatment and nanofiltration after ultrafiltration pre-treatment in four different pore sizes. After the treatment, flux, salt retention and COD removal were measured. According to the results, the decrease in pore size of nanofilter caused to improve chemical oxygen demand and salt retention [36].

A membrane bioreactor is defined as combining biological treatment and membrane filtration. Membrane bioreactor systems have been increasingly used as retention of solid particles with membrane ultra-filtration is higher than conventional biological process. Brik et al. investigated the performance of a membrane bioreactor for the textile wastewater originating from a polyester finishing mill. The level of percentage of chemical oxygen demand removal was found as 60–90% and color removal was measured as 87% [37].

Membrane bioreactor treatment to textile wastewaters has been investigated because of simple and significant removal of contaminants and cost-effective process. However, membrane fouling is one of the major drawbacks which leads to decrease in permeate flux. Jegatheesan et al. investigated aerobic and anaerobic membrane bioreactor process for textile wastewater treatment. It has been found that long sludge retention time increases the degradation of pollutants [38].

Lutz et al. performed zwitterionic copolymer membranes for industrial wastewater streams. These membranes were prepared with self-assembling zwitterionic amphiphilic random copolymer on porous supports. According to the results, these membranes are effective to polysaccharides, natural organic matter and fatty acids [39].

In other study, biological treated textile effluent is filtrated with nanofiltration membrane. Then color removal and chemical oxygen demand reduction were analyzed. It was found that hollow nanofiltration membranes caused effective color removal and chemical oxygen demand reduction [40].

Zhu et al. investigated the removal of reactive dye from textile waste water with nanofiltration. The nanomembrane was produced with hollow fiber in laboratory conditions. The efficiency of nanofiltration was evaluated according to dye removal efficiency. According to results, under the pressure of lower than 1 bar, the membrane filtrated all the dye molecules in the textile waste water. The efficiency of membrane increased with increasing in the transmembrane pressure [41].

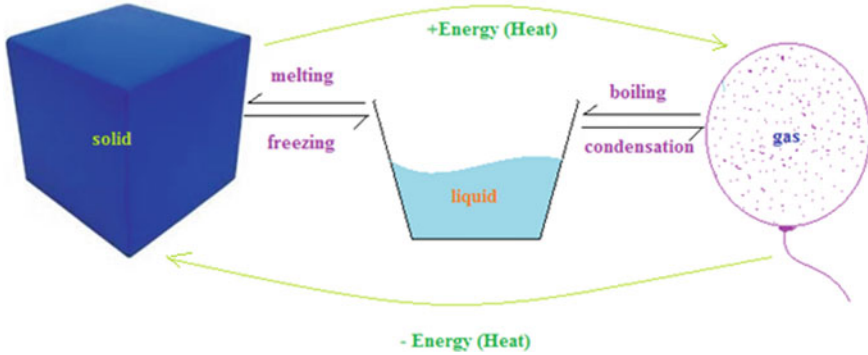
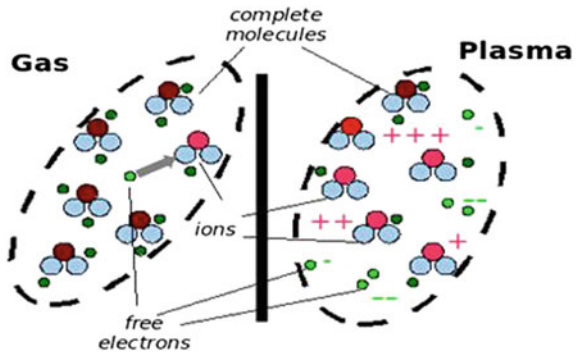


Fig. 7 States of matter

Fig. 8 The fourth state of material: plasma [42]



5 Plasma Technology

Plasma can be defined as the fourth state of material having the highest energy. In order to identify plasma, states of matter must be explained. When energy is given to a solid material, the distance between atoms increases, carrying out their vibrations more freely. In the present case, the solid material melts into liquid form. If energy delivery to this material goes on atomic mobility increases, and when the material receives the necessary energy for evaporation atoms begin to move freely in random directions, going from the solid phase to the gaseous state (Fig. 7).

Upon the maintenance of energy delivery, atoms and molecules begin to decompose into charged particles (ions and electrons), with the material going to the plasma phase.

Briefly, plasma described as ionized gas (Fig. 8).

For the first time, plasma was described by Sir William Crookes in 1879 with Crookes tube. The basis of the Crookes tube is cathode ray which was subsequently identified by Sir J. J. Thomson in 1897. In 1928, Irving Langmuir examined the plasma term in exact terms.

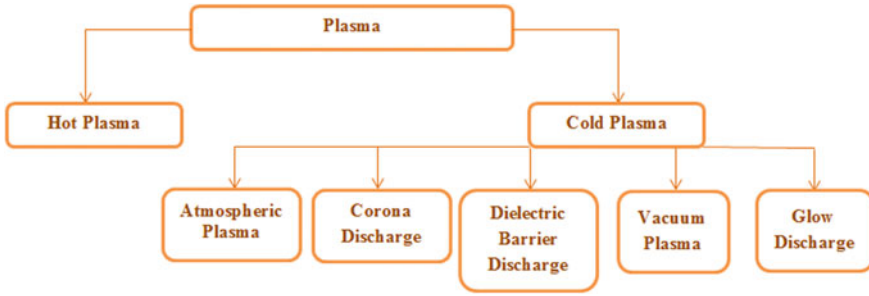


Fig. 9 Types of plasmas

Table 2 The advantages of plasma treatment compared with conventional method

Plasma technology	Conventional methods
– Water is not used in plasma application. Treatments are carried out in gas phase	– Water-based method
– Low water, energy and chemical consumption	– High water, energy and chemical consumption
– Short period of application	– Long period of application
– Plasma application does not affect the bulk properties of materials	– Bulk properties of materials are generally affected
– Complex and multifunctional	– Simpler
– Electric energy is used	– Heat energy is used

In plasma applications, reactive particles emerged, leading to modifications on the surface of materials. These modifications can be classified as surface activation, corrosion, grafting, cleaning and cross-linking.

Basically, plasma treatment can be categorized into two groups such as cold and hot plasma. In the textile industry, cold plasmas can be used because it does not cause damage to textile materials. Hot plasma applications lead to carbonization of textile materials. The types of plasmas are shown in Fig. 9.

Plasma technology is utilized in a wide range of textile industry applications due to its numerous advantages. Table 2 demonstrates the advantages of plasma technology compared with conventional methods in the textile industry.

Pre-treatment and finishing of textile materials by using non-thermal plasma applications have recently become more popular. Because of its numerous advantages compared with conventional process, plasma technologies have been preferred. Plasma surface modification does not require the use of water and chemicals. For this reason, plasma treatments are accepted as economic and ecological processes. Furthermore, plasma treatment led to decrease of contaminations as it does not require using water. In the textile industry, non-thermal plasmas are suitable because most of textile materials are sensitive to heat. This technique causes active functional groups to be formed on textile surfaces. In addition, after the non-thermal plasma treatment,

textile surfaces can gain wettability, adhesion of coatings, printability, induced oleophobic properties, changing physical or electrical properties, cleaning or disinfection of fiber surface [43].

5.1 Plasma Treatment to Cotton

Plasma treatment can be utilized to modify different types of textile products. In literature, there are a variety of researches using plasma treatment in order to modify cotton fibers. Plasma treatment provides removing PVA sizing [44], increasing hydrophilicity and wickability [45], gaining hydrophobic properties [46], developing adhesion properties [47] and increasing dyeability [48].

Cai et al. applied air/He and air/O₂/He plasma treatment on cotton fabric to desize of PVA. After the plasma treatment, percent desizing ratio and tensile strength were measured. The results showed that plasma treatment removed some PVA sizing and significantly improved percent desizing ratio by washing. The tensile strength of cotton fabric treated with atmospheric plasma is similar to that of unsized fabrics. Furthermore, air/O₂/He plasma is quite effective to remove PVA sizing [49].

In other study, raw cotton fabric samples were treated with air plasma and argon atmospheric plasma. After the plasma treatment, the hydrophilicity and wickability of samples increased and contact angles notably decreased. Furthermore, morphological changes were observed with scanning electron microscope [50].

Li et al. investigated that plasma surface treatment of cotton fabrics were performed in a hexafluoropropene (C₃F₆) atmosphere under different experimental conditions. X-ray photoelectron spectroscopy (XPS) analysis demonstrated that 50% of fluorine atoms were incorporated in the surface structure of two fibers and -CF, -CF₂, -CF₃ groups occurred on the surface. After the contact angle and wet-out time measurements, the fibers demonstrated high hydrophobic properties [46].

Selli et al. investigated RF SF₆ plasma treatment on cotton fabrics. The plasma treatment provided an efficient implantation of fluorine atoms on the surface of both polymers. After the plasma treatment, the fluorinated layer was observed on the surface of cotton fabrics. The fluorinated layer led to the increase in hydrorepellence behaviors of surface [51].

In another study, the hydrophilic improvement of the grey cotton fabric by low pressure dc glow discharge air plasma was investigated. The plasma treatment was achieved for different exposure times, discharged potentials and pressure levels. Effects of plasma treatment on wettability behaviors were investigated. The surface energy values were estimated using contact angle measurement. Furthermore, degradation and dyeability of the fabrics were determined. According to the results, the surface hydrophilicity and energy were found to increase [52].

Sun and Stylios investigated the effects of low temperature plasma treatment on cotton fabrics. In this context, hexafluoroethane (C₂F₆) and oxygen plasma treatment were applied to cotton fabrics separately. After the plasma treatment, samples were investigated with regards to the type of gas. The plasma treatment was determined

to cause changes on surface geometrical roughness. Furthermore, both rougher and smoother surfaces can be produced using plasma treatment. The plasma treatment led to chemical modification on surfaces [53].

In another study, cotton fabric samples were treated with radio-frequency plasma (in air) at different power levels and time intervals. After the plasma treatment, moisture content and surface resistivity behaviors were investigated with regards to the power level and treatment time. The surface resistivity was found to be affected by both power level and treatment time [54].

Peng et al. investigated the influence of moisture absorption of cotton fabrics on the effectiveness of atmospheric pressure plasma jet on desizing of polyvinyl alcohol. X-ray photoelectron spectroscopy analysis demonstrated that the plasma treated PVA has higher oxygen concentration than the control. Furthermore, the results indicated that the highest desizing efficiency was obtained [55].

In a different study, air and argon atmospheric plasma treatments were applied to bleached plain cotton fabrics. After the plasma treatment, pilling, thermal resistance, thermal conductivity, water vapour permeability, air permeability and surface morphology were investigated. The results showed that the pilling resistance of cotton fabric samples increased. Moreover, thermal resistance, water vapour permeability and surface friction coefficient increased with the plasma treatment. The SEM images demonstrated that the atmospheric plasma modified the fiber surface [56].

5.2 *Plasma Treatment to Wool*

Plasma treatment has been used by the industry for treatments of metals and other polymeric materials. In the textile industry, plasma treatment has particularly gained greater prominence.

Wool fabrics were treated with oxygen, carbon tetrafluoride and ammonia low temperature plasma. After the plasma treatment, the samples were dyed with natural dyes extracted from cochineal, Chinese cork tree, madder and gromwell. The results showed that the dyeing rate of plasma-treated wool fabrics increased. Furthermore, plasma-treated wool fabrics dyed with cochineal and Chinese cork tree were brighter compared with untreated wool [57].

Ghoranneviss et al. investigated the effects of plasma treatment on the natural dyeing properties of wool fabrics. Before the dyeing process, wool fabric samples were treated with argon plasma. Madder and weld were used as natural dyes and copper sulfate (CuSO_4) as a metal mordant. Furthermore, copper was used as the electrode material in a DC magnetron plasma sputtering device. After these processes, the color strength, fastness and anti-bacterial properties of samples were analyzed. The results showed that the plasma treatment led to the development of color strength and fastness properties of samples. Furthermore, the anti-bacterial efficiency of samples improved [58].

In another study, atmospheric pressure plasma was performed to pure cashmere and wool/cashmere textiles with a dielectric barrier discharge in humid air (air/water

vapor mixture). Treatment parameters were adjusted in order to develop the wettability of the fabrics. After the plasma treatment, characterization analysis was conducted out to investigate the wettability, surface morphologies, chemical composition and mechanical properties of the plasma treated samples. The analyses revealed a surface oxidation of the treated fabrics that enhanced their surface wettability. Furthermore, SEM analysis demonstrated that a minor etching effect occurred on the textile surface [59].

Zanini et al. investigated the hydro- and oleo-repellent modifications of pure cashmere and wool/nylon textiles by means of an atmospheric pressure plasma treatment after fluorocarbon resin impregnation. The plasma treatment was performed with a dielectric barrier discharge in humid air (air-water vapour mixture). The finishing process was carried out with a foulard system, with an aqueous dispersion of a commercial fluorocarbon resin. After these treatments, wettability, surface morphologies and chemical composition of the modified textiles were investigated in terms of the plasma treatment. According to the results, the plasma treatment caused to increase the hydro- and the oleo-repellent properties of the modified fabrics [60].

In another study, atmospheric pressure plasma treatments were performed to wool/cashmere (15/85%) textiles with a dielectric barrier discharge in nitrogen. The chemical properties of the plasma treated samples were investigated with FTIR/ATR spectroscopy, X-ray photoelectron microscopy and fatty acid gas chromatographic analysis. Furthermore, the mechanical properties of samples were analyzed with KES-F system. The analyses revealed the surface modification of the treated fabrics, which led to the improvement of wettability of samples [61].

Eren et al. synthesized different conducting polymers by atmospheric pressure plasma and coated these conducting polymers on wool fabrics with atmospheric plasma. Scanning electron microscopy, energy dispersive X-ray spectroscopy, Fourier Transform Infrared Spectroscopy and probe resistance measurements were used to investigate the properties of wool samples. After the plasma treatment, electric conductivity of samples increased [62].

In a further study, wool fibers were treated with plasma and a poly (propylene imine) dendrimer to develop dyeing properties. FESEM, EDX, AFM and FTIR analyses were then performed to investigate the effects of these treatments on the chemical and physical properties of wool fibers. According to the results, the etching effect occurred on the surfaces of wool fibers and the plasma treatment caused to increase the roughness of samples. Furthermore, oxygen plasma and dendrimer treatments improved the dyeability of wool fibers with cochineal natural dye [63].

Jeon et al. treated DBD plasma with oxygen, nitrogen, argon and air on wool fibers. In this study, the plasma treatment time was controlled. The increase in plasma treatment time led to the improvement of the wicking rate of wool samples. Furthermore, the surface morphology was investigated with SEM. According to the SEM results, the damages of surfaces increased with increasing treatment time. The wicking rates of wool fibers increase in the order: oxygen, argon, nitrogen and air plasma. As a result, the oxygen plasma is the most effective to change the wettability of the wool fibers [64].

Shahidi et al. investigated the effects of low temperature plasma on the wool fabric samples under different conditions. The reactive gases such as O₂, N₂ and Ar were treated on wool fabrics. After the plasma treatments, morphology, dyeability, hydrophilicity and fabric shrinkage properties of samples were analyzed. The results showed that surface topography and chemical composition changed after the plasma treatment. The dyeability analysis results illustrated that O₂ and Ar plasma treatments were more effective in terms of increasing the dye exhaustion of wool samples. Moreover, the samples had more brilliant colors with the plasma treatment. The plasma treatment led to the increase in the hydrophilicity of samples while developing shrink resistance and anti-felting behavior considerably [65].

In another study, wool fibers were treated with low temperature plasma treatment with different gases, namely oxygen, nitrogen and gas mixture (25% hydrogen/75% nitrogen). The results showed that chemical composition of the plasma treated wool fibers varied differently with different plasma gas [66].

Moreover, wool fabrics were treated with plasma of different gases (air, oxygen, water vapor (H₂O) and nitrogen) for different periods of time. The surface changes of wool samples were analyzed with XPS. According to the results, air plasma treatments oxidized and etched the F-acid mono-layer. Furthermore, after the nitrogen plasma treatment, new nitrogen groups were not observed on the surface. By contrast, oxygen gas led to the oxidation of the surface of wool fibers and their posterior etching [67].

5.3 Plasma Treatment to Synthetic Fibers

Jurak et al. prepared new mixed chitosan/phospholipid films and applied the films on plasma activated PET surfaces. The prepared surfaces were characterized with regards to the wettability and surface thermodynamics. According to the results, it was thought that the PET surfaces could be used in reducing inflammation and accelerating wound healing [68].

In another study, it was aimed to improve the adhesion properties of PET films using atmospheric plasma. PET is known as chemically inert to most coatings, but the surface can be modified with the atmospheric plasma treatment. Furthermore, after the plasma treatment, the surface becomes enriched with oxygen, rougher and more wetting. Lastly, adhesion test demonstrated the improvement of adhesion after the plasma treatment [69].

In another study, the effects of air plasma treatment on PET and starch modified PET were investigated. Air plasma treatment was applied in order to develop the interfacial adhesion of starch to PET. After the plasma treatment, wettability, thermal and mechanical properties of samples were investigated. After the plasma treatment for a short period of time, the contact angle of samples decreased immediately. Furthermore, plasma treatment led to the differences of elongation as well as small differences in thermal stability and flexural properties of PET [70].

Zhang et al. applied low-pressure oxygen and argon plasma to nylon and modified fabrics. After the plasma modification, the fabric samples were coated with single-walled carbon nanotubes by a dip-drying process. After the coating process, sheet resistance, fiber surface roughness and the attachment of single-walled carbon nanotubes onto nylon fabrics were investigated. The plasma treatment caused to increase the roughness of samples and the attachment of single-walled carbon nanotubes onto nylon fabrics. After the coating process, the sheet resistance of samples also improved [71].

In another study, multi-walled carbon nanotubes were modified by combination of oxygen + nitrogen in order to improve its dispersion in the nylon matrix and enhance the interfacial adhesion. After the plasma treatment, the tensile strength, Young's modulus, elongation at break and storage modulus were improved by ~66%, 64%, 69% and 39%, respectively. It was thought that the plasma treatment improved interfacial adhesion [72].

Sanaee et al. investigated the effects of oxygen and hydrogen radio frequency plasma on PET films with SEM, XPS and atomic force microscopy (AFM). It was found that the plasma treatment led to the reduction in penetration of air through the PET films. Furthermore, compared with hydrogen plasma, oxygen plasma resulted in a rougher surface [73].

In another study, nylon 6 fabrics were treated with low temperature plasma with three gases: oxygen, argon and tetrafluoromethane. After the plasma treatment, the properties of fabric such as surface morphology, low-stress mechanical properties, air permeability and thermal properties were analyzed. The different plasma gases resulted in different morphological changes. Low-stress mechanical properties were analyzed with Kawabata evaluation system fabric (KES-F). The results showed that surface friction, tensile, shearing, bending and compression properties of fabric samples changed with the plasma treatment. In addition, the plasma treatment caused to decrease the air permeability of samples probably due to plasma action resulting in an increase in fabric thickness and a change in the surface morphology. Finally, thermal properties of samples improved with the treatment [74].

McCord et al. treated the atmospheric pressure He and He-O₂ plasma to polypropylene and nylon 66 fabrics for selected time intervals of exposure. Scanning electron microscope showed no changes in the samples. After the plasma treatment, carbon and oxygen contents of nylon 66 altered. The oxygen and nitrogen contents of polypropylene fabric samples increased significantly. In addition, plasma treatment leads to decrease in tensile strength of nylon 66 fabric samples [75].

In another study, acrylic fabric samples were treated with a RF atmospheric pressure plasma, after which a fluorocarbon finish was applied to the samples. In the plasma application, helium and helium/oxygen gas were used for different periods of time. The oil and water repellency of samples were investigated with regards to the gas type and processing time. After the plasma treatment, the repellency properties of samples improved. Furthermore, plasma treatment caused to change the morphology of samples [76].

Liu et al. aimed to improve the antistatic properties of acrylic fibers by using nitrogen glow-discharge plasma. The treated surfaces are characterized by scanning

electron microscopy, specific surface area analysis and X-ray photoelectron spectroscopy. The plasma treatment led to the increase in surface roughness, wettability and antistatic ability [77].

6 Enzymatic Treatments

Enzymes are biocatalysts composed of metabolic products of live organisms acquired from bacterial derivatives. Catalysts are the substances involving in chemical or biochemical reactions and remaining unchanged at the end of the reaction [78].

All of the isolated enzymes have a protein structure or consist of a protein component. They are named by attaching an “ase” affix at the end of the substance that they affect or based on the reaction that they catalyze. The compound that an enzyme affects is called substrate and the number of the substrate molecules that they affect in a second is called the enzyme turnover number. These substances function as a group within a cell and the final product of an enzyme acts as the substrate of the next enzyme; for instance enzyme amylase converts starch to two-chain maltose and enzyme maltase converts one-chain maltose to glucose [78].

Enzymes are used extensively for many years in medicine, analyses, food chemistry, beverage industry and home-type detergents. 80% of detergents used at homes consist of enzymes. Modern gene technology and enzyme technology will consist of novel types with fixed production and potential extensive applications that will continue in the future [78].

Amylases used to decompose starch in textile industry are known since 1910s. Interesting applications were discovered for wool finish during the recent years. The flake layer on the surface is removed by the utilized enzymes in these methods and wool fabric surface is modified. Furthermore, anti-felting property is introduced and shininess and attitude is developed [78].

The oldest patent about these technologies was received 30 years ago. However, this enzymatic cellulose decomposition process did not find an industrial application field in Europe initially. The first successful applications in this field occurred in Japan [78].

The functions of enzymes can be listed as;

- They reduce activation energy of biological reactions.
- They function only in a specific type of reaction.
- They can function in the same type of reaction without decomposing.
- They enable the reactions to reach equilibrium quickly.
- They function in inorganic environments as well.
- They initiate their reactions at the external surface of the substance that they affect.

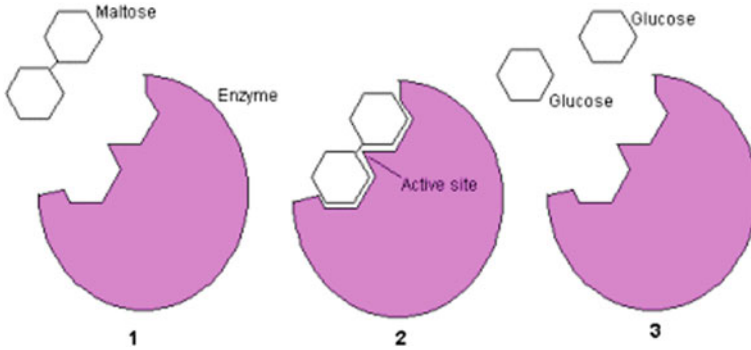


Fig. 10 The key-lock compatibility model [78]

6.1 Enzyme Structure

Genes encode all enzyme proteins. Hence, their amino acid sequence is unique. Some enzymes (e.g. pepsin and urease) are composed of only proteins. However, the other majority is composed of two different parts. These are;

- **Protein Component (apo-enzyme part of the enzyme):** This part determines which substance will be affected by the enzyme.
- **Coenzyme Component:** It is organic or inorganic and composed of phosphate in general, and it is an extremely small molecule in comparison to the protein component. Organic molecules required for enzyme action are called “coenzymes”. This component is responsible for enzyme action and carries out the main function. Some enzymes are active when specific ions are added in the material [78].

6.2 Enzyme Action Mechanism

Apo-enzyme component determines the type of substrate with which the enzyme will function. There is a relation between the apo-enzyme portion and substrate. German chemist Emil Fischer suggested that this resembles the key-lock fit. Coenzyme component functions closely to the chemical bond generally, for instance it breaks ester bonds. It is thought that apo-enzyme component of enzyme adheres or binds to the substrate molecule (at its active regions) (enzyme-substrate complex) and the coenzyme component combines or binds with the bonds on the substrate in real sense meanwhile and it digests it. A schematic illustration of the key-lock fit is shown in Fig. 10 [78].

6.3 Factors of Affecting Enzyme Action

6.3.1 Temperature

Enzymes are inactive at high temperatures. When the temperature goes up to 100 °C, the reaction rate doubles in other words the reaction rate-increase is proportional to temperature. However, it starts to drop at a specific point and stops completely. The temperature where enzymes act the best is called optimum temperature (generally 55–600 °C) [78].

6.3.2 pH

Enzymes are extremely sensitive to pH changes. They are inactive in extremely acidic and alkaline environments generally. Enzymes show highest activity in a specific pH value in some cases. This pH value is called optimum pH. For example, pepsin, which digests proteins, functions in acidic medium of stomach at pH 2. Various electrical charges are generated on the protein molecule depending on pH and the external surface form (tertiary structure) is generated accordingly and the substrate-enzyme compatibility is enabled. This electrical charge possibly improves enzyme-substrate attraction. Strong acids and bases coagulate enzymes [78].

6.3.3 Enzyme/Substrate Concentrations

If pH and temperature is kept constant, a reaction rate occurs depending on the ratio of enzyme/substrate concentrations. Excessive substrate or enzyme may affect this rate in various ways. Enzyme that is to be added in a medium containing abundant substrate will increase the final product amount [78].

6.3.4 Effect of Chemical Substances and Water

Many chemical substances inactivate enzymes, for example cyanide inhibits cytochrome oxidase enzyme that plays an important role in respiration. Death may occur. Fluoride affects enzyme steps converting glucose to lactic acid. Even the enzyme itself may create a toxic effect, for example if 1 mg of crystal trypsin is infused in mice, death occurs. Some snake, bee and scorpion toxins show enzymatic effect as well and disrupt blood cells or other tissues.

Since the majority of enzymes function in water, water amount is also an effective factor for enzyme function. Enzymes are inactive in medium consisting of less than 15% water generally. This factor is essential for jam and syrup production. Diluted jam, honey or syrups ferment and become sour due to this reason. Moreover, water ratio is desired to be less than 15% during grain purchases [78].

6.4 Enzyme Classification

Each enzyme has a 4-digit number, for example in 3.6.1.3 “ATP phosphohydrolase”, the first number indicates its class, the second number indicates its subclass, the third number indicates its group and the fourth number indicates its specific row number. According to this, the enzyme classes are as follows:

1. Oxidoreductases: They catalyze redox reactions.
 - (a) Dehydrogenases: They catalyze electron gaining reactions.
 - (b) Oxydases: They catalyze electron losing reactions.
 - (c) Reductases: They reduce substrates by means of a redactor. For example, acetylaldehyde reductase reduces acetylaldehyde to alcohol.
 - d) Transhydrogenases: They move hydrogen from one molecule to another and reduce it.
 - (e) Hydroxylases: They add one hydroxyl or water molecule to their substrates. For example, phenylalanine hydroxylase adds one hydroxyl group to phenylalanine and converts it to tyrosine.
2. Transferase Enzymes: They catalyze transfer of an atom or atom group from one molecule to another molecule (methyl, carboxyl, glycosil, amino, phosphate groups), except for hydrogen.

Decarboxylases: They catalyze CO₂ release from carboxylic acids.

3. Hydrolase Enzymes: They catalyze molecule breaking by adding a water molecule or by means of a water molecule. They also affect ester, peptide, acid-anhydrite and glycosidic bonds.
 - (a) Esterases: They break ester bonds (lipase, ribonuclease, phosphatase, pyrophosphatase, glycosidase).
 - (b) Proteases: They break peptide bonds (proteinase).
4. Liases: They break molecules without releasing water molecule. For example, C–C bond is broken by aldolase and decarboxylase. Similarly, there are enzymes breaking C–O and C–N bonds.
5. Isomerases: They make modifications within molecules and change their sequence in space, for example, rasemase and epimerase.
6. Ligases (Synthesases): They catalyze binding of substrate molecules to each other by spending energy, for example, they catalyze activation of amino acids and fatty acids [79].

6.5 Utilization of Enzymes in Textile

The enzymes and their usage in textile industry were given in Table 3 [80].

Table 3 The enzymes and their usage in textile industry

Enzymes	Textile process
Amylase	Desizing
Cellulose	Enzymatic washing of jeans, bio-process, finishing process, regenerated fabrics
Protease	Treatment of protein based fibers such as wool and silk
Catalase	Hydrogen peroxide removal after bleaching
Lactase	Removal of indigo colorants of jean fabrics
Peroxidase	Oxidation of colorants that are not bond covalently
Lipase	Desizing
Pectinase	For bio-cleaning of raw cotton or flax

6.6 Purposes of Bio-process for Textile Finishing

Textile enzyme manufacturers produced cellulases for improving characteristics of cellulosic fabrics and developed new fabric enzymes to be used in finish processes of cotton, linen, ramie and mixtures of these with synthetic fibers. Bio-finishing processes have an important role for textile finishing today. A cellulose preparation is manufactured by modification of nonpathogenic fungi. Enzymatic processes of cellulosic textiles are called bio-finishing process. The purposes of these processes are as follows;

- Cleaning of fabric surfaces and reducing fuzz.
- Improving some features including flexibility and softness.
- Improving fabric flow.
- Improving hydrophilic characteristic.
- Improving colorant attraction, color efficiency, smoothness and shine.
- Providing comfortable wearing characteristics.
- Successful application in fabrics including cotton, linen and viscose with low basis weight without conformity in their elastic and resistance features.
- For stone washing and old look purposes.
- Unmatched softness when combined with classic softeners.
- Resists are prevented by bio-finishing process and surface fuzz is reduced in preliminary processes of fabrics for sharp contoured prints.
- For removing nep and fibers on the cotton surface.
- For achieving touching, flow and natural softness by improving with comfort.
- For permanently preventing fibrillation and bead formation.
- For improving water absorption in especially towels and bath textiles.
- For creating new and original finish effects.
- For ensuring operability in all ecologic processes.

The effects acquired by bio-finishing are permanent even after multiple washing steps. Textile chemicals remain in the fabric and fabric look is destroyed after each wash in classic methods. This method is an alternative competitor of many textile chemicals with its modern content that can be completely digested biologically and does not create pollution. Enzymes provide water and energy savings and reduce waste amount and reduce environmental pollution in industry [80, 81].

6.7 Cellulase

Cellulases are colloidal proteins with high number of molecules in a metabolite form and with high metabolic rate and are obtained from *Aspergillus niger*, *Trichoderma longibrachiatum*, *Fusarium solani*, and *Trichoderma viride*. Each enzyme molecule in each unit time causes a change in high molecule number. Industrial cellulases are the complexes of cellulase, cellobiase and related enzyme compounds that are not completely uniform. Their molecular weight is 10,000–4,000,000. Enzymes resemble proteins and have primary, secondary, tertiary and quaternary structures. The properties of these substances can change due to alkali, acids, light, temperature, ionization radiation and biological effect factors. These substances have the ability to break 1,4 β -glucoside bonds of cellulose. An enzyme unit is one-unit of measurement. It is related with a group of 1 micromole reduced in the reference system of cellulose. This is its value at favorable pH and temperature conditions (pH 4.6, 40–550 °C).

A reaction field is undisrupted biological cells in the amorphous field of cellulose. Cellulose is not digested statically but it settles accidentally in general depending on the composition of cellulose complex that is dominant in specific porous places.

The effect mechanism of enzymes functions to generate enzyme-substrate complex by enzyme catalysis for instance. Enzymes consist of actual activity centers in a three-dimensional structural form such as grooves, clefts, spaces and packages. Enzyme function generates substrate complexes, for example cellulose-cellulose complex, and the number of factors is effective on this.

Cellulase multi-enzyme complexes have a structure that is not completely uniform to achieve special effects depending on the production methods, and they are also affected by the production conditions that can generate elective cellulose complex reactions. Moreover, substrate properties are also effective for generating elective conformity for enzymatic degradation due to the non-uniform structure of cellulose. In conclusion, thread type and structure, design of textile substrate, and dissociation effect are influential as well. Thin threads and open material structures, and especially each free, accessible, leaped fiber is fit for degradation.

Bio-reaction occurs due to reduction in activation energy for increasing the reaction rate which is a very simple expression of chemical degradation and corrosion in the enzyme-substrate relation mentioned above. In conclusion, the complex is degraded with the release of the reaction product and enzyme that is ready once again.

The application techniques are effective on enzyme activity and fundament. These are temperature, pH (550 °C, pH 4.6) and the diversity of chemical factors. For example, iron, manganese, magnesium and zinc ions and organic salts are affective on generating or inhibiting enzyme activity and on deactivation and improving their characteristics. Irreversible prevention of enzymes is called enzyme toxin [82].

Cellulase catalyzes cellulose chains and enables hydrolytic dissociation [83]. Cellulase has active locations like all enzymes and is a large protein and it catalyzes chemical reactions with its specifically positioned chemical groups. If temperature and pH are not favorable, these active locations change and enzyme activity drops.

It was seen that when American soldiers were at South Pacific Forests, their outfits were worn out extremely and the reasons for that were investigated. After studying thousands of samples, it was found out that the reason was an organism called *Trichoderma viride* (today it is called *Trichoderma reesei*). This organism plays a very important role for improving cellulose enzyme, moreover, it is known as the predecessor of fungi producing enzymes that are used today.

It is interesting that these researches started with the damage of cotton fabrics and they were conducted to prevent their effects that cause hydrolysis. However, we use them to improve their hydrolysis strength. This transition started during 1960s and the army started to produce food and energy products from solid waste by using cellulase enzyme in 1973. 20-fold powerful/effective organisms were generated by using mutant types of *Trichoderma reesei* (obtained in New Guinea).

Today, cellulase is used most extensively in stone washing process in textile industry. However, our knowledge on cellulase is substantially poor in comparison to other enzyme types because cellulose-cellulase systems consist of soluble enzymes that function on insoluble substrates. These systems are very complex. Due to this complexity, extensive researches were conducted and it was concluded in 1950 that this system was a combination of Cl enzyme (removing cellulose crystals = de-crystallizing) and hydrolytic enzymes known as Cx (converting cellulose to sugar). This explanation suggested then was discussed and modified for 40 years and some additions were made.

Enzyme complexes of large molecules are not able to enter interior parts of textile materials at the beginning. These are affective primarily on the surfaces where cellulose chains are broken. This is accidental generally. This situation depends on the origin of cellulase complex and especially on its penetration to thin threads and open structure. Microfibers are loose fibers. They break with the effect of biocatalytic degradation and with the mechanical effect on the surface, reduction in tearing strength, wear resistance and weight loss are carried out by process control. After this operation, fabric becomes loose. Smoother and clear surfaces are obtained since fiber ends are removed [82].

At the point reached based on these, the enzyme structure is explained as follows:

- Endoglucanases: They affect dissolved or undissolved glucose chains randomly.
- Exoglucanases (a) break off the glucose unit at the end of cellulose (b) cellobiohydrolases break off the cellobiose units (glucose dimers) at the end of cellulose chain.

– Beta glucosidases release D-glucose from the dimer [84].

These three enzyme classes show a synergistic effect and affect cellulase in a complicated way. In conclusion, decrystallization and hydrolysis of natural cellulose becomes possible.

Fungi and bacteria cause digestion of cellulose in nature. These organisms disrupt crystal structure of cellulose by means of some enzymes. Endoglucanases have random effects on cellulose chain or exocellulases affect the terminal groups in cellulose chain.

Cellulases are water insoluble polymers resembling many other enzymes or they are polymeric substrates longer than the enzyme and these are organized as two characteristic places. A catalytic site is connected by flexible bonds to separate the cellulose bonding site. Collaboration is needed between two functional types of two different cellulases for effective digestion of natural cellulose and two different sides of synergetic effect are shown. The collaboration is between endoglucanase and cellobiohydrolase (endo/exo synergetic effect).

It supports creation of the number of free, sensitive terminals for endoglucanase movement and there is collaboration between different CBH. The reason for this synergetic effect and the effects of individual enzymes on crystalline cellulose are not known precisely. CBHs attack cellulose chain at its unreduced terminals [85].

In a study, the stability of cellulase produced from *T. reesei* and its effects on pre-treated cellulosic material were studied and it was seen that enzyme stability was good until 450 °C and there was gradual inactivation in enzyme solution at 55–600 °C. The enzyme was completely inactivated in applications at 700 °C for 1 h. It was seen that maximum enzymatic hydrolysis was achieved at pH 6.5 and 500 °C [86]. The effects of mono-components, cellobiohydrolases produced from purified *Trichoderma reesei* and endoglucanases on cotton fabrics were also studied by analysis of weight loss of fabrics, reduction of sugars, and molecular weights of water-soluble oligosaccharides and their generated cotton powders. It was seen that the amounts of sugars reduced in endoglucanases in treatments with cellulase applied with and without mechanic effect and the amounts of dissolved oligosaccharides were high. It was determined that there was reduction in molecular weight of poplin cotton powders for all cellulase types in enzymatic treatments applied without mechanical effect [87]. It is known that structural characteristics of cellulose were effective on the sensitivity of cellulose for enzymatic hydrolysis. The most important characteristics of cellulose fibers including surface area and crystallinity were studied during hydrolysis period, and enzymatic hydrolysis of cellulose and change of structural parameters were studied [88–90].

Catalytic activity of cellulase produced from pure *Trichoderma reesei* in the solution and adsorbed on cotton fabric and the effect of high temperatures on its bonding ability was investigated [91].

X-ray, CP-MAS NMR and structural and morphologic characteristics of four different cellulosic materials were studied and cellulase produced from *Trichoderma viride* and cellobiase enzyme produced from *Aspergillus niger* was applied to cellulosic material obtained from two sources [92].

Commercial cellulases consist of different cellulase mixtures. The characteristics of fabrics treated with these mixed cellulases were studied. The effects of treatment with cellulose mono-components on the molecular and supra molecular structures of cotton cellulose were studied. Desized, bleached print fabrics that were subject to a basic process were produced from ring and OE thread. These fabrics were subject to an enzymatic process with endoglucanase I and II and cellobiohydrolase I and II produced from *Trichoderma reesei*. The application was carried out by using acetate tampon in stainless steel containers containing steel balls. The effects of the enzymatic process were studied in terms of weight loss, reduced sugar formation, fabric breaking strength and tearing strength, copper number, water absorption, hydrogen bonding means and cellulose micro structure and fiber pore size distribution [93].

An enzyme produced from *Penicillium funiculosum* F4 was applied to cotton fibers of four different origins. Sugar was reduced and hydrolyzed in almost all of them within 6 h. There were differences seen in hydrolysis of cottons of different origins. These differences were attributed to the different structural arrangement of cellulose on secondary cell wall of cotton [94].

Cellulase enzymes produced from *Aspergillus niger* and *Trichoderma viride* microorganisms were immobilized and the obtained enzyme preparation was used for digestion of wastes of CMC, cellobiose and filter papers [95].

7 Conclusion

Since prehistoric times, textile materials have been used to cover oneself and protect oneself from climate conditions. With the industrial revolution, textile process has industrialized and textile industry has become a potential environmental pollutant. After the textile wet process, wastewater containing of higher polyaromatic molecular organic compounds have been generates. The quantitative and qualitative profile of textile wastewater show a change according to raw material, production management, technologies, products being manufactured, type and capacity of treatment systems. In this study, the reduction methods of textile wet process pollution were summarized [96]. Owing to the many advantages of ozone, ozone gas is utilized in numerous fields of textile industry such as pre-treatment process and finishing process. Membrane filtration has been accepted as a very efficient and economical method to clean textile waste water. Plasma treatment is a dry and eco-friendly technology as alternative the traditional wet-chemical process.

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