INFLUENCE OF FIBER DYEING PROCESS ON INNER STRUCTURE OF SOME COTTON FIBERS PRODUCED IN TURKEY

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In this paper, the influence of fiber dyeing on the internal structure of cotton fibers was investigated. For this purpose, some cotton fibers originating from growing areas in the Aegean region and around Kahramanmaraş city in the Mediterranean region were used. The physical properties of the cotton fibers were characterized by an Uster HVI 1000 Instrument. Whole cotton fibers were pretreated, dyed and washed using the same process parameters. The inner structures of undyed and dyed cotton fibers were analyzed by the X-ray diffraction method. The peak positions, full width at the half-height of maximum peaks (FWHM) (β) and d-spaces of cotton fibers were obtained by X-ray diffraction. Crystal sizes were calculated using Scherrer's equation. The crystal sizes, β and d-spaces of undyed and dyed cotton fibers were compared. It was found that the inner structure parameters of the cotton fibers were altered after the dyeing processes.

Keywords: cotton fiber, fiber dyeing, reactive dye, inner structure, X-ray diffraction, crystal size, d-spacing

INTRODUCTION

Cotton is, by far, the most important and dominant natural textile fiber. Now, it is only exceeded in volume by polyester fiber.[1-4] In 2015, the ratios of cotton and polyester fibers in global fiber consumption were around 27% and 55%, respectively (Fig. 1).[4]

Cotton is the purest source of cellulose. Cotton fibers mainly consist of α-cellulose (88-96.5%). Cotton cellulose has high molecular weight and structural order, *i.e.*, it is highly crystalline, oriented and fibrillar. Cotton, with this high availability and structural order of the most abundant natural polymer, is, not surprisingly, viewed as a premier fiber and biomass.[5]

Cellulose is a linear syndiotactic homopolymer, composed of D-anhydroglucopyranose units, which are linked together by β-(1→4)-glycosidic bonds. Each anhydroglucose unit includes three hydroxyl groups, one primary on C-6 and two secondary on C-2 and C-3. The abundant hydroxyl groups and the chain conformation allow extensive intra-molecular and inter-molecular hydrogen bonding to further increase the rigidity of the structure of cellulose. Hydroxyl groups also allow for dye molecules to form bonds.[5-8]

The fine structure of native cellulose fibers has important implications in the biological processes of plant growth, chemical or enzymatic transformation of cellulosic biomass, as well as for the conception of new materials and understanding of physical properties of a wide range of cellulose-based materials.[9] Molecular modeling of the chain conformation of cellulose and the settlement of cellulose in the base centered monoclinic unit cell are shown in Figure 2 (a)[10] and (b),[11-12] respectively. The effects of heating and chemical reactions on cotton cellulose depend on its super-molecular structure, as well as on the activity of the C-2, C-3 and C-6 hydroxyl groups. Chemical reactions or heating effects start in the more accessible amorphous region and the surfaces of crystalline domains.[5]

Dyes may be defined as substances that, when applied to a substrate, provide color by a process that alters, at least temporarily, some crystal structure of the colored substances.[13-14] Reactive dyes are dyes that form a covalent bond with cotton fibers. The key parts of the dye molecule are the chromophore and the reactive group.[15] Reactive dye is one of the most widely used synthetic dyes for cotton dyeing, owing to its wide color gamut, brilliant color, excellent wet-fastness and easy application.[16]

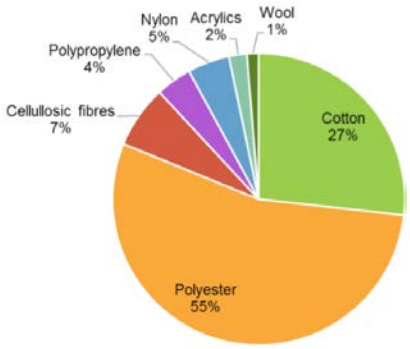
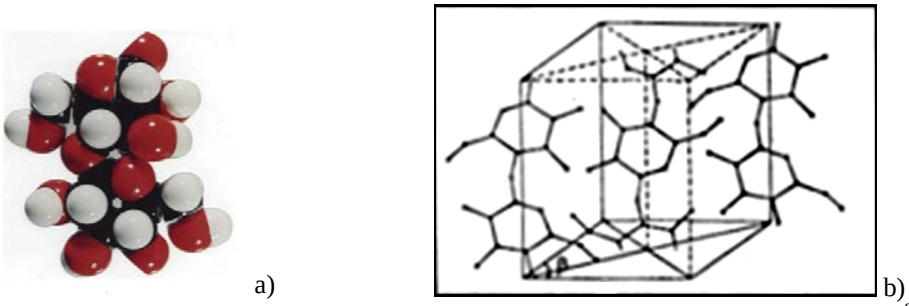


Figure 1: Global consumption of fibers at mills in 2015[4]



a) b)

Figure 2: a) Molecular modeling of chain configuration of cellulose in three dimensional space;[8] b) settlement of cellulose in the base centered monoclinic unit cell[9-10]

Cotton fabrics are highly popular due to their excellent properties, such as versatility, softness, hygroscopicity, breathability, affinity to skin, biodegradability and regeneration property.[8] Colored cotton fibers are mostly used in fancy yarn production. Among the types of fancy yarn, mélange yarn is known for its attractive color and appearance. Mélange yarn is a type of spun yarn made from two or more fiber groups with different colors or dye affinities.[15,17-19]

The aim of this research was to describe the structure of Turkish cotton fibers before and after dyeing processes. The structural parameters play an important role in determining both physical and chemical properties of textile fibers. Therefore, it is important to recognize the structural properties of cotton fibers before using them in textile production. Turkey is one of the major cotton-producing countries in the world. For this reason, the investigation of the structure of Turkish cotton fibers is very important. In this study, which is part of a more extensive work, the inner structures of raw and dyed cotton fibers were examined. The dyeing properties of different cotton types, another part of this comprehensive project, will be examined in another paper.

EXPERIMENTAL

Materials

The cotton fiber samples used in this research were collected from some cotton varieties grown in different locations of the Aegean region and Kahramanmaraş city and its environs. These cotton fiber samples were varieties of Aksel, Carmen, Celia and Flora (the Aegean region) and varieties of Adana-98, BA-308 and Stoneville-453 (Kahramanmaraş city and its environs). From these cotton samples, Carmen and Adana-98 cottons were registered at Nazilli Cotton Research Center in Turkey.

In the processes of pretreatment, dyeing and washing, a wetting agent (Torawet SK-37), a degreasing agent (Weltex PY), sodium hydroxide (NaOH), a stabilizer (Iyonex Fe), hydrogen peroxide (H_2O_2), acetic acid (CH_3COOH), antiper enzyme (Perozym HO CONC), salt (Na_2SO_4), soda (Na_2CO_3) and reactive dye (Synozol Gold Yellow HF-2 Gr 150) were used.

Methods

In this research, the same processes of pretreatment, dyeing and washing were applied for all the cotton fibers. Thus, the effect of the parameters of these processes was excluded.

The conditions and prescriptions for the pretreatment, dyeing and washing processes applied to the cotton fibers were taken from the industrial manufacturing process used at ÇMS Tekstil San. Tic. A.Ş., based in Kahramanmaraş, in Turkey. These processes were performed by an ATAÇ Lab Dye HT laboratory scale dyeing machine.

Pretreatment processes of cotton fibers

The cotton fiber samples were pretreated according to the recipe and conditions given in Figure 3. Wetting agent (1 g/L), degreasing agent (0.5 g/l), NaOH (3 g/L), stabilizer (1 g/L), H_2O_2 (5 g/L), acetic acid (0.5 g/L) and antiper enzyme (0.15 g/L) were used in the pretreatment processes of cotton fibers. The liquor ratio of the pretreatment bath was 1:7. The same prescription, conditions and chemicals were used for all cotton fibers. In the first bath (Fig. 3 a), cotton fibers were bleached using H_2O_2 at pH 10-11 and a temperature of 100 ºC. In the second bath (Fig. 3 b), rinsing was carried out for 10 minutes at 80 ºC. In the third bath (Fig. 3 c), using acetic acid, the pH was adjusted to 5, which the most suitable for the antiper enzyme, and the remaining H_2O_2 was removed.

Dyeing processes of cotton fibers

Pretreated cotton fibers were dyed according to the recipe and conditions given in Figure 4. Reactive dye (1%), salt (40 g/L), wetting agent (1 g/L) and soda (20 g/L) were used in the dyeing process. The dyeing process of cotton fibers was carried out as shown in the flowchart in Figure 4.

Washing processes of cotton fibers

After the dyeing process, the cotton fiber samples were washed, neutralized and softened according to the conditions given in Figure 5.

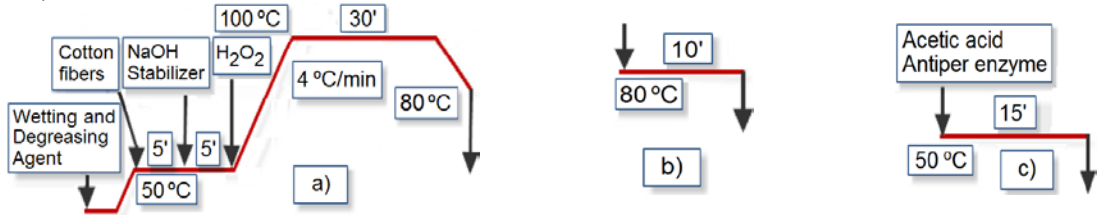


Figure 3: Recipes for a) pretreatment, b) rinsing, c) peroxide removing processes

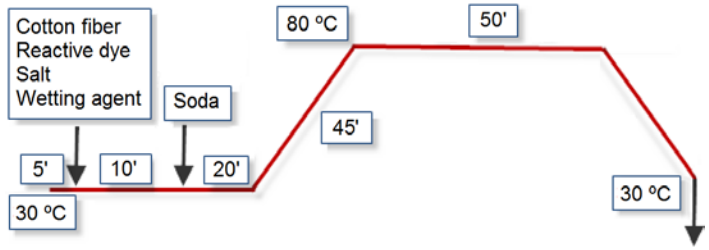


Figure 4: Flowchart of reactive dyeing process

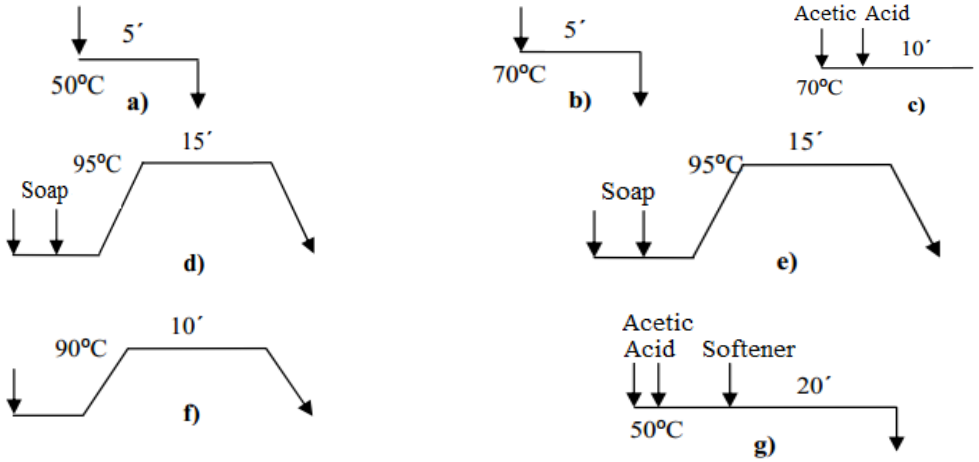


Figure 5: Flowchart of washing processes; a) and b) rinsing, c) neutralization, d) and e) soaping, f) rinsing, g) softening

Measurement of physical properties

The physical properties of the cotton fibers were measured by using a High Volume Instrument (Uster HVI 1000).

Wide-angle X-ray diffraction (WAXD)

Cotton fiber powder from each sample was placed into a specimen holder. A Panalyt X'Pert PRO X-ray diffractometer was employed to obtain the X-ray diffraction patterns of the investigated cotton fiber samples. CuKα (λ = 1.5406 Å) radiation was generated at an accelerating potential of 40 kV and a tube current of 30 mA. Diffraction intensities were counted at 2 °/min scanning speed, in the two theta (2θ) angle range from 5° to 45°.

For each fiber sample, the peak positions, interplanar d-spacings and the full width at half-height of the maximum peaks (FWHM) (β) were obtained by the X-ray diffractometer. Average crystal sizes (t_c) were calculated from the X-ray graphics, using the Scherrer equation (Eq. 1).[20-24] Peak breadths can provide information on both the crystallite size and on the disorder. The Scherrer equation (Eq. 1) relates the minimum crystallite size *tc* to the breadth.[24]

$$t_c = \frac{K.\lambda}{\beta.Cos\theta} \quad (1)$$

where t_c is crystal size, K is the "shape factor", λ (= 1.5406 nm) is the wavelength, β is the full width of peak at the half-height (rad), θ is peak position in the diffraction pattern (half of the 2-θ value). The value of K often gives values of about 0.9, but can range from 0.6 to 2.08.

RESULTS AND DISCUSSION

The spinning consistency index (SCI), micronaire (Mic), maturity index (Mat), fiber length (Len), fiber amount (Amt), fiber uniformity index (Unf), short fiber index (SFI), fiber strength (STR), fiber elongation (Elg), moisture (Moist), reflectance degree (Rd), yellowness (+b), trash count (Tr Cnt), trash area (Tr Area) and trash grade (Tr Grade) values of the cotton fibers measured by Uster HVI-1000 are given in Table 1. The most important physical property of cotton fibers for the dyeing process is maturity. The maturity index of cotton fibers used in the study varies between about 0.85 and 0.93.[25] According to Uster technologies, maturity index values between 0.86 and 0.95 refer to mature cotton fibers. As a result, all cotton fibers, except Celia, are mature cotton fibers.

Table 1
HVI Test results of cotton fibers

Fiber		SCI	Mic	Mat	Len	Amt	Unf	SFI	STR	Elg	Moist	Rd	+b	Tr Cnt	Tr Area	Tr Grade
	Mean	**176**	**4.57**	**0.92**	**29.83**	**752**	**86.0**	**6.5**	**36.9**	**5.6**	**7.6**	**81.9**	**7.0**	**24**	**0.22**	**2**
Adana-98	S.D.	6	0.09	0.01	0.17	11	0.7	0.1	1.2	0.3	0	0.1	0.1	3	0.01	0
	CV %	3.6	1.9	1.1	0.6	1.3	0.8	0.9	3.3	5.4	0	0.1	0.8	12.9	4.5	0
	Mean	**169**	**3.97**	**0.88**	**28.69**	**744**	**85.1**	**6.7**	**35.6**	**6.6**	**6.7**	**78.8**	**9.1**	**6**	**0.09**	**1**
Aksel	S.D.	5	0.1	0.01	0.33	46	0.9	0.6	0.5	0.4	0.1	0	0	2	0.02	0
	CV %	2.7	2.5	1.2	1.2	6.1	1	9.1	1.3	5.7	0.9	0	0	24.1	16.4	0
	Mean	**163**	**4.89**	**0.93**	**30.98**	**657**	**85.1**	**6.3**	**35.2**	**5.8**	**7.5**	**77**	**8.8**	**22**	**0.30**	**3**
BA-308	S.D.	5	0.17	0.01	0.24	29	0.7	0.3	1.7	0.7	0.1	0.1	0.1	1	0.01	0
	CV %	3.2	3.5	0.6	0.8	4.5	0.8	5.1	4.7	12.2	0.8	0.1	1.3	4.5	1.9	0
	Mean	**144**	**4.92**	**0.92**	**27.92**	**643**	**84.1**	**7**	**32.6**	**6.4**	**6.9**	**76.8**	**8.6**	**5**	**0.13**	**1**
Carmen	S.D.	7	0.04	0	0.25	114	1.2	0.7	0.5	0.4	0.2	1	0.4	1	0.07	1
	CV %	4.6	0.8	0	0.9	17.8	1.5	9.4	1.4	6.2	3.4	1.3	4.2	21.7	54.3	43.2
	Mean	**174**	**3.31**	**0.85**	**28.41**	**526**	**85.1**	**6.3**	**35**	**5.9**	**6.2**	**80.6**	**8.5**	**10**	**0.27**	**2**
Celia	S.D.	10	0.1	0.01	0.98	20	0.6	0.3	2.5	0.5	0	0.1	0.1	1	0.01	1
	CV %	6	3.1	0.7	3.4	3.9	0.7	4	7	8.8	0	0.1	0.7	10	2.1	24.7
	Mean	**149**	**3.89**	**0.86**	**27.97**	**625**	**84.1**	**7.2**	**30.5**	**6.8**	**6.6**	**78.4**	**8.6**	**11**	**0.18**	**1**
Flora	S.D.	12	0.2	0.01	0.87	56	1.2	0.4	1.1	0.5	0	0.3	0.3	6	0.06	1
	CV %	8	5	0.7	3.1	9	1.4	5.7	3.5	7.8	0	0.3	2.9	60.3	35.9	43.2
	Mean	**144**	**4.63**	**0.9**	**28.85**	**621**	**84.2**	**6.9**	**31**	**6.6**	**7.6**	**76.1**	**8.5**	**16**	**0.33**	**3**
Stoneville-453	S.D.	8.9	8.7	1.1	2.6	5	1.1	5.1	3.7	6.3	0.8	0.2	0.7	1	0.01	0
	CV %	8.9	8.7	1.1	2.6	5	1.1	5.1	3.7	6.3	0.8	0.2	0.7	3.5	3.5	0

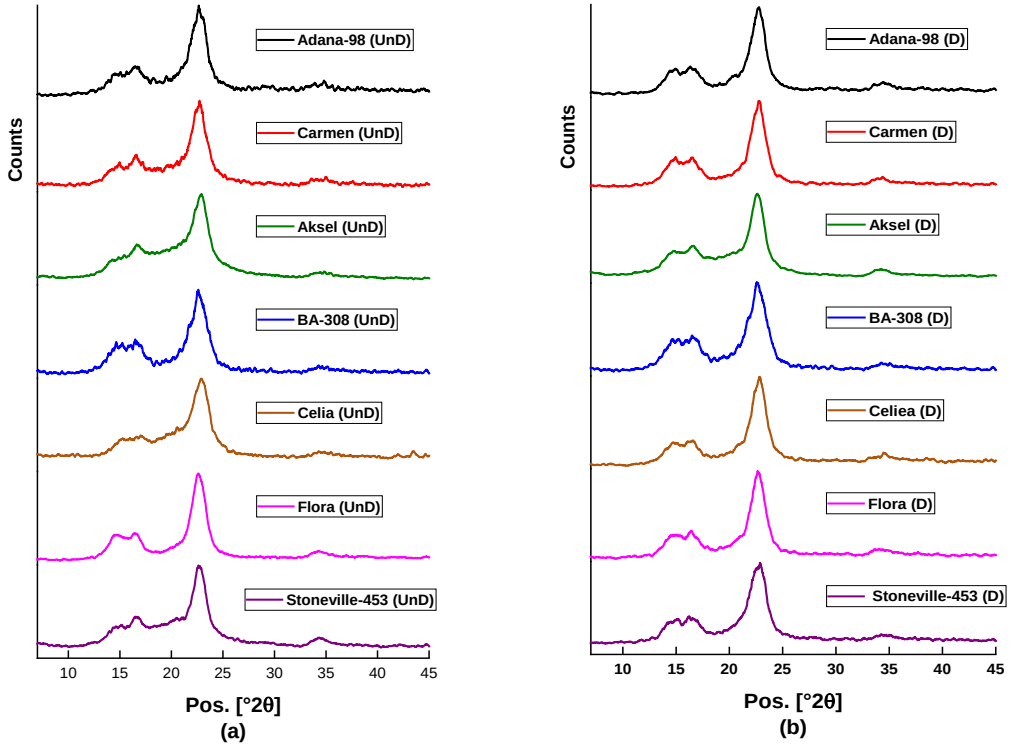


Figure 6: WAXD traces of a) undyed cotton fibers and b) dyed cotton fibers

Table 2
X-ray diffraction data of undyed and dyed cotton fibers

Fiber	Peak position (2θ) (°)		d-Spacing (Å)		FWHM (β) (rad)		Crystal size (t_c) (Å)	
	Undyed	Dyed	Undyed	Dyed	Undyed	Dyed	Undyed	Dyed
Adana-98	22.6684	22.7706	3.9227	3.9054	0.2362	0.6298	339.2255	127.2458
Aksel	22.8493	22.5964	3.8921	3.9351	0.7085	0.3936	113.1270	203.5442
BA-308	22.6212	22.6212	3.9308	3.9308	0.3936	0.3936	203.5530	203.5530
Carmen	22.7398	22.8136	3.9106	3.8981	0.4723	0.2362	169.6699	339.3119
Celia	22.8768	22.8490	3.8875	3.8921	0.3149	0.3149	254.5392	254.5267
Flora	22.4668	22.5700	3.9575	3.9363	0.1968	0.3149	406.9966	254.4023
Stoneville-453	22.6334	22.8895	3.9287	3.8853	0.3149	0.2362	254.4305	339.3573

Wide angle X-ray diffraction (WAXD) patterns for undyed and dyed cotton fiber samples are given in Figure 6. The values of maximum 2θ peak positions, d-spacings, FWHM (β) and crystal sizes for undyed and dyed cotton fibers obtained from X-ray diffraction graphics are given in Table 2. The characteristic diffraction peaks of 002 planes for all the raw and dyed cotton fibers were obtained from the wide angle X-ray diffraction patterns. For both undyed and dyed cotton fibers, the maximum 2θ peak values showed a shift in the X-ray diffraction patterns, but all these peaks were seen in the range of 22° and 23°. These results are compatible with the peak values of cellulose given in the literature.[5,10-11,24,26]

The changes of d-spacings for undyed and dyed cotton fibers are shown in Figure 7. After dyeing process, it was shown that the d- spacings of cotton fibers (Adana-98, Carmen, Flora and Stoneville-453) were generally decreased.

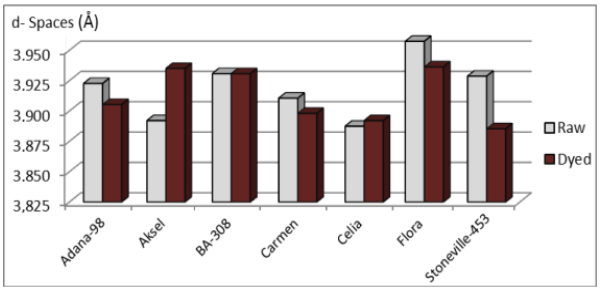


Figure 7: Comparison of d-spacings of undyed and dyed cotton fibers

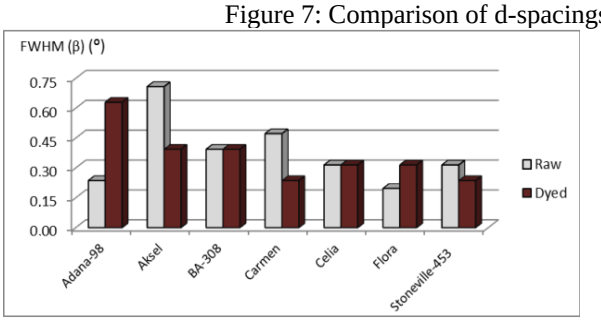


Figure 8: Comparison of FWHM (β) values for undyed and dyed cotton fibers

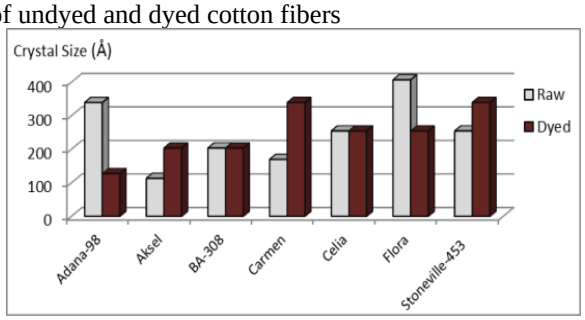


Figure 9: Comparison of crystal sizes for undyed and dyed cotton fibers

The full width at the half-height of the maximum peak (FWHM) (β) in the X-ray spectra shows the crystal perfection of fibers. When the peak (β) expands, the crystal perfection decreases.[20-21,23] The change in the FWHM (β) values for undyed and dyed cotton fibers are shown in Figure 8. After the dyeing process, it was observed that the FWHM (β) values of Adana-98 and Flora increased, which those of Aksel, Carmen and Stoneville-453 decreased.

It is understood from the Scherrer equation that the crystal size varies inversely with FWHM (β). Crystal size also depends on the 2θ value. When the crystal regularity increases, crystal size increases. The changes in the crystal sizes of undyed and dyed cotton fibers are shown in Figure 9. After the dyeing process, it may be noted that the crystal size decreased in the cotton fibers with large crystal size (Adana-98 and Flora), but it increased in the cotton fibers with small crystal size (Aksel, Carmen and Stoneville-453), compared to the respective crystal size of their undyed counterpart.

CONCLUSION

The aim of the present work was to understand the changes in the inner structure of cotton fibers induced by dyeing processes. The results of the wide angle X-ray diffraction analysis of cotton fibers showed that the inner structure parameters of cotton fibers are altered after dyeing. It was found that d-spacings, FWHM (β) and crystal sizes of cotton fibers were affected by the dyeing process. It was shown that the d-spacings of cotton fibers (Adana-98, Carmen, Flora and Stoneville-453) generally decreased, while the FWHM (β) values increased for some types of fibers (Adana-98 and Flora), but decreased for others (Aksel, Carmen and Stoneville-453). The crystal size of cotton fibers decreased in cotton fibers with large crystal size (Adana-98 and Flora), but increased in cotton fibers with small crystal size (Aksel, Carmen and Stoneville-453).

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