OZONE: NEW TENDENCY IN TEXTILE FINISHING

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Abstract

Nowadays, countries have been facing many environmental problems such as global warming, water pollution, air pollution. The environmental problems are major issues that affect humankind and must be addressed. So, most of the governments in the world have started to pay more attention to the environmental protection and encourage the private sector, public institutions and non-governmental organizations to organize and take part in environmental protection activities. Rising public awareness for environmental protection and competitive requirements in global market has led the textile industry to manufacture products with improved environmental profiles too. At this point, one of the new tendencies in textile finishing has arisen. As a result of many studies, it can be told that use of ozone gas in the treatment of textile materials like cotton, jute, angora, denim looks much promising because of being environmentally and also saving time, water and chemicals. This study concerns that use of ozone gas in a closed system as an alternative or supportive process to the conventional bleaching. Also, some requirements and advantages occurred with use of ozone was examined. This study becomes important because of having extensive content about ozone which is new promising agent for textile finishing.

1. INTRODUCTION

The name of ozone originates from the Greek “ozein” (to smell). The German chemist Christian Schönbein described “ozein” odor during electrolysis of water in 1840 [1, 2]. Ozone (O_3) is a triatomic molecule composed solely of three oxygen atoms [1].

Ozone can be condensed to a dark indigo-blue liquid, which can also be frozen. It quickly decays into diatomic oxygen. Thus, it can not be stored and transported; it has to be made on site. This is carried out by electrical discharges which is conclueded as an ozone-oxygen mixture [3]. Physical properties of ozone are shown in Table I.

Table I. Physical properties of ozone [4]

Physical Property	Value	Physical Property	Value
Molecular weight	48.0 g/mol	Density, gas (0^0C, 101 kPa)	2.144 kg.m^{-3}
Boiling point (101 kPa)	-111.9^0C	Density, liquid (-112^0C)	1358 kg. m^{-3}
Melting point	-192.7^0C	Viscosity, liquid (-183^0C)	$1.57*10^{-3}$ Pa.s
Critical temperature	-12.1^0C	Heat of vaporization	15.2 kJ.mol^{-1}
Critical pressure	5.53 Mpa		

Ozone is a stronger oxidizing agent than molecular oxygen or hydrogen peroxide and reacts with most substances at room temperature [5]. Its oxidation potential (2.07V) is greater than that of hypochlorous acid (1.49V) or chlorine (1.36V) [4]. Ozone reacts with most elements of the periodic table, except for the noble metals, fluorine, and the inert gases. It reacts with practically all organic and organometallic functional groups, including C=H, C=O, C=N, C=S, and C=M bonds [5].

In general, reactions of ozone with various compounds occur in two different ways, one involving direct reactions of molecular ozone and the other being a free radical-mediated destruction [4]. Ozone mostly finds use in industrial applications because of higher oxidation potentials.

2. THE USE OF OZONE IN DIFFERENT INDUSTRIES

Ozone can find usage in many different applications. Nowadays, it is widely utilized in soft drink industry [20], bottled water industry [21], and beer and wine industry [22]. Ozone is a suggested agent for several applications in the food industry such as food surface hygiene, sanitation of food plant equipment, reuse of waste water, lowering biological oxygen demand and chemical oxygen demand of food plant waste [23, 24]. It is also used for sterilization of liquids, air purification, sanitation purposes, odor control, killing the house dust mites, and waste water treatments [25-29].

On the other hand, ozone's medicinal effects were discovered in the 19th century and clinically applied during World War One. Since then, ozone application for external infections such as infected wounds, diabetic ulcers, and burns is established. The recent discovery that ozone is produced in vivo as a fundamental immunological defense against pathogenic organisms is critically important for the clinical use of ozone [30-32]. Finally, ozone has been used to bleach different wood products and pulp [3, 33-36].

3. OZONE APPLICATIONS IN TEXTILE INDUSTRY

Besides all the applications of ozone mentioned above, textile industry has tried to adapt it into the finishing processes. For example, it can clean commercial laundry with little or no need for hot water, reducing chemical and water demand because of its disinfecting and cleaning power. Ozone facilitates normal washing process because it alters insoluble soils into soluble products that can be removed from fabrics easily. Any laundry that handles large amounts of textiles can be performed easily by aid of ozonation process [37-40].

Also, in recent literatures, it has also been used for decolorization, and there are several studies on the reaction between ozone and dyes. Each dye has its own molecular structure and differs somewhat in the degree of reactivity with ozone [41-45]. It is possible to oxidize indigo dye by ozonation [46]. Although, oxidative bleaching of denim garments mostly has been performed with sodium hypochlorite, it is expected that use of sodium hypochlorite will be restricted in the future because of its ecological incompatibility. Therefore, it is thought that ozonation can find widespread use in the denim sector [47-49].

Wool fabric shrinkage can be controlled by the treatment with ozone and also its dyeability and printability properties can be improved [50-54]. Moreover, ozone gas has been used for modification of fabric's surfaces and also to change dyeability properties [55-60].

Besides all the applications of ozone mentioned above, researches and studies are continuing from a finishing mills point of view. Ozone gas is a promising agent and it is thought that it will be adapted as an alternative or supportive process to the conventional methods in the textile mills. The discussion that follows mainly introduces the applications of ozone in bleaching treatment because ozone with higher oxidation potential has been both extensively and intensively used in this area.

3.1.The Use of Ozone in the Bleaching Process of Cotton Fabric

Cotton acts an important part in the world in terms of its economic and social importance for countries. Cotton is a natural cellulosic fiber and it finds acceptance as an environmentally responsible product because of being biodegradable and coming from a renewable resource. However, during the production stage, cotton has to be subjected to the different kinds of wet processes such as scouring and bleaching, which constitutes an environmental pollution [6]. As a result of environmental susceptibility growth and severe competition requirements, the textile industry has to find more economical and ecological processes which require small amounts of water, low temperature and process time without the use of toxicological chemicals. Ozonation can be a promising process because of fulfilling these objectives. Therefore, comprehensive studies [61, 62] related with ozonation of greige cotton fabric were performed. Within the context of studies, effects of ozonation on fabric's properties were investigated. And also, requirements for ozonation of greige cotton fabric were determined.

In the light of our previous studies [61, 62], it is cited that there was an increase in the whiteness degree of fabric with the increase in exposure time of ozonation. For example, the increase in whiteness degree of cotton fabric with 60 % water pickup value (W.P.V.) improved from 19.12 % to 33.62 % when the ozonation time extended from 1 min. to 5 min [61]. Although, longer ozonation time supplys higher whiteness degree, it can not meet economic prospects. Therefore, different factors (fabric's water pick up value (W.P.V.), pH of impregnated water, medium temperature, etc.), except ozonation time, were emphasized to get higher whiteness [61, 62].

The results of experiments showed that the W.P.V. of fabric has an important effect on whiteness during ozonation. Put another way, the whiteness degree increases with the increase in W.P.V. of fabric until a critical value (60 %). After this critical value, the increase in the W.P.V. of fabric has a negative effect on whiteness. When the fabric with 0 % W.P.V. is ozonated for five minutes, whiteness degree of it increased about 9 %. But this value was nearly 33.5 % when the fabric with 60 % W.P.V. was used instead of the fabric with 0 % W.P.V.. But, the whiteness of fabric which has higher W.P.V. than 60 % starts to decrease sharply. Authors gave an impulse to opinion related with effect of W.P.V. on whiteness during ozonation. It was thought that the increase in water content up to 60 % provides penetration of ozone gas into the fiber. Thus, ozone reacts with colored compounds easily. But after this value of water content, undesirable ozone decomposition starts and so, the increase in whiteness starts to reduce [61, 62].

On the other hand, effect of water pH used for impregnation and medium temperature on whiteness was investigated during ozonation. The lowest whiteness degree belongs to the fabric impregnated with water at pH 10–11 in which the increase in whiteness degree is about 21.91 %. Authors attributed the reason of it to the more hydroxide ions present in solutions at high pH values [61, 62]. Because hydroxide ions act as an initiator during the destruction of ozone [4, 63]. Some studies and literatures cited that lower pH levels were more efficient in terms of ozonation process efficiency [41]. Similarly, bleaching efficiency of ozone was the highest when the pH of water used for impregnation was 6.5-7.5 or 2-3. Also, it was observed that there was no significant difference between whiteness degrees of fabrics which are impregnated with water at neutral and acidic pH before ozonation. So, it is recommended that fabric can be impregnated with water at pH 6.5-7.5. Because no pH regulator is required, and also this is more economic and easier to study [61, 62]. It is well known that ozone gas is susceptible to high temperatures. Consequently, it can decompose in a short time at high medium temperatures, so the increase in whiteness degree is about 4.25 % after ozonation at 50–52^{0}C [64]. Nearly same whiteness degrees were obtained with the ozonation at 23-25^{0}C and 10-12^{0}C. It can be recommended that ozonation of cotton fabric can be performed at 23-25^{0}C because of no need extra energy for cooling the medium [61, 62].

Moreover, the results were compared with conventionally bleached fabrics. It was seen that the whiteness degree of ozonated cotton fabric was higher than the whiteness of conventionally bleached fabric. Also, the loss in polymerization degree of ozonated cotton fabric was higher [61, 62].

3.2.The Use of Ozone in the Bleaching Process of Jute Fabric

Jute is the second most important natural fibre after cotton [65]. It has previously been used only to produce agricultural packaging materials (potato sacks), yarn, ropes, fabric, carpet, rugs, and sacks. However, in recent years, the use of jute has exceeded from its traditional frame and has been used to produce a wide range of diversified products (geo-textiles, automotive non-woven interiors, door panels, particle board, fire retardant fibers, etc.). The fibres are also woven into curtains, chair coverings, hessian cloth, and backing for linoleum [66].

Lignin-removing bleaching is generally applied to jute fiber to convert the lignin into soluble substances that can be removed by washing and white color of fiber emerges [67]. Chemicals such as chlorine are not preferred for use in bleaching process because they cause large reduction in strength properties of fibers. To avoid the disadvantages inherent in the use of hypochlorite solutions in bleaching bath, an alternative agent, hydrogen peroxide, has been used. Hydrogen peroxide is generally acceptable from a toxicological and environmental standpoint, but treatment with it requires high levels of energy and is relatively expensive [68, 69]. All these facts are considered and ozone which provides hopeful results for cotton bleaching was also studied.

The results related with ozonation of jute were analogous with the results obtained after cotton ozonation. Process conditions (pH of impregnated water = 6.5-7.5, WP.V. of fabric = 60 %, medium temperature = 23-25^{0}C) without ozonation time were same as optimized ozonation conditions of cotton fabric. Results of experiments demonstrated that when these conditions were provided, best whiteness degree was obtained. Ozonation time must be adjusted according to the concentration of ozone fed to the system and required whiteness [70].

The results show that ozonation process of jute fabric provides an acceptable degree of whiteness, hydrophilicity, and strength loss in a short duration. It was observed that the whiteness obtained by ozonation for 120 min was higher than the whiteness of fabric bleached for 240 min by conventional methods. Results of ozonation for 90 min were comparable to results of conventional bleaching methods for 240 min. To carry on the ozonation process increases the whiteness and hydrophilicity of jute fabric, but reduces breaking strength [70].

Fourier Transmittance Infrared Spectroscopy was used to determine the change in lignin content of jute fabric after ozonation. It is also evident from the results of FTIR that CH_3 and CH_2 found in the lignin and cellulose were diminished with ozonation [71-74]. Also, it was found that the characteristic absorbance of aromatic C=C bonds found in lignin disappeared after ozonation [71-75]. Authors explained this situation by the delignification of jute with ozone [70]. This idea was also supported by literatures. It is demonstrated that ozone reacts initially and most rapidly with olefinic groups present in lignin and then with aromatic groups. In the absence or inaccessibility of these structures, ozone will also react with many different carbon-hydrogen bonds typical of those found on the lignin side chains [76]. According to the results of experiments, it was found that the lignin of the jute was reduced with all bleaching processes studied, but much more with ozonation. Meanwhile, lignin content of fabrics was detemined. While the lignin content in greige jute fabric was 11.8 %, this value reduced to 8 % and 3 % after conventional bleaching and ozonation respectively. On the other hand, the structure of the cellulose was damaged and this damage was most evident in ozonated samples. The intrinsic viscosity of samples was determined using the standard NFT 12-005 method [77]. It was found that the DP of the greige jute decreased nearly 58 % after ozonation and 45 % after combined conventional bleaching [70].

Moreover, ozonated fabric showed less surface roughness than fabric bleached with conventional processes. The main causes of roughness—mechanical effects and wet medium—are characteristic features of conventional bleaching processes. It was therefore to be expected that the roughness was more evident on the fabrics bleached with conventional methods than on the one treated with ozone [70].

3.4. Advantages and Disadvantages in Use of Ozon in Textile Industry

Some advantages and disadvantages of ozone gas as a bleaching agent in textile industry are stated below;

- Ozone bleaching of natural fibers like cotton, jute, angora etc. provides higher whiteness degree than conventional bleaching processes.

- Strength loss of ozonated fabric is very high, but it is interesting to bleach natural coloured fibers because of its bleaching capacity. Also, researchs to minimize the damage caused by ozone are continued.
- It is very interesting for hygienic nondurable products like sheets, gauze bandage, tissues, bib, hydrophilic cotton etc., because ozone is a disinfectant agent.
- Ozonation is one of the useful processes in denim finishing, because different patterns and bleaching effects can be obtained in a short time ecologically.
- Ozone causes damage at cuticle layer of animal fiber. So, it provides unfelted fiber like chlorined animal fiber. But, ozone is more ecological than hypochloride.
- Water and chemical consumption of ozonation process is lower than conventional bleaching methods.
- Bleaching time is shorter than conventional bleaching methods.
- Yellowing problem can occur after ozone bleaching. But different aftertreatments help to prevent it.
- If the system is fully-closed, ozonation process will be harmless to human health in the mill. At the end of the bleaching, performing some aftertreatments such as UV or high temperature treatments is enough to decompose ozone into O_2 molecules and oxygen atoms. Ozone decomposes rapidly, and therefore, it leaves no harmful residual that would need to be removed from the wastewater after treatment. So it is an ecological bleaching agent contrary to chlorined bleaching agent. Haloganeted Organic Compounds (AOX) are not problem in ozone bleaching.
- Material of finishing machine has to be made of stainless steel because of high oxidation potential of ozone. It causes corrosion of some metals and gives damage to plastics. Therefore, conventional finishing machines have to be adapted to ozone bleaching.

4. CONCLUSION

The appearance in recent years of new laws regulating processes generating pollution is the result of a new social awareness about ecology and the environment. This trend toward ecology, with the support of new laws, is bringing pressure to bear on industry and obliging it to make changes, adaptations, and/or improvements to its processes in order to attain procedures that are more environmentally friendly. At this point, ozone occours as an alternative agent for textile material's ecological bleaching.

The strong oxidizing and bleaching properties of ozone might allow reduction or even elimination of toxicological chemicals, thus lowering the chemical loads in discharge wastewaters. Meanwhile, ozone requires only electricity which is readily available from hydro, solar, wind or fuel electric generators. Ozonation process requires a very low quantity of water, and bleaching is achieved in a very short time at room temperature without requiring any heating or cooling energy. Because of these benefits, it can be reported that an acceptable degree of whiteness (ready for dyeing) can be obtained by ozone bleaching in a very short time, especially for cotton and jute products. However, the important disadvantage of ozonation is reduction in fabric's strength. In future studies it would be interesting to observe the stabilization effect of different textile bleaching stabilizers and chemicals in order to control the bleaching mechanism, and as a result to decrease DP losses after ozone bleaching.

Consequently, ozonation within a closed system can be called as an environmental application for textile's bleaching processes.

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