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Improvement A Sustainable Pretreatment Process Including Enzymatic Treatment and Ozone Bleaching for The Jigger Machine

Navruz ÜDÜRGÜCÜ[1*], Onur BALCI[2], Burcu SANCAR[3]

[1,2]Kahramanmaraş Sütçü İmam University, Faculty of Engineering and Architecture, The Department of Textile Engineering, Avşar Campus, Kahramanmaraş-Türkiye
[3]Adıyaman University, Faculty of Engineering, Department of Textile Engineering, Adıyaman-Türkiye

[1]https://orcid.org/0000-0002-0741-1174
[2]https://orcid.org/0000-0001-6885-7391
[3]https://orcid.org/0000-0001-5120-268X
*Corresponding author: nevruzpaksoy@hotmail.com

Research Article

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ABSTRACT

The present study aimed to improve a sustainable pretreatment process with enzymes and ozone gas at the jigger wet process machine for the 100% cotton woven fabric. To achieve this purpose, the stage where the ozone bleaching should be applied in the pretreatment process was first investigated. After the pretreatment processes, the effects of the processes on the pretreatment and mechanical performances of the fabric samples were researched. The pretreatment performance of treatments was researched through the residual starch, hydrophilicity, and whiteness (Berger value) tests, while the mechanical performances were examined via breaking and tearing strength, abrasion resistance, pilling, and SEM analyses. After all performance tests, to investigate the importance of the pretreatment process on the effectiveness of dyeing, the samples were dyed at the same jigger machine. In addition, the yellowing tendency of the pretreated samples depending on the time after the ozone bleaching was also researched. The results demonstrated that the stage where the ozone bleaching is applied was crucial, and the best results were obtained when the ozone bleaching was applied before the combined desizing and bioscouring treatments (Process 2). Besides, the ozone gas had no crucial negative effect on the mechanical performances of the fabrics, and the ozone-bleached fabric samples had no yellowing tendency when a process was applied after ozone bleaching.

Jigger Makinesi İçin Enzimatik ve Ozon Ağartma İşlemleri İçeren Sürdürülebilir Ön Terbiye Prosesi Geliştirilmesi

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ÖZ

Bu çalışma, jigger yaş işlem makinesinde %100 pamuklu dokuma kumaşlar için enzim ve ozon gazı içeren sürdürülebilir bir ön terbiye prosesi geliştirmeyi amaçlamıştır. Bu amaçla ilk olarak, ön terbiye prosesinde ozon ağartmanın uygulanması gereken adım araştırılmıştır. Uygulanan ön terbiye işlemleri sonrası proseslerin kumaş numunelerinin ön terbiye ve mekanik performanslarına etkisi incelenmiştir. İşlemlerin ön terbiye performansları haşıl kalıntısı, hidrofilite ve beyazlık (Berger değeri) testleri; mekanik performansları ise kopma ve yırtılma mukavemeti, aşınma dayanımı, pilling testleri ve SEM analizleri vasıtasıyla araştırılmıştır. Performans testleri sonrası ön terbiye prosesinin boyama etkinliği üzerindeki önemini araştırmak amacıyla, ön terbiye işlemi gören kumaş numuneleri jigger makinesinde boyanmıştır. Ayrıca ön işlem gören kumaşların zamana bağlı olarak sararma eğilimleri de incelenmiştir. Sonuçlar, ozon ağartmanın uygulandığı işlem adımının oldukça önemli olduğunu, en iyi sonuçların tek adımda haşıl sökme ve biohidrofilleştirme işlemi öncesi ozon ağartma işlemi uygulandığında (Proses 2) elde edildiğini göstermiştir. Ayrıca, ozon gazının kumaşların mekanik özellikleri üzerinde önemli bir negatif etkisi olmadığı ve ozon ağartması sonrası işlem uygulandığında ozon gazı ile ağartılmış kumaşların sararma eğilimi göstermediği belirlenmiştir.

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1. Introduction

In the textile finishing processes, the conventional pretreatment and dyeing stages cause high water pollution because of the high demand for water and chemicals (Eren et al, 2017; Körlü, 2018). In the conventional pretreatment process of cotton woven fabric, desizing and scouring need the high amount of water and chemicals (Perincek et al, 2007; Paksoy, 2014; Hussain et al., 2018; Paksoy et al., 2020). After desizing and scouring processes, bleaching is inevitable for fabrics will not be dyed or dyed at light color. In conventional hydrogen peroxide bleaching which has common-usage, environmental concerns associated with the use of stabilizers with poor bio-degradability in the bleaching bath have increased (Perincek et al, 2009). In addition, it is necessary to apply the process at high temperature (Sancar Beşen, 2012; Cardoso et al, 2016; Maqsood et al, 2017; Hareem et al, 2019; Arooj et al, 2019; Bahtiyari et al., 2020). To resolve these problems, the enzymes in the desizing and scouring processes and the ozone gas in the bleaching process have been widely used for many years as environmentally friendly materials and processes (Prabaharan et al., 2001; Perincek et al., 2013; Sancar et al., 2013; Bahtiyari et al., 2014; Paksoy, 2014; Benli et al., 2015; Sancar Beşen, 2016; Erdem et al., 2018; Eren et al., 2018; Turhan et al., 2018; Paksoy et al., 2020). Ozone bleaching is an environmentally friendly method since cotton materials can be bleached at room temperature without necessity of using harsh chemicals (Paksoy et al., 2020). In addition, less water is also used at the ozone bleaching process (Perincek et al., 2007; Eren et al., 2018; Hareem et al., 2019; Paksoy et al., 2020; Palabıyık et al., 2022; Gedik et al., 2023).

When the literature is investigated, it is concluded that in order to achieve sufficient hydrophilicity and whiteness degrees for cotton greige fabrics, ozone bleaching was either applied to the textile materials after the scouring process (Eren et al., 2010; Piccoli et al., 2015; Paksoy et al., 2020) or any supportive materials as surfactants (Eren et al., 2014; Arooj et al, 2021), and ultrasound energy (Benli et al., 2015) had to be used in the ozone bleaching. However, none of the researchers has ever investigated the effects of where the ozone bleaching is applied on the pretreatment performers such as desizing degree, hydrophility, and whiteness results. Paksoy et al. (2020) demonstrated that the ozone bleaching process can be applied at the jigger machine and that ozonation parameters are effective on the bleaching degrees (Paksoy et al., 2020).

The main goal of the present study is to improve a sustainable pretreatment process, including enzymatic treatment and ozone bleaching at the jigger, and to find the stage where the ozone bleaching should be applied in that pretreatment process. For this aim, the ozone bleaching was carried out at three different stages as “after combined desizing and bioscouring treatment (Process 1)”, “before combined desizing and bioscouring treatment (Process 2)”, and “after desizing treatment, before bioscouring treatment (Process 3)”. The ozone bleaching treatments were applied in the air to the moist fabric samples and in the water. The effects of the processes on the pretreatment performances and mechanical performances of the fabrics were investigated. In addition, the yellowing situations of the pretreated samples depending on time was also followed. Because the success of pretreatment process has depended on the dyeing results, the fabric samples were dyed, and the effect of the pretreatment process on the color was also investigated. The dyeing processes were carried out at two concentrations (light and dark shade) at the jigger machine, and then the dyeing homogeneity and color fastness (washing, water and perspiration fastness to color) of the dyed samples were researched.

2. Material and Method

2.1. Material

In the experiments, enzymes such as amylase (Rucolase HPZ), pectinase (Rucolase PTZ) and catalase (Rucolase CAP) which were supplied by Rudolf Duraner were used. Besides, hydrogen peroxide, sodium carbonate, wetting agent, sodium hydroxide, organic stabilizer, salt (sodium chloride), washing agent, Levafix Blue CA reactive dye, Levafix Yellow CA reactive dye, and Levafix Fast Red CA reactive dye (DyeStar) were used. 100% cotton woven raw fabric (3/1 S twill, 167 g/m^2) with starch sizing on it was also used.

In the ozone bleaching processes, ozone generators with capacities of 6 g/h and 12 g/h were used. Besides, 18 g/h of ozone capacity was also used by connecting the outputs of two generators in series. The applications were applied at the laboratory-type jigger machine (ATAÇ), the technical drawing of the machine can be seen in Figure 1.

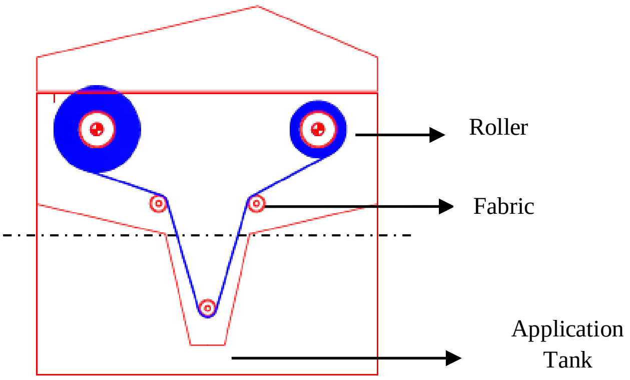


Figure 1. The technical drawing of the jigger machine

Rubber and stone diffusers were used in the jigger machine to transfer the ozone gas into the machine. The settlement of the diffusers transferring the ozone gas can be seen in Figure 2. The ozone gas was directly applied to the samples in the machine.

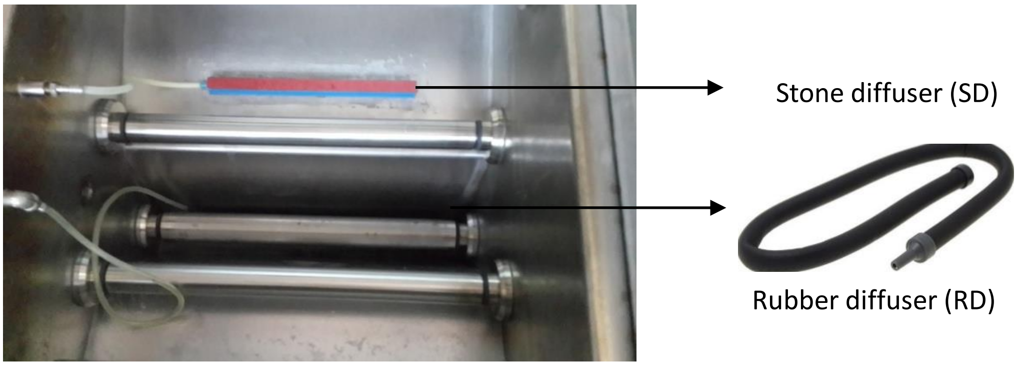


Figure 2. The settlement of the diffusers transferring the ozone gas

2.2. Method

In the ozone bleaching treatments, the produced ozone gas having three capacities (6, 12 and 18 g/h) was fed either through the stone diffuser or the rubber diffuser, as shown in the four methods in Figure 3. Thus, the ozone bleaching was applied with an 18 g/h ozone capacity.

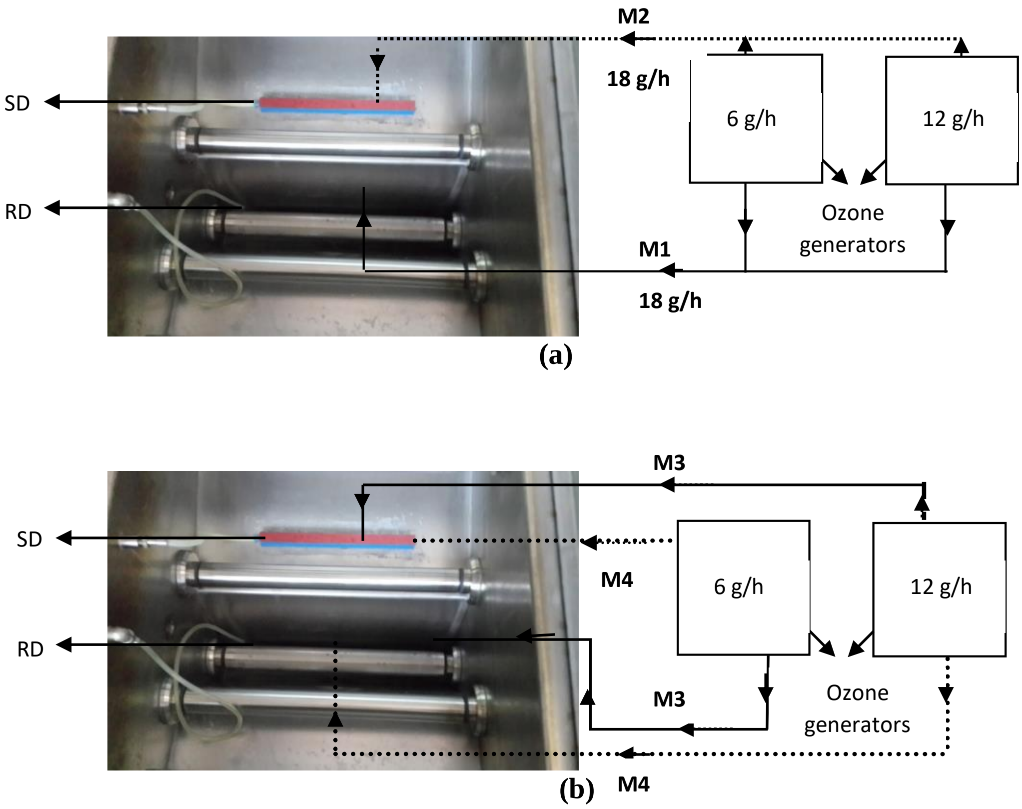
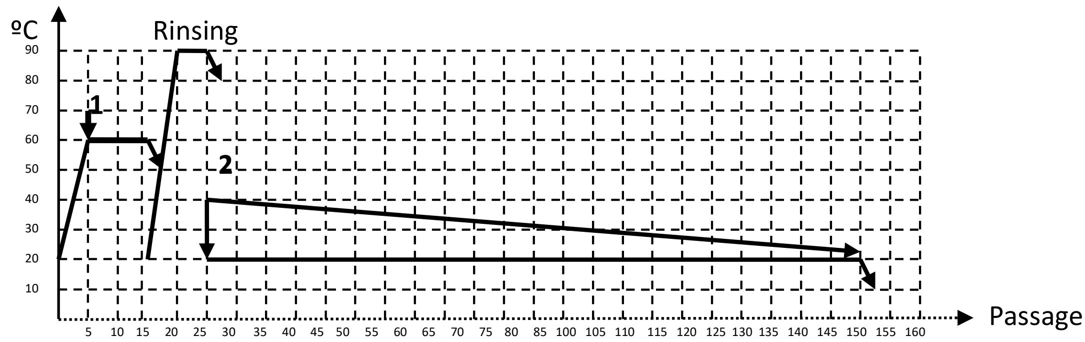


Figure 3. The methods of ozone feeding to the jigger

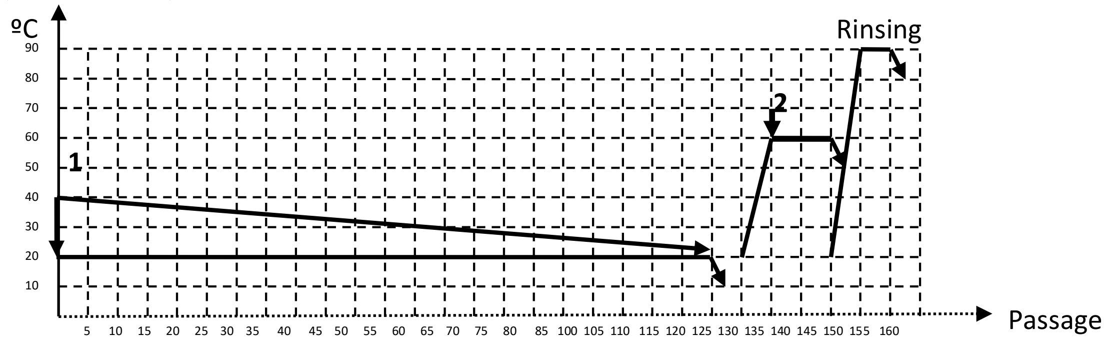
The pretreatment processes were applied in three different ways named as Process 1, Process 2, and Process 3. The ozone bleaching was carried out at different stages of the pretreatment processes. In Process 1, the ozone bleaching was applied after the combined desizing and bioscouring treatment

(Figure 4a). In Process 2, the ozone bleaching was applied before the combined desizing and bioscouring treatment (Figure 4b). In Process 3, the ozone bleaching was applied after the enzymatic desizing treatment, but before the bioscouring treatment (Figure 4c). The desizing and bioscouring treatments were applied enzymatically by using amylase and pectinase enzymes. 30 liters of water were used for all treatments.

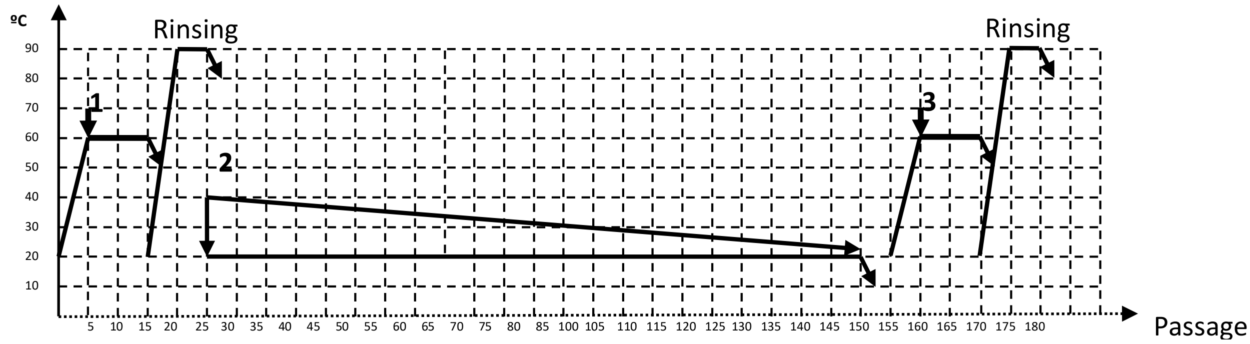
Process 1, Process 2, and Process 3 and their working parameters are shown in Figures 4a, 4b, and 4c, respectively.



1: 1 g/L amylase, 3 g/L pectinase, 2 g/L wetting agent (pH 8-8.5 with sodium carbonate) (desizing+bioscouring process)
2: Ozone bleaching
(a – Process 1)



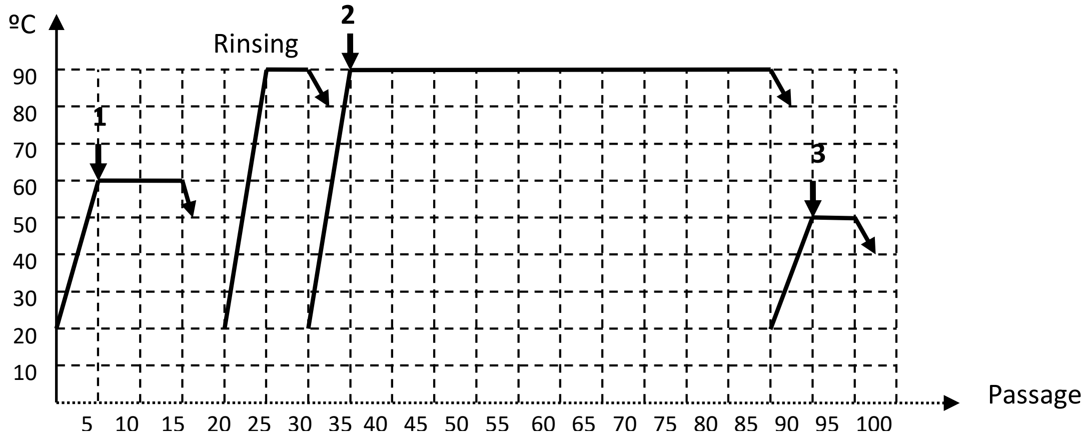
1: Ozone bleaching
2: 1 g/L amylase, 3 g/L pectinase, 2 g/L wetting agent (pH 8-8.5 with sodium carbonate) (desizing+bioscouring process)
(b – Process 2)



1: 1 g/L amylase, 2 g/L wetting agent (pH 8-8.5 with sodium carbonate) (desizing process)
2: Ozone bleaching; **3:** 3 g/L pectinase, 2 g/L wetting agent (pH 8-8.5 with sodium carbonate) (bioscouring process)
(c – Process 3)

Figure 4. The processes and working parameters (a) Process 1, (b) Process 2, (c) Process 3

The conventional bleaching was also carried out as a reference to compare the ozone bleaching (Process 1-2-3). The conventional hydrogen peroxide bleaching treatment was applied after combined desizing and bioscouring treatment. The working parameters of the reference bleaching process can be seen in Figure 5. The hydrogen peroxide bleaching treatment was applied at 90 ºC. After the treatment, the catalase enzyme was applied to decompose the residual of hydrogen peroxide.



1: 1 g/L amylase, 3 g/L pectinase, 2 g/L wetting agent (pH 8-8.5 with sodium carbonate) (desizing+bioscouring process); **2:** 3 g/L H_2O_2, 2 g/L NaOH, 1 g/L wetting agent, 0,5 g/L stabilizer (hydrogen peroxide bleaching)
3: 0.2 g/L catalase (pH 6-6.5 with sodium carbonate)

Figure 5. Conventional reference bleaching process

Based on the best whiteness results of the previous studies, the ozone bleaching treatments were applied in the air to the moist fabric samples and in the water at 120 and 150 passage numbers (Paksoy, 2014; Paksoy et.al, 2020). For the ozone applications in the air to moist fabric, the dry fabrics were immersed into the water and squeezed directly up to 60% pick up while the applications in the water were applied in the water-filled tank. All ozone bleaching treatments were applied at room temperature. The experimental plan for the ozone application treatments is given in Table 1.

Table 1. Experimental plan of the study

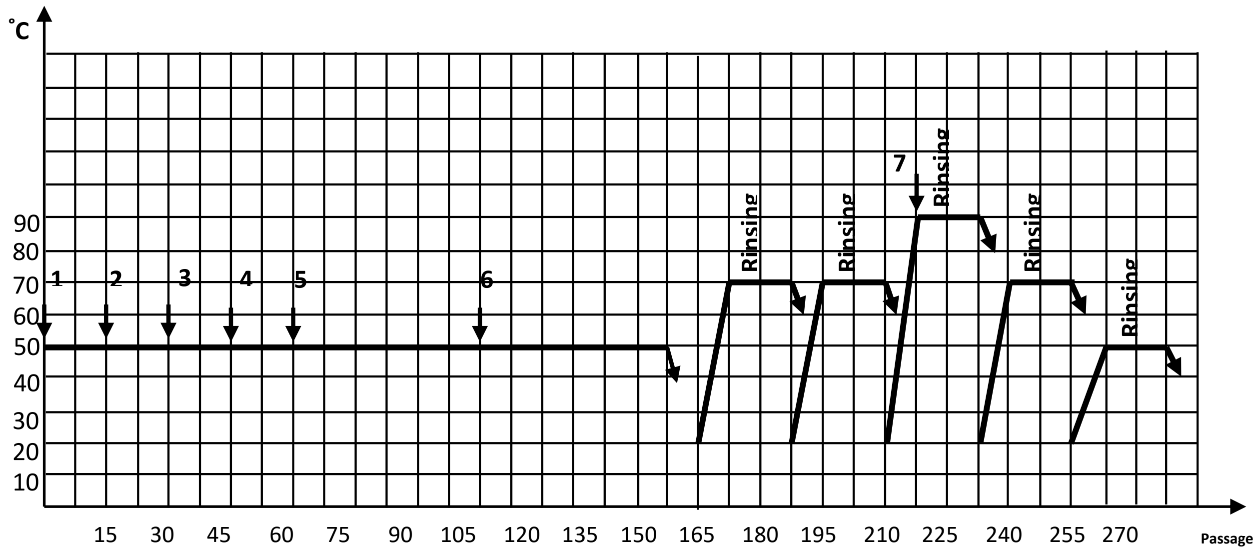
Process 1		Process 2		Process 3			
Exp. number (in the water)	Exp. number (in the air)	Exp. number (in the water)	Exp. number (in the air)	Exp. number (in the water)	Exp. number (in the air)	Number of passages	Method of ozone feeding
1A	1B	1C	1D	1E	1F	120	M1
2A	2B	2C	2D	2E	2F	150	M1
3A	3B	3C	3D	3E	3F	120	M2
4A	4B	4C	4D	4E	4F	150	M2
5A	5B	5C	5D	5E	5F	120	M3
6A	6B	6C	6D	6E	6F	150	M3
7A	7B	7C	7D	7E	7F	120	M4
8A	8B	8C	8D	8E	8F	150	M4

After the pretreatment processes, the pretreatment performances of the fabric samples were examined via measurements of residual starch, hydrophility, and whiteness degree (Berger value). In addition, the mechanical performances of the samples were also investigated through breaking strength, tearing strength, abrasion resistance, pilling tests, and SEM analysis. Besides, the yellowing tendency of the ozone-bleached fabric samples versus time were followed via measurement of whiteness degree at 5-day intervals during 15 days, since the ozone residual on the samples may cause the fabric to be yellower depending on time and ozone.

Because the success of pretreatment process depends on the dyeing performance of the fabric, the pretreated fabric samples according to Process 1 and Process 2 were then dyed, since Process 1 and Process 2 were more sustainable processes in terms of time and water consumption. Besides, the reference bleached fabric samples were also dyed as reference dyeing. The trichomic dyeing treatments at two different concentrations as light (0.6%) and dark shade (2.1%) were applied according to dyeing recipe and graph given in Table 2 and Figure 6, respectively. The dyeing treatments were done at the jigger machine.

Table 2. Dyeing recipe

Shade	**Concentration (owf%)**	**Dyestuff and owf%**		**Salt (g/L)**	**Sodium carbonate (g/L)**
Light	0,6%	Levafix Blue CA	% 0,2	50	6
		Levafix Yellow CA	% 0,2		
		Levafix FastRed CA	% 0,2		
Dark	2,1%	Levafix Blue CA	% 0,7	60	6
		Levafix Yellow CA	% 0,7		
		Levafix Fast Red CA	% 0,7		



1: ½ Dyestuff
2: ½ Dyestuff
3: ½ Salt
4: ½ Salt
5: ½ Sodium carbonate
6: ½ Sodium carbonate
7: 1 g/L washing agent
Figure 6. The dyeing graph

After dyeing processes, the CIELab color values and the changes in the color of the dyed samples versus holding time were researched. In addition, the color fastness to washing, water, and perspiration (acidic and alkaline) were also tested.

2.3. The Characterization Tests

2.3.1. Residual starch test

The residual starch was examined by dropping I_2/KI solution onto the different areas of the samples as a starch size indicator and comparing the color occurring on the fabric with Tegewa scale (Figure 7). The scale has values ranging from 1 to 9. One means that whole starch is present on the fabric and nine means that all starch is removed from the fabric's surface (Patel et.al, 2013). The percentage of the residual starch was determined according to values equaled to Tegewa scale given in the Table 3.

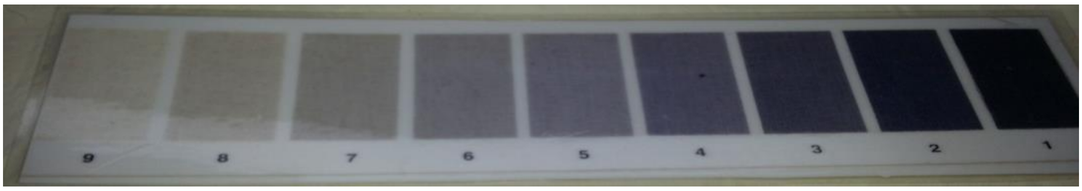


Figure 7. Tegewa scale

Table 3. The percentage of size residual according to the Tegewa scale (Patel et al., 2013)

Tegewa scale	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Size residual (%)	2,5	1	0,6	0,35	0,2	0,125	0,085	0,06	0,04

2.3.2. Hydrophility test

The dropping and rising tests were carried out according to TS 866 and DIN 53924 Standards, respectively. The capillarity performance of whole samples was measured by the help of rising results. Each test was carried out three times, and the average of the results was calculated.

2.3.3. Whiteness degree

The whiteness degrees (as Berger value) of the fabric samples were measured under D65 daylight and aspect of 10° via Minolta 3600 A spectrophotometer. In addition, in order to observe the yellowing situations of the ozone-bleached fabric samples versus time, the whiteness degrees of the samples were measured at 5-day intervals for 15 days. Each sample was measured three times, and average of the results was calculated.

2.3.4. Breaking and tearing strength test

The breaking strength was measured according to EN ISO 13934-2 (75 mm) Standard via James Heal TİTAN device, while the tearing strength was measured according to EN ISO 13934-1 Standard via Elmatear device.

2.3.5. Abrasion resistance and pilling tests

The abrasion resistance test was carried out according to EN ISO 12947-1 Standard, while pilling test was done according to TS EN ISO 12947-2 Standard via Martindale device.

2.3.6. SEM (Scanning Electron Microscope) Analysis

The SEM images of the chosen fabric samples were taken in order to investigate whether ozone gas caused damage on the fibers or not (Zeiss Evo LS10). Before the analysis, the fabrics were rendered conductive by being coated with gold.

2.3.7. CIELab values

The CIELab values of the dyed samples were measured with Minolta 3600 A spectrophotometer under D65 daylight and aspect of 10° and the color differences were calculated according to CIELab 1976 formula. Any samples were measured three times, and average of the results was calculated. In addition, the dyeing homogeneity of the samples was also observed.

2.3.8. Fastness tests

The color fastness to washing, water, and perspiration (acidic and alkaline) of the dyed samples were tested according to EN ISO 105 Standards.

2.3.9. Statistical analysis

The statistical analysis was carried out using the results of the whiteness degree of the fabric samples to determine the effects of the investigated working parameters (input) on the results (output) by one-way ANOVA via Design Expert 7.0.

3. Results

3.1. The Hydrophility and Residual Starch Results of the Pretreated Samples

The results of hydrophility and residual starch of the fabric samples pretreated according to Process 1 are given in Table 4. According to Table 4, the absorption and capillarity of the reference fabric are 1.04 seconds and 1.93 seconds, respectively. Both the absorption time and capillarity for the samples pretreated according to Process 1 are higher than those of the reference fabric. Thus, it can be said that hydrophility results of the fabric samples pretreated according to Process 1 are poor, and these fabrics are not appropriate for dyeing processes. The results are thought to be based on the natural oils and waxes on the fabrics, which cannot be removed properly by either the combined desizing and bioscouring process or ozone bleaching at room temperature. The different hydrophility results demonstrate that the oils and waxes are probably decayed with ozone bubbles, but they cannot be removed from the fabric since any rinsing treatment was not applied after the ozone treatment as mentioned in a previous study (Turhan et al., 2018). In addition, it can be said that the method of ozone gas feeding (qq v. the hydrophility results of 1 coded sample and 7 coded sample), and the ozone bleaching conditions (qq v. the hydrophility results of A coded samples and B coded samples) are crucial for the hydrophility results for the fabrics pretreated according to Process 1, and the ozone bleaching treatments in the air provide better hydrophility results. When results of residual starch are focused, it is clearly seen that the values of the samples are close to the reference fabric, so it is possible to say that the ozone bleaching after the desizing treatments has not negative effect on the desizing results.

The results of hydrophility and residual starch of the samples pretreated according to Process 2 can be seen in Table 5. When Table 5 is focused, it is seen that the hydrophility results of the fabric samples pretreated according to Process 2 are better than those of Process 1 (while the results of absorption time <10 s for Process 2, they are >10 s for Process 1) and their results are closer to the reference fabric. The situation can be verified with the removal of the decayed oils and waxes by ozone gas from the fabrics with the combined desizing and bioscouring treatments and then rinsing treatments. In addition, the form of the droplets on the samples is more regular, and it can be said that the samples are pretreated more homogenously according to Process 2 than Process 1. Generally, the ozone bleaching treatments in the air produce better hydrophility results like those of Process 1 (qq v. the hydrophility results of C coded samples and D coded samples). The results can be explained by the efficiency of the ozone gas on the moist fabric mentioned in previous studies (Perincek et al., 2009; Gülümser et al., 2009; Erdem et al., 2018).

Table 4. Hydrophility and residual starch results (Process 1)

Exp. number (Table 1)	Dropping test			Capillarity (s)	Tegewa	Residual starch (%)
	Absorption time (s)	Diameter (cm)	Diffusion form of the droplets			
Reference	1,04	2,6	Regular	1,93	9	0,040
1A	45,95	3,0	Irregular	22,62	7	0,085
2A	56,74	3,1	Irregular	30,00	8	0,060
3A	16,59	2,8	Irregular	16,45	8	0,060
4A	20,08	2,7	Irregular	21,07	8	0,060
5A	23,92	3,0	Irregular	18,92	9	0,040
6A	20,65	2,9	Irregular	14,18	9	0,040
7A	17,58	2,8	Irregular	15,92	8	0,060
8A	23,91	2,6	Irregular	19,56	8	0,060
1B	17,50	3,5	Irregular	15,92	8	0,060
2B	13,01	3,2	Irregular	14,36	8	0,060
3B	13,53	3,3	Irregular	15,56	8	0,060
4B	17,84	3,0	Irregular	13,91	7	0,085
5B	15,41	3,3	Irregular	13,16	8	0,060
6B	20,15	3,3	Irregular	18,41	8	0,060
7B	9,47	3,4	Irregular	13,48	8	0,060
8B	15,57	3,0	Irregular	13,04	9	0,040

Table 5. Hydrophility and residual starch results (Process 2)

Exp. number (Table 1)	Dropping test			Capillarity (s)	Tegewa	Residual starch (%)
	Absorption Time (s)	Diameter (cm)	Diffusion form of the droplets			
Reference	1,04	2,6	Regular	1,93	9	0,040
1C	3,57	3,0	Irregular	15,53	7	0,085
2C	6,44	2,8	Irregular	16,89	7	0,085
3C	3,28	3,1	Irregular	11,09	8	0,060
4C	4,58	3,2	Irregular	10,37	8	0,060
5C	4,82	2,7	Regular	13,00	7	0,085
6C	5,87	3,0	Irregular	9,39	7	0,085
7C	9,84	3,1	Irregular	22,04	5	0,200
8C	10,34	3,0	Irregular	20,22	5	0,200
1D	2,25	2,4	Regular	4,88	4	0,350
2D	1,91	2,6	Regular	4,53	5	0,200
3D	2,00	2,6	Regular	4,71	4	0,350
4D	1,76	2,8	Regular	4,72	5	0,200
5D	3,03	2,6	Regular	5,10	5	0,200
6D	2,00	2,6	Regular	4,80	5	0,200
7D	1,30	2,8	Regular	3,92	6	0,125
8D	1,61	2,7	Regular	3,42	6	0,125

The results of hydrophility and residual starch of the fabric samples pretreated according to Process 3 are given in Table 6. According to Table 6, it is seen that the hydrophility results of the samples pretreated according to Process 3 are better than those of Process 1. The situation can be explained by the removal of the decayed oils and waxes by ozone gas from the fabrics with the bioscouring treatments and then rinsing treatments. Besides, the hydrophility results affect mostly from the method of ozone feeding depending on the ozone bleaching conditions. Since the ozone gas dissolved in the water comes into contact with the fabric, the ozone gas fed from the bottom of the tank provides better hydrophility results, while that fed from the outside of the tank is more appropriate for the ozone bleaching in the air.

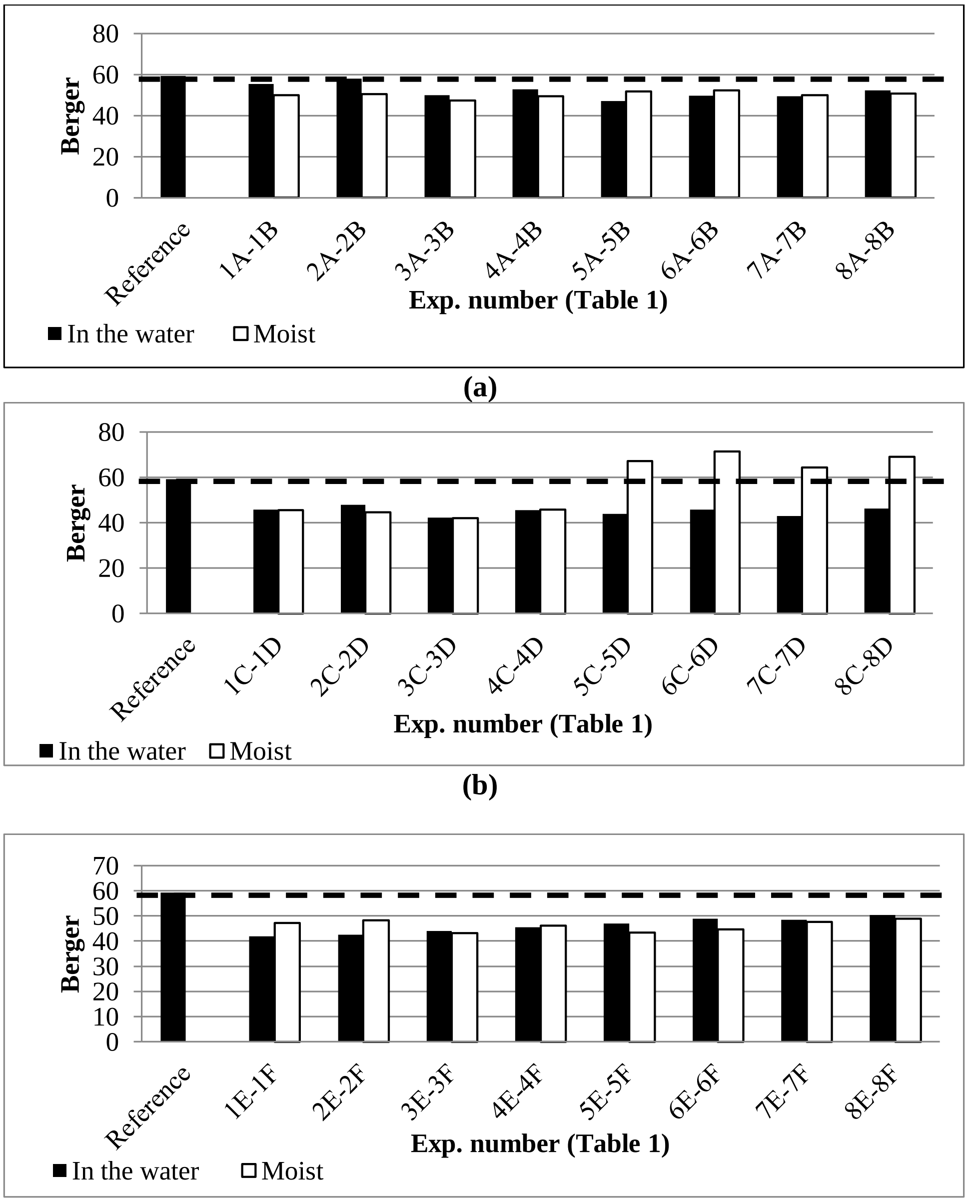
Table 6. Hydrophility and residual starch results (Process 3)

Exp. number (Table 1)	Dropping test			Capillarity (s)	Tegewa	Residual starch (%)
	Absorption Time (s)	Diameter (cm)	Diffusion form of the droplets			
Reference	1,04	2,6	Regular	1,93	9	0,040
1E	1,38	2,5	Regular	3,42	8	0,060
2E	2,08	2,7	Regular	4,34	9	0,040
3E	1,52	2,6	Regular	2,40	9	0,040
4E	1,56	2,9	Regular	5,92	8	0,060
5E	9,09	2,7	Irregular	15,82	9	0,040
6E	10,33	2,8	Irregular	15,14	8	0,060
7E	7,80	2,5	Irregular	26,35	9	0,040
8E	18,92	2,4	Irregular	19,98	8	0,060

1F	1,96	2,7	Irregular	8,61	8	0,060
2F	6,34	2,5	Irregular	9,87	8	0,060
3F	1,78	2,5	Regular	4,74	8	0,060
4F	1,64	2,7	Regular	7,13	8	0,060
5F	12,70	3,0	Regular	18,83	8	0,060
6F	4,80	2,8	Irregular	14,52	8	0,060
7F	3,54	2,9	Regular	12,85	8	0,060
8F	3,99	2,8	Regular	12,45	8	0,060

3.2. The Whiteness Degree Results of the Pretreated Samples

The Berger results of the samples pretreated according to Process 1, Process 2, and Process 3 were given as Berger values in Figures 8a, 8b, and 8c as graphs, respectively.



(c)

Figure 8. The Berger values of the samples *(a) Process 1, (b) Process 2, (c) Process 3*

According to Figure 8, the Berger value of the reference fabric is 59.27, and the values of the samples pretreated according to Process 1 and Process 3 is lower than the reference fabric, while some samples pretreated according to Process 2 have higher values (5D-6D-7D-8D). The Berger value of the fabric samples pretreated according to Process 2 and having ozone bleaching in the air, at which the ozone gas was fed both through stone diffuser and rubber diffuser, reach to 71.38. The results demonstrate the significance of ozone bleaching condition and the method of ozone feeding. The lowest bleaching results are obtained for the samples pretreated according to Process 3. Therefore, it is possible to say that the stage where the ozone bleaching is carried out is crucial for the bleaching. Generally, the samples bleached in the air according to Process 2 and Process 3 have higher Berger values than those in the water, while the values are lower for the samples pretreated according to Process 1. The Berger values of the samples pretreated according to Process 1 and having ozone bleaching treatments in the water are close to those of the reference fabric. The results means that ozone bleaching condition is crucial according to the pretreatment process, and it is thought that the results are derived from the stage where the bioscouring treatment is applied, or, in other words, the hydrophility situations of the fabric samples. The samples having bioscouring treatment before ozone bleaching are bleached with hydrophilic structure (Process 1), and the ozone bubbles dissolved in the water can penetrate easily into the hydrophilic fabric samples, resulting in grater bleaching effects. Furthermore, increasing the number of passages from 120 to 150 has positive effect on the bleaching results, implying that the ozone application time is also crucial for bleaching. The results are confirmed by the ANOVA analysis established by using Berger values of the fabric samples. The inputs and codes given to the parameters are shown in Table 7. According to ANOVA results given in Table 8, it is possible to say that both the investigated main factors and double interactions of them have effects on the bleaching results, statistically. The most effective main factors on the results are ozone bleaching condition > pretreatment process > method of ozone feeding > number of passages, respectively. When the interactions are focused, it is seen that the most effective one is "CD" double interaction, which means that the bleaching results are affected mostly by the ozone bleaching conditions depending on the pretreatment process. Table 8 also shows the significance of "BCD" ternary interaction. This interaction concludes that the pretreatment process, ozone bleaching condition, and method of ozone feeding should be considered together for obtaining the desired whiteness results.

Table 7. The codes given to the parameters

Parameter A: Number of the passage	**Parameter B: Method of ozone feeding**	**Parameter C: Ozone bleaching condition**	**Parameter D: Pretreatment process**
120 150	-M1 -M2 -M3 -M4	- In water - In the air	Process 1 Process 2 Process 3

Table 8. ANOVA results of the established model by using Berger values

Parameter		**F value**	**p value**	**State**
Model		108,3357	< 0,0001	**Significant**
A	Main factors	79,65434	< 0,0001	**Significant**
B		124,1454	< 0,0001	**Significant**
C		194,0345	< 0,0001	**Significant**
D		185,307	< 0,0001	**Significant**
AB	Interactions	2,728008	0,0763	Insignificant
AC		0,892373	0,3581	Insignificant
AD		2,379855	0,1227	Insignificant
BC		110,3974	< 0,0001	**Significant**
BD		94,32689	< 0,0001	**Significant**
CD		297,3985	< 0,0001	**Significant**
BCD		121,2576	< 0,0001	**Significant**

The normal probability diagnostic of the analysis can be seen in Figure 9. The normal probability indicates whether the residuals follow a normal distribution, in which the points will follow a straight line. This plot consists of the number of standard deviations of the actual values from their respective predicted values. Ideally, it should be straight line, indicating no abnormalities (Sancar and Balcı, 2013). According to Figure 9, it can be said that there are no problems on any plots, and it is also good signal for the reliability of the experimental results.

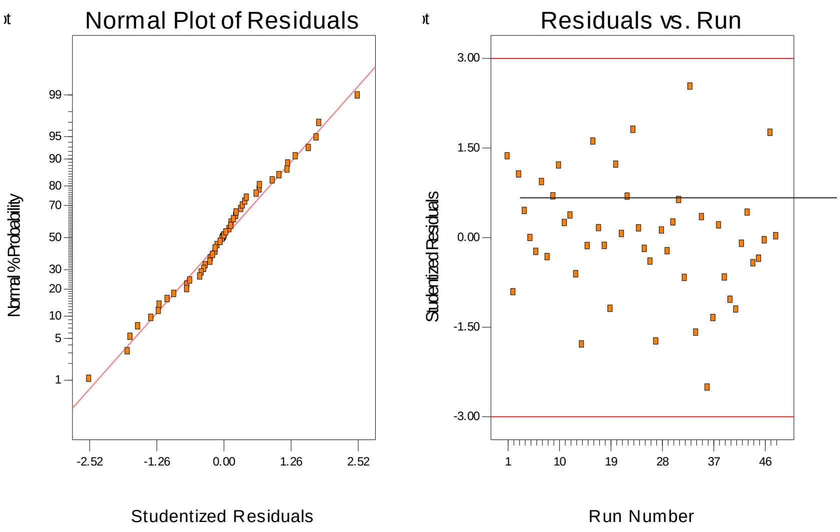


Figure 9. The normal probability diagnostic of the analysis

When the results of pretreatment performances such as whiteness, hydrophility, and residual starch of fabric samples pretreated according to Process 1, Process 2, and Process 3 are compared, the results of Process 3 are found to be inferior to the others. In addition, in Process 3, since the desizing and bioscouring treatments are applied separately, more water and time are used up. Therefore, it is concluded that Process 3 is not sustainable, so the tests and the following studies are carried out with fabric samples pretreated according to Process 1 and Process 2.

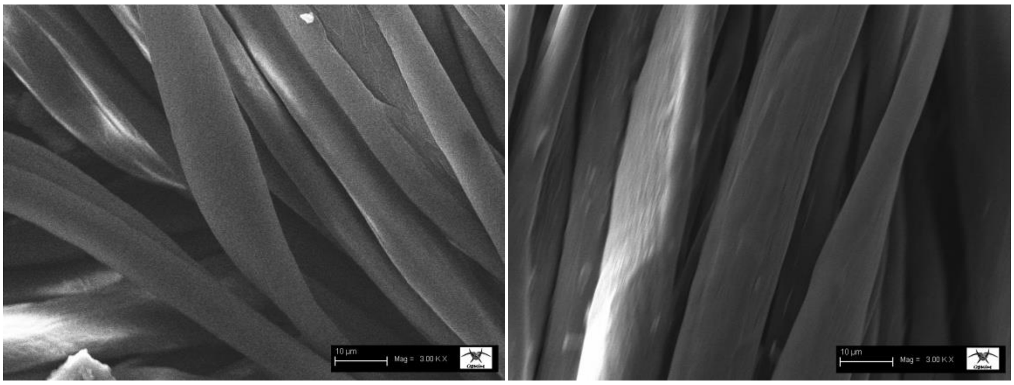
3.3. Mechanical Properties Results of the Pretreated Samples

The mechanical properties of the pretreated fabric samples according to Process 1 and Process 2 were investigated through breaking strength, tearing strength, abrasion resistance, and pilling tests, and the results are given in Table 9. Based on the mechanical test results, there are not crucial differences between the results of the samples pretreated according to Process 1 and Process 2 and those of the reference fabric. As a result, it can be said that the sustainable pretreatment processes do not cause a crucial mechanical damage to the fabrics. Since the desizing and bioscouring treatments were already applied with enzymes, the problem could have been derived from ozone bleaching treatments. For that reason, to investigate whether ozone bleaching treatment damaged the fibers, the SEM photos of the reference fabric and a fabric sample pretreated according to Process 2 (6D) were also taken. According to SEM photos seen in Figure 10 and Table 9, it is possible to say that the ozone bleaching treatments have not caused any crucial damage to the fibers, as mentioned in previous studies (Sancar Beşen et.al, 2016; Turhan et.al, 2018).

Table 9. Mechanical properties result of the pretreated samples

Exp. number (Table 1)	Breaking strength (N)		Tearing strength (gf)		Abrasion resistance				Pilling (2000 cycle)
					5000 cycles		15000 cycles		
	Warp	Weft	Warp	Weft	First weight	Final weight	First weight	Final weight	
Reference	58	24	2354	1658	0,186	0,181	0,187	0,175	4
1A	59	25	2354	2193	0,188	0,178	0,185	0,177	3
2A	61	25	2407	2084	0,189	0,183	0,195	0,182	2
3A	59	26	2407	2565	0,190	0,186	0,189	0,179	3
4A	55	26	2354	2247	0,187	0,180	0,185	0,180	2/3
5A	59	27	3420	2407	0,187	0,184	0,184	0,174	2/3
6A	57	24	2460	2193	0,184	0,182	0,186	0,173	3
7A	61	27	2617	2407	0,185	0,181	0,184	0,172	3
8A	57	20	3027	2670	0,187	0,181	0,184	0,181	3/4
1B	60	28	2617	2670	0,183	0,179	0,186	0,179	4
2B	55	27	2617	2247	0,185	0,184	0,183	0,177	3/4
3B	49	28	2460	2193	0,188	0,181	0,189	0,173	3/4
4B	62	27	2565	2139	0,183	0,181	0,185	0,176	3/4
5B	55	19	2977	2247	0,183	0,180	0,185	0,169	3
6B	56	23	2721	2565	0,183	0,179	0,186	0,172	2/3
7B	56	21	2460	2300	0,185	0,177	0,185	0,170	3/4
8B	50	25	2460	2513	0,186	0,181	0,187	0,177	2/3
1C	63	26	2513	2565	0,187	0,184	0,187	0,180	3

2C	59	25	2670	2300	0,189	0,186	0,186	0,179	3/4
3C	58	18	2513	2247	0,191	0,185	0,182	0,176	2
4C	56	22	2824	2565	0,192	0,185	0,187	0,181	2/3
5C	51	26	2773	2247	0,185	0,180	0,184	0,177	3
6C	69	24	3420	2721	0,190	0,184	0,190	0,181	4
7C	60	26	2513	2193	0,187	0,184	0,191	0,181	3/4
8C	54	28	2565	2300	0,187	0,184	0,187	0,183	2/3
1D	58	21	2247	1920	0,185	0,177	0,187	0,175	3/4
2D	61	24	2193	1642	0,186	0,179	0,185	0,172	3
3D	60	21	2407	2139	0,181	0,177	0,182	0,173	4
4D	60	24	2407	2247	0,182	0,170	0,183	0,170	4/5
5D	60	26	2617	2084	0,185	0,181	0,185	0,178	4
6D	64	20	2565	2300	0,182	0,180	0,186	0,179	3/4
7D	47	16	2084	1865	0,180	0,177	0,185	0,174	3/4
8D	52	14	2460	1698	0.180	0,178	0,184	0,171	3/4



(a) **(b)**

Figure 10. The SEM photos of (a) Reference fabric, (b) Ozone bleaching treatment applied sample

3.4. Yellowing Tendency of the Pretreated Samples Versus Time

Since the ozone-bleached cotton fabric samples have a yellowing tendency during storage (Perinçek et.al, 2009; Eren et.al, 2016), the whiteness degrees of the pretreated fabric samples according to Process 1 and Process 2 were measured at 5-day intervals for 15 days. The change in the Berger values (dBerger) was calculated by using the Berger values of the 1st day as reference. The change in the Berger values of the samples versus time can be seen in Figure 11, and it is obviously seen that the whiteness degrees of the samples decrease and the samples tend to yellowing over time. In addition, the yellowing situations of the samples change depending on the pretreatment process, and it can be said that the samples with a higher yellowing tendency are those pretreated according to Process 1. The situation can be explained by the applied treatments after the ozone bleaching, as indicated in the previous studies (Perinçek et al., 2009; Eren et al., 2016). Perinçek et al. suggested that any kind of treatment should be applied for preventing yellowing of ozonated cotton fabric during storage (Perinçek et al., 2009). According to that suggestion, since combined desizing and bioscouring treatment was applied after ozone bleaching in Process 2, the ozone gas decayed to oxygen quicker because of the wet process at high pH (8-8,5) and temperature (60 ºC), thus the ignorable yellowing occurred (dBerger<1). It is also concluded from Figure 11 that the yellowing occurs more in the fabric samples treated with ozone bleaching in the air than in those treated in water, which are clearer in Process 1 results. The differences are thought to be derived from the lower half-life of the ozone gas in the water. The ozone gas decays to oxygen in the water faster than in the moist medium (https://www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm), thus the higher ozone residual on the fabric samples bleached in the air caused more yellowing over time.

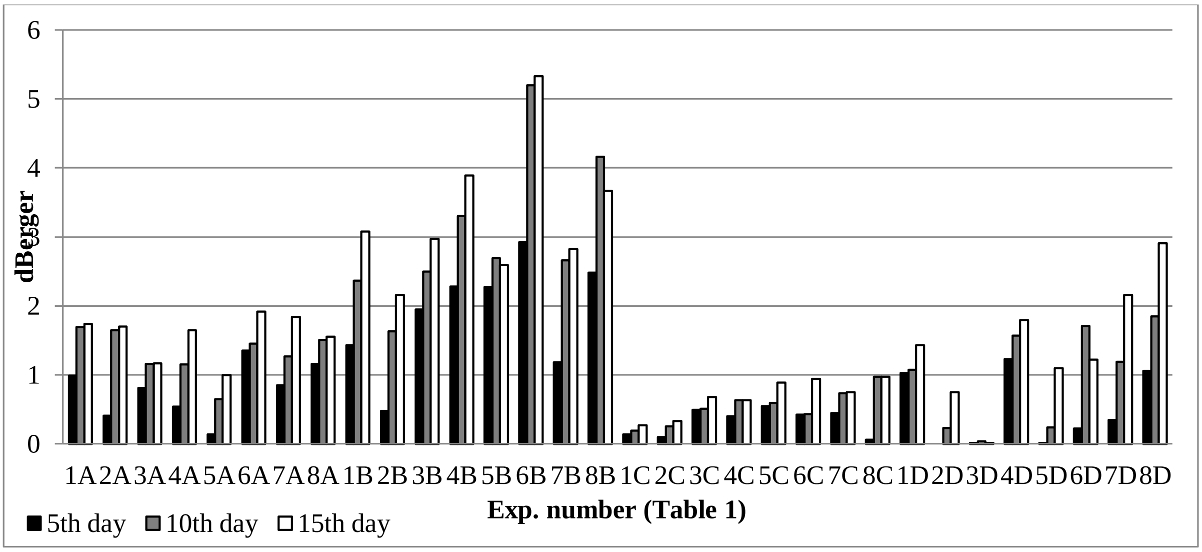
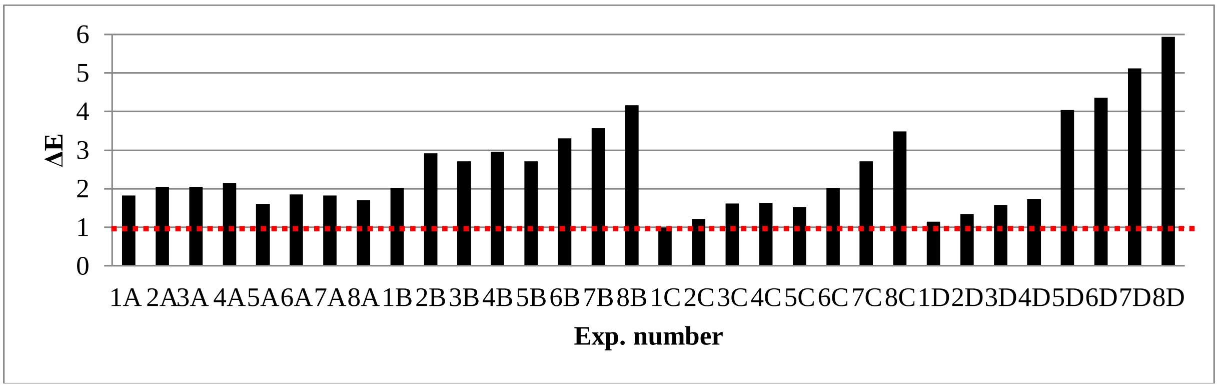


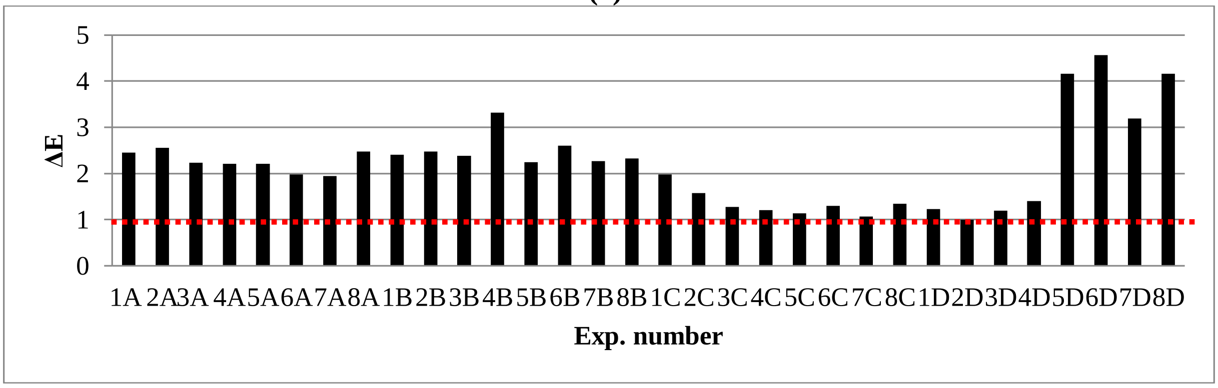
Figure 11. Change in the Berger values versus time

3.5. CIELab Values of the Dyed Samples

The CIELab values of the dyed samples were measured, and color differences values were calculated. The results of color differences (ΔE) of the dyed samples compared with the reference dyeings of 0.6% and 2.1% are given as graphs in Figure 12. According to Figure 12, it can be said that generally the ΔE values of the fabric samples pretreated according to Process 1 and Process 2 were higher than limiting value (ΔE should be less than 1). The color differences are derived from the hydrophility and whiteness properties of the gray fabrics. The color measurements of the fabric samples from the different locations and the visual evolution showed that the fabric samples pretreated according to Process 2 can be dyed more homogeneously than those of Process 1, because the hydrophility values of the samples pretreated according to Process 2 were better and the diffusion form of the droplets was regular. Therefore, it can be concluded that Process 2 is a preferable process than Process 1.



(a)



(b)

Figure 12. ΔE results of the dyed samples for owf of (a)0.6% (b)2.1%

3.6. Fastness Results of the Dyed Samples

The results of the washing, water, and perspiration fastness (acidic and basic) of the dyed samples show that whole results are 4 and 4/5 levels. Thus, it is possible to say that the improved sustainable pretreatment process in the present study is appropriate for pretreatment of the 100% cotton fabrics for dyeing with high fastness results.

4. Conclusion

In this study, it was aimed to improve a sustainable pretreatment process including enzymatic treatment and ozone bleaching at the jigger machine, and the effect of the stage where the ozone bleaching treatment should be applied was investigated. For this purpose, the 100% cotton woven raw fabrics were pretreated according to three different processes, as given below.

- Process 1: The combined desizing and bioscouring treatment then ozone bleaching
- Process 2: The ozone bleaching, then combined desizing and bioscouring treatment
- Process 3: The desizing treatment, ozone bleaching, then bioscouring treatment

In the processes, the desizing and bioscouring treatments were applied with enzymes. The ozone bleaching treatments were applied in the air to the moist fabric samples and in the water by feeding ozone gas with different methods to the jigger machine. In addition, conventional bleaching treatment was also carried out to compare the results as reference. After the pretreatment processes, the effects of the process on the pretreatment and mechanical performances of the fabric samples were examined, and the yellowing tendency of the samples versus time was also investigated. The pretreated samples were then dyed, and the dyeing homogeneity of the samples was also observed. The results are summarized as follows:

- The stage where the ozone bleaching treatments are applied is crucial for the success of the process.
- The hydrophility and size residual results of the pretreated samples according to Process 2 are better than other processes. The ozone bleaching treatments in the air provide more homogeneous hydrophility results.
- The natural oils and waxes on the cotton can be decayed through ozone gas, and to remove them, any wet treatments should be carried out after ozone bleaching.
- According to the Berger values, the whiteness degrees of the samples pretreated according to Process 2 are better than other processes, and higher Berger values can be obtained by Process 2 than reference bleaching, especially for ozone bleaching in the air.
- The mechanical performance results and SEM analysis show that the ozone bleaching treatment had no crucial effect on the mechanical properties of the samples.
- The yellowing tendency results of the pretreated samples versus duration time indicate that the most yellowing effects occurred for the samples pretreated according to Process 1. The ozone gas decays to oxygen quicker because of the wet process at high pH (8-8,5) and temperature (60 ºC); thus, the samples pretreated according to Process 2 have an undetectable yellowing tendency.
- According to the dyeing results of the pretreated samples, the fabric samples pretreated according to Process 2 can be dyed more homogeneously because of the better hydrophility performance.
- When compared to the reference pretreatment process, while 90 liters of water (the volume of laboratory type jigger is 30 liters) are used in Process 2, 120 liters of water are used in the reference one. The water consumption also drops by 30 liters when ozone bleaching is applied in the air in Process 2. In addition, while the reference bleaching process is applied at 90 ºC, the ozone bleaching is applied at room temperature, consuming more energy than Process 2. Therefore, it is possible to say that Process 2 is a sustainable pretreatment process that includes enzymatic pretreatment and ozone bleaching.

As a conclusion, the stage where the ozone bleaching treatment is applied has high importance for the success of the process. Process 2 in which the ozone bleaching treatment is applied before the combined desizing and bioscouring process, is the most appropriate one due to superior hydrophility, whiteness, yellowing tendency, and dyeing performance results. In addition, the condition of ozone bleaching treatments is also crucial for the results and it is recommended to apply in the air in terms of both obtaining better results and consuming less water and energy.

5. Acknowledgement

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