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Optical Studies of Cotton Fabrics Dyed with a Natural Dye

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

In the present work, cotton fabrics were dying with a natural colorant from Calligonum comosum plant under different conditions to determine the ultraviolet protection factor (UPF) values and the effect of light exposure and laundering on the sun blocking properties of these dyed cotton fabrics. Three different dyeing conditions, such as: different bath temperatures, different pH values of the dye bath and different dyeing times, were applying during dyeing the cotton fabrics. The role of these dyeing conditions on the UPF was examining via color strength analyses as well as their effects on the reflectance spectra were investigating using spectrophotometer tool, CIE tristimulus values and the color parameters. The dye-ability strength and fastness to light and wash of these cotton fabrics were also carrying out spectrophotometrically. The results showed that dyeing cotton fabrics with Calligonum comosum dramatically increased their protective abilities and were considering as an effective protection against ultraviolet rays. Moreover, the data obtained indicated that the optical properties are very different because of changing dye bath conditions. In addition, it was hoping that data obtained in the present study would be useful for dermatologists advising patients regarding the UV-protective properties of clothing made from natural fibers and dyed with natural colorants.

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1. INTRODUCTION

Solar ultraviolet radiation (UVR) was dividing into three parts: UV-A (400-315 nm), UV-B (315-290 nm) and UV-C (290-200 nm). These UVR were presenting in natural terrestrial sunlight in different amounts. Due to the filtering activity of the upper atmosphere, and the local conditions (latitude, altitude, clouds, etc.), UV-C and most of UV-B were filtering by the ozone layer and did not reach the earth [1]. UV-A was causing little visible reaction on the skin but was showing to decrease the immunological response of skin cells, while the rest of UV-B was most responsible for the development of skin cancer [2]. Therefore, ultraviolet radiation was considering harmful to human health.

Recently, considerable attention was paying to the barrier properties of textiles as a protection against UV radiation [3]. As the intensity of ultraviolet (UV) radiation increases every year, effective methods to block UV rays to protect human skin, plastics, timber and other polymer materials were urgently soughing. UV radiation can cause severe damage in these products in forms of discoloration, chalking and reduced mechanical properties. This situation was aggravating every year due to the recent ozone depletion caused by the increased generation of man made free radical catalyst gas molecules [4]. UVR was responsible for the generation of free radical species, such as nitric oxide, nitrous oxide and organo-halogen compounds, that they are supposed to participate in the development of various pathologies such as: cancer, aging, Alzheimer's disease inflammatory disorder, and so on. Therefore, the development of effective UV-shielding materials was of great importance to our health, society and environment.

In order to decrease the health risk due to overexposure to UV radiation, the World Health Organization (WHO) has also recommended the use of loose-fitting, full-length clothes with a high protection factor [5]. However most sport wear and light clothing commonly worn in the summer time do not guarantee an efficient shield against UV. Textiles serve as important materials for UV protection in many applications.

Textiles serve as important materials for UV protection in many applications. The UV blocking properties of textiles were improving by changing their parameters, such as: thickness, fabric opening, fiber types and colors. When radiation of specific wavelength and energy strike the fiber surface, there were three possible outcomes: The light may reflect, absorb, and/or transmit through the fibers. The amount of each depends on many factors [5-8]: (1) Fiber type (2) Fiber smoothing and porosity; and (3) The presence of different auxiliaries and finishes such as delustrants, dyes, and UV absorbers. These compounds had the ability to absorb the harmful UV radiation in the region of 250-400 nm and rapidly convert it to harmless heat.

Ultraviolet protection factor (UPF) was a scientific term used to indicate the amount of ultraviolet protection provided to skin by fabric. UPF was defining as the ratio of the average effective UV radiance calculated for unprotected skin to the average UV radiance calculated for skin protected by the test fabric. An effective UV radiation dose (ED) for unprotected skin is calculated by convolving the incident solar spectral power distribution with the relative spectral effectiveness function and summing over the wavelength range 290-400 nm [6].

One of the most important elements in the prevention of skin cancer was the use of comfortable UV-protective clothing. Owing to their low weight, cotton fabrics, and especially viscose fabrics made from filament yarns, were ideal for summer clothing and in fact enjoy a high degree of acceptance among consumers. Cotton fabrics were characterizing by a combination of properties such as abundance, fine cross section, high strength and durability, ability to absorb moisture and ease of dyeing. However, cotton had certain drawbacks, the most outstanding of which were the low wrinkle resistance and inability to maintain shape or crease. Wang et al. [9] found that summer T-shirts manufactured from white cotton and mercerized cotton print cloth offered limited protection against UV radiation as determined by spectrophotometric analysis. In addition, laundering with detergent and water improved UPF slightly by causing fabric shrinkage. Moreover, Wang and his co-workers were reporting that, dyeing fabrics or adding a UV-absorber agent during laundering substantially reduced UV transmission and increased UPF.

On other hand, inorganic UV blockers were more preferable to use in comparison with organic UV blockers, as they were non-toxic and chemically stable under exposure to both high temperatures and UV radiation. Inorganic UV blockers were usually certain semiconductors oxides, such as TiO_2, ZnO and Al_2O_3 [10-14]. It is determined that, nano-sized TiO_2 and ZnO were more efficient at absorbing and scattering UV radiation than conventional size, and were thus better able to block UV [13,14]. Therefore, UV protecting cotton fabrics were developing by the application of nanoparticles [15]. In addition, undyed fabrics showed better loading of nanoparticles as compared with the dyed fabrics, e.g., TiO_2 nanocoated fabrics were founding to be durable to domestic washing.

In the present work, cotton fabrics are dyed with a natural colorant from *Calligonum comosum* plant under three different conditions (different bath temperatures, different pH values of the dye bath and different dyeing times) to determine the ultraviolet protection factor (UPF) values and the effect of light exposure and laundering on the sun blocking properties of these dyed cotton fabrics. Moreover, the dye-ability strength and fastness to light and wash of these cotton fabrics were also carrying out spectrophotometrically.

2. EXPERIMENTAL DETAILS

2.1 Materials and chemicals

Pure cotton fabrics (100%) are kindly supplied by Golden Tex. Company, Egypt, weight 120 g/m^2 according to ASTM Test Method D3776-96 [6], thickness 0.261 mm according to ASTM Test Method D1777-96) [6], number of yarns/cm in warp direction was 30 and in weft direction was 31 (thread counts are measured according to ASTM Test Method D3775 -98) [6].

The prepared fabrics are carried in a laboratory by scouring with a solution containing 2 g/L of non-ionic detergent with liquor ratio 1:50 at 60°C for 15 minutes. Finally, the samples were washing with water, and then were drying at ambient conditions. The dye used was extracting from the barks of a plant named *Calligonum comosum*.

2.2 Extraction of Dye

Calligonum comosum plant barks were crushing and 20 g of it is weighted and dissolved in 100 mL distilled water to obtain concentrated dye solution. The solution was leaving for 24 hours for complete extraction. The dye liquor was heating slowly until 100°C then stilled at this temperature for one hour to get the required quantity of the extracted dye. The extraction is cooled, then filtrated to get rid of unwanted portions. Finally, the dye liquor was measuring to the original level by adding distilled water.

2.3 Characteristics of the Extracted Dye

Two techniques were using to identify the extracted dye:

2.3.1 Ultraviolet-visible spectroscopy

The absorbance spectrum of the extracted dye of *Calligonum comosum* plant barks allover the UV-VIS range using LAMBADA 35 Spectrophotometer, Perkin-Elmer, USA, was showing in Fig. 1. From the figure, it is clear that, the dye has maximum absorbance at wavelength (λ_{max}) = 460 nm in the visible range.

2.3.2 Fourier trans form infrared (FTIR) spectroscopy

The most characteristics functional chemical groups present in *Calligonum comosum* dye are recorded in the wavelength range 4000-500 cm^{-1} and are tabulated in Table 1 by using Nicolet 380 FTIR Spectrophotometer, USA, of 4 cm^{-1} resolution of and a number of scans of 32, with Attenuation Total Reflection (ATR) and Zinc selenide crystal.

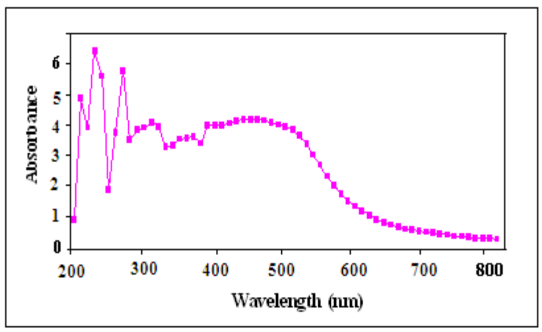

Fig. 1. The absorbance spectra of the extracted dye from *Calligonum comosum*

Since natural dyes do not have affinity for cellulosic fibers, an alum mordant was using to impart affinity. Fabrics were mordant prior to dyeing by treating with alum at boil for 45 minutes. The liquor ratio was 1:40 and alum concentration was 10% on weight of the fabric. After mordanting, fabrics were squeezing thoroughly and were dyeing using the conventional exhaustion dyeing method [16] in a laboratory dyeing apparatus.

Table 1. FTIR analysis of *Calligonum comosum* dye showing its peak intensity values of its characteristics functional bands

Wavenumber (cm^{-1})	Characteristic functional bands	Peak intensity value (%)
3411.91	O-H Stretching band	99.0
2925.54	C-H Vibration	62.0
1650.97	C=O anti symmetric stretching	100.0
1403.18	C-C benzene ring vibration	73.5
1240.53	C-O stretching vibration	63.0
1076.56	Sulpher cystine monoxide	71.5
522.44	O-H twisting	70.1

2.4 Samples

Cotton fabrics were dividing into four groups (A, B, C and D): Group A was dyeing with *Calligonum comosum* dye in a medium of pH = 7 for 60 minutes and at different temperatures 20, 40, 60, 80 and 100°C. As the dye has OH group and carboxyl group, so, the pH value of the dye bath was fixing at 7 to obtain a neutral dye bath medium. The second group (B) was dyeing by *Calligonum comosum* dye at a temperature of 100°C and for 60 minutes in a dye bath of different pH values 5, 6, 7, 8, and 9. It is preferred to dye group (B) at 100°C since higher temperature manifests the dye easily in the fabric. The third group (C) is dyed by *Calligonum comosum* at temperature 100°C and medium of pH value = 7 and for different times 15, 30, 45, 60, 75 and 90 minutes. Group D was dyeing by using three post mordents, such as: alum, $FeCl_2$, and $FeSO_4$. The fabrics of group D were introducing into the dyeing solutions at room temperature. Then, the temperature was rising to the boiling temperature and the dyeing was continuing for 60 minutes. The liquor-fabrics ratio was 40:1.

All the samples were dyeing in stainless steel canister of an ATLAS Launder Meter, and finally, the dyed samples were rinsing in de-ionized water, washed using a non-ionic detergent and air dried at ambient conditions. Three replications were doing for each dyeing condition.

2.5 Testing and Analysis

2.5.1 The ultraviolet protection factor (UPF)

To obtain meaningful of the ultraviolet protection factor (UPF) results, it was essential that samples sent for UPF testing were representative of the bulk of material. Due to manufacturing variations, UPF for one batch of material may not apply to different batches of the same material. UPF is measured using UV-VIS Double Beam Spectrophotometer (Perkin-Elmer, Lambda 35, Diffuse transmission technique) according to the American standard (ASTM D6603-2000) and AATCC test method [AATCC 183- 2000]. Then, the UPF was calculating using the following equation:

$$\mathrm{UPF} = \frac{\int_{\lambda_1}^{\lambda_2} \mathrm{E}(\lambda).\mathrm{S}(\lambda)\, d\lambda}{\int_{\lambda_1}^{\lambda_2} \mathrm{E}(\lambda).\mathrm{S}(\lambda).\mathrm{T}(\lambda)\, d\lambda} \quad (1)$$

Where: E(λ) is the relative erythermal effectiveness function, S(λ) is the solar spectral irradiance in $Wm^{-2}nm^{-1}$, T(λ) is the spectral transmittance of fabric and λ denotes the wavelength of the UV radiation (290 nm ≤ λ ≤ 400 nm). The numerator of equation (1) described the quantity of the UV radiation reached the skin if unprotected and the denominator described the quantity of the UV radiation reached the skin protected by the garment [17,18].

The UPF values were calculating for UV-A in the range 315-400 nm, and for UV-B in between 295 and 315 nm. The percent UV transmission is determined for UV-A and UV-B radiations from the transmission spectra of the cotton fabric samples from the following relation:

$$\text{Percent UV transmission} = \frac{\sum_{\lambda_1}^{\lambda_2} T(\lambda)}{(\lambda_2 - \lambda_1)} \quad (2)$$

The tested samples are classified [15,19] according to their UPF values as tabulated in Table 2.

Table 2. Sample UV protection classification according to their UPF

UPF value	UV protection
<15	Poor
15-24	Good
25-39	Very good
>39	Excellent

2.5.2 Color data analysis

2.5.2.1 Reflectance measurements

The reflection spectra of all samples in the visible range (380-700 nm) were measuring before and after dyeing using a Double Beam Recording Spectrophotometer Shimadzu UV-300 Japan attached by an integrating sphere; MgO was taking as the standard white. These reflectance spectra were using to deduce the color parameters (a, b, L and the color difference ∆E). In addition, the values of color yield or color strength (K/S) for the investigated samples were calculating from these reflectance curves.

2.5.2.2 Color strength determination

The color strength (K/S) of the dyed cotton fabrics under the different conditions of dyeing is determined from the tristimulus values of the samples measured in the visible spectrum region 380-780 nm and the reflectance percentage (R%) at the maximum absorption (460 nm) using Optimatch 3100 Spectrophotometer SDL, England. In addition, K/S was taking as a measure of dye ability. Relative color strength of the dyed cotton fabrics is determined using Kaubelka-Munk equation [20-22]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (3)$$

K is known as the absorption coefficient (is depended on the dyestuff) and S is the scattering coefficient (is depended on the substrate).

2.5.2.3 Light fastness determination

All the samples under test were exposing to artificial day light for 160 hours using Tera Light fastness Test [23] at a temperature of 25±2°C and a relative humidity of 65±5%. A standard blue scale was hanging alongside the samples. The light fastness of all the samples was assessing after exposure using ASTM Standard method Vol. 23, 1990, according to the visual assessment of inspection against the blue patterns [24]. The rating is based on the blue scale ranging from 1 (considerable change) to 8 (no change).

2.5.2.4 Durability

The durability of the treated fabrics against repeated launderings are evaluated by washing the fabric according to AATCC test method [AATCC 61(2A)-2003] using an ATLAS Launder Meter. One cycle of laundering was considering equivalent to 5 home machine launderings at 49 ±2°C for 45 minutes. The 1993 AATCC Standard Reference Detergent without fluorescent whitening agent (WOB) was using in this test method. The samples were washing 0-30 times [25].

3. RESULTS AND DISCUSSION

It is found that all the cotton fabrics dyed with the natural dye *Calligonum comosum* attained colors ranges from faint brown or brown or dark brown.

3.1 Group A

3.1.1 Reflectance percentage analysis

Fig. 2A shows the reflectance percentage (R%) as a function of wavelength for undyed (blank sample) and dyed with *Calligonum comosum* cotton fabrics of group A (samples: 1, 2, 3, 4 and 5) in a medium of pH =7 and dyeing time of 60 minutes at different dye bath temperatures 20, 40, 60, 80 and 100°C. It was clear from the figure that undyed sample has the highest reflectance value. A high drop in this value was attaining by all the samples dyed by *calligonum comosum* dye, but the sample dyed at 20°C has the highest reflectance value between the other dyed samples, all the curves of them have the same trend. Each dye has an optimum dyeing temperature and until that was attaining, dye uptake will continue to increase with increase in temperature [26], because increasing temperature reduce the aggregation in dye bath and increase the amount of dye available to the fiber in dye bath.

3.1.2 Color strength (K/S) determination

To assess the relative color strength of dyed cotton fabrics, K/S values are determined from the diffuse reflectance of the cotton fabrics measured at wavelength 460 nm (Fig. 3) using Kubelka- Munk (Equation 3). The results were tabulating in Table 3. The K/S results are similar to CIE-LAB coordinates. However, the numbers of the hydroxyl groups in cotton are much enough to attract the dye molecules and bind them through hydrogen bonding or through Van der Waal's forces to give this highest dye-ability. Also, the high value of K/S for all the samples is greatly dependent on the nature of the dye class used and can be related to the dye structure which allows forming a covalent bond between its chemical groups and non-charged or ionized hydroxyl (-OH) groups [27].

It is also clear from the figure that, the color strength (K/S) of all the dyed cotton at the different dye bath temperatures (20, 40, 60, 80 and 100°C) increases by increasing temperature. This finding can be due to a number of parameters e.g. affinity, heat of sorption and accessibility. Moreover, dyeing temperature is one of the most important parameters, which affect the exhaustion of natural dyes onto substrates. In addition, the highest (K/S) values for samples dyed at higher temperature can attribute to the fact that this dye gives a bright color at this temperature [28], besides it can be absorbed easily on cotton.

3.1.3 Ultraviolet protection factor (UPF) determination

It is clear from Table 3 that, increasing the dyeing temperature up to 80°C causes an increase the UPF value of the dyed fabrics (from good to very good) above that of the blank one (12.63, i.e., poor). Such increase in the UPF values may attribute to higher dye attraction onto the dyed fabrics and enhancing the reaction efficiency between the dye and the fabric, since enhancing the reaction efficiency was accompanying by an obvious increase in the carboxyl content of the dyed fabrics. At dye bath temperature 100°C, the dyed samples show decrease in the UPF values (27.02 in the range of good) when compared to that fabrics dyed at 80°C.

As cotton dyed samples under different dye bath temperature could be classified as having good UV protection factor (UPF values between 15 and 24) to very good UV protection factor (31.40 at 80°C). These results are in agreement with the data previously reported by Reinert et al. [29]. Reinert and co-workers showed that dark colored fabrics of cotton, silk, polyamide and polyamide/elastan gave more protection against intense UV radiation. In addition, the present data are in agreement with the data previously reported by Gies et al. [30], which indicated that dyeing fabrics in deeper shades and darker colors improves sun protection properties. Thus although the studies by Reinert et al. [29] and Gies et al. [30] are done with synthetic dyes, their conclusions seem to hold with natural colors as well.

The improvement of UV-protection property of dyed fabrics was relating to the high bulky structure effect of the natural dyes to cause blocking of the holes in the fabric to avoid the holes effect. These criteria minimized the transmission of UV-radiation through the fabric structure, i.e., better UPF rating [25,31].

3.2 Group B

3.2.1 Reflectance percentage analysis

Figure 2B represents a relation between the reflectance percentages at the visible range from which the color strength was calculating for group B. It was clear that, the values of reflectance nearly coincides at high wavelength range (620-780 nm) and then have different values at low wavelength range (380-620 nm).

3.2.2 Color strength (K/S) determination

Table 3 and Fig. 4 show the values of the color strength, which were taking as a measure for the dye ability of the examined substrates, dyed at different pH values of the dye bath. In general, it was clear that, the color strength decreases markedly by increasing the pH value [31-33]. This may attribute to the less availability of the dye molecules near the fiber, which was minimizing by increasing the pH value of the dye path. At a dye bath of pH = 8 or 9 the value of K/S show slight increase in its value but does not reach that occurred at pH = 5 or 6. The pH of dye bath was one of the most important parameter that must control to obtain good shade and wash down characteristics [32,33]. Since, some dyes were highly sensitive to pH, so, liquor used for dyeing must be buffered [34].

3.2.3 Ultraviolet protection factor (UPF) determination

Table 3 represents the effect of pH value of the dye bath on the UV protection (UPF) of the blank and dyed fabrics by *Calligonum comosum* dye. It is clear that increasing pH dye bath value leads to a decrease in the UPF values and reaches the minimum at dye bath of pH = 7. Above this pH value UPF starts to increase at pH =8 and reach higher value at pH = 9. Also, from Table 3, the dyed cotton fabrics at pH value from 6 to 9 were rated as offering very good UV-protection moved to excellent UV Protection classification with respect to cotton fabric dyed in a dye bath of pH = 5 (47,09). Again, it found that dark colors within the same fabric type transmit less UV radiation than light colors and consequently have higher UPF. Such increase in the UPF is due to the increase in the numbers of -OH molecules in the dyed fabrics.

3.3 Group C

3.3.1 Reflectance percentage analysis

Fig. 2C represents a relation between the reflectance percentages at the visible range from which the color strength was calculating for group C.

3.3.2 Color strength (K/S) determination

The color strength values K/S for group C were calculating from Fig. 2C. A relation between K/S and time of dyeing is present in Fig. 5. The color strength (K/S) of the cotton samples dyed for dyeing times 45 and 60 minutes were higher than the color strength of that dyed at 15 and 30 minutes establishing colorants resulted in deeper colors on that fabrics, K/S drops at dyeing time of 75 minutes and more drops occur at 90 minutes.

3.3.3 Ultraviolet protection factor (UPF) determination

Considering Table 3, the cotton samples dyed for different times (15-90 minutes), the increase in UPF values of dyed fabrics for times above 45 minutes was dramatic, and all of them gained excellent degree (52.05-60.37) except that at 30 minutes (very good = 37.24). The K/S values of the dyed fabrics, which are a measure of color depth, seem to support the claim that higher color depths increases UPF values (Table 3). For example, in the case of the dyed sample at pH = 5 and 6, when the K/S value increased from 2.164 to 2.320, UPF value raised from 31.31 to 47.09. However, the relationship of K/S with UPF is limited to the same fabric type and the results cannot generalize across of different weave structures [3]. A primary reason for this observation is that the UPF values are dependent on a multitude of fabric construction factors such as pores in the fabric, thickness and weight in addition to processing parameters such as dyeing and finishing. Another probable reason is the dependence of K/S on the absorbing properties of colorants in the visible region of the spectrum and that may not influence the absorption characteristics of colorant in the UPF region.

Table 3. Variation between K/S and UPF values for the four studied groups

Samples conditions	UPF	K/S at λ=460 nm
Dyeing temperature (ºC)		
20	12.63	0.926
40	21.63	2.153
60	28.29	2.949
80	31.40	2.877
100	27.02	3.123
pH value		
5	47.09	2.32
6	31.31	2.164
7	25.97	1.737
8	28.55	1.577
9	37.63	1.633
Dyeing time (minutes)		
15	52.05	4.664
30	37.24	4.422
45	58.74	5.001
60	59.22	8.14
75	60.37	5.549
90	56.62	3.234
Cotton + alum	21.92	1.312
Cotton + $FeCl_2$	33.39	1.537
Cotton + $FeSO_4$	24.97	1.962

3.4 Group D

3.4.1 Reflectance percentage analysis

A relation between the reflectance percentages at the visible range from which the color strength was calculated for group D is represented in Fig. 2D.

3.4.2 Color strength (K/S) determination

With respect to the K/S values of group D which contains cotton fabrics dyed with *Calligonum comosum* dye then mordant with different mordants (Fig. 6),calculated from the relation presented Fig. 2D, it is noticed that all these values are less than those of the above three groups. The highest K/S value was relating to $FeSO_4$ mordant, this is clear in its fabrics color; mordant dyed cotton fabrics with alum have the lowest one. K/S values of the dyed cotton fabrics mordant with $FeCl_2$ are located between the two above-mentioned mordant.

3.4.3 Ultraviolet protection factor (UPF) determination

By following UPF values of these three samples, it is noticed that dyed cotton fabrics by *Calligonum comosum* and mordant with $FeCl_2$ has the highest UPF value (33.39 - very good), while those mordant with alum has good values (21, 92 and 24.97, respectively), i.e., UPF values of this group range from good to very good. No relation given to relate between K/S values and UPF values for these dyed mordant cotton fabrics.

Metallic salt mordant are commonly responsible for the formation of co-ordinate bonds with the functional groups of dye molecules and the textile substrate [35]. In addition, it is observed that, mordant may increase, dye exhaustion; shade variation; fastness and other fiber properties [36,37]. The use of metallic mordant introduced an additional role in the functional treatment of textile materials.

3.5 Percentage UV-A/UV-B ratio

The percentage of UV-A and UV-B transmission values were using to calculate the UPF values and sometimes useful in better understanding the sun protective properties of fibers. An in-depth examination of the UVR transmission data afforded little attention insight into the sun blocking of these cotton fabrics.

The values of the ultra protection factor (UPF) and the percent of UV transmission for UV-A and UV-B ranges were calculating using Equations 1 and 2, respectively, and tabulated in Table 4. The values reflect the higher protection against UV radiation provided by dyeing the cotton fabrics by this natural dye (*Calligonum comosum*).

It is clear from Table 4 that, since for all the dyed fabrics, the relative erythemal spectral effectiveness is higher in the UV-B region compared to the UV-A region, the UPF values depend primarily on transmission in the UV–B region. Group B fabric has significant transmittance and consequently a low UPF value (only good).

As is evident from the transmission data and the corresponding UPF values all the dye conditions used in the study caused a dramatic reduction in UV radiation transmission through the dyed cotton fabrics. The increase in UPF values in the presence of colorant was especially significant for the cotton dyed samples for different dye time (15-90 minutes) which were classified as having excellent UV protection (UPF values 40 or greater). Therefore, undyed fabrics offer much lower protection against UV radiation if any in comparison with dyed fabrics. Dyes react like additives, and improve UV protection abilities, because they absorb UV radiation in the visible and UV radiation band.

3.6 Durability

3.6.1 Color fastness

The obtained data indicated that, the four groups of the cotton fabrics dyed with *Calligonum comosum* have color fastness ranges between 5 and 7.

The color fastness of colored textile defined as its resistance to change in hue, value and chroma when subjected to a particular set of conditions, e.g., light, washing, respiration, rubbing, etc. The character of bonds between the dye and the fiber were influence the dyeing light fastness to the extent that this bond may serve as a bridge for transferring the excitation energy between the two components of the dye-fiber system. The stronger of the formation of bond between the dye and the fiber, the greater was the light fastness of the dyed substrate and the easier of the transfer of excitation energy from the dye molecule to the fiber [24,25,38]. If this bond promotes energy transfer, the light fastness increases and if it impedes the energy transfer, the light fastness decreases. The hue of the fibers in most cases becomes deep. Single dye may have different light fastness on different fibers. The light fastness increases with increase in crystallinity of the dyed fiber by virtue of diffusion restriction effect, which lowers the rate of water vapor or air (or both) transported to the excited dye molecules.

A general rule followed the most dyes is that the light fastness improves with rise in fiber treatment and the amount of voids present on its surface, the greater the voids volume the higher the light fastness of the dyed fiber due to increase association of the particles [5].

The strength and amount of the covalent bonding formed between the dye and the substrate had affected considerably the light fastness property. In case of cellulose the dye, a primary OH groups, covalently bond which has in its chemical constituents anthraquinones and flanovonids.

The stronger the covalent bond the higher the aggregation of dye molecules in the substrate and the more the consumption of the activation energy for dissociating the bond and consequently the less observing fading.

3.6.2 Wash fastness

The factors affecting light fastness of the dyed materials have a similar effect on the washing fastness properties but the physical chemistry determining washing fastness properties is simpler. It observed that some natural dyes, which contain ionizable carboxyl groups undergo marked change in hue rather than a reduction in the original color, this is due to the high pH of soap solution used in washing test. The affinity of dyes for fabrics reduces the rate of absorption and desorption from the fabric. The dye attractive forces tend to keep the dye molecules attached to the fabric and retard their diffusion along the pores of the fabric [39].

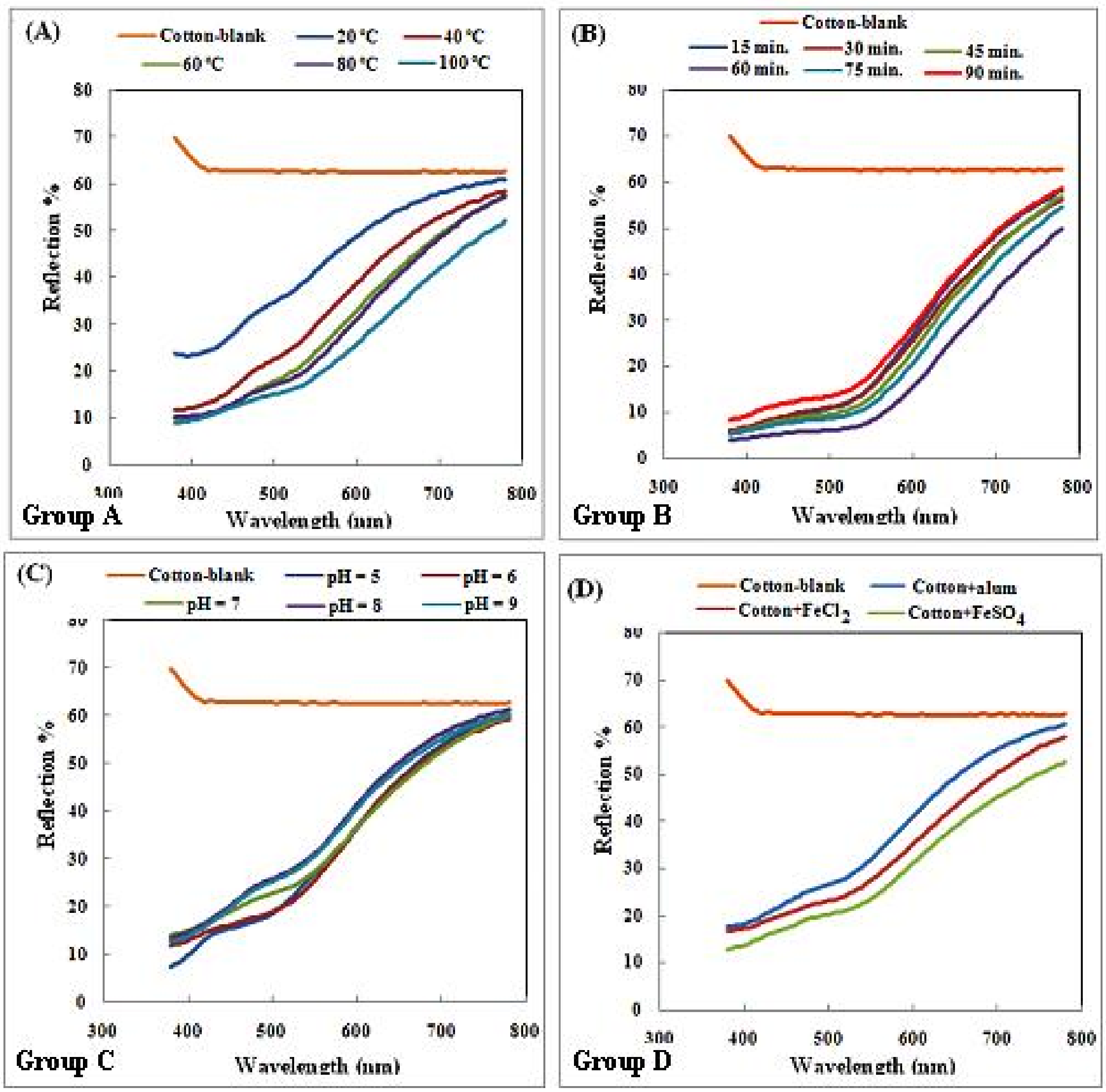

Fig. 2. Relation between reflectance percentage and different dyeing conditions for groups A, B, C and D

Table 4. The percent UV transmittance for the four cotton fabrics groups

Samples condition	UV transmission %		UV-A/UV-B
	UV-A	UV-B	
Blank	48.85	43.48	1.123
Dyeing temperature (°C)			
20	7.78	9.14	0.851
40	4.45	5.11	0.871
60	3.4	3.71	0.916
80	3.03	3.36	0.902
100	3.52	3.88	0.907
pH value			
5	1.95	2.52	0.774
6	2.97	3.95	0.752
7	2.61	3.25	0.803
8	3.33	3.93	0.847
9	2.49	3.04	0.82
Dyeing time (minutes)			
15	1.81	1.99	0.91
30	2.59	2.78	0.932
45	1.60	1.56	1.026
60	1.58	1.5	1.053
75	1.56	1.59	0.981
90	1.66	1.81	0.917
Cotton + alum	4.38	5.37	0.816
Cotton + $FeCl_2$	2.84	3.41	0.833
Cotton + $FeSO_4$	3.82	4.73	0.808

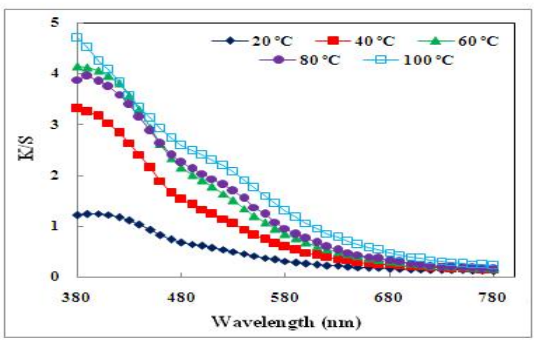

Fig. 3. Relation between K/S values and dyeing temperature for group A

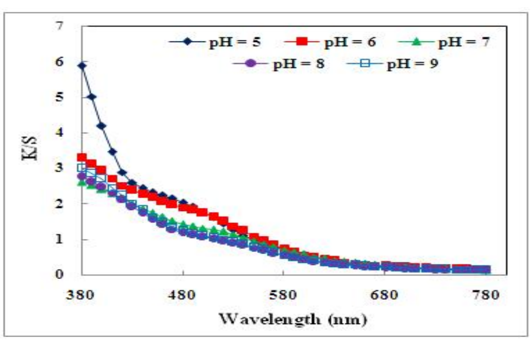

Fig. 4. Relation between K/S and pH values for group B

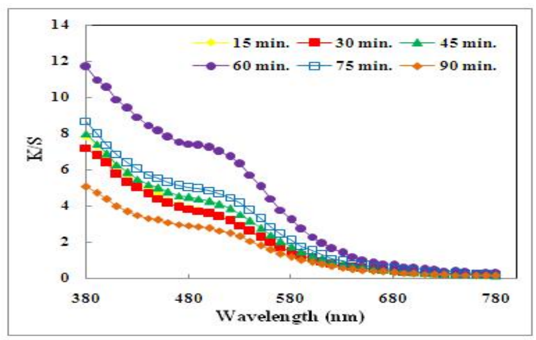

Fig. 5. Relation between K/S for different dyeing time for group C

Generally, in natural dyes, it is possible to combine good washing fastness with good fastness to light. The rating f washing was doing on the bases of the change of color as well as the staining on the adjacent fabrics. The washing fastness grade was assessed via the gray scale which ranges from 1 to 5), where 5 (excellent), 4 (good), 3 (fair), 2 (poor), and 1 (very poor), while, the staining 5 (negligible or no staining), 4 (slightly staining), 3 (noticeable staining), 2 (considerable staining), and 1 (heavy staining). Several samples undergo tone change on washing. The poor washing fastness may be due to the washing off, the uncomplexed dye from the fabrics or due to some reaction between dye and soap solution used for washing.

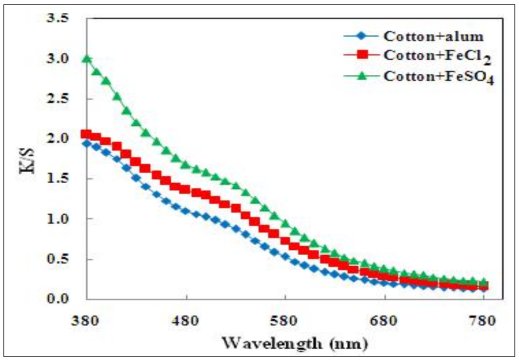

Fig. 6. Relation between K/S and different mordants (group D)

The obtained results showed that all samples dyed with *Calligonum comosum* had acquired washing fastness between 3 and 4 and staining between 2 and 3.

UPF of the all dyed fabrics were monitoring as a function of repeating washing cycles. Analysis of UPF values of the four groups shows that neither light exposure nor laundering significantly affected its mean UPF value. Despite some shrinkage, cotton samples is so transparent to UVR radiation that its UPF remains virtually unchanged by the shrinkage associated with laundering.

Comparison tests, performed to determine where significant difference existed, showed that laundering resulted in marginal increases in the UPF values for all of the examined cotton fabrics. The increase in UPF and decrease in the percentage of UV-A and UV-B transmission values following laundering the fabrics may attribute to shrinkage, which reduced fabric porosity as previously reported by Algab et al. [6].

4. CONCLUSIONS

From the obtained results, it can be concluded that:

- *Calligonum comosum* plant in the form of barks is a new eco- friendly natural dye. This plant was using to dye cotton fabrics, which help avoiding synthetic dyes disadvantages. Limited legal environmental conditions were following with low costs, and the procedures of dyeing were applying easily.
- UPF and K/S were determined by spectrophotometric tool which shows accurate values, these measurements can be used for improving cellulosic fabrics characteristics
- In this study, the UPF was calculating using UV diffuse transmission measurements.
- The intensity and percent transmission of UV-A through the fabrics used in this study are substantially greater than that of UV-B.
- The UV tests indicate a significant increment of the UV absorbing activity in the dyed cotton fabrics such results can exploit for the protection of the body against radiation.
- The dyed cotton fabrics with this natural dye show good light fastness. Moreover, the dyed fabrics were laundering up to 30 washing cycles without reduction in UPF values at the different dyeing conditions.
- It was hoping that data from this study would be useful for dermatologists advising patients regarding the UV-protective properties of clothing made from natural fibers and dyed with natural colorants.
- Further studies needed to elucidate the relative roles of UV-A and UV-B in causing human melanomas and no melanoma cancers of the skin.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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