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Abstract

Wet processing of textile materials consumes a large amount of electricity, fuel, and water. Therefore, greenhouse gas emissions and contaminated effluent are environmental problem. The most of the governments in the world warn all the industrial sectors containing textile manufacturing to be careful about environmental pollution. Increasing in public awareness of environment and competitive global market forces the textile industry to manufacture textile products environmentally. Environmental pollution in textile wet processes can be reduced by four main ways. They are process optimization (reducing in water, chemical energy consumption, and time loss), use of ecofriendly chemicals, reuse of water, and new technologies like ozone and plasma technologies, transfer printing, enzymatic processes, etc. This chapter is about the use of ozone in the textile industry.

Keywords: textile, wet processing, ozone, ozone treatment, environment

1. Introduction

The aim of wet processes is to improve the appearance, texture, or performance of a textile material. Wet processes consist of pretreatment, dyeing, printing, and finishing processes. Wet processes compose of application of chemicals, fixation, washing, and drying stages generally [1, 2].

The textile dyeing and finishing industry is one of the largest water users. It uses huge amount of water throughout all processing operations [2]. A lot of dyestuffs, chemicals, auxiliaries, etc. are applied to textile materials in water baths. Ecological problems are commonly related with water contamination in the textile dyeing and finishing industry. Wastewater of the textile industry is hot, has strong odor, and colored by dyestuffs, which are used as a part of dyeing and/or printing process [2–4].

Clean production methods consider all possibilities that will lessen the effects of pollution problem in wet processing of textiles and will save water and/or energy. The main methods are below [5]:

1. Process optimization (water and time saving in every possible area, use of less chemical, working in lower temperatures).

2. Use of environmentally friendly chemicals.
3. Reuse of water.

4. New technologies in wet processing (enzymatic processes, ultrasound, ultraviolet, plasma and ozone technologies, dyeing in CO₂-containing environment, etc.).

In this chapter, the use of ozone as some ecofriendly production method in wet processing of textiles is investigated.

2. Ozone

Ozone is a strong oxidant agent, which can be produced synthetically, as well as is being naturally available in the atmosphere. Ozone layer behaves like a shield against ultraviolet radiation. Because it absorbs UVB and UVC light during the cycle (Figure 1) of formation and destruction of ozone in the atmosphere [6–8].

Christian Schönbein described “ozein” odor during electrolysis of water in 1839. Thomas Andrews found out that ozone was formed only by oxygen in 1856. In 1863, Soret defined the relationship between oxygen and ozone. He determined that 3 volumes of oxygen produce 2 volumes of ozone. Ozone is thermodynamically unstable and spontaneously reverts to oxygen (Figure 2). It dissolves very quickly in pure water and respects for Henry’s law. Ozone immediately reacts with inorganic and organic substances dissolved in biological water generating a variety of free radicals [9, 10].
2.1 Generation of ozone

Ozone must be generated “in situ” because it is very reactive gas and cannot be stored and transported to anywhere. So, it has to be generated [3]. The basic methods for generating ozone artificially are below [5–7, 9, 12–15]:

- **Photochemical ozone generation**: Oxygen atoms formed by the photodissociation of oxygen by short-wavelength UV radiation react with oxygen molecules to form ozone. The theoretical quantum yield of ozone by photochemical technique is 2%. Nevertheless, the actual yield is approximately 0.5% in practice. Because, the low-pressure mercury lamps produce not only the 185-nm radiation responsible for the production of ozone, but also the 254-nm radiations that destroy ozone. Medium-pressure UV produces higher levels of 185-nm radiation, and it generates more ozone. The low concentrations of ozone from UV generators limit their usage for water treatment to special applications. But it can be used in air treatment effectively.

- **Electrolytic ozone generation**: An electrolytic cell is used for electrolytic ozone generation. Electrolysis involves converting oxygen in the water to ozone by passing the water through positively and negatively charged surfaces. Electrolysis of water can generate high concentrations of ozone. However, the output is low and the method is more expensive than the corona discharge process. Small electrolytic units can be used for treatment of ultrahigh purity waters in pharmaceutical and electronic industries.

- **Radiochemical ozone generation**: High-energy irradiation of gaseous or liquid oxygen by radioactive rays can help the formation of ozone. Energy efficiency of the method is greater than that of ozone produced by electric discharge. However, it has not yet been commercialized due to complex structure, problems associated with recovery of ozone, and separation of by-products and radioactive material.

- **Ozone generation by corona discharge (silent electrical discharge)**: Ozone is generated by providing air or oxygen gas into the generator. And oxygen or air is converted into ozone by the electric discharge. Primary components in air are firstly separated into reactive atoms or radicals by effect of the intense electric field. Then, these reactive atoms can react among themselves. Ozone generation by corona discharge is especially the most widely used method for water treatment.

2.2 Measurement methods

It is necessary to determine the concentration of ozone produced by an ozone generator because of efficiency of processes, costs, excessive ozone, and environmental drawback [14, 16]. Many analytical methods for the determination of ozone concentration have been described in the literature. However, most of them are not specific and often give incorrect results [17]. Analysis of ozone is difficult because of the instability of pure ozone, volatilization from solution, the rapid decomposition of ozone in water, and the reaction with trace contaminants in water, etc. [18]. Ozone can be analyzed by methods given below [15]:

- titrimetry,
- direct and colorimetric spectrometry,
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• amperometry,
• oxidation-reduction potential (ORP),
• chemiluminescence,
• calorimetry,
• thermal conductivity,
• gas-phase titration with NO, and
• isothermal pressure change on decomposition.

The last four methods are not commonly used for analysis. It is necessary to be aware of its reactivity, instability, volatility, and the potential effect of interfering substances to measure the amount of ozone in water correctly. Ozone sometimes is sprinkled in drops by using an inert gas for analysis in the gas phase or on reabsorption in a clean solution in order to eliminate interferences [14].

2.2.1 Iodometric methods

Gaseous ozone from ozone generator is absorbed by aqueous potassium iodide solution. On the other hand, a preformed ozone solution can be alternatively treated with aqueous potassium iodide solution. The liberated iodine is measured by spectrometer or titration with sodium thiosulfate. The pH value of iodine solution is adjusted to 2. Then, it is titrated with titrant solution sodium thiosulfate and starch indicator [14, 19–21]. Theoretically, one molecule of ozone releases one molecule of iodine as the triiodide ion. It is a standard method [21]. Oxidants like H\textsubscript{2}O\textsubscript{2} and NO\textsubscript{x} are problem for the measurement method because of their interference with the analysis. The method is sensitive to pH, buffer composition, buffer concentration, iodide concentration, sampling techniques, temperature, and time [14, 19, 21].

Aqueous ozone solution is added to 2\% potassium iodide in 0.1 M neutral phosphate buffer containing a known amount of arsenic (III). And then, the excess As (III) is back-titrated with standard iodine using a starch end point [21, 22].

Standard method for residual chlorine analysis is adapted for residual ozone as Palin DPD (N,N-diethyl-p-phenylenediamine) method. Ozone oxidizes iodine ion in phosphate buffer of pH 6.4. Then, the released iodine oxidizes DPD, and it is measured colorimetrically or is titrated with standard ferrous ammonium sulfate due to the formation of pink Wurster cation [21].

The other adapted standard way is amperometric method. Ozone oxidizes iodide ion in acetate buffer of pH 4.0–4.5 in the presence of sodium thiosulfate, phenylarsine oxide (PAO), or inorganic arsenic (III). These reagents are titrated with standard iodine to an amperometric end point without acidification. Grundwell et al. compared (Table 1) the four currently popular iodometric methods for aqueous ozone analysis in 2008 [21].

2.2.2 Direct spectrometry

Ozone has a peak absorption at 254 nm wavelength, and it is the ultraviolet spectrum, so absorbance of the gaseous ozone can be measured at 254 nm by direct UV spectrometry. The method is sensitive in the molar absorptivity. Interference of CO, hydrocarbons, NO\textsubscript{x}, or H\textsubscript{2}O vapor has no noticeable effects on measurement.
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UV absorbance measurement method is mainly useful for gas analysis. This method also can be used for measuring aqueous ozone solution. However, interference from turbidity, dissolved inorganics, and organics is a problem. Ozone is sprinkled into the gas phase in order to eliminate interference for measurement. If the sample is liquid, the best sample for this method will be clean water free of UV-absorbing impurities [14, 19, 23–25].

2.2.3 Colorimetric spectrometry

Several different colorimetric methods are used for measuring ozone residuals. But most of them are sensitive to significant interference from secondary oxidants [14].

The first reagents for measuring ozone in air and exhaust gases are indigo and its water-soluble derivatives, the sulfonated indigo compounds like indigo disulfonate, indigo carmine, and indigo trisulfonate. Water-soluble derivatives of indigo, indigo disulfonate, and indigo trisulfonate are pH or redox indicators. Purity and age of the indigo trisulfonate are very important for the method because they affect the stoichiometry of the reaction [17, 19].

The indigo molecule contains only one double bond (C=C). It reacts with ozone in order to produce sulfonated isatin and similar substance (Figure 3). Maximum absorbance of indigo is at 600 nm [17, 26]. If the pH value is below 4, sensitivity of the method does not vary with ozone concentration, small changes of temperature of reaction, or the chemical composition of the water. The advantage of the method is applicable for lake water, too hard groundwaters, and biologically treated domestic wastewater. Indigo trisulfonate method is quantitative, selective, fast, and simple. Classical instrumentation of water work laboratories is enough for measurement. The method is based on the decolorization of the dye by ozone. The loss of color is directly proportional to the concentration of ozone, and pH value of the sample is adjusted to about 2 in order to minimize destruction of the ozone by hydroxide ions [17, 19, 21]. The concentration is the difference in absorbance between sample and blank [16]. Mn$^{2+}$ ion is a problem in this method. Because, oxidation products from the reaction of Mn$^{2+}$ ions with ozone can demolish indigo trisulfonate. So, glycine is added to the sample in order to demolish the ozone

![Figure 3. Ozonation of potassium indigo trisulfonate [26].](image-url)
selectively. Then, indigo reagent is added to the sample to measure the seeming ozone concentration because of the reaction with manganous ion oxidation products. This value is subtracted from the value of the sample without glycine [19].

Indigo method is applied to “AccuVac Ampul” ozone measurement. For the measurement, all the chemicals are packaged under vacuum into an ampule. The ampule is like a cuvette, and it is used precisely for the spectrophotometric determination of the dissolved ozone [25].

2.2.4 Electrochemical methods

These methods can include amperometric titration, which is mentioned under the title of iodometric methods. Amperometric analyzers use an electrochemical cell to determine the ozone. There are two types of analyzer [25]:

- The bare-metal electrodes, which are in direct contact with the water;
- The electrochemical cell separated from the process water by a semipermeable membrane.

In the literature, there are various electrochemical methods using a solid redox polymer electrolyte-based amperometric sensor, a lignin-modified, glassy carbon electrode, and multiwalled carbon nanotubes to analyze ozone [16].

General advantages of electrochemical methods are low cost, easy operation, potential for miniaturizing and automation, simple portable devices for fast screening purposes, and in-field/onsite monitoring [16]. But every 1 or 2 months, amperometric analyzers have to be calibrated against a reference method such as UV, or the colorimetric indigo methods [25].

2.2.5 Chemiluminescent methods

Light is produced on the reaction of ozone with ethylene in gas phase. It is chemiluminescence. This type of analyzer is based on chemiluminescence and it is measured with a photomultiplier tube. It is comparable to the ozone concentration. Aqueous solutions of ozone emit light on the reaction of ozone with miscellaneous dyes. They are benzoflavin, acridine yellow, indigo trisulfate, fluorescein, etc. [14].

3. Ozone applications in the textile industry

There are two types of ozone application in the textile industry. They are:

- application in the gas phase and
- application in aqueous phase.

For wet processes, aqueous ozone is more practical than gaseous ozone because working principle of finishing machines is suitable for solution. Use of gaseous ozone needs special airproof machines because of occupational health and comfort. Material of leakproof gasket has to resist gaseous ozone.

Gas phase: Half-life of gaseous ozone is more than that of aqueous ozone. So, it decomposes slowly [13]. Gaseous ozone is easily affected by the catalyst. Light, trace organic matter, nitrogen oxides, mercury vapor, and peroxides act as catalysts for homogeneous catalysis. Metals and metal oxides are catalysts for heterogeneous catalysis.
catalysis. If there is no any effect of the catalyst on the mixture, it will be stable. Porous solid substrates can adsorb gaseous ozone [14]. Textiles are the sample of porous solid substrates.

**Aqueous phase:** Solubility of ozone in water is better than the oxygen [27]. However, ozone dissolves moderately in water. It follows Henry’s law [13]. The solubility of ozone depends on pressure, temperature, and ionic strength [14]. Efficient moving of ozone to solution needs dispersion of gaseous ozone into small bubbles. Positive-pressure ozone contractors, negative-pressure reactors (Venturi), and injectors achieve it [13]. At room temperature, decomposition of ozone in pure water is very slow. However, ozone decomposes with the catalysts like hydroxyl ion, trace metals, H$_2$O$_2$ /HO$_2$¯, organic substances, heat, and UV light [14].

The parameters affecting the physical mass-transfer rate of ozone into water are:

- gaseous ozone concentration,
- temperature,
- pressure,
- solution composition (pH, ionic strength, reactive substances),
- gas dispersion,
- turbulence,
- type of contactor [14].

Recently, scientific studies about the use of ozone in textile manufacturing are very popular. But the use of ozone in textile manufacturing is not common in practice. It is only commercially common in denim and garment washing. Therefore, the use of ozone in denim washing is discussed in a special title. The other titles are based on fiber types.

### 3.1 Use of ozone in denim washing

The denim garments are very popular, and they are preferred by people of all ages, classes, and genders. Depending on the desired effect, denim garments are treated with different substances [28, 29]. A lot of dry and wet processing techniques are used for desired effects [30]. Wet processes in denim washing are not environment friendly. High water and energy consumption, large amount of wastewater, and solid waste like pumice stones are generally environmental problem in denim washing [29, 30]. Sodium hypochlorite is a very common bleaching agent in denim washing. Especially AOXs (adsorbable halogenated organic compounds) are the most important environmental problem. Therefore, chlorine-free bleaching technologies are a good solution for AOX. Ozonation is an alternative bleaching method [28]. Ozonation is a simple and “green” process because it does not require steam and water. Therefore, it greatly reduces process time, water, chemical and energy consumption, and amount of wastewater [31, 32]. Ozone decomposes indigo and other dyes because of high oxidation potential. In addition to denim washing, it is generally applicable to treatment of other textiles like T-shirts, shirts, chinos, and casual wear. In ozonation, the ozone generated in the equipment can commercially provide bleaching effect. It is like washing machine without water for fading of color [31]. And ozone is generally applied to whole of the garment in this ozonation
machine. However, local bleached spots on the fabric can also be created by ozone. Ozone gas is scattered onto the denim fabric at a controlled velocity [32]. Özdemir et al. studied on ozonation parameters of denim fabric. They used prewashed denim fabric for ozonation. They inform that water content of the denim fabric is very important for efficiency of ozonation, and 50–60% water pick up value (W.P.V.) is the best for bleaching efficiency. The higher W.P.V. affects the bleaching efficiency of ozonation negatively. For ozonation, acidic and neutral pH values are better than basic pH value. Temperature is one of the most important parameters because higher temperatures decrease the half-life of ozone. Ozonation of wet denim is especially for bleaching [28].

Hmida and Ladhari studied the parameters affecting dry and wet ozone bleaching of denim fabric. Their results about the effect of W.P.A. on bleaching efficiency are also compatible with Özdemir’s results. They claim that water film covers the surface of the fabric and swelling of the fibers is achieved. Then, ozone can penetrate into fibers, and bleaching efficiency on wet denim is better than that of dry denim. On the other hand, backstaining problem is solved by ozonation of dry denim [31, 33].

In the other study, denim fabric was treated with the combination of ozonated water, ultrasound, and hydrogen peroxide. According to the results, ozone is more effective with the aid of ultrasonic energy because the ultrasonic cavitations improve the penetration of ozone into the fabric, and then, ozone decomposes indigo [5, 32]. Bağiran et al. compared ozone to other bleaching agents in denim washing. According to results, ozone is one of the strong agents. It follows potassium permanganate and benzoyl peroxide. But, the most important advantage of ozone is environment friendly, and it is a good alternative to the others. Benzoyl peroxide and ozone are the causes of gray tint in bleached denim fabric. The others are the reason for blue tint of bleached denim. After ozonation, loss of strength is not too high because ozone is unstable, and it decomposes indigo primarily [34].

In practice, ozone is applied to garments. However, there are a few studies on ozonation of yarn [35, 36]. Beşen and Balci try to fade indigo-dyed yarn before weaving and garment processes. The indigo-dyed yarn is ozonated in hank form. Their results about the effect of the ozonation condition on bleaching efficiency are generally compatible with Özdemir’s results. On the other hand, the origin of the raw material directly affects the fading degree of the yarn. According to the results, the count of the yarn is the most important parameter on the decrease in strength of the yarns depending on the ozonation process. However, strength loss is not so important. As a conclusion, the ozonation condition can be determined according to desired effect from the yarns. They claim that different fading effects can be achieved by ozonation before weaving process [35].

He et al. investigated effect of ozone on three typical denim yarns (cotton, lyocell, and polyethylene terephthalate (PET)) during the color-fading process. They claim that ozone only smoothly impacts the crystalline structures of these yarns. PET is not affected by ozone because of its aggregate structure. This structure prevents the oxidation and decomposition of PET. They suggest that ozonation for cotton, lyocell, or other cellulosic yarns should be limited within 10 min at the pH > 7 with a careful selection of water content [36].

3.2 Ozonation of cellulosic fibers

A lot of researchers study on ozonation of cellulosic fibers, especially cotton. Periççek et al. studied on the use of ozone gas in bleaching cotton fabrics. Cotton fabric containing 60% water at pH 7 can be bleached in a short time with ozonation treatment. Room temperature is the optimum for ozonation. After ozonation in a
short time, the whiteness of the fabric is acceptable for dyeing and DP losses are not so important [5, 10].

Eren and Öztürk also investigated ozonation of cotton fabrics. According to their results, the starch size removal of the greige cotton samples and the water absorbency of the greige and desized cotton samples are increased by ozonation. But ozonation does not remove the motes successfully. Bleaching effect of ozonation is successful because of high oxidation potential of ozone [37].

Maqsood et al. suggest ozonation of cotton fiber for medical textiles and production of nanocrystalline cellulose or nanofibrils of cellulose in their paper [38].

Turhan and Soydaş discussed ozonation of cotton terry fabrics. As the results of the study, ozone cannot sufficiently remove impurities like sizing agents, natural waxes, and oils. Therefore, they suggest desizing the terry fabric before ozonation and rinsing the fabric after ozonation [39].

Perinçek et al. also investigated the effects of new advanced processes on cotton woven fabric. The new advanced processes contain ozonation, ultrasound, and ultraviolet. In this study, cotton fabrics are bleached by combining ozone with ultrasound and ultraviolet. According to results, advanced processes can be used in pretreatment of cotton fabrics. However, advanced processes at 63–65°C are not sufficient for desizing the cotton fabrics and need desizing agents. After ultrasonic treatment followed by ozonation, whiteness and hydrophilicity of the fabric are sufficient for dyeing. The combination of ozone and ultraviolet processes for high whiteness of the fabric is recommended. However, breaking strengths and hydrophilicity values have to be considered carefully [3].

Perinçek recommended a removing method of optical brightener from cotton fabric in her paper. It is difficult to remove optical brightener efficiently from the fabric when any problem is seen on the fabric due to high stability of optical brightener. Hazardous chemicals are generally used to remove it. Therefore, ozonation process has ecological advantage. The results show that ozonation can be used for decolorizing the optical bleached samples. Increasing ozonation time increases the efficiency. However, bursting strength loss of fabric should be taken into consideration due to the oxidation of cellulose. Meanwhile, a new patterning method for optical bleached fabrics is proposed in the paper. It provides fashionable products (Figure 4) like batik or tie-dyed cloths [40].

Figure 4. The photographs of fabrics treated by developed method (I: optical bleached fabric is tied in knots, tightly bound with thread; II: a = optical bleached fabric before ozonation; II: b/c = optical bleached fabric after ozonation in accordance with developed method [40]). (Thanks to Textile and Apparel for copyright).
Gashti et al. studied on surface oxidation of cellulose by ozone gas. The aim of the study is to investigate the influence of ozonation on the performance of the fluorocarbon monomer on cotton. As a result of the study, fluorocarbon efficiency on cotton is remarkably improved by ozonation before fluoromonomer grafting. The contact angle tests and microscopic appearances show that contact angle increases because of the higher efficiency of the water repellent polymer on the treated cotton by ozone [41].

In Bahtiyari and Benli’s study, ozone ultrasound humidifier combines to bleach the cotton fabric before dyeing with green walnut shells. As a result, treated cotton with ozone can be dyed with green walnut shells, and the colors of the natural dyed fabrics are good. Even if no mordanting agent is used in natural dyeing, the fastnesses are sufficient [42].

Bahtiyari and Benli proposed a green process line in their paper. In their study, cotton fabrics are treated by ozone gas and ultrasound before natural dyeing without mordant (Figure 5). Natural dyes are nutshell, orange tree leaves, and alkanet roots. Finally, ozone and ultrasound are used for the pretreatment of cotton before natural dyeing without mordanting agent. At the same time, fastnesses of all the dyed samples are generally sufficient, except light fastness. But light fastness of dyed samples with pomegranate peels is only sufficient [43].

Erdem and Bahtiyari combined ultrasound and ozone during the pretreatment of cotton slivers. Ultrasound is used in scouring process, and as expected, ozone is for bleaching process. As a result of the study, hydrophilicity of the cotton is achieved by pectinase enzyme/ultrasound combination. Meanwhile, bioscourd cotton is dyed by using pomegranate peel and green tea. In the end of the study, they suggest their process line for production of medical and cosmetic textiles [44].

Benli and Bahtiyari applied ozone to natural dyed cotton fabrics in their study. Aim of the study is to establish an alternative natural dyeing method without mordanting agents. Ozonation ways are given below:
After the dyeing and washing processes, application of ozone gas to dyed fabrics, which are wet.

Before washing process, application of fresh and cold water through ozone gas to dyed fabrics.

After dyeing, application of fresh and cold water through ozone gas to dyed fabrics. Then, washing of the treated fabrics.

Different ozone application ways present various shades and effects due to chemical structure of natural dyes. Different types of fastnesses are examined in terms of ozone application ways and various mordanting agents. Generally, all dyed samples have high fastness except for light fastnesses. Direct ozonation of wet dyed samples improves the rubbing fastness values [45].

Kan et al. examined the effect of plasma-induced ozone treatment on the color fading of reactive dyed cotton fabric. According to the results, color fading effect is increased by increasing ozonation time, and air ratio has considerable effect on color fading. Color levelness of the ozone-treated fabrics is excellent [5, 46].

Eren et al. studied the color stripping of reactive dyed cotton by ozonation. The parameters are ozonation time and type of reactive dyes. The longest ozonation time gives the best color stripping result. COD value of effluent from ozonation is less than that of conventional reductive treatment [47].

 Yiğit et al. discussed ozonation for discharge printing of reactive dyed cotton in their paper. The aim of the study is to use ozone gas instead of reductive agent and caustic soda in discharge printing. Color discharge increases at higher gas flow rates and prolonged ozonation times. According to results, ozone gas can be used for discharge printing. However, contour sharpness of conventional discharge printing is much better than that of ozonation. It is not as excellent as contour sharpness of conventional discharge printing [48].

Zhong et al. investigated color-fading process of sulfur-dyed cotton fabric by a plasma-induced ozone. As the results, the plasma-induced ozone color-fading treatment can be used to remove the color from the dyed fabric and the effect is uniform and even [49].

Perinçek et al. studied the ozonation of jute. The results indicate that the ozonation conditions for the best whiteness degree are fabric at pH 7, 60% WPV, and temperature of 23–25°C. The lignin content and DP values of fabrics are reduced by ozonation [50].

Perinçek et al. also combined ozonation and hydrogen peroxide bleaching in their paper. Linen fabrics are bleached in two steps. First, the linen fabric is treated by ozone. Then, it is bleached by hydrogen peroxide. The treatment conditions are optimized statistically [51].

Kurban et al. examined the ozonation of nettle biofiber in their study. Different bleaching methods are applied to nettle fiber fabric. They are:

- ozonation,
- ozonation in the presence of ultrasonic homogenizer,
- combination of the conventional bleaching and ozonation process, and
- combination of laccase enzyme and ozonation process.

As a result of the study, ozonation improves the whiteness of nettle fiber fabric. Among all the bleaching ways, the highest whiteness is obtained from combination of the hydrogen peroxide bleaching and ozonation process [52].
3.3 Ozonation of protein fibers

One of the early studies is about ozonation of wool garments. The aim of the study is to obtain shrink-resisted wool garments and fabric. Therefore, a continuous or batch treater was designed, and wool fabric and garments hung in cabin containing ozone. It was found out that circulation of the vapor around the garments and fabric is inevitable for rapid reaction. Fabric construction is very important for desired degree of shrink resistance. It is claimed that ozone-steam process is a solution to the felting problem of wool [53].

Rahmatinejad et al. discussed innovative hybrid fluorocarbon coating on wool treated with UV/ozone. The application of fluorocarbons on the wool fabrics is a problem because of chemistry and structure of the fiber surface. Therefore, UV/ozone treatment is proposed as a solution to this problem. Firstly, wool is modified by UV/ozone treatment. Hydrophilicity of treated wool is remarkably better than untreated wool. UV/ozone treatment can be applied to one side of the fabric and hybrid functional fabrics with two different properties on each side of the fabric are thus obtained [54].

The chlorine/Hercosett process is the most common treatment for the wool dyeing. It causes environmental problems because of the pollution of wastewater with absorbable organic halides (AOX). Therefore, ozonation is an alternative surface modification method for improving wool dyeability [6].

Micheal and El-Zaheer examined the effect of ultraviolet and ozone combination for different times on wool. As a result of the study, wetting of the wool is improved by the ultraviolet/ozone process because of surface modification. It means that there is an increase in amorphous areas of the treated wool. Ultraviolet/ozone oxidizes cystine bond on the surface of the wool fabrics and generates free radical species. They support dye uptake [6].

Shao et al. investigated the effect of UV/ozone exposure and peroxide pad-batch bleaching on the printability of wool. It is found that peroxide pad-batch bleaching can prevent the yellowness caused by UV/ozone treatment and improved the wet-tability of the treated wool in a short time. Printability performance of treated wool is similar to that of chlorinated wool [55].

Sargunamani and Selvakumar investigated the effects of ozonation on raw and degummed tassar silk fabrics. Ozone treatment is compared with soap degumming and hydrogen peroxide treatment. Soap treatment of silk is less harsh than ozonation. Peroxide treatment causes lower yellowing index compared to ozonation [6, 56].

Balci et al. discussed the effects of plasma and ozone treatments on silk in their paper. In this study, raw and degummed silk fabrics are treated with low-frequency oxygen plasma and ozone. The processes are applied to the fabrics individually and alternately. According to the results, fabrics treated with ozone have more yellowing index that of plasma treatment. Increasing the treatment time of plasma and ozonation processes causes increase in yellowness and decrease in whiteness [57].

In this study, Perinçek et al. examined role of the fiber moisture, pH, and treatment time during ozonation on the dyeing properties of Angora rabbit. It is observed that ozonation increases the whiteness degree and dyeability property of the fibers. Ozone oxidizes cysteine linkage in the surface of fiber to cysteic acid [6, 58].

Perinçek et al. combine ozone and ultrasound in their paper. First, Angora rabbit fibers are bleached by ozonation. Then, treated fibers are dyed by the aid of ultrasound. It is indicated that the ozonation and ultrasonic dyeing improves the dyeability of Angora rabbit fiber considerably [59].

Atav and Yurdakul investigated the ozonation of mohair fibers. The optimum conditions of ozonation process are W.P.V. 60%, pH 7, and 30 min. Dyeability of the mohair fibers is improved by ozonation [6].
Perinçek et al. discussed bleaching of soybean fabric by different treatments combined with ozonation in their paper. Combined process is ozonation, oxidative, and reductive bleaching. Process steps are shown in Figure 6.

Consequently, combined bleaching processes improve whiteness and hydrophilicity degree, wettability of the soybean fabrics significantly [60].

Benli and Bahtiyari examined dyeing of casein fibers with natural dye after ozonation. Casein fabrics are bleached by ozone. However, whiteness degrees of the treated fabrics are limited [61].

3.4 Ozonation of the other fibers

Hydrophilicity of synthetic polymer surfaces can be accomplished by ozone. The reactive molecules on 3-D structures are covered uniformly during the ozonation. Ozone treats not only the surface and penetrates through the polymer bulk. Ozone self-decomposes rapidly in water producing free radicals, a stronger oxidant than ozone itself. This property was utilized to produce hydrophilic and highly reactive high-density polyethylene (HDPE) films [62].

Yang et al. studied the effect of ozone on aramid fibers. They found out that surface morphology of aramid fabrics does not have obvious change after the treatment. Wicking effect increases slightly with increasing ozonation time. Ozonation treatment does not have significant effect on the tenacity and elongation of the fibers. However, the tenacity and elongation of aramid yarns improve significantly after ozonation and increase with increasing ozonation time. The authors claim that ozonation process extracts foreign matters from the surface of the fiber and establishes oxygen-containing functional groups. The importance of oxygen-containing functional groups is to support adhesion to the matrix [63].

Rahmatinejad et al. investigated enhancement in polyester materials’ hydrophobicity by surface modification via chemical pretreatment, UV/ozone irradiation, and fluorocarbon finishing combinations. The study concentrates on the application of UV/ozone radiation together with various chemical pretreatments
on fabrics and their effects on the fluorocarbon finishing performance. In surface modification, UV/ozone irradiation prior to fluorocarbon treatment results in more hydrophobic polyester fiber surface than only fluorocarbon-treated fabric. Because of erosion, redeposition, and the melting effects of UV/ozone-irradiation, proper unevenness of the fiber surface is formed by UV/ozone radiation [64].

Elnagar et al. studied dyeability of polyester and nylon fabrics treated with UV/ozone radiation. Mordant is ferrous sulfate. Natural dyes are curcumin and saffron dyes. The results show that dyeability of both fabrics with curcumin and saffron natural dyes increases with aid of UV/ozone [65, 66].

Atav and Namırtı investigated effect of ozonation process on dyeing of polyamide fabrics with walnut rind natural dye. Color yield is increased by ozonation before dyeing polyamide fabric, and ozone gas does not affect the color nuance and fastness properties negatively [67].

Lee et al. discussed ozone-gas treatment of nylon 6 and polyester fabrics in their paper. It is appeared that the O1s relative intensity increases for nylon 6 and polyester fabrics. Oxygen is included in the form of OCOH and OCOOH. Therefore, hydrophilicity of treated fabrics is higher than untreated ones. Ozonation changes the crystalline and amorphous regions, especially for polyester fiber. Moisture regain, water absorption, and dyeing properties increase despite an increase in the crystallinity. On the other hand, ozonation affects the brittle hand of the fabric [68].

Lee et al. studied ozonation of cationic dyeable polyester and poly(butylene terephthalate) fibers too. Although water absorption is improved by ozonation, crystallinity index increases a little bit. They claim that ozonation changes fiber surface. On the other hand, internal structure of both fibers is also changed by the treatment. Therefore, it has effect on the dyeing properties of the fibers. After ozonation, dyeing rate with the cationic dye increases exceptionally. However, increasing dyeing rate with disperse dye is not so significant [69].

Eren and Aniş suggest ozone treatment of polyethylene terephthalate fibers after dyeing as a novel after-clearing method. Results indicate that the trimer removal rates of ozone treatment are quite similar to the conventional reduction clearing for 1-min and higher for 3-min ozone treatments. The treatment time at 130°C is also efficient on the amount of surface trimer [70].

Eren studied on combination of after-clearing and decolorization by ozonation after disperse dyeing of polyester. He claims that encouraging results from decolorization and wash fastness tests are obtained with a 3-min ozonation period in the dyebath at room temperature. Decolorization and COD removal ratios are up to 67 and 62%, respectively [71].

Eren et al. discussed after-clearing of disperse dyed polyester with gaseous ozone in their paper. They propose that a new ozonation method is adopted to continuous treatment lines. Proposed method is different from exhaust application method in early papers [71, 72]. Ozone gas from the generator blasts through the wet fabric. Depending on the type of the disperse dyes, ozonation time is different for wash fastness results which is comparable to that of conventional reduction clearing method. According to results from tensile strength tests and scanning electron microscopy analysis, ozonation does not cause any serious damage to the fabrics [73].

3.5 Advantages and disadvantages of use of ozone in the textile industry

Wet processing of textile materials consumes large amounts of electricity, fuel, and water. Therefore, greenhouse gas emissions and contaminated effluent are environmental problem. Ozone treatment proposed a solution to environmental pollution from textile wet processes [5, 74, 75]. Use of ozone in the textile industry has advantages and limitations [4].
Advantages of ozonation in the textile industry [4, 5, 13, 74]:

- lower water and chemical consumption and time loss of ozonation process than conventional wet processes,
- no need to store chemicals compared to the other conventional methods,
- no dangerous waste because of decomposition of ozone into oxygen,
- no halogenated organic compounds (AOX) in waste water,
- combination with novel technologies like UV, plasma, and ultrasound,
- different pattern and fading effects soon in denim washing,
- improving dyeability of fibers,
- more ecological antifelting treatment than conventional methods,
- higher whiteness than conventional bleaching processes, and
- treatment of hygienic nondurable products like sheets, gauze bandage, tissues, bib, hydrophilic cotton, etc., due to disinfectant property of ozone.

Limitations of ozone treatment [4, 5, 13, 14, 32, 74, 76, 77]:

- prevention of yellowing problem with after-treatment like catalase treatment, reductive washing, etc.
- high strength loss in textile materials due to illiterate use of ozone,
- difficulty in using ozone gas due to suitability of textile finishing machine for wet processes,
- except for stainless steel, corrosion in metal parts of finishing machine due to high oxidation potential of ozone,
- damage possibility of plastics of the finishing machine due to high oxidation potential of ozone,
- high capital investment for new machinery setups,
- necessity of onsite generation because of unsuitable for storage,
- unsuitable for storage due to decomposition of ozone quickly,
- use of ozone in illiterate way due to occupational health and safety,
- needs regular monitoring and alarm system in the mill for any leakages, and
- flammability and explosivity of ozone.

Finally, ozonation within a closed system can be called as environmental process [4]. However, limitations of the ozone have not to be forgotten by users.
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