STUDY OF THE RELATIONSHIP BETWEEN FIBER PROPERTIES AND DYE ABILITY FOR COMMERCIAL EGYPTIAN COTTON

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Abstract

The relation between cotton fiber properties and dye-ability has been studied for eight Egyptian cotton varieties representing a wide range of fiber properties grown during four successive seasons. The dye-ability was studied for both mercerized and un-mercerized cotton samples. A relationship was found to exist between dye absorption, chemical activity (accessibility %) and fiber maturity% of the commercial Egyptian cottons. These studies indicate that there is a strong correlation between fiber maturity, accessibility and dye-ability at equilibrium. The results obtained showed that the dye-ability of the mercerized cotton varieties had the highest values than the un-mercerized cottons due to the chemical and physical structure of the fibers. The cotton fibers have a natural porosity consisting of pores and micro capillaries whose accessibility can increase. Mercerized Egyptian cotton fibers are more absorbent and have greater affinity for dyestuff. The results obtained revealed that dye uptake increased gradually in the Egyptian cotton with increasing fiber maturity%.

INTRODUCTION

Dyeing is a heterogeneous process that takes place at the interphase between the dyeing solution and the fiber. Its proceeding includes (i) diffusion of the dye into the bulk liquid phase; (ii) adsorption of the dye on the fibers outer surface: (iii) diffusion in the bulk of the fiber; and (iv) adsorption on the inner surface of the fiber.

Depending on the dyeing conditions each one of these steps can become limiting and hence determines the overall rate relations of the process. The degree of the dyeing fixation is mainly affected by the chemical structure of the fibrous polymer which determine the affinity of the dye towards the fibers, the number and the type of the potential active cites where physical and chemical of the dye molecules adsorption take place.

According to Vigmann (1958), the cellulose macromolecule includes anhyro-glucoscide residues interconnected by 1-4-β-glucoscide linkages each of which containing three-hydroxyl groups. These groups have different reactivates towards the dye molecules and the studies carried so far showed that the fixation precedes predominantly through the hydroxyl group at C6.

The physical structure of the fibers is of importance, as well as, it determines the accessibility of the active cites. Only some of the dye molecules sorbed on the fibers surface are able to interact with them. A favorable disposition is required. The physical properties of the fibers can be divided to surface and bulk ones. The cotton fibers have a natural porosity- a system of pores and micro capillaries whose accessibility can increase depending on the dyeing conditions.

Dyeing of the cotton fibers takes place in alkaline medium, which results in a considerable swelling of the fibers and increase of their inner surface. As the fixation is preceded by dye molecule diffusion and sorption, their chemical structure and size are important too. Pal (1959) pointed out the relation between cotton fiber properties and dye absorption of American upland type cotton.

An analytical procedure was described by Rebenfeld and Wu (1961) for placing the differential dye test for cotton fiber maturity on a quantitative and objective basis. The procedure involves the extraction of the two dyes from a differentially dyed sample and spectrophotometrically analyzing the red and green dye uptake. The G/R value, defined as the ratio of green and red dye uptake, was shown to be a sensitive index of cotton fiber maturity. The mechanism of the differential dye test is discussed in terms of dyeing rates and fiber structure. The effects of swelling treatments on the differential dyeing test were also discussed.

Inglesby and Zeronian (1996) disclosed the accessibility of cellulose as determined by dye adsorption. The problem of correctly assessing the maturity (the degree of development of the fiber wall) of a sample of cotton remains a serious issue for the world textile industry. The presence of immature cotton fibers in a lay down poses significant problems in processing performance and in the quality of the finished textile. These problems may include neps, weak places in yarns, ends-down in spinning, excess waste, and dyeing imperfections such as white specks and barré.

Thibodeaux et al. (1999) reported on the use of a reference technique for measuring cotton maturity, based on image analysis of thin fiber sections to develop a set of standard calibration cottons having a wide range of fineness and maturity values. Abdel-Aziz et al. (2001) found that accessibility % for untreated Egyptian cotton fibers Giza 88, Giza 86 and Giza 89 varieties were 57.21, 53.16 and 56.40%, respectively.

Cotton fibers were subjected to cleaning process and then characterized for maturity, Yakoabu et al. (2006). Dcrystallisation and swelling processes with custic soda, ethanol, propa-2-nol, and trichloro-ethane on the native fibers were carried out. As a kinetic variable is used, the Kubelca-Munk function (K/S) is direct relation to fibers dye concentration, Vassleva et al. (2008). It was found that the process rate is described by the power kinetic equation valid for exponentially in homogeneous surfaces and is determined by entropy factors according for the number of active sites, their accessibility and the steric hindrance present. Mercerization is one of the most important processes of finishing cotton materials. It imparts luster to the fiber, increases its hydroscopicity and strength and improves its dye ability, Sadov et al. (1973). Hatch (1993) reported that, mercerized fibers and fabrics are more absorbent and have greater affinity for dyestuff. Mercerized fabrics are less expensive to dye because they require only 7/10 as much dyestuff as un-mercerized fabrics to achieve a given shade. Mohamed (2002) showed that, the value of color strength (k/s) for mercerized cotton fabrics which dyed with henna (as a natural dye) was increased compared with un-mercerized cotton fabrics.

Gosh (1998) found that fiber dye uptake increased gradually with increasing maturity (micronaire values), and also reported that dye sorption is depended on the mature substrate concerned along with the quality of the cotton particular fiber maturity.

The aim of the present investigation was to study the relation between cotton fiber properties and dye absorption for eight commercial Egyptian cotton varieties representing a wide range of fiber properties grown during four successive years. The absorption was studied for both mercerized and non-mercerized cotton samples.

MATERIALS AND METHODS

Materials

A. Fibers

This study was carried out on eight fiber samples of commercial Egyptian cotton varieties Giza 45, Giza 70, Giza 88, Giza 86, Giza 85, Giza 89, Giza 80, and Giza 90 obtained from Cotton Research Institute, Agriculture Research Center during four successive seasons from 2006 to 2009.

B. Chemical reagents

All chemicals used were of analytical grade using doubly distilled water (18.5 $M\Omega.cm^{-1}$). NaOH was analytical grade (Koch-Light Co.), Hydrogen peroxide (30% LR grade) from Aldrich. Sodium carbonate (LR grade), sodium silicate (136 Tw, 27% SiO_2), the wetting agent was the commercially Triton 100 supplied by Merck. Acetic acid and soap. The dye used in this work was Procion Crimson CX-B.

Methods

A. Scouring, bleaching and mercerizing treatments

Scouring of the fiber samples was performed with 3% NaOH containing 1.5-2% of the wetting agent and steamed in a laboratory steamer at 100C, for 10 minutes. The samples were washed with water, neutralized with dilute acetic acid, further washed with water, and finally dried in air.

The scoured samples were immersed in alkaline bleach liquor (180 ml ddH_2O), containing Na_2CO_3 (0.2 g/l), NaOH (1.5 g/l), SiO_2 (0.4 g/l), $MgSO_4$ (0.2 g/l), Triton 100 (0.5 g/l), and H_2O_2 ($10ml^{-1}$) was added to the bleaching liquor, then, boiled for 90 minutes. The samples were removed from the liquor and neutralized with aqueous solution containing 0.1% acetic acid followed by a through hot water (80-85 C) to ensure removal of residual chemicals. Samples were dried in an oven at 100C, for 60 minutes.

The bleached samples were treated with aqueous solution of NaOH (20%) at room temperature (mercerization treatment). The samples were removed from the liquor and neutralized with aqueous solution containing 0.1% acetic acid followed by a through hot water (80-85 C) to ensure removal of residual chemicals. Samples were dried in an oven at 100C, for 60 minutes.

The samples were dyed in solutions of Procion Crimson CX-B. The dyeing was carried out at a liquor ratio of 1:20, in a sealed stainless steel dye bath. The temperature and duration of dyeing were 80°C and 45 min. respectively. After dyeing, the dyed samples were taken out and rinsed thoroughly in tap water, and dried freely in open air, then subjected to soaping off in a boiled solution containing 5 g/l non-ionic surfactant for 15 min. at the liquor ratio of 1: 50. The soaped-off dyed samples was then rinsed in tap water and dried freely in open air.

B. Tests and analysis

The chemical activity of the fiber (accessibility %) was estimated according to the method described by Valentine (1954) which calculated by using equation and constant values as follows:

Moisture sorption = moisture regain * 162 / 1800

Accessibility % = moisture sorption * 100 / 1.53

The maturity% was estimated according to the

The color strength expressed as (K/S) was measured using Perkin-Elmer double beam spectrophotometer of model Lambda 35 that is equipped with integrating sphere according to the Kubelka-Munk equation that given by:

$$K/S = (1-R)^2/2R - (1-R0)^2/2R0$$

Where *R* is the reflectance of the colored fabric, *R0* is the reflectance of the uncolored fabric, and K/S is the ratio of the absorption coefficient (*K*) to scattering coefficient (*S*): the higher the value, the greater the color strength.

The color difference ΔE were measured by using the Win lab software according to delta-E 1976 using the following equation.

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2}$$

The statistical procedures outlined by Little and Hills (1978) were applied to the data obtained in this study.

RESULTS AND DISCUSSION

1- Effect of the growing season on color strength (K/S)

Table 1 and Figure 1 shows that the color strength (K/S) values mostly differed significantly among varieties and the four successive seasons. The obtained data showed that the mercerized Egyptian cotton varieties attained the highest color strength values. The average values of Giza 85, Giza 86, Giza 90 and Giza 89 during the successive seasons were 11.39, 11.36, 11.29 and 11.28 respectively, while Giza 80 had the lowest value 8.5. The color strength of Giza 45 shows low value 10.2, compared with the other extra-long stable varieties. This result may be due to the lower average fiber maturity% value during the four successive seasons (83.8). On the other hand, the mercerized samples show higher increase in the color strength than the un-mercerized samples. The mercerization process involves partial destruction of inter molecular bonds. The fibrous transformation from cellulose I to cellulose II occurs during mercerization, which consists of a swelling of the initial fibers in alkali, followed by recrystallization during subsequent washing, and subsequently increases the chemical activity due to the free hydroxyl groups (amorphous cellulose). The results in table 1 show that there were high significant average percentages of dye-ability between the mercerized and un-mercerized of the variety itself and the different commercial varieties samples during the four successive years before and after dyeing. These results may be due to the environmental conditions, the soil nature, and the crop management during different growing seasons. The dye-ability of the mercerized samples for the commercial varieties increased in the range of 75-77%. These results are economically very important in textile industries for decreasing the costs of dyeing for the same shade by mercerization. This means that the dyeing companies can save about half of their costs by reducing the concentration of the dyes. Another important result is to reduce the effluent pollution as an eco-friendly treatment for textile industry.

In cellulose I, the chains within the unit cell are in parallel conformation. Penetration of the dye in the swollen amorphous region of the cellulose where they are held by hydrogen bonding increase the dye uptake more than the non-mercerized samples. The results obtained showed that the same trend was found except for Giza 45, where the color strength had the high value 18.3. This result indicates that factors other than fiber maturity and accessibility may be involved in determining the color strength or the dye absorption of the cotton fibers.

Table 1. Color strength (K/S) of the Egyptian cotton fibers during four successive seasons (2006-2009) before (B) and after (A) mercerization

Seasons	G 45 %			G 88 %			G 70 %			G 86 %			G 85 %			G 89 %			G 90 %			G 80 %		
	B	A	%±	B	A	%±	B	A	%±	B	A	%±	B	A	%	B	A	%±	B	A	%±	B	A	%±
2006	10.1	17.7	75.2	11.87	19.31	62.7	10.5	17.9	70.5	10.1	17.76	75.8	10.1	17.76	75.7	10.03	18.7	86.4	9.43	15.44	63.7	9.31	15.13	62.6
2007	9.3	17.4	87	9.3	17.33	86.3	9.7	17.5	80.4	10.1	17.76	75.8	10.03	17.7	76.5	9.7	17.5	80.4	9.12	16.2	77.6	7.28	13.56	86.3
2008	9.25	17.25	86.5	9.4	17.4	85.1	10.1	17.76	75.8	10.7	18.1	79.7	9.8	17.6	79.3	10.1	17.7	75.2	9.12	16.2	77.6	7.13	13.25	75.8
2009	11.67	20.54	76	11.59	20.39	75.9	12.75	22.45	76.1	13.5	23.59	74.7	14.2	25.03	76.3	13.7	23.94	74.7	10.89	19.16	75.9	9.03	15.85	75.5
Average	81.4			77.5			75.7			76.5			76.9			79.2			73.8			75.1		

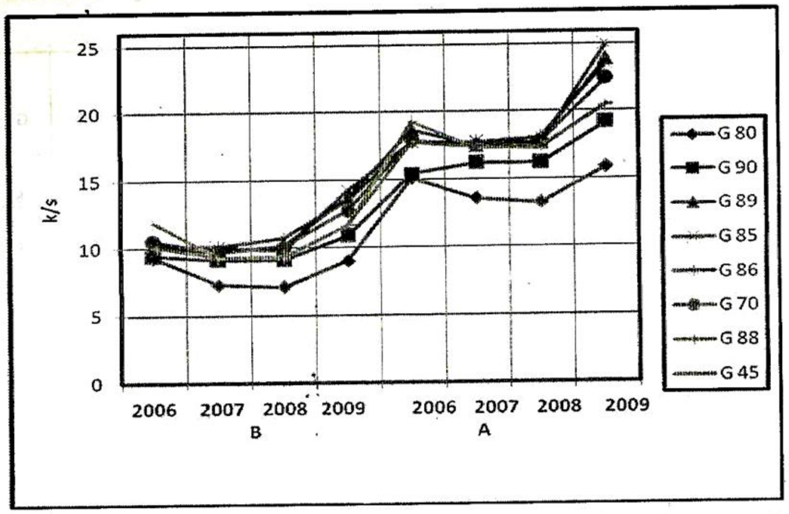

Figure 1. Color strength (K/S) of the Egyptian cotton fibers during four successive seasons (2006-2009) before (B) and after (A) mercerization

2- Effect of the growing seasons on the fiber maturity percent

Fiber maturity is the proportion of fiber cross section occupied by cellulose and is influenced by variations in photosynthesis affecting assimilate supply to growing fibers. The degree of fiber maturity impacts dye absorbency and retention. The data recorded in Table 2, and Figure 2 clearly revealed that the average values of the maturity % are affected by different growing years. This may be due to changes in the climatic conditions from year to year and also the soil composition. The results indicated that Giza 85, Giza 89, and Giza 86 had the highest maturity% values, 88.3, 87.6, and 86.6 respectively, while Giza 45, Giza 90, and Giza 80 had the lowest maturity% values, 83.3, 83, and 83.3 respectively. Thus, it is generally can be concluded that the varietal differences in cotton maturity% of Egyptian cottons are in general not genetically controlled, and influenced by different parameters.

Table 2. Maturity percent (M%) of the Egyptian cotton fibers during four successive seasons (2006-2009)

Seasons	G 80	G89	G 90	G 88	G 45	G 70	G 86	G85	G89
2006	84	85	84	87	86	84	83	86	85
2007	82	84	83	80	82	82	85	85	84
2008	84	86	82	84	81	85	89	84	86
2009	85	85	82	84	81	86	88	84	85

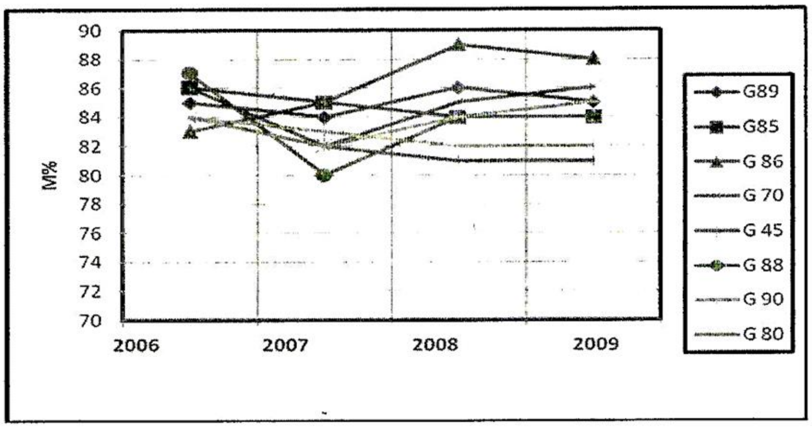

Figure 2. Fiber maturity% of the Egyptian cotton fibers during four successive seasons (2006- 2009).

3- Effect of the growing year on the chemical activity (C.A)

As shown in Table 3 and Figure 3, the chemical activity values ranged between 43.7 to 46.02% and 59- 76% for the un-mercerized and mercerized Egyptian cotton varieties during the four successive seasons respectively. The results obtained revealed that the chemical activities (accessibility %) varied from season to another for each cotton cultivar, means that there was an environmental effect on the chemical activity. The increase in chemical activity (accessibility) following mercerization was more related to the reduction in crystallite size rather than to the change in the total crystallinity. It appeared that the crystallinity of mercerized cotton was slightly increased during dyeing. The cotton fibers have a natural porosity which contains of pores and micro capillaries whose accessibility can increase. Mercerized Egyptian cotton fibers are more absorbent and have greater affinity for dyestuff. It was noticed that the samples mercerized and not dried adsorbed more dye than their counterparts given the same swelling treatment but dried after mercerization. The presence of dye in a sample mercerized and undried before dyeing did not affect its crystallinity. From the dye adsorption (K/S) data it was concluded that structural collapse of the fiber is greater for the mercerized product than its un-mercerized counterpart after it is dried.

Table 3. Chemical activity% of the Egyptian cotton fibers grown during four successive years (2006-2009) before (B) and after mercerization **(A)**

Seasons	Tr.	G 80	G 90	G 88	G 45	G 70	G 86	G85	G89
2006	B	43.6	44.7	45.4	45.8	42.1	46.23	41.9	42
2007		43.1	44.3	44.4	45.5	46.1	46.9	45.9	46.6
2008		43.2	43.6	43	48.5	44.8	43.9	44.7	42.7
2009		41.9	44.6	41.6	43	46.9	46.2	45.2	44.7
2006	A	62.28	63.85	64.8	65.42	65.28	66.04	67.1	60
2007		61.57	63.28	63.42	65	60.14	67	59.85	66.57
2008		61.57	62.28	61.42	69.28	65.85	62.71	63.85	61
2009		59.85	63.7	59.42	61.4	67	66	64.71	63.85

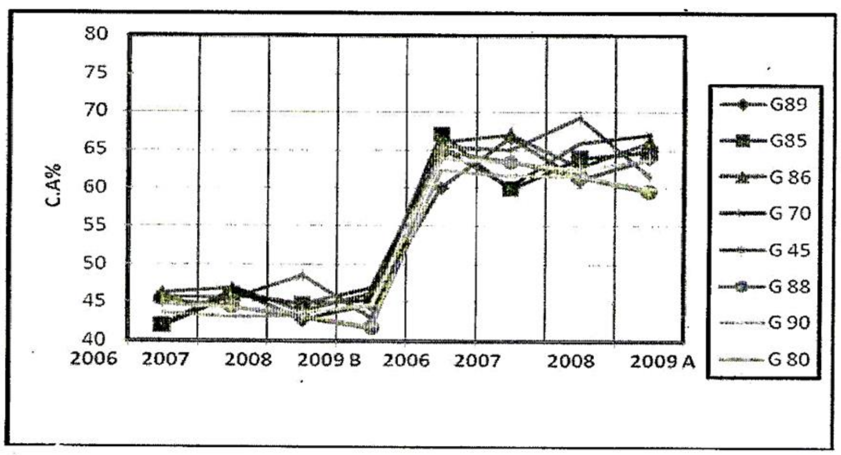

Figure 3. Chemical activity% (C.A) of the Egyptian cotton fibers during four successive seasons (2006-2009) before (B) and after (A) mercerization.

4- Effect of the growing year on the colour difference ΔE

It is known that ^E is a single number that represents the distance between two colors. So, the color difference is due to the variation in the L* a* and b* color spaces. The ^ E corresponds to the color strength of the cotton verities. The data as shown in figure 4 represent that ^E has the greatest values for Giza 85, Giza 89, and Giza 86 for both the un-mercerized the mercerized varieties. During the four successive years, the lowest values for both un-mercerized and mercerized cotton varieties were Giza 80, and Giza 90 respectively.

Table 4. Color Difference of the Egyptian cotton fibers during four successive Seasons (2006-2009) before (B) and after (A) mercerization

Seasons	Tr.	G 80	G 90	G 88	G 45	G 70	G 86	G85	G89
2006	B	82.59	83.04	105.42	95.59	93.25	95.59	95.59	89.7
2007		65.28	77.42	83.42	83.42	87.01	90.59	89.7	87.01
2008		62.72	77.42	82.42	81.97	89.51	94.83	86.05	89.6
2009		81.29	98.42	104.68	105.32	115.06	120.93	127.2	122.72
2006	A	135.08	134.06	171.61	157.31	158.99	157.83	157.83	166.18
2007		121.55	126.03	155.98	155.98	156.87	159.2	156.87	156.06
2008		118.7	126.03	155.88	154.53	159.1	161.25	156.8	159.69
2009		143.11	181.43	183.98	185.43	202.57	212.86	225.58	216.02

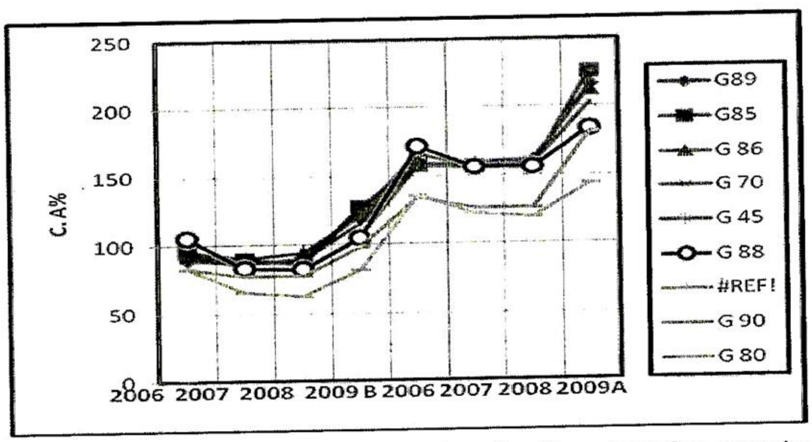

Figure 4. Color difference (ΔE) of the Egyptian cotton fibers during four successive seasonss (2006-2009) before (B) and (A) after mercerization .

5- Correlation coefficient between maturity%, chemical activity%, and color strength (dye uptake) of the eight Egyptian cotton varieties over different four seasons

It's of particular concern to note that the color strength differed with high significant over years with the different ratios of maturity% and chemical activity % for the un-mercerized and mercerized cottons. Consequently, it could be generally concluded that, the color difference of Egyptian cotton also change significantly with the maturity %, and the chemical activity%. The data represent in table 1 revealed that there is a strong correlation between maturity, accessibility and dye-ability. A highly significant correlation values were found between maturity with chemical activity, color strength and color difference for both mercerized and un-mercerized cotton varieties during the four successive seasons. Accessibility had a high significant values for maturity, and color difference and significant values for the color strength. This is due to the competition of the dye molecule and the additive salts in the dyeing bath to bond with the free hydroxyl.

Table 5. Correlation coefficient between studied traits for four Egyptian cotton varieties and four successive seasons

	M%	C. A (B)	C. A (A)	K/S (B)	K/ S (A)	ΔE (B)	ΔE (A)
M %	NS	0.22**	NS	0.57**	0.60**	0.48**	0.51**
C. A (B)	0.22**	NS	0.61579**	0.20687*	0.19795*	0.22**	0.24**
C. A (A)	0.24**	0.61579**	NS	0.41**	0.53**	0.35**	0.40**
K/S (B)	0.57**	0.20687*	0.41**	NS	0.93**	0.85**	0.88**
K/S(A)	0.60**	0.19795*	0.53**	0.93**	NS	0.90**	0.90**
ΔE (B)	0.48**	0.22**	NS	0.85**	0.90**	NS	0.98**
ΔE (A)	0.49**	0.24**	NS	0.88**	0.91**	0.98**	NS

NS = Non-significant C.A= Chemical activity ΔE = Color differences

* = Significant K/S = Color strength A = After merceization

** = High significant M% = Fiber maturity% B = Before mercerizatio

CONCLUSION

The relation between cotton fiber properties and dye absorption has been studied for eight Egyptian cotton varieties representing a wide range of fiber properties grown during four successive years. The dye absorption was studied for both mercerized and un-mercerized cotton samples. A relationship was found to exist between dye absorption, accessibility% and maturity% of the commercial Egyptian cottons. This study has indicated that there is a strong correlation between maturity, accessibility and dye absorption at equilibrium. The results obtained showed that:

1- Dye absorption of the mercerized cotton varieties had the highest values among the un-mercerized cottons.
2- The color strength (K/S) mostly differed significantly among varieties and the four successive seasons.
3- The increase in chemical activity (accessibility) following mercerization was more related to the reduction in crystallite size rather than to the change in the total crystallinity. It appeared that the crystallinity of cotton slack mercerized was slightly increased during dyeing.
4- The average values of the maturity% affected by different growing years. They may be belonging to change the climatic conditions from year to year and also the soil composition.
5- The statistical data presented strong correlation between maturity, accessibility and dye absorption at equilibrium.
6- The dye-ability of the mercerized samples for the commercial varieties increased in the range of 75-77%. These economically results are very important in textile industries for decreasing the costs of dyeing for the same shade by mercerization.
7- It is possible reduce the effluent pollution as an eco-friendly treatment for textile industries by reducing the dye concentration.

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دراسة العلاقة بين خواص تيلة الأقطان المصرية و قابليتها للصباغة

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يهتم هذا البحث بدراسة و إيجاد العلاقة بين بعض خواص تيلة القطن مثل (درجة نضج التيلة– النشاط الكيميائي) و والقابلية للصباغة. تم دراسة هذه العلاقة علي ثمانية اصناف من الاقطان التجارية المصرية وهي جيزة ٤٥ و جيزة ٧٠ و جيزة ٨٨ من الاصناف فائقة الطول و جيزة ٨٩ و جيزة ٨٦ و جيزة ٨٥ من الاصناف الطويلة بحري و جيزة ٨٠ و جيزة ٩٠ من الاصناف الطويلة قبلي و ذلك خلال المواسم من ٢٠٠٦و ٢٠٠٧ و ٢٠٠٨ و ٢٠٠٩.

تم اجراء المعاملات الاولية علي جميع العينات بالظروف القياسية العالمية المعروفة مثل الغلي لازالة المواد غير المرغوب فيها مثل الشموع و المواد غير السليلوزية ، والتبييض لازالة المواد الملونة والتحرير (المرسرة) ، ثم تم اجراء عمليات الصباغة بالصبغة النشطة (Procion crimson CX-B) علي جميع العينات. تم قياس قيم نضج التيلة و درجات النشاط الكيميائي قبل و بعد المرسرة و كذلك تم تقدير و قياس درجة عمق اللون (K/S) و درجة الاختلاف اللوني (ΔE) و الابعاد اللونية (L, a, b) ايضا لجميع العينات الممرسرة و الغير الممرسرة خلال الاعوام الاربعة.كما تم اجراء التحليل الاحصائي للنتائج.

يمكن تلخيص النتائج فيمايلي:

١– قابلية الصباغة للعينات الممرسرة اعلي منها بالنسبة للعينات غير الممرسرة.

٢– قابلية الصباغة تختلف اختلافاً معنوياً قوياً للاصناف خلال الاربعة اعوام المتتالية نتيجة الاختلاف في قيم نضج التيلة و قيم النشاط الكيميائي المختلفة للاصناف.

٣– يزداد النشاط الكيميائي خلال عمليات المرسرة نتيجة الزيادة في مجوعات الهيدروكسيل الحرة و نقص في نسبة السليلوز المتبلور في الصنف.

٤– متوسط قيم النضج المختلفة تختلف اختلافا معنويا باختلاف الاعوام نتيجة للاختلافات المناخية و التركيب الكيميائي للاصناف.

٥– دلت الدراسات الاحصائية للنتائج على وجود علاقة قوية بين نضج التيلة والنشاط الكيميائى وقابلية الصباغة .

٦– متوسط نسبة زيادة القابلية للصباغة للعينات الممرسرة للأصناف المستخدمة تراوحت بين ٧٥–٧٧% خلال الأربعة مواسم مقارنة بالعينات الغير الممرسرة. هذه نتيجة اقتصادية هامة للصناعة لخفض التكاليف نتيجة نقص كمية الصبغات المستخدمة مع الحفاظ علي نفس عمق اللون و التجانس اللوني.

٧– نتيجة اخري هامة و هي العمل علي تحويل الصناعات النسجية الي صناعة صديقة للبيئة بخفض معدلات خفض الصرف الصناعي المسسبب لتلوث البيئة نتيجة اختزال تركيزات الصبغات المستخدمة.