

Quantification of The Light Fastness of Colored Substrates by Applying Fading Rate Constant Values

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VISUAL assessment of light fastness of colored substrates against the Standard Blue Scale is considerably not accurate due to the difficulties in the differentiation between small color changes either at lower or higher shades. In this work, nylon fabric and polyamide films (PA) samples, and cellulose diacetate (CDA) films were dyed with different disperse dye concentrations, also wool, viscose and unmodified and modified cotton samples were dyed with reactive dye at same concentrations. The dyed samples were exposed to artificial day light for various periods (20-160 hours) were examined. Color strength, the light fastness and the fading rate constant (K) of these samples were evaluated. It was concluded that for a series of dye concentrations, same light fastness rating were observed and/or with an appreciable change. Since 'K' is a concentration dependent, it decreases by increasing the dye concentration and at each dye concentration a definite 'K' value was obtained. Also, direct relation was found to exist between light fastness rating values and 'K' values. For each light fastness rating of the Standard Blue Scale, there exist a range of 'K' values. Thus, low 'K' values showed high light fastness of the order (7). K values are precise and more accurate and reflect the real change in the light fastness of colored textiles.

Keywords: Colored textile, Blue scales, Light fastness, Fading rate constant, Reactive dye, Disperse dye and Films.

When dyed textile fabrics are exposed to light, a major change in the molecular structure of the polymer occurs, which then leads to gradual loss of the mechanical integrity, difference in their color strength and light fading. This change of color is the result of a complex process which is attributed to a large variety of factors. The light fastness of colored substrate

depends mainly on the two main characteristics, the fiber-dye-ambient medium, *i.e.* the quantum efficiency and the absorption rate. Among the factors affecting the photo fading of colored textiles are the character of the bond between the dye and the fiber, the physical state of the dye, the chemical structure of the dye and/or the substrate⁽¹⁾, the diffusion restriction effect, dye concentration, chemical modification, the quality of the radiation as well as temperature and humidity⁽²⁾. Many trials were carried out to evaluate a standard method for assessing the light fastness of the dyed fabrics⁽³⁾. The modern system for the light fastness testing was introduced by the Deutsche Echtheitskom mission, who adopted the principle, now in use in many countries, of exposing the test pattern alongside a set of standard patterns of graded fastness. This method depends on human vision, *i.e.* comparing the change in color of the dyed exposed samples with that of the standard blue or gray scales⁽⁴⁾. There are many errors in this method due to the variation from one investigator to another, the nature of the color and the illumination under which these fastnesses were assessed. The fading rate constant (K) is considered a good representative for the light fastness measurement^(4,7) and can be evaluated from the slope of curves plotted between $(\log C_t/C_0)$ against the exposure time, where C_t and C_0 represent the dye concentration on the fabric after and before exposure time (t) respectively⁽⁸⁾.

Most light-sensitive colorants exhibit similar fading behaviors on exposure to light. Giles and co-workers classified these trends as Type II or Type III fading rates. Materials with higher light sensitivity usually experience a rapid change in color during the early stages of exposure, followed by a slower rate after maximum fading has occurred; this curve has been described as Type II. The dye is typically found in aggregate form inside the fiber substrate, with a small part of the colorant molecularly dispersed. Dyes exhibiting higher light fastness are characterized by a constant rate of fading, which is classified as Type III. This trend is mostly observed for dyes that form large aggregates inside the fiber, for which the surface area accessible to the environmental elements is reduced resulting in slower fading rates. Although the light fastness of organic dyes is related to both their chemical structure and physical state, it is known that the physical state of the dye within the fiber has a greater influence on its stability⁽⁹⁾.

Experimental

Materials and chemicals

Mill desized scoured and bleached cotton and viscose were supplied by Misr Co., Mahall El-Kobra, Egypt. While wool and nylon fabrics were supplied from El-Shorbagy Co., Egypt. Cellulose diacetate (CDA) and polyamide (PA) films were supplied by Hocest Co. Egypt.

1-choloro-2-dimethyl amino ethane hydrochloride ($\text{Cl-CH}_2\text{-CH}_2\text{-NH}(\text{CH}_3)_2\text{Cl}$) supplied by Fluka AG Buch SC. and used as aminated reagent in the modification process. Sodium chloride, zinc acetate, sodium carbonate are of laboratory grade chemicals were used as salts in dyeing process.

Dyes

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The following dyes were used:

Reactive dyes: Cibacron blue (B.E) (C.I.39) supplied by Ciba Giegy, and Levafix Brilliant Red (E-4BA) (C.I. 158) supplied by Bayer.

Seven simple mono-azodisperse dyes: p-hydroxyl azo benzene having NO₂ and Cl₂ substituents in the ortho, meta and para positions were prepared and purified in situ. Na₂CO₃ and dispersing agent (Lissapol N) were used for the dyeing processes.

Preparation of DMAE cellulose

This was prepared according to the reported Hartmann process using two different nitrogen contents (0.386-0.795)⁽¹⁰⁾.

Dyeing methods

Four groups of substrates were used in this study as follows:

- i) The first group of substrates contains CDA and PA films dyed with seven simple azo dyes at six different dye bath concentrations using the exhaustion dyeing method (group I)⁽¹¹⁾.
- ii) The second group includes cotton, viscose and wool fabrics dyed with Levafix brilliant red reactive dye using the conventional exhaustion method (group II).
- iii) The third group includes cotton modified with DMAE and finished using zinc acetate (Zn(OAc)₂) and Na₂CO₃ as catalysts and dyed with Cibacron blue reactive dye Cibacron blue with two nitrogen contents (group III).
- iv) The fourth group of nylon fabric dyed with simple monoazo disperse dye (group IV).

Testing & Analysis

a) Light exposure

Irradiation of the dyed samples was performed by using Tera Light Fastness Tester having artificial day light source⁽¹²⁾. Exposure continued for different intervals (20-160 hours) at ambient temperature of 25 ± 2°C and relative humidity of 60 ± 5%. The Blue Scale was hanged alongside with the examined samples under the same conditions for all exposure times.

b) Color strength and light fastness determination

The color strength (k/S) values for all of the examined dyed samples based on the reflection spectra at the proper wave length before and after each exposure time (20, 40, 80, 120 and 160 hours) – were determined using the Kubelka Munk equation⁽¹³⁾. The light fastness was assessed after each exposure using ASTM standard method⁽¹⁴⁾

Results and Discussion

In this work, we conducted some investigations on the light fastness ratings (L.F) of different dyed textiles and films substrates using traditional accelerated ageing methods to evaluate the precision of fading rate constant (K) in assessing the change occurring during light exposure of these dyed materials. Thus, the materials used in this study are divided into

four groups; group I: CDA and PA films dyed with seven simple mono azo disperse dyes, group II: cotton, viscose, wool dyed with Levafix brilliant red reactive dye, group III: modified cotton -using two different nitrogen contents under the effect of two different catalysts- dyed with Cibacron blue reactive dye, and group IV: nylon fabric dyed with disperse dye.

In considering the data of Fig.1 (a & b) belonging to group I, it is obvious that, the light fastness of almost all dyed films using different dye concentrations for the seven azo dyes has nearly two or three L.F. rates on the Standard Blue Scale, while on calculating K, each dye concentration represented by color strength (K/S) value has a definite K value, and in some case we can find only one L.F. rate for all the dye concentrations (K/S). Besides, the L.F. values increase with increasing dye the concentration while K takes the reverse trend, the main cause being an increase in average size of the submicroscopic particles which the dye forms in the fiber. In case of PA film (Fig. 1-a) there is a gradual decrease in the K values alongside with increasing of the L.F. values referring to homogeneity of the dye particles distribution. While, dealing with CDA film (Fig. 1-b) show that, all the dyed samples show a gradual decrease in the K values except in case of the samples dyed with m-chloroazo benzene, where there is an increase in the K values with increasing the dye concentration followed by gradual decrease which reflect the non-homogeneity of the dye particles inside the fiber pores. Moreover, in case of the samples dyed with p-hydroxy p-nitroazo benzene, the L.F. values of the dyed exposed samples are steady referring to more uniform and highly aggregated state.

As it is known, L.F. ratings increase on increasing the dye concentration, while K takes the reverse behavior. Both L.F. and fading rate constant (K) clarify the dye distribution on the samples, *i.e.* Lower L.F. means mono dispersed dye particles while higher L.F. means aggregation with different size. Also, the type of bond between the dye and substrates play an important role on both L.F. and K values. Moreover, the size of the aggregated particles evaluates the homogeneity of the distribution on the surface^(15,16).

Regarding to Fig. 2 (group II) the highest L.F. values obtained from wool fabric followed by viscose then cotton. On the other hand, it is found that there are only two L.F. ratings of the wool samples (5 & 6) with no intermediate values along the dye concentration, but in case of either viscose or cotton, there are three or four L.F. ratings with the different dye concentrations. This could be related to the large aggregates of the dye particles inside the pores of wool fabrics, as wool has the biggest pore size and light fastness of the dyed textiles which is related to the chemical structure and physical characteristics of the fiber itself. The fading on cellulose substrates may be attributed to an oxidative process, whereas on protein fibers the process has a reductive nature. The size and the form of the aggregates determine the extent of the exposed air-dye interface, and this in turn determines the rate of photodegradation⁽¹⁷⁾.

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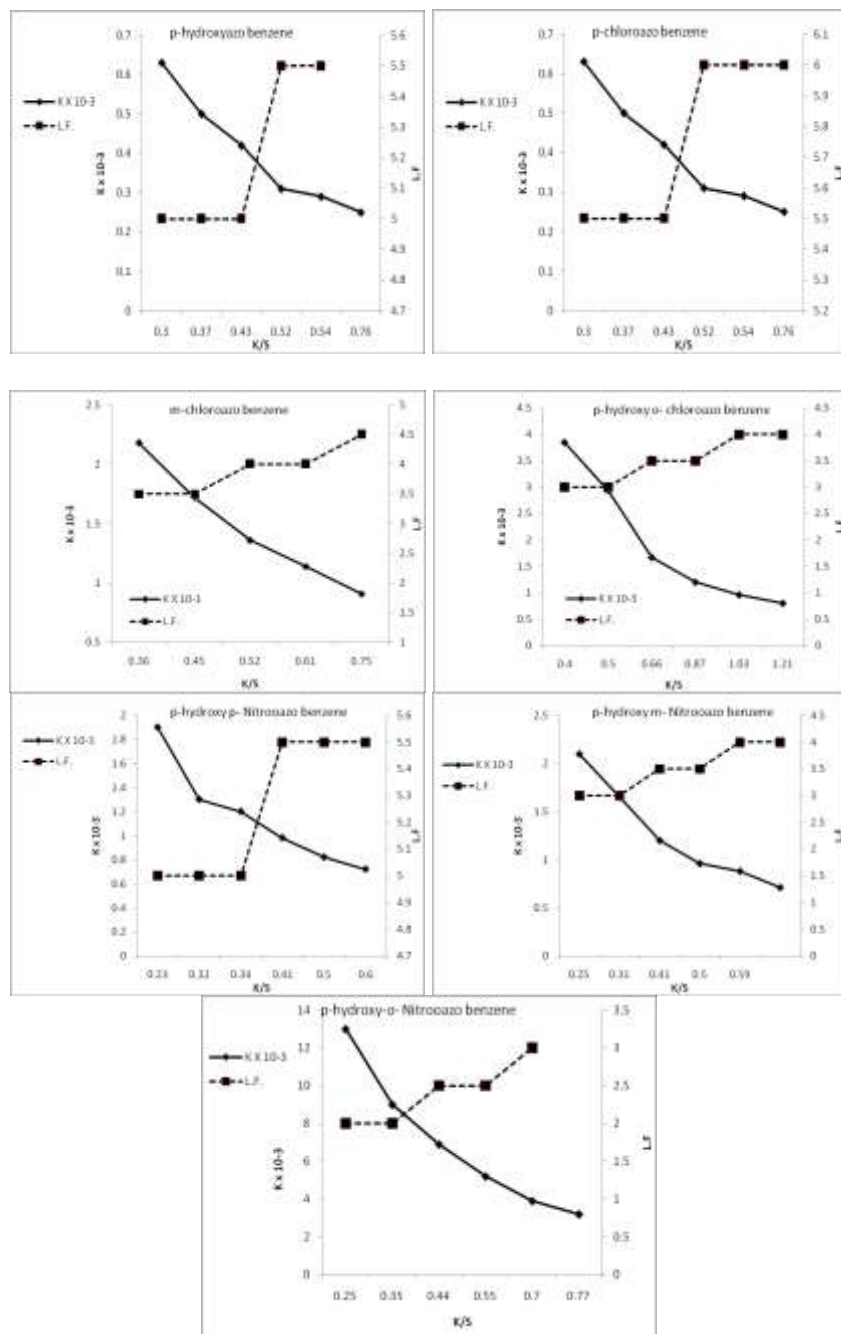


Fig. 1-a. (Group I): Variation of fading rate constant and light fastness of the poly amide (PA) film dyed with seven different disperse azo dyes using different dye bath concentrations.

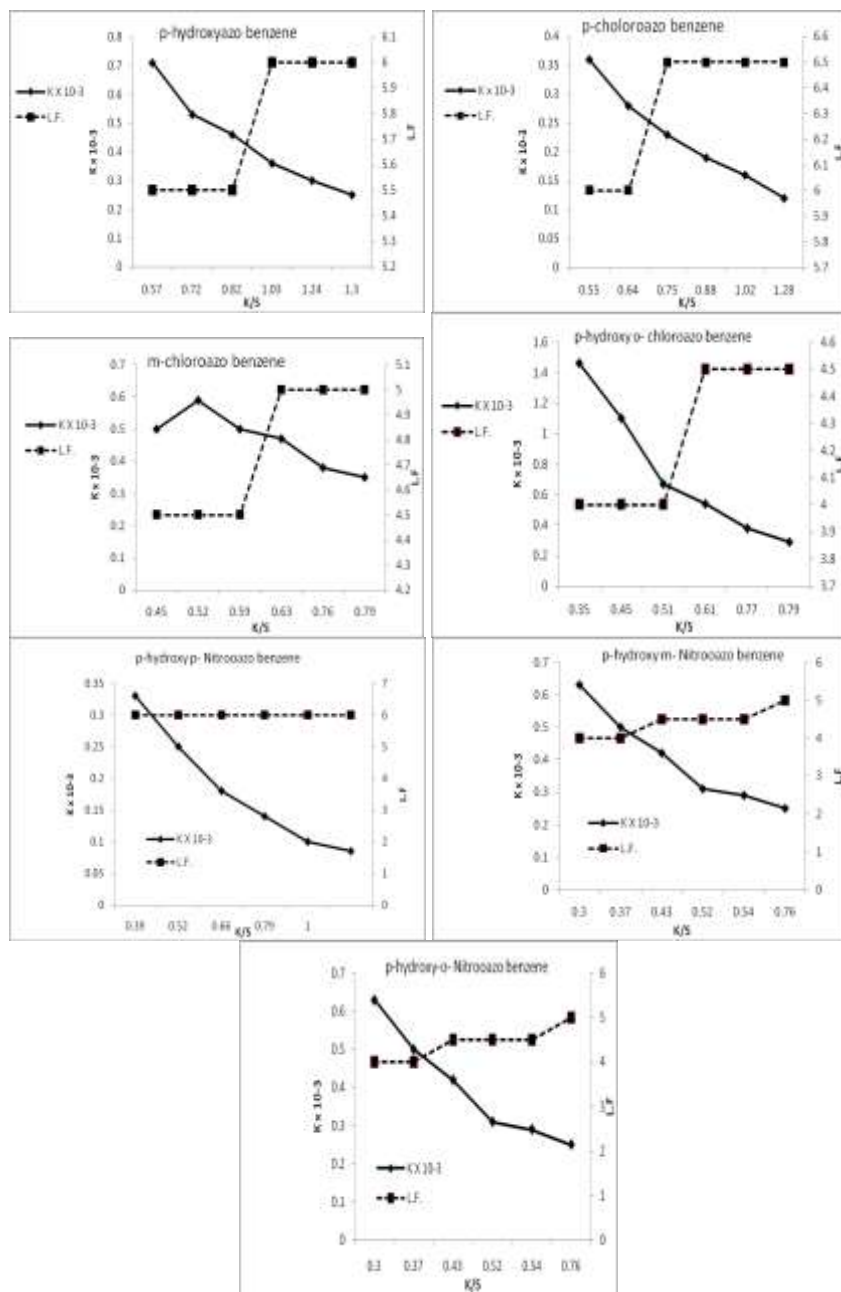


Fig. 1-b. (Group I): Variation of fading rate constant and light fastness of the cellulose diacetate (CDA) film dyed with seven different disperse azo dyes using different dye bath concentrations.

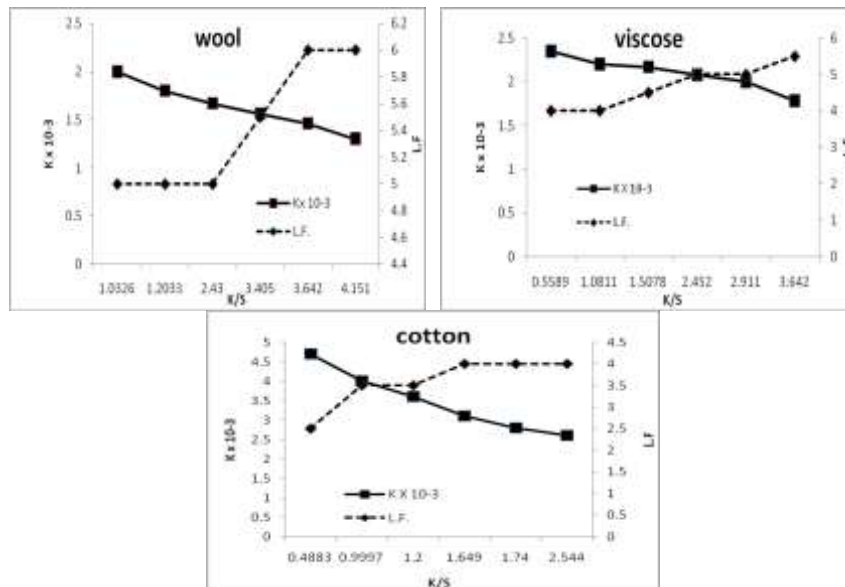


Fig. 2 (Group II): Variation of fading rate constant and light fastness of the wool, viscose and cotton fabrics dyed with Levafix reactive dyed.

When concerning group III assigned to the modified cotton fabric under the effect of two different catalysts using two different nitrogen contents, (Fig. 3 a-c), it is noticed that, the modified cotton samples having lower K values than those of the unmodified ones, meaning higher L.F values in all examined samples. This means the successes of the amination process in enhancing the light fastness of cotton samples. Also, the amination process has a clear effect on increasing fiber porosity which leads to increasing the aggregated dye particles inside the fiber pores reflecting higher L.F values. On the other hand, the samples dyed using zinc acetate as catalyst (Fig. 3c), show a dramatic decrease in K values (not a gradual one like other other modified investigated samples) accompanied by increase in the L.F values than those dyed in the presence of Na_2CO_3 as catalyst. This could be attributed to the fact that, the presence of Na_2CO_3 in the dyeing media cause dye hydrolysis leading to decreasing in the dye aggregation and so rendering the fastness of the modified samples.

The data represented in Fig. 4 (group IV) concerning nylon fabric dyed with mono azo disperse dye, depict that, the light fastness ratings are high and steady while the K values show a gradual decrease all over the dye concentrations, this again refer to the large aggregated dye particles inside the fiber pores⁽¹⁸⁾. It was presumed that the characteristics of the aggregates influence fading by influencing the aggregate lattice energy, *i.e.* the energy to break away a dye molecule⁽¹⁹⁾. The penetration of a dye into the fiber polymer structure from the dye-fiber interface is known as dye diffusion. Fick's second law states that the rate at which the dye diffuses across a unit area in the fiber is proportional to the concentration gradient across that area, the proportionality constant being the diffusion coefficient⁽²⁰⁾.

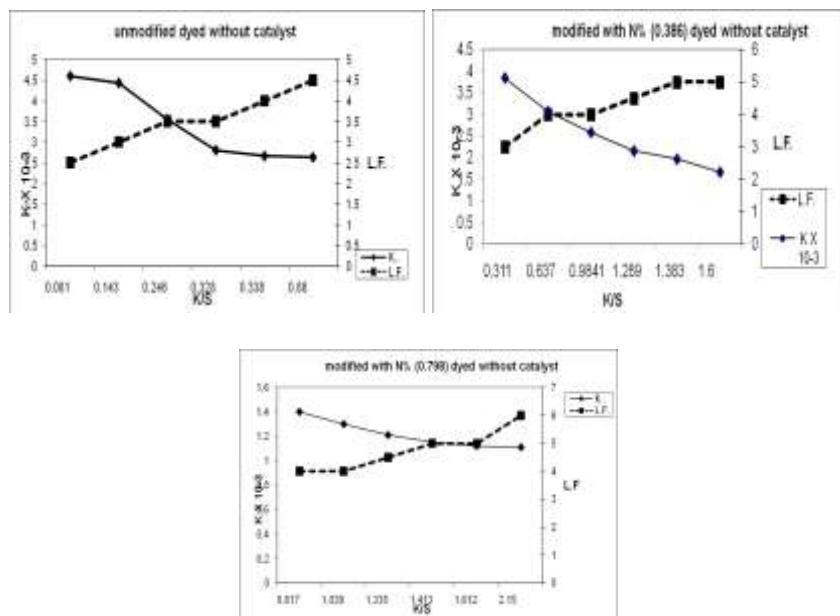


Fig. 3-a. (Group III): Variation of fading rate constant and light fastness of cotton (lino) fabric dyed with Reactive dye Cibacron blue using two nitrogen contents without catalyst.

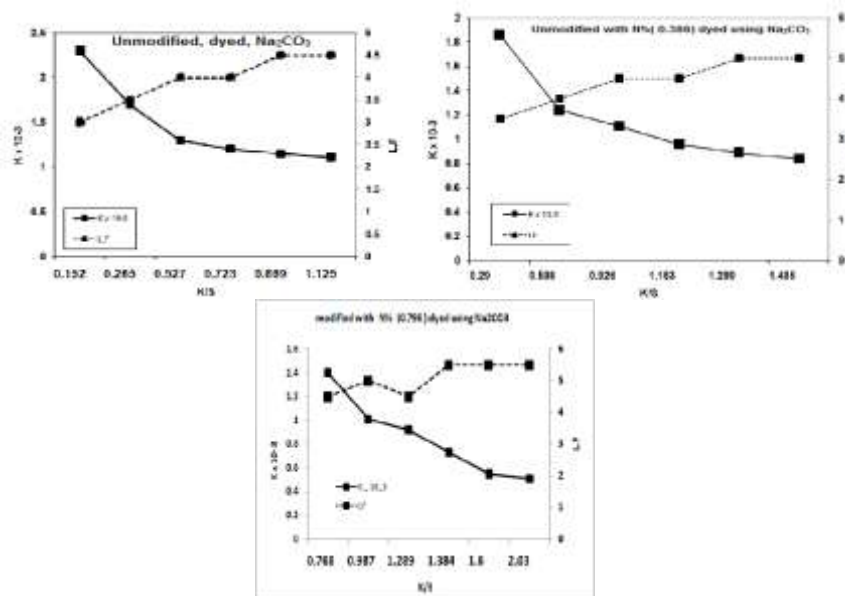


Fig. 3-b. (Group III): Variation of fading rate constant and light fastness of cotton (lino) fabric dyed with Reactive dye Cibacron blue using two nitrogen contents and Na_2CO_3 catalyst.

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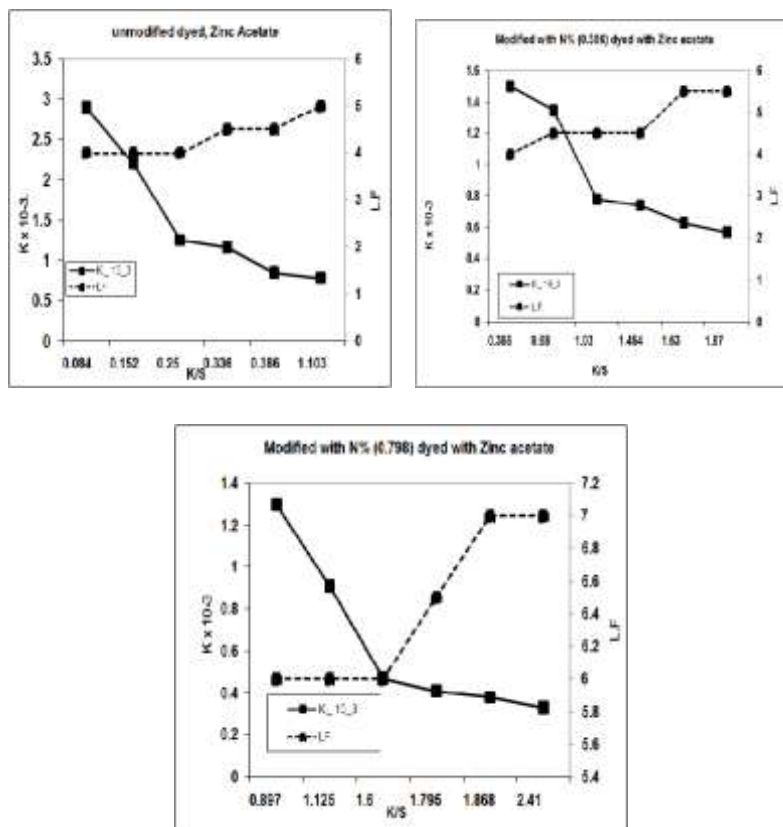


Fig. 3-c. (Group III): Variation of fading rate constant and light fastness of cotton (lino) fabric dyed with Reactive dye Cibacron blue using two nitrogen contents and Zinc acetate catalyst.

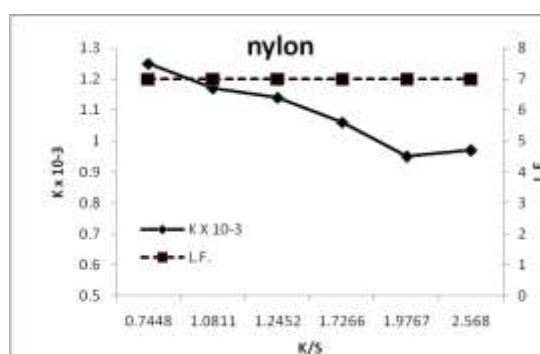


Fig. 4. (Group IV): Variation of fading rate constant and light fastness of nylon fabric dyed with simple monoazo disperse dye using different dye bath concentrations.

Conclusion

This research work aimed to find a general method to represent the fading of the dyed substrates (L.F) by taking advantage of the fading rate constant (K) values for any kind of dyed materials. PA and CDA films dyed with seven simple mono azo dyes, also wool, cotton and viscose fabrics dyed with red reactive dye were prepared. Moreover, modified cotton using two different nitrogen contents -under the effect of two catalysts- dyed with blue reactive dye, and also, nylon fabric dyed with simple mono azo dye were prepared and investigated. The relation between the L.F ratings and K values under the effect of different dye bath concentrations was represented and discussed. It was found that, regardless the type of the dyed material or the applied dye class, there is a definite fading rate constant (K) value for each dye bath concentration, while two or three light fastness (L.F) values were assessed for the same dye concentration. This result assured the fact that, the fading rate constant (K) values represent the change occurring in the light fastness much more accurate than the light fastness rating values. These variations may be attributable to the effect of dye particles aggregation and its type inside the fiber pores, which produces alterations on the perceived dye distribution (homogeneity) on textiles.

The evidence indicates that, the aggregation of the dye in a polymer substrate play an important role in controlling photofading. Generally, aggregated dyes exhibit a much higher light fastness than fully dispersed dyes.

The advantage of using this method of evaluating the color is that, it helps to explain the fading of a material in a more precise way and allows understanding of any variation that may arise during exposure⁽²¹⁻²²⁾.

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التقدير الكمي للثبات الضوئي للمنسوجات الملونة بتطبيق ثابت معدل الاضمحلال

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من المتعارف عليه ان يتم تقدير الثبات اللوني للعينات بالطريقة البصرية باستخدام المقياس الأزرق القياسي حيث لا يمكن تقدير التغير الطفيف في الالوان في كثير من الاحيان بسبب اختلاف درجة الرؤية بين الأشخاص واختلاف تركيز الصبغة مما يؤدي الى اختلاف درجات التقييم لنفس العينة باختلاف المقيم لها. ومن هنا كانت اهمية التقدير الكمي وليس البصرى للعينات المصبوغة باختلاف انواعها وذلك من خلال حساب ثابت معدل الاضمحلال

K

التجارب المعملية:

تم صباغة خامات مختلفة باستخدام فئات مختلفة من الصبغات. وتم تقسيم العينات الى اربعة مجموعات:

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المجموعة الاولى: وتشمل صباغة كل من بولى اميد وسيليلوز داي اسيتات
simple disperse azo على شكل فيلم باستخدام صبغة
المجموعة الثانية: وتشمل صباغة كل من قماش الصوف، القطن والفسكوز
red reactive dye باستخدام
المجموعة الثالثة: تشمل صباغة قماش القطن المعدل تحت تأثير تركيزين
Zinc مختلفين من النيتروجين في وجود عنصرين مختلفين كعامل حفاز
Blue reactive بصبغة Na_2CO_3 - acetate
simple mono/mجموعة الرابعة: وتشمل قماش النايلون المصبوغ بصبغة
disperse

تم استخدام ستة تركيزات مختلفة من كل صبغة على الخامات المصبوغة ثم
تعريض العينات المدروسة الى التقادم الضوئي المعجل لفترات زمنية مختلفة (20،
40، 80، 160، 120 ساعة) مع تعريض المقياس الازرق القياسى تحت نفس
لكل العينات المصبوغة والمعرضة تم K/S الظروف. بعد قياس الشدة اللونية
وكذلك حساب ثابت معدل L.F. تعيين الثبات اللوني لها بالطريقة البصرية
ورسم العلاقة بين تركيز الصبغة متمثلا في الشدة اللونية للعينات K الاضمحلال
L.F و K المصبوغة مع كل من

اهم النتائج:

كشفت النتائج التي حصلنا عليها ان:

- مهما كان نوع الخامة المصبوغة او نوع الصبغة المستخدمة فان كل قيمة من يقابلها قيمة واحدة لمعدل K/S تركيز الصبغة متمثلا في قيمة الشدة اللونية للعينات قد يتراوح بين L.F في حين ان قيمة الثبات اللوني K الاضمحلال اللوني قيمتين او ثلاثة مهما اختلف تركيز الصبغة
- تقل القيمة العددية لمعدل الاضمحلال اللوني بزيادة تركيز الصبغة في حين تزيد قيمة الثبات اللوني او تظل ثابتة لكل العينات المصبوغة
- تعد درجة تغلغل جزيئات الصبغة ومدى تجانس توزيعها على سطح الخامة المصبوغة من اهم العوامل المؤثرة على درجة الثبات اللوني لها هو الاكثر دقة عند تقدير K ولذلك فان تعيين قيمة معدل الاضمحلال اللوني مهما اختلف نوع الصبغة او نوع الخامة المصبوغة L.F قيمة الثبات اللوني