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Characterization of a new natural dye applied on wool fabrics

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ABSTRACT

The present work involves the dyeing of pure wool fabrics with a natural dye extracted from the violet flowers of Calotropis procerea plant Erichrome black T as a pre-mordant. The effect of dyeing time, temperature and pH value of the dye bath, using, on the reflectance spectra of the fabrics was followed using spectrophotometer tool and CIE tristimulus values. The color yields of the dye on the wool fabrics were found to be highly dependent on these different dyeing conditions. The beneficial effects of varying conditions of dyeing on the color parameters L, a, b, h, c and the change in color difference (ΔE) were also investigated. Light and washing fastness were carried according to ISO standard recommendations to evaluate the amount of fading in terms of color difference to deduce the influence of dye-fiber bonding. The Fourier transform infrared (FTIR) spectra of dyed wool fabrics were followed at each dyeing conditions. The results indicated that, the behavior of the change in the peak intensity values of different functional groups present in the wool fabrics are completely different by changing dyeing conditions. The obtained results indicate that the improvement in dyeing process may be due to the change in the molecular configuration as a result of the variation in the chemical bonds in wool fabrics, the dye and/or the mordant. This means that the increase in the amorphous region of the dyed samples, the oxidation of the cystine linkage on the surface of the wool fabrics, and the formation of free-radicals species encouraged dye penetration and aggregation inside the fiber pores as well as bond formation. The standardization of dyeing and mordanting mechanisms are discussed, as well as the evaluation of the dyeing parameters and fastness properties and reported CIELab data.

KEYWORDS

Calotropis procerea plant;
Wool fabric;
Optical properties;
Dyeing conditions.

INTRODUCTION

Wool is the fiber from the fleece of the domesticated sheep. It is a natural protein, multiple cellular, subtle fibers; its density is 1.31 g/cm^2 which tends to make wool as a medium weight fabric. The wool fabric is a crimped, fine to stick, regular fiber. Wool fiber may be varying from off-white to light cream in color. This variation in color is due to the disulphide bond, which seems to be able to act as chromophores. When the fiber is cream to dark cream in color, this is due to polymer degradation on the surface of the fiber, as the wool polymer is chemically very sensitive to atmospheric oxygen and air pollutants. Brown, yellow, orange, or green wool can be obtained by using natural plant dyes[1]. Recently, wool has been used as an adsorbent to remove heavy metal pollutant from industrial effluents and to purify contaminated water supplies.

Natural dyes have been used for many purposes such as coloring of natural fibers: wool, cotton and silk as well as fur and leather. The dyes were also used to color cosmetic products and to produce inks, watercolors and artists paints. The use of natural dyes declined rapidly after the discovery of synthetic dyes. An international awareness of environmental, ecology and pollution control created an upsurge in the interest in natural dyes. The dye industry is more forced to reduce toxic effluents and stop the production of dangerous dyes or pigments. Natural dyes/colorants derived from flora and fauna are believed to be safe because of their non-toxic, non-carcinogenic and biodegradable nature. They do not cause pollution and waste water problems and represent more environmentally friendly alternative to synthetic dyes. Some of them have reported to possess anti-UV and anti-microbial properties[2].

Synthetic dyes cause skin complaints and illness and cancer, and some cases of dermatitis and respiratory sensitivity have been reported. Consumers require safer clothing products especially for babies and children.

Natural dyes and dyeing process were studied together with finding the optimized process in terms of resource use, quality of goods, energy and water consumption and environmental aspects to meet the demand of both industry and consumers. The requirement of using natural colorants in textile sectors are quality of color including color shade, fastness properties as well as color appearance in terms of reproducibility and economic benefit for example, acceptable costs for process engineering and dyeing process[3,4]. An important aspect in the selection of a certain source of plant material is the maximum color depth that can be achieved. Higher color depth is expected from an increase in extract concentration and the use of high concentration of mordents[5].

The buying decision of consumer depends on the emotional component. Consumers associate natural dyes with health and color aspects and can be represented as ecological awareness, responsibility and fairness. However consumers still concern about natural dyes in terms of causing allergic reaction and fastness properties[6]. Natural dyes have a limited range of color. The introduction of hybrid dyeing concepts allows widening the range of available colors.

The aim of the present work was to study the effects of dyeing time, dye bath temperature, and the pH value of the dyeing medium of wool fabrics by means of spectrophotometer tool and CIE tristimulus values: reflectance percent (R%), relative Lightness (L), color parameters such as: red-green parameter (a), yellow–blue parameter (b), hue (h), chromaticity (c) and color difference (ΔE). In addition, new color centers in the investigated dyed wool fabrics are formed as a result of the change in the chemical bonds between Calotropis procerea dye, the fixing agent and the fabric samples which cause a change in the molecular configuration of the wool fabrics.

EXPERIMENTAL

Materials

Pure wool fabric (100%, weight 137 g/m^2, thickness ~ 0.35 mm, number of threads in weft direction 25 and in wrap direction 30 were used in the present study and was supplied by Goldentex Co. (Cairo – Egypt). The fabric was scoured with a solution containing 0.5 g/L of sodium carbonate and 2 g/L of non-ionic detergent using liquor ratio 1:50 at temperature 60 ºC for 15 minutes. Finally, all the samples were thoroughly washed with tap water and dried at ambient conditions.

The dye used was extracted from the violet flowers of Calotropis procerea plant. The leaves of this plant produces yellow colors, while the flowers used in this study give degraded shades of violet colors according the dyeing conditions.

Extraction and preparation of the dye[7,8]

Adding 20 g of Calotropis procerea (CP) crushed flowers to 100 mL distilled water give aqueous extract of the dye. The mixture was stirred, heated and hold to boil for 30 minutes, allowed to stand for 15 minutes and then filtrate to drain off undesired portion. The filtrate was used for dyeing; dyeing was carried out at 60 ºC for one hour using liquor ratio 1:50. In case of mordanting, pre-mordanting was chosen as the most suitable process.

Identification of extracted dye

The extracted dye was identified by characterization through various techniques:

Ultraviolet-visible spectroscopy: The absorbance spectrum of the extracted dye of Calotropis procerea flowers allover the UV-Vis range using LAMBDA 35S Spectrophotometer-Perkin Elmer, USA, is shown in Figure 1. The dye has maximum absorbance at wavelength (λ_{max}) = 310 nm in the UV range and of absorbance 4.3557. Most of the violet dyes showed a similar spectrum in the near of visible range.

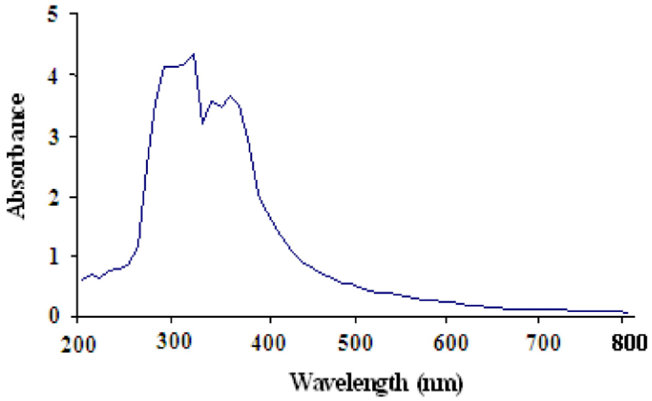


Figure 1 : The absorbance spectrum of extract of Calotropis procerea flowers natural dye allover UV-Vis range

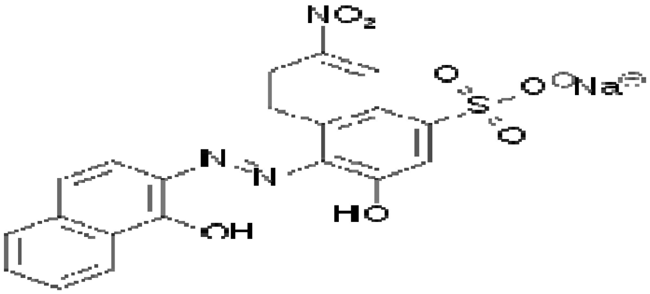
Fourier transform infrared (FTIR) spectroscopy: The FTIR spectrum of extracted and purified dye is recorded using Perkin-Elmer Spectrophotometer model 1650–USA with a wavelength range of 4000-500 cm^{-1}, and the most characteristic functional chemical groups present in the dye are tabulated in TABLE 1. Also, the wool fabrics samples under investigation were analysed for their chemicals groups by the same spectroscopy.

TABLE 1: The peak intensity values characteristic functional bands of Calotropis procerea natural dye

Wavenumber (cm^{-1})	Characteristic functional bands	Peak intensity values (%)
3409.53	OH-stretching band	75.76
2926.45	CH-vibration	88.36
2359.48	CH_2 symmetric stretching	98.41
1731.76	C=O stretching vibration	94.12
1623.77	Carbonyl bond C=O antisymmetric stretching	86.24
1421.28	C-C benzene ring vibration	89.74
1240.00	C-O stretching vibration	93.01
1053.91	Sulpher cystine monoxide	82.34
607.467	OH-Twisting	92.80

Dyeing and fixing methods

The wool samples under test were separately dyed by the pre-extracted dye in a laboratory dyeing apparatus using the conventional exhaustion dyeing method. To obtain better results the wool samples were pre-mordanting at 40 ºC for 60 minutes using an exhausting agent Erichrome black T mordent (0.1%) with liquor ratio 1:50 then the samples were removed, squeezed and air dried[9]. Some information about the pre-mordant is found as:



Eriochrome Black T

IUPAC name

Sodium4-[(1-hydroxynaphthalen-2-yl-hydrazinylidene]-7-nitro-3-oxo-Y-naphthalene-1 sulfonate

Systematic name

Sodium4-[2-(1-hydroxynaphthalen-2-yl)hydrazin-1-ylidene]-7-nitro-3-oxo-3,4-Dihydronaphthalene -1-sulfonate Sodium 4-[2-(1-hydroxynaphthalen-2-yl) hydrazin-1-ylidene]-7-nitro-3-oxonaphthalene-1-sulfonate

Molecular formula	$C_{20}H_{12}N_3O_7SNa$
Molar mass	**461.381 g/mol**

AppearanceDark red/brown powder

The Pre-mordantd wool fabrics were subdivided into three portions. One portion (group I) was dyed by Calotropis procerea dye in a medium of pH = 7 for 60 minutes and different temperatures 20, 40, 60, and 80 ºC. The second portion (group II) was dyed by calotropis procerea at temperature 60 ºC and medium of pH = 7 and at different times 15, 30, 45 and 60 minutes. The third portion (group III) were dyed by Calotropis procerea dye at a temperature of 60 °C for 60 minutes in a dye bath of different pH values 5, 6, 7 and 8.

Optical measurements

To determine color quality, color measurements permit an assessment of the color of the dyed samples. The CIELab coordinates describe the Color parameter of dyeing: L value defines lightness (with values from 100 to 0 representing white to black respectively), 'a' value denotes the red/green value (positive sign = red and negative sign = green) and 'b' the yellow/blue value (positive sign = yellow and negative sign = blue), the color difference (ΔE), 'c' value (chroma) is a measure of saturation of color and h (hue angle) is derived from the two coordinates a and b which are related to perceived color[10-12]. The relative brightness value (y_r) was given by the multiplication of luminance factor and reflection at the wavelength in the range (380-780 nm) according to the CIE. Four measurements were made on each of the samples and the variation in the percentage reflection values over range of 400-700 nm was recorded. The color difference (Δ E) was evaluated spectrophotometerically via CIELab system from the following equation:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{½} \qquad (1)$$

where $\Delta L = L_s - L_r$, $\Delta a = a_s - a_r$ and $\Delta b = b_s - b_r$, s and r represent the sample and the reference specimens, respectively.

Color data analysis

The color strength (K/S) of the dyed and dyed mordanted fabrics under the previous different conditions was determined from the tristimulus values of the samples measured in the visible spectrum region 380-780 nm and the reflectance (R%) at the maximum absorption (λ_{max} = 320 nm) using Optimatch 3100 Spectrophotometer, SDL, England and was taken as a measure of dyeability. Relative color strength (the color yield) of the dyed fabrics was determined using Kubelka–Munk equation[13,14]:

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

K is known as the absorption coefficient (is dependent on the dye stuff) and S is the scattering coefficient (is dependent on the substrate).

Fastness determination

The durability of dyed wool fabrics was also evaluated in terms of fastness towards lighting, using the blue scale according to ISO105-B02 standard recommendations. Light fastness is the resistance of a material to a change in its characteristics as a result of light exposure. The fastness grade is evaluated by comparing the color change of the test specimen to that of a simultaneously exposed blue wool light fastness standards[10].

Wash fastness tests were carried out according to the ISO105-C10 method. A specimen of the textile in contact with one or two specified adjacent fabrics is mechanically agitated under specified conditions of time 30 minutes and 50 °C for temperature in a soap or soap and soda solution, then rinse and dried. The change in the color of the specimen and the staining of the adjacent fabric were assessed with the reference to the original fabrics, using the grey scale or instrumentally.

RESULTS AND DISCUSSIONS

Fourier transform infrared (FTIR) spectroscopic analysis

Fourier transform infrared spectroscopy (FTIR) has long been recognized as powerful tool for elucidation of structural information. The position, intensity, and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers at the molecular level. FTIR generally, infrared radiation ranges from 10.000 to 100 cm^{-1} is absorbed and converted by an organic molecule into energy of molecular vibration. The main two types of molecular vibration are stretching and bending. Stretching vibration is a rhythmical movement along the bond axis resulting in an increase or decrease of the interatomic distance. While bending vibration results from a change in the bond angle between bonds with a common atom. Only those vibrations that result in a rhythmical change in the dipole moment of the molecules are observed in the IR spectra and is a point of interest[15].

The FTIR spectra of the dyeing and mordanting of wool fabric in the wavenumber range 4000-500 cm^{-1} are shown in Figures 2a, 2b and 2c. From the figures, it is noticed that, wool spectrum exhibits broad band near 3450-3370 cm^{-1} due to the OH–stretching vibrations of free and hydrogen bonded groups (most probably due to the humidity absorbed by the KBr during the preparation of the pellets). Also, the band in the region 1699-1650 cm^{-1} is most probably due to the same cause. Absorption arises from CH stretching occurs in the region of 3020-2750 cm^{-1} which contains two distinct peaks at 3012 and 2940 cm^{-1} resulting from asymmetrical stretching modes of CH bonding, respectively.

Spectroscopic technique has been employed to study the effect of dyeing and mordanting of wool fabric on the peak intensities of different functional groups present in that fabrics. TABLE 2 shows the change in peak intensity values of the major absorption bands relating to the main functional groups existing in wool fabrics. On comparing the behavior of the characteristic bands during the different condition of dyeing and mordanting, they are completely different due to the effect of dyeing process in changing the nature of the fabric constituents[16].

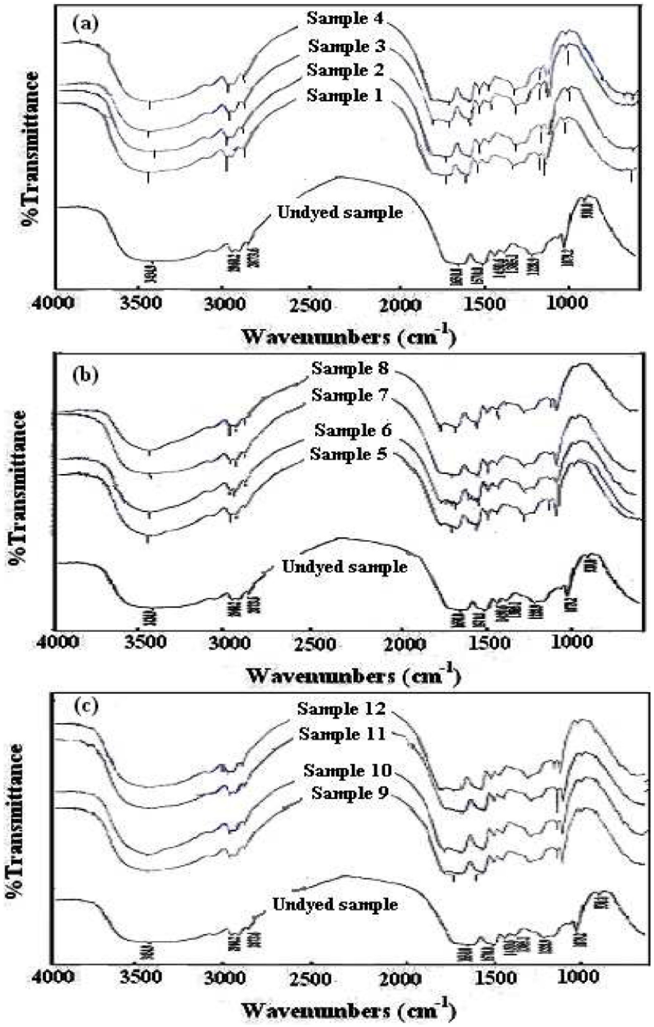


Figure 2 : Variations in FTIR spectra of wool fabrics : (a) Group I, (b) group II and (c) group; III

By following the variation in the peak intensities of the wool fabrics chemical functional groups, it can be deduced that:

For the assignment of the chemical group 3450-3370 cm^{-1}:

Group I:

The highest intensity of it is that for sample 1 (20 °C) followed by sample 4 (80 °C) followed by sample 3 (60 °C) and the lowest intensity is that for sample 2 (40 °C).

Group II:

The highest intensity values of this chemical group follow the order: sample 6 (30 minutes) > sample 8 (60 minutes) > sample 5 (15 minutes) > sample 7 (45 minutes).

Group III:

Sample 10 (pH = 6) has the highest intensity for this chemical group then sample 11 (pH = 7) then sample 12 (pH = 8) and the lowest intensity is that for sample 9 (pH = 5).

For the assignment of the chemical group 3020-2750 cm^{-1}:

This functional chemical group has the same trend as that for the above one.

For the assignment of the chemical groups 1699-1650, 1600-1540 and 1200-1190 cm^{-1}:

For wool fabrics groups II (change in time) and group III (change in pH value), their chemical groups take the same order that for the two above chemical assignments, while group I takes the order as: sample 3 (60 °C) > sample 1 (20 °C) > sample 4 (80 °C) > sample 2 (40 °C).

For the assignment of the chemical group 1120-1070 cm^{-1}: For this chemical group, the peak intensity for wool fabric of group III (change pH value) has the same trend as the other above chemical groups. Wool

TABLE 2 : The peak intensity values characteristic functional bands of dyeing and mordanting of wool fabrics

Dyeing conditions		Sample	Peak intensity values of the fundamental groups							
			520.6 (cm^{-1})	930.8 (cm^{-1})	1079.2 (cm^{-1})	1228.9 (cm^{-1})	1570.0 (cm^{-1})	1650.0 (cm^{-1})	2960.2 (cm^{-1})	3434.9 (cm^{-1})
		Blank	**9.53**	**25.26**	**12.72**	**10.78**	**8.32**	**8.22**	**11.62**	**8.89**
Dyeing temperature (°C)	20	1	33.25	52.58	39.29	35.68	31.75	31.37	38.62	33.05
	40	2	26.54	48.37	34.77	28.02	23.62	23.63	30.06	25.04
	60	3	37.98	57.77	45.05	38.19	33.47	32.81	35.79	29.44
	80	4	32.83	54.88	42.02	34.81	30.49	30.62	36.15	30.12
Dyeing time (minutes)	15	5	30.37	50.39	37.08	32.32	28.36	27.31	32.15	24.65
	30	6	49.37	-	51.67	51.46	47.68	46.66	51.02	43.98
	45	7	17.83	-	21.54	20.81	17.15	16.91	22.31	17.53
	60	8	50.46	-	54.32	50.63	46.53	45.11	45.24	36.92
pH value	5	9	26.60	46.35	32.24	28.02	24.05	23.74	30.03	24.94
	6	10	45.30	61.14	49.01	45.48	41.66	40.97	46.58	40.09
	7	11	33.25	52.58	39.29	35.68	31.75	31.37	38.62	33.05
	8	12	28.83	47.62	33.56	28.71	24.28	24.50	30.63	25.65

fabric group I (changing temperature) has the peak intensities of values: sample 3 (60 °C) > sample 4 (80 °C) > sample 1 (20 °C) > sample 2 (40 °C). Group II follows the order sample 8 (60 minutes) > sample 6 (30 minutes) > sample 5 (15 minutes) > sample 7 (45 minutes).

In addition, it is noticed from TABLE 2 that, strong local interaction between the dye and other groups to different chains in wool will take place at the expense of the intermolecular interaction between these chains.

Optical measurements

Group I

The diffuse reflectance percentage (R%) as a function of wavelength in the visible range 380-780 nm for dyed wool fabrics group I (including samples 1, 2, 3 and 4), which is dyed by Calotropis Procerea flowers and pre-mordanted by Eriochrome black T in a medium of pH = 7 and time of dying 60 minutes at different dye bath temperatures 20, 40, 60 and 80°c is shown in Figure 3.

It is clear from Figure 3 that, the reflectance% decreases by increasing temperature of dyeing bath. R% of sample 1 and sample 2 (temperatures 20 °C and 40 °C) is nearly the same, wavy with changing wavelength, increases markedly from wavelength 600 nm till 780 nm and have so high value than samples 3 and 4. With respect to the samples dyed in a dye bath of tempera-

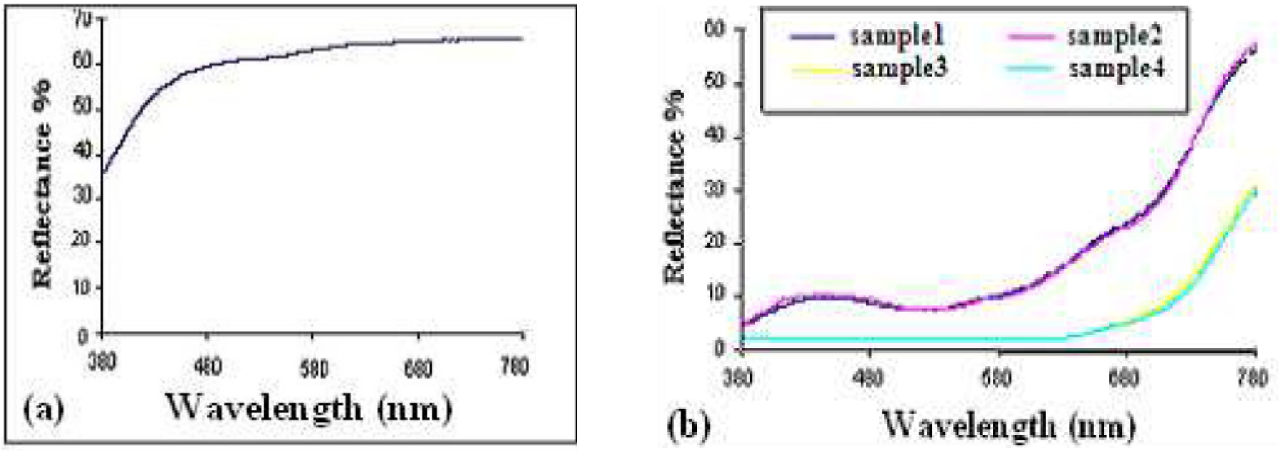


Figure 3 : The reflectance % curves of un-dyed (a) and dyed (b), wool fabrics as a function of wavelength for group I

ture 60 and 80 °C (sample 3 and sample 4, respectively), the reflectance is steady% and have very small value till 680 nm, increases till 780 nm and reaches 30% of reflection at this end of the visible region. So, there is a high color variation as a function of wavelength by increasing temperature.

The relative brightness values (y_r) calculated from R% values as a function of wavelength is shown in Figure 4 for samples 1, 2, 3 and 4. The peak position of all the samples is located at 560 nm, so these samples at different temperature of dye bath have similar behavior. Little change is noticed when the dyeing bath temperature of these wool fabrics are 20 and 40 C. At 40 °C the relative brightness is lesser than that at 20 C. Huge drop happens in relative brightness for wool samples dyed at 60 and 80C, respectively.

TABLE 3 represents the variation in the color parameters: L (brightness), a and b (color components), c (chroma), h (hue) and ΔE (color difference), of wool samples of group I (samples 1, 2, 3 and 4) as a function of dye bath temperature. From the table, it is noticed that the brightness (L) has the same values for both wool samples 1 and 2 (dyed at 20 and 40°C, respectively), this value drops noticeably when wool is dyed at 60 °C and remains constant when the dye bath temperature is 80 °C. This drop means that these wool samples (3 and 4) become darker. The value of color component 'a' also stay constant for wool samples dyed at 20 and 40°C (samples 1 and 2, respectively) and drop by the same trend as (L) when using dye bath of temperature 60 and 80 °C. The drop means the green color dominates in these samples in account of the red color. The behavior of the color component 'b' takes wavy manner reaches negative at some dye bath temperatures (i.e., blue-yellow). The hue of the wool fabrics decreases steeply by increasing the dye bath temperature, while the chroma (c) takes the same trend as both L and 'a'.

The relative color strength (K/S) was determined from the diffuse reflectance of the fabrics measured at wavelength 320 nm, using Kubelka-munk equation. From Figure 5, for group I (samples 1, 2, 3 and 4), the color strength (K/S) of sample 3 (dyed at 60 °C) is higher than the other three samples of the group (dyed at 20, 40 and 80 °C). K/S value for this group takes the order: sample 3 (60 °C) > sample 4 (80 °C) > sample 1 (20 °C) > sample 2 (40 °C). Dyeing wool fabrics at 80°C (sample 4) is not preferable, which it

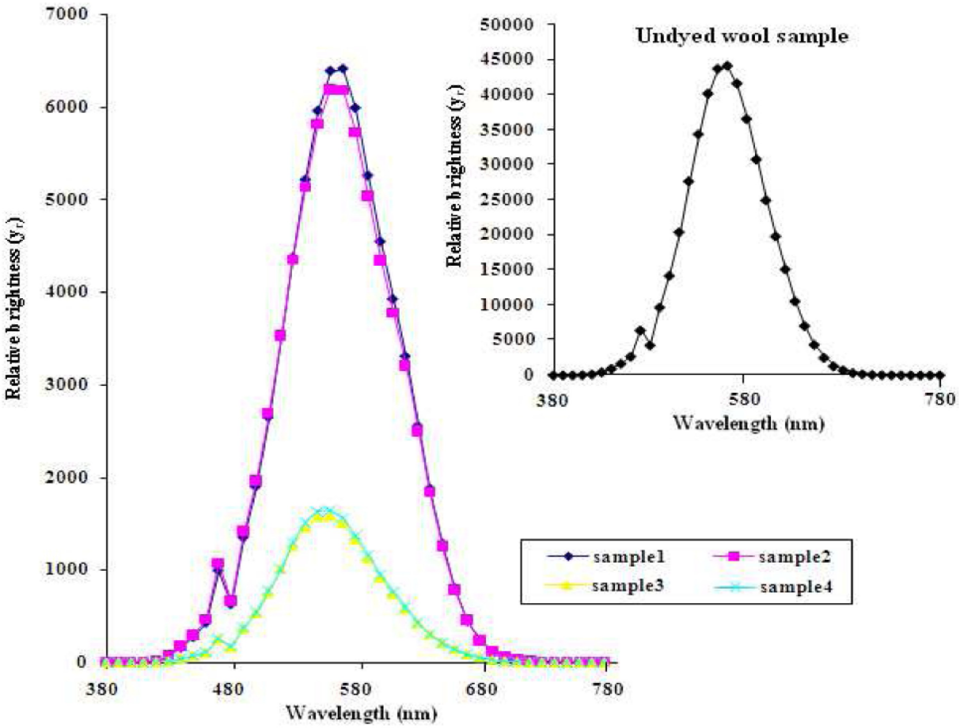


Figure 4 : The relative brightness values (y_r) of wool fabrics as functions of wavelength for group I. The inset represents the un-dyed wool sample

TABLE 3 : The variations in the color parameters: L, a, b, c, h and ΔE of the three groups of wool fabrics

Dyeing conditions		Sample	L	a	b	c	h	ΔE
		Blank	**82.88**	**-0.32**	5.58	5.59	93.92	0
Dyeing temperature (^{o}C)	20	1	37.30	11.69	1.82	11.83	8.84	47.13
	40	2	37.08	11.69	-1.10	11.74	354.63	46.04
	60	3	17.09	2.29	0.71	2.40	342.82	66.00
	80	4	17.45	1.95	-0.50	2.01	345.67	65.65
Dyeing time (minutes)	15	5	18.05	3.75	-1.21	3.94	342.17	65.07
	30	6	18.67	4.57	-2.23	5.12	333.01	64.43
	45	7	17.27	2.98	-1.28	3.25	336.70	65.80
	60	8	16.86	2.11	-0.86	2.27	337.85	66.21
pH value	5	9	20.07	6.09	-3.23	6.94	331.37	63.11
	6	10	18.18	4.44	-2.79	5.24	327.88	64.89
	7	11	17.43	3.44	-1.53	3.77	336.00	65.64
	8	12	17.88	3.39	-1.71	3.80	333.27	65.19

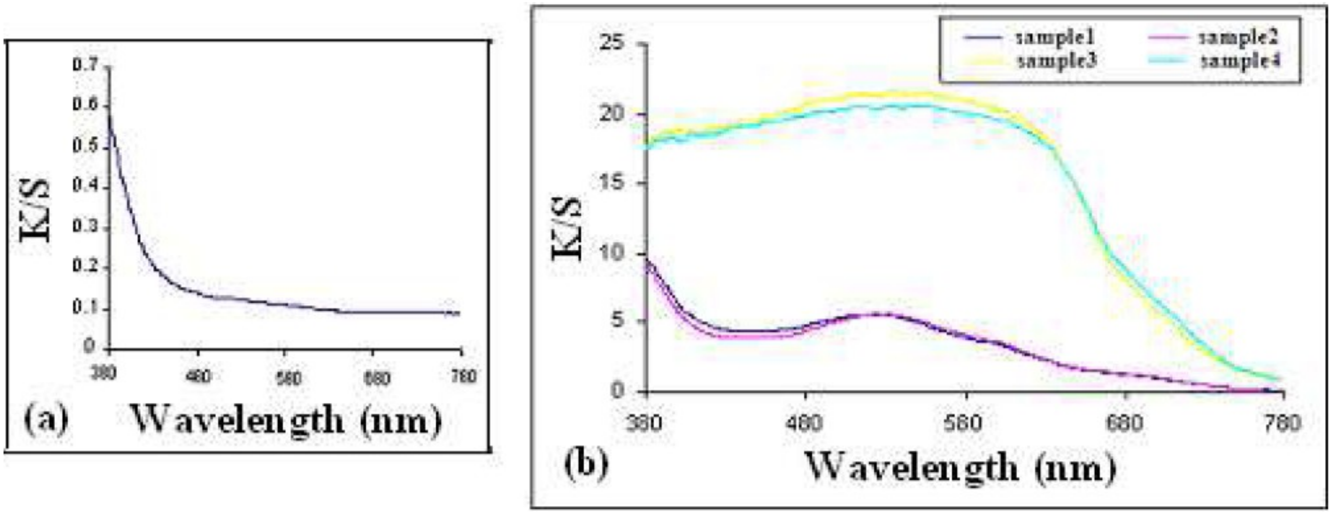


Figure 5. The change in the relative color strength (K/S) of un-dyed (a) and dyed (b), wool fabrics as a function of wavelength for group I

may cause wool shrinkage.

Group II

The diffuse reflectance percent (R%) as a function of wavelength in the visible range 380-780 nm for wool fabric group II (including samples 5, 6, 7 and 8) which is dyed by Calotropis procerea at temperature 60 °C and dye medium of pH = 7 for different times 15, 30, 45 and 60 minutes and pre-mordanted by Erichrome Black T (0.1%), is shown in Figure 6. Similar behavior with respect to the wavelength changes is clear from the spectra of the reflectance values of each individual sample. This proves a steady color variation as a function of wavelength.

It is noticed from the figure that, from 380 nm till 630 nm R% stays constant and may be unnoticeable drop in some parts of the range. After 630 nm the reflectance % increases noticeably reaching its maximum at780nm. The R% value for this group increases by increasing time reaches maximum when dyeing time is 60 minutes.

Figure 7 represents the relative brightness value (y_r) calculated from R% values as a function of wavelength for group II. The peak (at about 560 nm) has the same position with changing times for all the samples. This figure shows a noticeable decrease in relative brightness values with increasing dyeing time till 60 minutes.

TABLE 3 records the variations in the lightness (L),

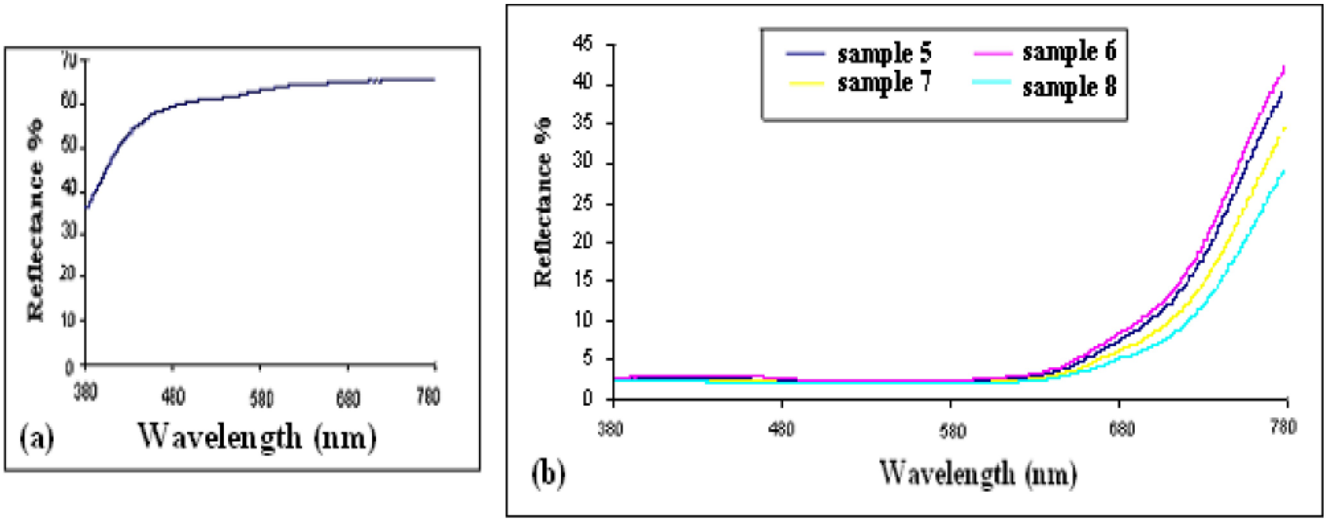


Figure 6 : The reflectance % curves of un-dyed (a) and dyed (b), wool fabrics as a function of wavelength for group II

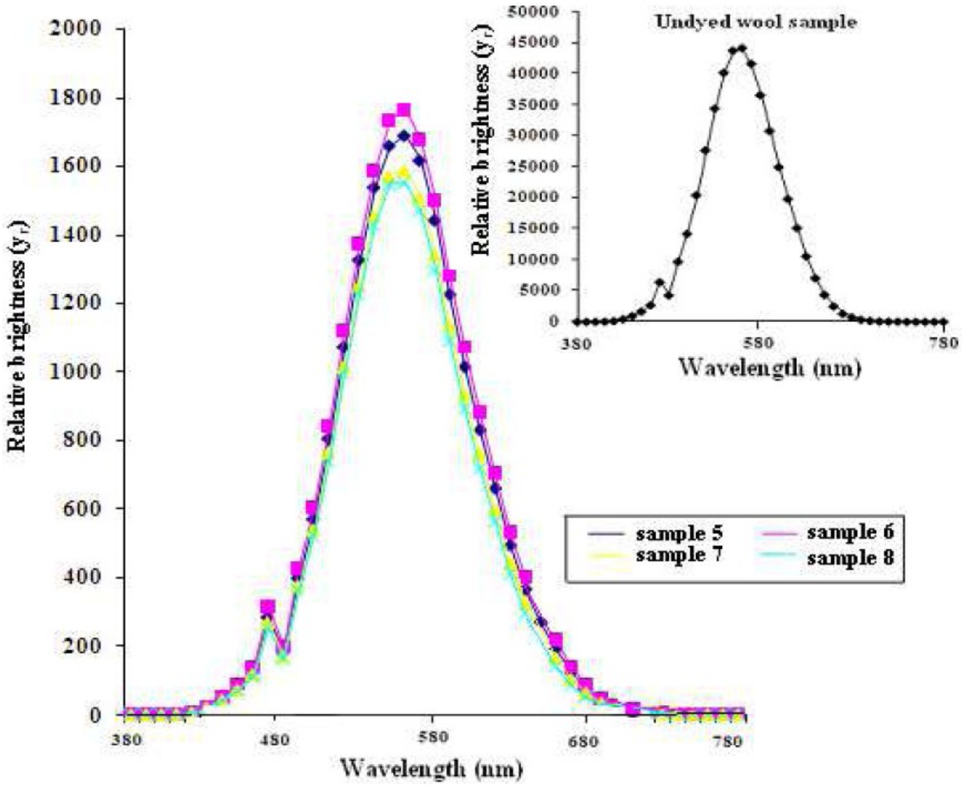


Figure 7 : The relative brightness values (y_r) of wool fabrics as functions of wavelength for group II. The inset represents the un-dyed wool sample

the color parameters (a, b, c and h) and the color difference (ΔE) of wool sample of group II (samples 5, 6, 7 and 8) as a function of dyeing time. From the table it is noticed that: The brightness (L) shows an increase in value at both dyeing time 30 and 45 minutes, while its value is small at 15 and 60 minutes. The value of the color parameter 'a' increases by increasing time of dyeing to 30 minutes, then drop markedly at 45 and 60 minutes. This drop means decrease in red component instead of green one. The values of the color parameter 'b' show the same values at dyeing time 15 and 45 minutes, but it drops drastically at 30 minutes of dyeing time, and then there is an increase in its value at 60 minutes. The drop means that there is an increase in the blue component instead of yellow one, and vice versa. In addition, from the table, the chromaticity (c) increases when dyeing takes 15 minutes and this increase continue till the dyeing time reach 30 minutes. At 45 minutes of dyeing time the chromaticity (c) drops noticeably and more drops occurs when dyeing takes 60 minutes. On the other hand for the hue (h), no measurable change is noticed due to the change in time of dyeing. There is a small drop at 30 minutes but the values at 15, 45 and 60 minutes are nearly the same.

The relation between the color yield (color strength, K/S) and wool fabrics time of dyeing of group II is shown in Figure 8. From the figure, the value of K/S drops when dyeing time is 30 minutes than its value at dyeing time of 15 minutes, its value return up at 45 minutes exceeding its value at dyeing time of 15 minutes. Another drop occurs when the wool fabrics are dyed at 60 minutes but its value is still above that for samples 5 and 6 (15 and 30 minutes).

Group III

Figure 9 shows the reflectance percent (R%) as a function of wavelength in the visible region 380-780 nm for wool fabrics group III (including samples 9, 10, 11 and 12) dyed by Calotropis procerea flowers and pre-mordanted by Eriochrome black T (0.1%), at temperature 60 °C for time 60 minutes and dye bath medium of different values pH 5, 6, 7 and 8. As noticed in groups I and II a steady color variation by increasing wavelength is observed because the reflectance spectra have the same behavior for each individual sample. Sample 9 (pH = 5) has the highest R% value, while

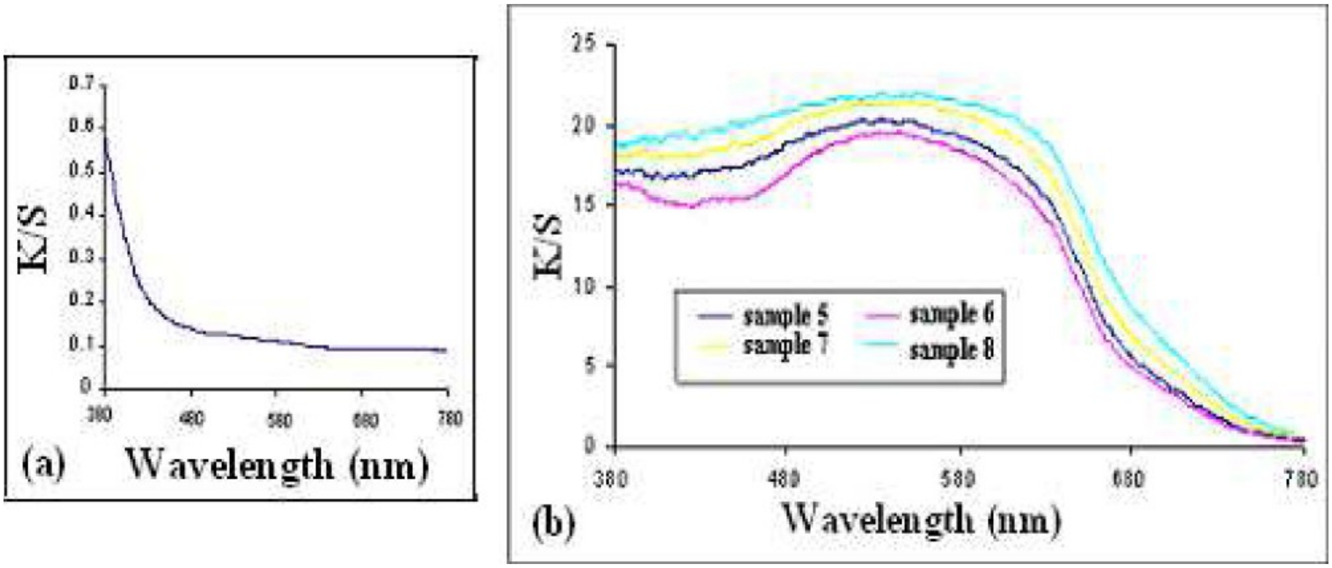


Figure 8 : The change in the relative color strength (K/S) of un-dyed (a) and dyed (b), wool fabrics as a function of wavelength for group II

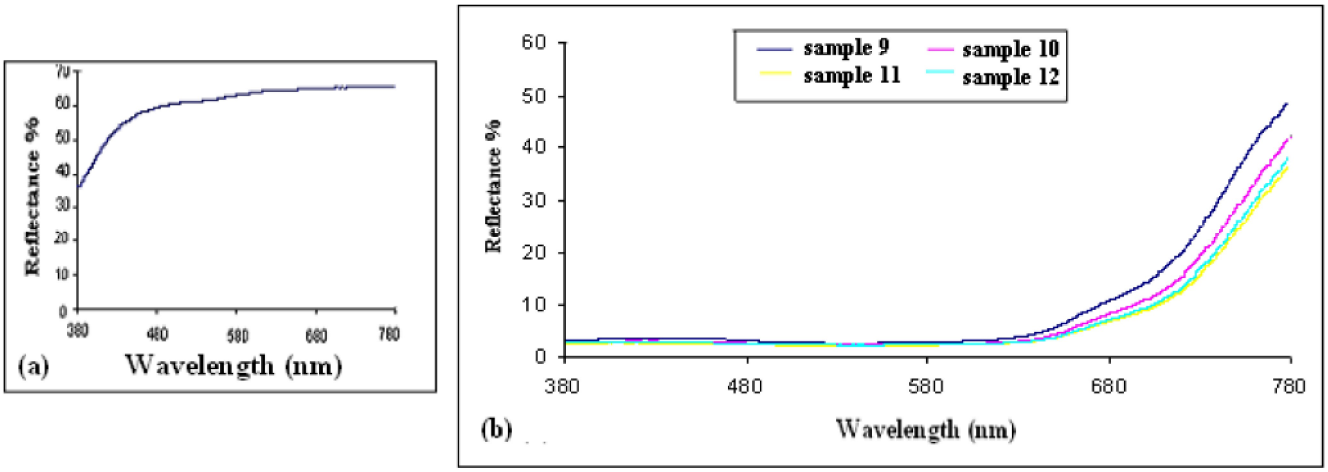


Figure 9 : The reflectance % curves of un-dyed (a) and dyed (b), wool fabrics as a function of wavelength for group III

sample 11 (pH = 7) has the lowest R% value.

Figure 10 shows the relative brightness value (y_r) calculated from R% values as a function of wavelength for wool fabrics of group III, the peaks have the same position at about 560 nm with changing pH values of the dye bath medium. It is clear from the figure that, a decrease in y_r values with increasing pH values from 5 till 7, then a little increase in y_r when using a dye bath of pH = 8.

TABLE 3 represents the variation in the Lightness (L), the color parameters (a, b, c and h) as well as the color different (ΔE) of wool fabrics of group III (samples 9, 10, 11 and 12) dyed with Calotropis Procerea and pre-mordanted by Erichrom black T (0.1%) as a function of different dye bath medium pH values (samples 5, 6, 7 and 8). It is noticed that, L shows little increase when pH values increase from 5 to 6 then decreases at pH values for both the wool fabrics dyed in a bath medium of 7 and 8, which means that the wool samples became darker at these two samples (7 and 8). With respect to the color parameters: 'a' values take the same trend as L, i.e., the green component dominates at pH value = 5 or 6 and the red component dominates at pH value = 7 or 8. The color parameter 'b' has different behavior than L and 'a', it increases markedly at pH value of bath dyeing 5, 6 or 7, but little decrease occurs when pH value is 8. This decrease do not reach the same value of the sample dyed at pH value = 5 or 6. The high increase in 'b' represents the increase in the yellow component instead of the blue one. Also, from the table, the hue (h) values of this group take a wavy behavior. The chroma (c) increases at pH = 6 than its value at pH =5, but a drastically drop occurs at both pH = 7 and 8. This drops exceeds the value of the chroma (c) at pH = 5.

Figure (11) represents the variation of the color yield (color strength, K/S) when changing the value of the dye bath pH values from 5 to 8 for group III (wool fabrics samples 9, 10, 11 and 12). All the samples take the same trend, K/S decreases by increasing the wavelength from 380 till 430 nm; an increase at 440 till 560 nm; and steeply decrease till the end of the visible region (780 nm). The K/S values increase for samples 9, 10 and 11 (pH = 5, 6 and 7) then a decrease occurs at pH value = 8 but not reaching the value of pH = 5 or 6.

The high K/S values can be attributed to the fact

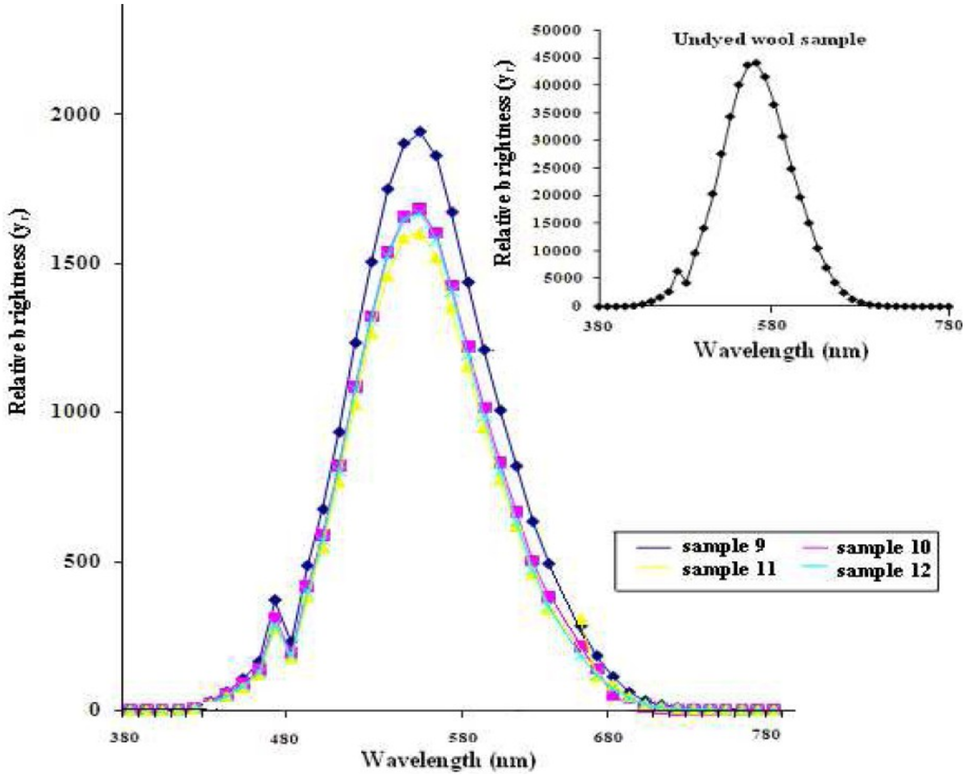


Figure 10 : The relative brightness values (y_r) of wool fabrics as functions of wavelength for group III. The inset represents the un-dyed wool sample

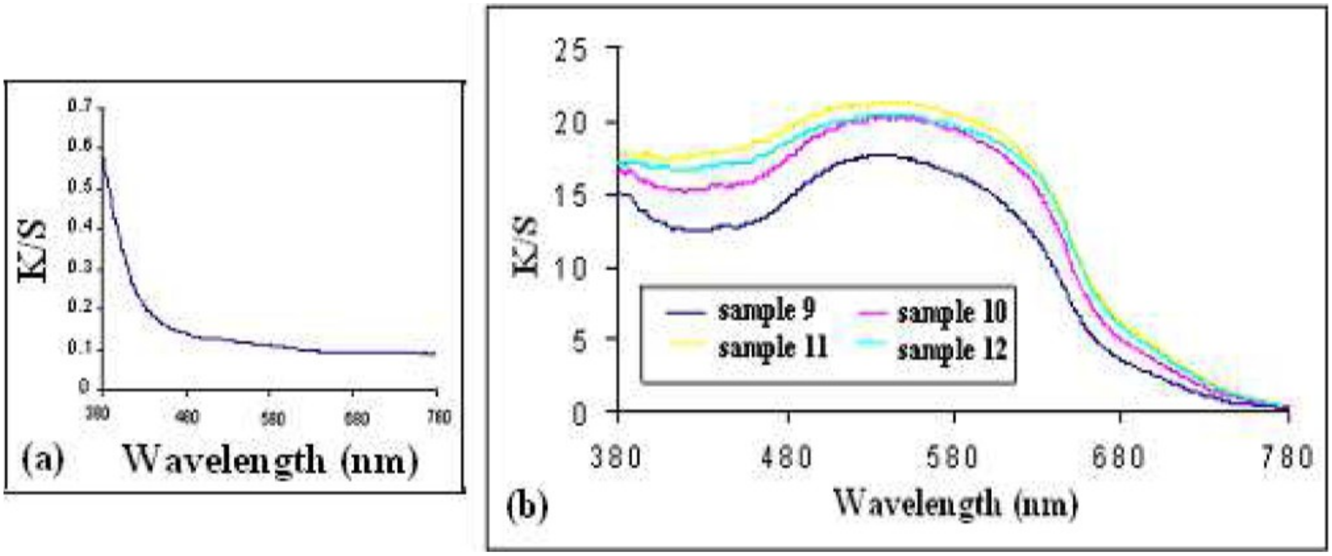


Figure 11 : The change in the relative color strength (K/S) of un-dyed (a) and dyed (b), wool fabrics as a function of wavelength for group III

that this dye gives a bright color on the dyed fabric[17], besides it can be absorbed on wool through interaction with terminal (NH_2) amino groups and also through non-ionic interactions with groups along the chain[18]. However, the number of groups in wool is much enough to give this highest dye ability. Also, the high value of K/S for the wool samples can be related to the dye structure which allow to form a covalent bond between its groups and non-charged ($-NH_2$) amino or ionized hydroxyl (-OH) or thial group (-SH) in wool fabric and the reaction pertain to nucleophilic substitution reaction in the aromatic series[19]. Also, 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. By legislation, temperature of waste water released has to be reduced below 40 °C. This problem can be solved by using recovery systems and stabilization ponds to reduce and level out water temperature, adjust pH value and separate the sediments and solid residues from the wastewater.

On considering the effect of mordant on the dye ability of wool, it is clear that, K/S values increase by adding it where there is an increase in the peak intensity values of the different functional groups that characterize this fabric as CH_2– anti–symmetric stretching, carbonyl band C=O stretching and O-CH_2 anti-symmetric stretching, leading to increase its dipole moment and this in turn encourages the attraction, exhaustion and diffusion of the dye molecules to the fabric surface[20]. So, the extent of the increase in dye ability is greatly dependent on different condition applied.

Fastness characteristics

Assessment of fastness, involves a visual determination of either change in shade or staining of an adjacent material and the graduation of the gray tones in the scales, is defined as the smallest difference in depth, which is of commercial significance. TABLE 4 shows light and washing fastness properties of blank and the three groups I, II, III of dyed wool fabrics under different temperature, time, and pH values of dye bath. The results show that, light fastness was good to very good according to blue scale rating. This may be due to increasing aggregation of dye particles inside the fiber pores, which lower surface per weight ratio of the dyed fabrics[21]. It strengthens the covalent bond formed between the dye and thiol radicals due to the photooxidation of cystine in wool fabrics. Also, the higher light fastness properties of Calotropis procerea dye can be attributed to the strong ionic bonding. This enhances the stability of the compounds by a reduction in electron density at the chromopheres.

TABLE 4 shows the wash fastness properties of the blank and the three groups of pre-mordanted and dyed wool fabrics under different conditions of temperature, time, and pH value of dye bath. Samples 3, 4, 6, 7 and 11 give very well to excellent rating. The

TABLE 4 : The variations of the wash fastness properties of the blank and the three groups of pre-mordanted and dyed wool fabrics

Dyeing conditions		Wool sample	Light fastness	Wash fastness
		Blank	**5**	**4**
Dyeing temperature (^{o}C)	20	1	5-6	4
	40	2	5-6	4
	60	3	7-8	4-5
	80	4	7-8	4-5
Dyeing time (minutes)	15	5	5-6	4-5
	30	6	7-8	4-5
	45	7	7-8	4
	60	8	5-6	4
pH value	5	9	5	4
	6	10	5-6	5
	7	11	7-8	5
	8	12	7-8	4

other samples give rating good to very good. This is due to the strong ionic bond between dye molecules and NH^{2+} groups in the wool fiber. Also, the chemical groups such as C=C and C=O in this natural dye adsorb in the fiber and increase washing fastness due to its bounds and saturation properties.

CONCLUSION

This is the first report where Calotropis procerea extract used in wool dyeing has shown as a source of a natural, non-toxic dye. In this work, the different functional groups were identified by spectrophotometeric methods; all of these purified products were from flavonoid groups.

The color bases extracted from Calotropis procerea plant contain –OH groups, which because of their high polarity increased the absorption and color intensity. The dyeing results reveal that the exhaustion rate increases. This leads to a considerable decrease in the amount of the extracted dye used to reach the same desired results.

The above experiments showed that natural dyeing can give good fastness properties to wool fiber using the Calotropis procerea plant as a dye source and this finding has good potential for commercial dyeing, thus making textile dyeing more eco-friendly. Furthermore, most of the properties of natural dyes were competitive with acid dyes. Thus this dye has good potential to act as co- partner with acid dyes.

Calotropis procerea show good shade reproducibility and satisfying levelness with significant fastness properties.

The observed changes in the color parameters by changing dyeing conditions (temperature, time and dye bath pH values), may be due to the changing in the physical bonds and then changes in the molecular configuration of the wool fabrics which may lead to formation of new color centers.

By following the K/S values for the three groups I, II and III, it is noticed that, the highest values of K/S occurs at 60 °C, 45 minutes and pH = 7. But this does means that the samples must be dyed at these values, because every value of temperature, time or pH gives nice shade of violet colors.

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