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Ozonation: a Green Source for Oxidized Cotton

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Abstract
Research was carried out on the oxidation of cellulose by ozone treatment. It is considered as environment friendly in comparison with the existing oxidation methods used in industry for a long time. This treatment is used in different applications such as the scouring / bleaching of cotton fabrics and in improving the properties of Kraft pulp cellulose in the paper industry. In this study, the effect of Ozone treatment on cotton yarn properties was investigated. This investigation can help in obtaining the maximum crystalline percentage of cotton for the production of nano-crystalline cellulose. Two-ply cotton ring spun yarn was treated with ozone gas for different time periods. Yarn tensile properties, wickability, the copper number and physical appearance were observed. It is evident that yarn tensile properties deteriorate drastically after a certain time, while the wickability and copper number increase simultaneously.

Key words: *ozone, oxidized cotton, copper number, nano crystalline cellulose.*

Introduction

Nowadays environmental protection is a necessary issue to be considered and investigated. In this field, excessive use of dangerous chemicals, their effect on the environment and post effects such as the disposal of waste water are factors which must be considered seriously. There is huge pressure on scientists to give some alternatives to these harmful chemical treatments, which is why they are exploring some physical or biological treatments. These alternatives may be costly but can still be utilised where the environment is concerned. Thus the main aim of the researchers is to suggest some alternative methods less harmful to the surroundings and less costly as well.

Ozone gas is an irritating gas of pale blue colour. It is heavier than air and is produced using an ozone generator, in which dry air or oxygen is passed through a very strong electric field which splits the diatomic oxygen molecule (O_2) into two highly excited oxygen atoms (O-) under the corona discharge principle. By combining these unstable oxygen atoms with other oxygen molecules, ozone gas is produced [1, 2], which is highly reactive and chemically unstable for storage and transportation.

Ozone treatment is a workable source for some treatments in different areas such as the pretreatment of waste water or treatment of waste water for reusing in processes [3 - 6]. This gas is also being tried for the pretreatment of different dyes like Azo dyes to facilitate the biological treatment of waste water disposed from dyeing process because this pretreatment oxidises those dyes into more degradable compounds [7]. Researchers are attempting the optimisation of cotton fabric bleaching parameters like the water content in cotton woven fabric, pH and the temperature using ozone gas [8, 9]. Ozone was also used instead of conventional desizing, scouring and hydrogen peroxide bleaching to attain an acceptable degree of whiteness before dying and to save the energy required for the finishing process, as well as chemicals and water [10]. This gas is also used for finishing processes, replacing the hazardous chemicals of some textile fabrics made of fibres other than cotton such as polyester, Angora rabbit hair, raw and degummed mulberry silk and jute fibres to optimise different process parameters such as fabric moisture, pH, ambient temperature and treatment time [11 - 14]. The multiple reuse of water bath for the bleaching of cotton fabrics has also been attempted, as well as in the field of drinking water for colour and odour elimination [15, 16].

As ozone gas is used in water treatment and fabric finishing processes, etc., it is interesting to use this gas to treat fibres. In this study, ozone gas was used for the advanced oxidation of cotton fibre. This oxidised cotton may be utilised for different applications such as in medicine or for the production of cellulose nanofibrils or nano- particles. Two-ply cotton ring spun yarn was selected so that changes in the material after treatment were easily quantifiable.

Material and method

In this study, cotton fibres (Medium Staple Pakistan Cotton) with average values of 28 mm staple length and 1.65 dtex (fibre linear density) were used to produce 25.5 tex ring spun yarns with 711 t.p.m. (Z twist). Afterwards these single yarns were folded and twisted to produce two-ply yarn with 364 t.p.m. (S twist). 8 yarn samples, 0.5 grams each, were mounted separately on special stainless steel holders and kept in closed containers filled with the ozone gas. The setting of the ozone generator - „TRIOTECH GO 5LAB-K" (Czech Republic) was kept same for all samples: 1.5 minutes for the ozone charging time, and 4.5 mg/litres of ozone gas. The samples were kept in their containers for different time periods and then taken out according to the plan shown in ***Table 1***.

Samples were conditioned at 20 ± 2 °C and relative humidity 65 ± 2%. Yarns tensile properties were measured using an Instron 4411 (England) at a speed of 110 mm/min and 500 mm gauge length. For measuring wicking properties, samples with a pretension of 15 mN/tex were

Table 1. *Experimental plan.*

Cotton yarn	Sample number	Ozone treatment time, h
Untreated	01	0
Treated (with O_3)	02	24
	03	48
	04	144
	05	336
	06	504
	07	672
	08	840
	09	1008

hung and immersed in a liquid consisting of 90% water and 10% isopropanol, and the intake height was observed for each sample after 24 and 48 hours. The copper number was also measured using a (CSN 80 0600) standard Czech test method for the determination the weight of copper in cellulose materials [17]. Samples were viewed under a scanning electron microscope (SEM) to check changes in the yarn surface appearance due to the treatment effect.

Table 2. *Test results for the tensile properties, intake height and copper number of untreated (control) and ozone treated (specific times) yarn samples.*

Description	Sample number	Tensile Properties		Intake height, mm		Copper number
		Tenacity, cN/tex	Elongation at breaking, %	24 hrs	48 hrs	
Untreated	01	16.92	6.13	0	0	0.12
Ozone treated	02	15.74	5.23	0	0	0.13
	03	14.82	5.83	0	0	0.22
	04	15.96	5.71	0	0	0.27
	05	14.05	5.35	0	0	0.20
	06	0.32	3.83	2	2	0.60
	07	0.41	4.63	7	8	0.26
	08	0.36	4.03	5	6	0.40
	09	0.32	3.82	6	8	0.66

Results and discussions

Table 2 shows the tensile properties, intake height and copper number for untreated (control) and ozone treated yarn samples. It is obvious from the results that after a specific time of treatment, there is a sudden and significant change in the different properties of the yarns. As shown in ***Figure 1***, it is clear that up to 336 hours of ozone treatment, the yarn tenacity deteriorates slightly by 16.9%, except the reading at 144 hours, which is not in line with the decreasing trend; this might have happened due to the variation in yarn. After 336 hours of Ozone treatment, a drastic deterioration of 97.7% in yarn tenacity was observed, which may be due to the weak links introduced in the fibre amorphous region, as we know that the strength of a yarn is the combined effect of the fibre strength and cohesive forces between fibres enhanced by twist inserted in the yarn. Actually ozone treatment is used to check the oxidation of cotton fibre dedicated for nonwoven manufacturing for medical purposes or for the production of micro/nano crystalline cellulose. In this experi-

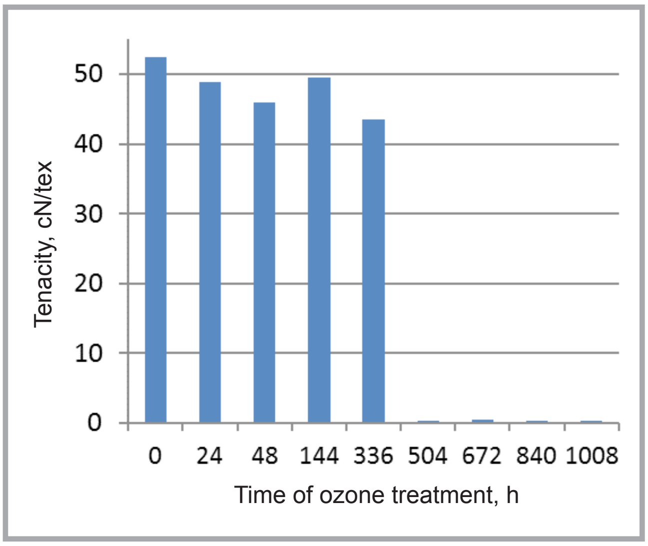

Figure 1. *Effect of ozone treatment on yarn breaking tenacity.*

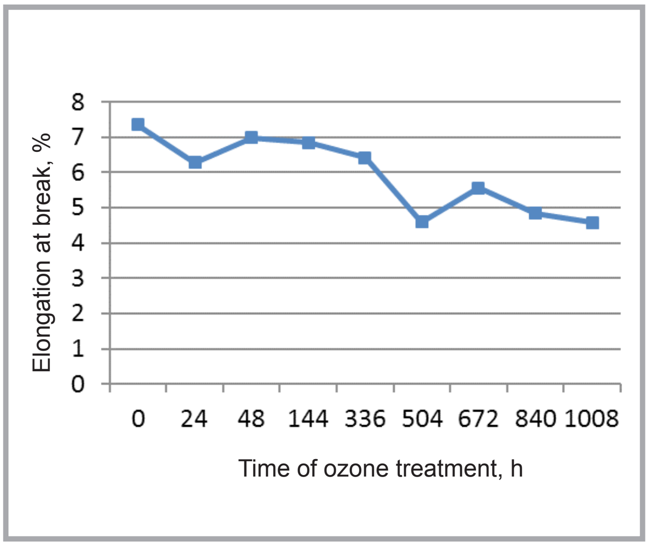

Figure 2. *Effect of ozone treatment on yarn elongation at break.*

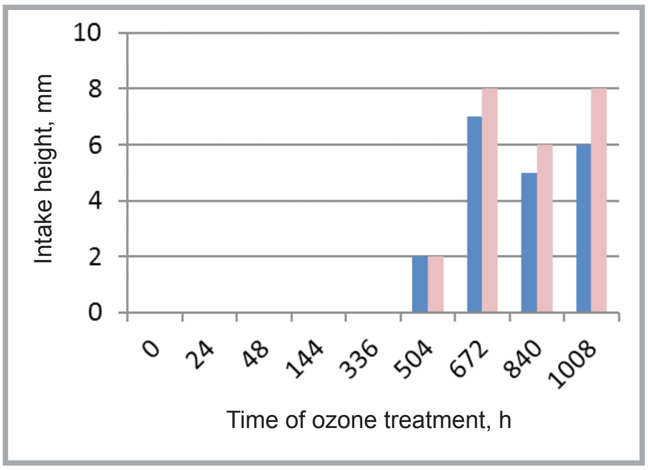

Figure 3. *Intake height observed at different time periods.*

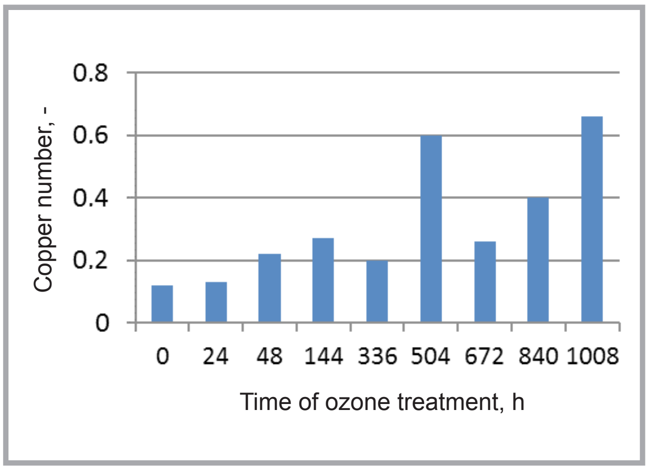

Figure 4. *Copper number values measured for different samples.*

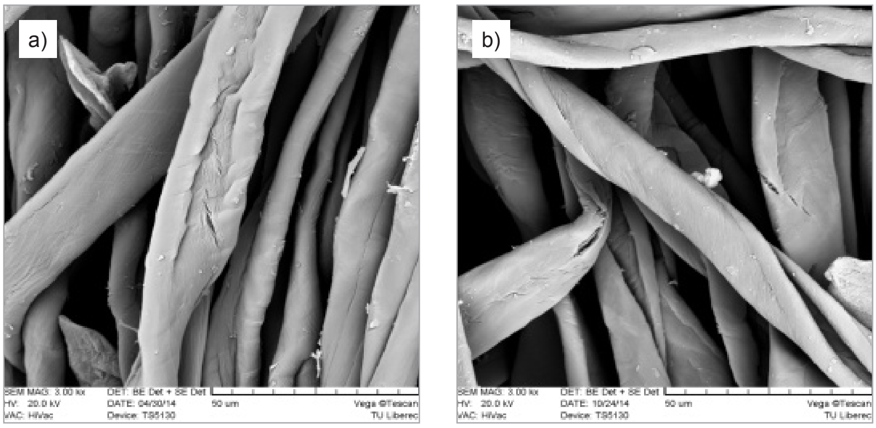

Figure 5. *SEM images of samples: a) untreated, b) treated 1008 hour; (3000×).*

ment cotton yarn was used only for easy quantification of the changes produced by ozone treatment. It is evident that approximately no changes were seen in the yarn tenacity after 504 hours till the end of the experiment. ***Figure 2*** shows a decreasing trend of elongation at break throughout the whole experiment time, which is due to the damage to the amorphous region in the fibres and weak links developed. As shown in ***Figure 3***, the intake height was observed for each sample after 24 and 48 hours. Results show that the intake height is zero till 336 hours, then increases to 2 mm, and continues increasing gradually with the increasing treatment time. This phenomenon happens due to oxidation, which weakens the amorphous regions of the fibres, hence the liquid can find its way to be transported easily through. The copper number is the weight of copper from the Cu^{2+} to Cu^{+} state, which is reduced by 100 gm of dry cellulose and is a measure of its inter and intra chain breakdown. It is an expression of the reducing power of degraded cellulose. The oxidation of cellulose can produce the ring fission of glucose residues, resulting in the formation of aldehyde groups at carbon atoms 2 and 3 [18]. It was measured to assess the degradation of cellulose by ozonation and the formation of aldehyde groups in this experiment. Results show that the copper number increased after 336 hours of treatment by 200% as shown in ***Figure 4***. The value of the copper number at 504 hours of ozone treatment is abnormally high, which may be due to some noise or human error. This reading could not be repeated as the whole sample was utilised in the copper number test. ***Figure 5*** shows the fibre surface appearance of the untreated and treated samples after 1008 hours of ozone treatment. SEM images show no difference in the fibres' surface appearance between the untreated and treated samples. Thus it is clear that the chemical structure of the fibres changed but is not reflected on the surface's appearance.

Conclusions

In this study, the effect of ozone treatment on cotton yarn properties was investigated. It is clear that yarn tensile properties deteriorate drastically after a certain time, while the wickability and copper number increase simultaneously. It can be concluded that ozone gas is an alternative and environment friendly method for the oxidation of cotton. Besides the bleaching and scouring of cotton fabrics, ozone gas can also be used for cotton fibre treatment, which can then be used in some useful areas like medical textiles or for the production of nano-crystalline cellulose or nano-fibrils of cellulose.

Future work

As this experiment is time consuming, it is suggested to reduce the treatment time by increasing the quantity of ozone gas or by some other changes such as the moisture content, temperature and pH.

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