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Comparison between the optical properties of cotton and wool fabrics dyed with a natural dye using different mordents

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ABSTRACT

Cotton and wool fabrics were dyed by Calligonum Comosum extracted from the barks of the plant. The dyed cotton and wool fabrics were mordanted by different mordants that are: Alum (potassium aluminum sulfate), ferrous chloride and ferrous sulfate which were applied separately. The effect of different mordants on the reflectance spectra was investigated using spectrophotometer tool and CIE tristimulus values. The color parameters including L, a, b, h, c and ΔE were determined. A comparison between the effect of mordanting on both the cotton and wool fabrics by the same three mordants was done. The data obtained indicated that the optical properties are totally different as a result of the nature of wool which is a protein fabric and cotton which is a cellulosic fabric. The different mordants gave different colors and shades which encourage the use of natural dyes instead of synthesis dyes; also, the absorption coefficient (α) was calculated in the visible range. The decrease in transmission and increase in absorption coefficient with the change in the mordant type may be due to the change in the molecular configuration as a result of the change in the chemical bonds in the fabric, dye and the mordant. The optical studies can differentiate between different kinds of fabrics with different kinds of mordants present in small proportions.

KEYWORDS

Calligonum Comosum plant;
Cotton fabric;
Wool fabric;
Optical properties;
Dyeing conditions.

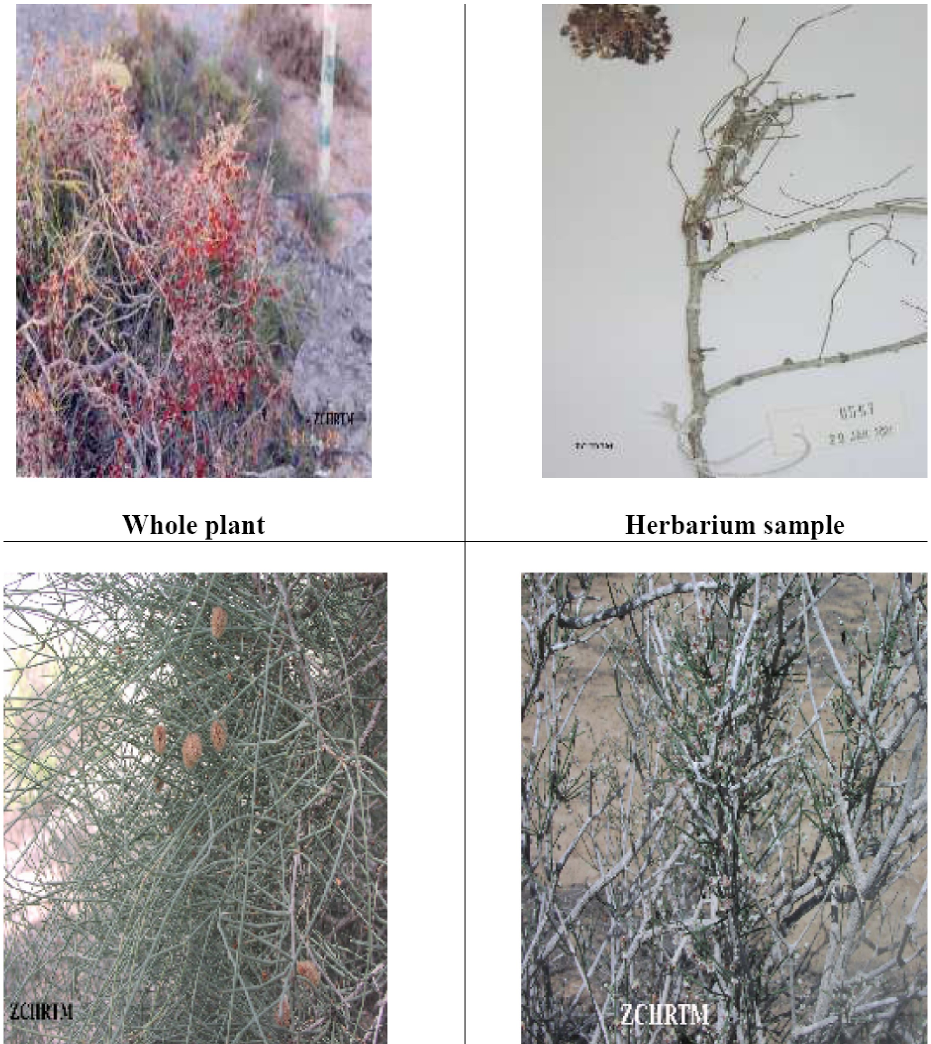
INTRODUCTION

Charateristics of the dye used

Scientific Name : Calligonum comosum L'Her.
Synonym : C. polygomoides subsp. comosum (L'Her.) Soskov
Local Name : Arta', A'bal, waragat Alshams
Arabic Name : Arti, Arta',waragat alshams, Ramo, Tape

Description[1,2]

Woody based ascending shrub, glabrous much branched, erect up to 250 cm high, older branches rigid with whitish gray bark and swollen knotty nodes, young shoots green flexible 1-2 mm in diameter, branching and angled at nodes. Leaves minute, soon deciduous and usually absent. Flowers 0.5 cm across, on pedicels about equaling or somewhat exceeding the perianth lobe from leaf nodes, sometimes clustered; perianth lobes



Whole plant | Herbarium sample

Fruit | Flowers

Family (Polygonaceae)

oblong, obtuse c. 2.8-3.0 mm long, white pink or white-greenish with darker medial part; anthers many, bright –red in color. Fruit capsule, red or greenish yellow with 4 pairs of longitudinal wings, covered with short-branched stiff red bristles, 1-2 cm long, becoming dirty yellow when mature.

Habitat and distribution

It is a plant of tropical and subtropical regions wide-spread in UAE. Frequent to common in deeper sand, dunes, plains and valleys; cultivated around desert plantations as windbreaks; tolerates saline conditions:

Part Used: aerial parts, fruits and young twigs.

Chemical constituents: anthraquinones and flanovonids[2,3]

Plants have been the basis of sophisticated medical systems for thousands of years and they have an essential role in healthcare. The World Health Organization has estimated that 80% of the earth's inhabitants rely on traditional medicines for primary healthcare, and the plant products are highly important in the remaining 20% of the population. Natural products have made an enormous impact on the discovery of anticancer compounds.

In fact, possibly 60% of all cancer drugs that are used clinically are either natural products or owe their origin to a natural source[4]. It was reported that Calligonum comosum possesses anti-ulcer and anti-inflammatory reactivity[5].

Cotton cellulosic based material is the most wide used for textile manufacture. It is a natural biomaterial, it is as important as chemical resources to replace petroleum-based material[6]. Cotton and linen are used in furniture's, Packing paper and medical products[7], by converting it to cellulose derivatives and regenerated materials. Because of cellulosic materials good mechanical properties, low cost, light weight, moderate strength, high specific modulus,renewability, biodegradability, lack of health hazards and recycle-ability[8]; cellulosic fibers constitute an interesting alternative to the inorganic counterparts used to reinforce polymer matrix to prepare composite material to apply the environmental awareness all over the world. The molecular structure has an ultra-fine network composed of ribbon-like micro fibrils whose three dimensional network endows cellulosic fibers unique properties including high tensile strength and high specific surface area. The dyeability of cotton fabrics with a natural dye faces problems because cotton posses only hydroxylic groups in its structure which prevent fiber dye bonding. Many researchers try to improve dye bonding and dye adsorption on fabrics through chemical modification. The structure of cotton consists of monomeric units of β-D-glucopyranose linked through 1-4 β glucoside bonds[9].

Wool, protein fibers is a natural biological polymer, consists of crystalline and amorphous phases, multiple cellular, subtle fibers medium weight. Wool has complex structure due to its different important groups and the intermolecular force of attraction that are formed[10], i.e. the polar peptide groups (-CO-NH-) and the oxygen of the carbonyl groups (-CO-) of slightly negative charge which will form hydrogen bond with the slightly positively charged hydrogen of the amins groups (-NH-) of other peptide groups. Cystine, containing the sulfur attached to the amide group is capable of forming disulfide crosslinking tends towards greater chemical stability, resulting in less dye absorption. The cystine linkage is sensitive to chemical attack and is removed and/or modified by a aqueous chlorination and high radiant energy. Also, the very absorbant nature of wool is caused by the polarity of the peptide groups, the salt linkage and the amorphous nature of its polymeric system. Wool has high nitrogen content (16%), high moisture content (10-14%)[11], high ignition temperature (570-600 °C)[12], low heat of combustion (20.5KJ/g), low flame temperature (677 ºC) and high limiting oxygen index (25-28%). Wool is not exclusively a keratin protein, it is also has external lipid content and a small amount of specific internal wool lipids (1.5%). These internal lipids have ceramide content, with smaller amounts sulfates.

The dyeability[10], the light fastness characteristic and color parameters, …. etc, depends strongly on the wool fiber surface. The oxidation of cystine content on the surface of the wool fabrics is responsible for its hydrophobic nature and limited wettability and dyeability forming cystic acid and this modifying or volatilizing the surface lipids.

There are two kinds of natural dyes: substantive and adjective-substantive dyes (Lichens, acrons, sumac, oak galls and walnut hulls for instance) need no mordants to help them adhere to the fiber. The dye must form strong chemical bonds with the basket material to set the color permanently. It enters deeply into the fiber, and when the dye is added, they combine to form a color, since the mordant is thoroughly embedded, so is the color.

Mordants prepare the fiber to receive the dye stuff and help in bonding between the dye and the fabric. Compounds of Alum (potassium aluminum sulfate), tannin (tanic acid) and iron (ferrous sulfate) are the safest choices[13]. Many Factors influence the dyeability and light fastness of the dye used for the two fabrics, among them are the chemical and physical state of both the dye and the fabric, environmental factors, the source and the intensity of light, and other additives in the dyeing bath[14].

To decrease the effect of photo-degradation, acid hydrolysis, oxidation and biodegradation which are the main reaction acting on the cellulose and wool structure and causing its alteration, different mordants are used before and after or during fabric dyeing. Mordants were firstly used to obtain different shades from a single source of dye. Some researches[15,16] have concluded that the mordant is more important than the dye itself in determining the color fastness of the dyed materials according to its type, concentration, method of application, pH of dyeing media and the nature of both substrate and dye used. A mordant can itself be fixed on the fiber and also combine with the dye – stuff, therefore a link is formed between dye-stuff and fabric which allows certain dye with no affinity for the fabric to be fixed. There is some difference in fastness properties by the use of various metals salts as the mordanting agents. The main objective of the present research is to evaluate the effect of different mordants namely Alum (potassium aluminum sulfate), Ferrous chloride and ferrous Sulfate on the absorptivity of dyed cotton and wool fabrics using optical measurements and absorption coefficient calculations.

The variation on the optical parameters and the difference in color (ΔE)[17] are taken to represent the variation in the chemical groups for different mordants. Also the formation of new color centers in the investigated dyed fabrics was followed by the calculated absorption coefficient. These color centers are formed due to the change in the molecular configuration as a result of the change in the chemical bonds between the Calligonum Comosum dye, the mordant and the fabrics samples under test

Different types and selective mordants or their combination can be applied on the textile fabrics to obtain varying color/shade, to increase the dye uptake and to improve the color fastness behavior of any natural dye.

EXPERIMENTAL

Materials and chemicals

Fabrics: The following fabrics are used throughout this study:

Cotton: Pure cotton fabrics (100%) weight 120 g/m^2, thickness was 0.21 mm, number of yarn/cm in warp direction was 30 and in weft direction was 31.

Wool: Pure wool fabrics (100%) weight was 176.61 g/m^2 and thickness 0.65 mm, number of yarn/cm in warp direction was 25 and in weft direction was 24.

These fabrics were kindly supplied by Golden Tex. Company, Egypt. Cotton and wool fabrics were purified in laboratory by scouring with a solution containing 2 g/L of non-ionic detergent with liquor ratio 1:50 at 60ºC for 15 minutes. Finely, the samples were thoroughly washed with water and then dried at ambient conditions.

The dye: The dye used was a natural dye named Calligonum Comosum.

Mordants: Mordants were potassium aluminum sulfate $Al_2K_2(SO_4).24H_2O$, ferrous chloride $FeCl_2$ and ferrous sulfate $FeSO_4.7H_2O$ all are used in a pure state.

Dye extraction procedure

50 gm of the crushed barks of this dye were soaked in 500 ml of distilled water and allowed to boil for one hour. The solution was filtrate to drain the undesired portions to obtain clear mother solution for dyeing process[18].

Extracted dye characteristics

The extracted dye was characterized by two techniques:

Ultraviolet-visible spectroscopy

The absorbance spectrum of the extracted dye from Calligonum Comosum dye allover the UV-Vis range using LAMBDA 35 Spectrophotometer-Perkin Elmer USA was followed and shown in Figure 1. The dye has maximum absorbance at wavelength λ_{max} = 450 nm in the UV range of absorbance.

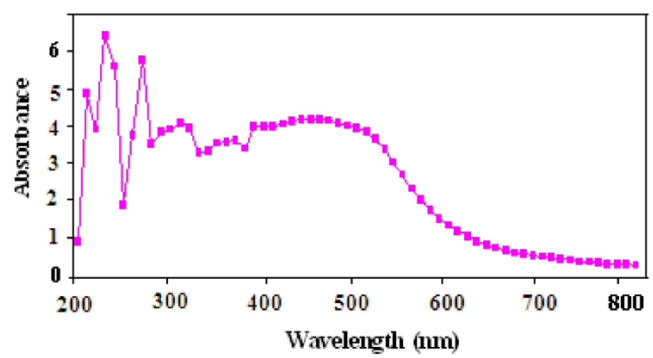


Figure 1 : The absorbance spectrum of the extracted dye from Calligonum Comosum

Fourier transform infrared (FTIR) spectroscopy

The FTIR Spectrum of extracted and purified dye is recorded using Perkin Elmer Spectrophotometer model 1650-USA with a wave number range of 4000-500 cm^{-1}. TABLE 1 represents the most characteristic functional chemical groups present of Calligonium Comosum dye. Also, the wool fabrics samples under investigation were analysed for their chemicals groups by the same spectroscopy.

Dyeing and mordanting method

The cotton and wool under test were separately dyed by the preextracted dye in a laboratory dyeing apparatus using the convertional exhaustion dyeing method[9] and different mordants were added to the dye bath separately with fixed concentartion.

Full Paper

TABLE 1 : FTIR analysis of Calligonium Comosum dye showing its peak intensity values of its characteristic functional bands

Wave number (cm^{-1})	Characteristic functional bands	Peak intensity value (%)
3411.91	O-H Stretching band	99
2925.54	C-H Vibration	62.0
1650.97	C=O antisymmetric stretching	100
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

Alum (potassium and aluminum sulfate) of concentration 5 g/liter was applied as pre-mordant. Both ferrous chloride and ferrous sulfate of concentration 5 g/liter were applied as post mordants. All cotton samples dyeing were carried out using pH = 7, at temperature 100 ºC for 60 minutes, and liquor ratio of 1:40. The same conditions were used for wool samples but the temperature was 80ºc and the liquor ratio was 1:50. Finally the dyed mordanted samples were thoroughly washed and dried at ambient conditions.

Optical measurement

UV-VIS-NIR scanning spectrophotometer type shimadzu uv 311 PC Japan covering the range 190-3000 nm was used to record the reflection spectra in the visible range. MgO was used as standard white for the zero and 100% setting of the apparatus. The tristimulus value (x,y,z) of the CIE for all the cotton and the wool samples were calculated from their corresponding reflection curves by summing the multiplication of the luminance factors and reflection at the wavelength[19-21]. The hunter coordinates L, a and b of the dyed mordanted samples by Calligonium Comosum were calculated from the tristimulus values x,y,z using the following equations 8and were converted to L, a and b coordinates[22]:

$$L = 10\sqrt{Y} \quad (1)$$

$$a = 17.5(1.02-y)/\sqrt{Y} \quad (2)$$

$$b = 7(y-0.84\,z)/\sqrt{Y} \quad (3)$$

$$\text{Color difference } (\Delta E) = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (4)$$

The positive values of 'a' and 'b' indicate redness and yellowness respectively, and their negative values indicate greenness and blueness, which are more toward the dull side. The lower the value of L the greater is the depth of the dye.

Four measurements were made on each sample and the variation in the absorption coefficient (α) was calculated from the reflection spectra obtained for cotton and wool fabrics using the equation:

$$\alpha = (1/d)\,\ell n\,[(1-R)^2/T] \quad (5)$$

Where T is the transmittance (neglected in this calculation), R is the reflectance percentage and d is the Thickness of the investigated fabric in cm.

RESULTS AND DISCUSSION

Reflection measurements of cotton fabric

Figure 2 represents the reflection spectra (in the range 400-700 nm) of the dyed cotton fabrics with Calligonium Comosum also those mordanted by the three mordants: alum, ferrous chloride and ferrous sulfate. It is clear that the samples mordanted by alum acquired higher reflection values than their mates. From the figure, it is noticed that the cotton samples dyed with Callognum Comosum and mordanted with alum have the highest R% while those dyed and mordanted with $FeSO_4$ have the lowest R%. This is in agreement with Figure 3 relating the absorption coefficient (α) and wavelength (λ).

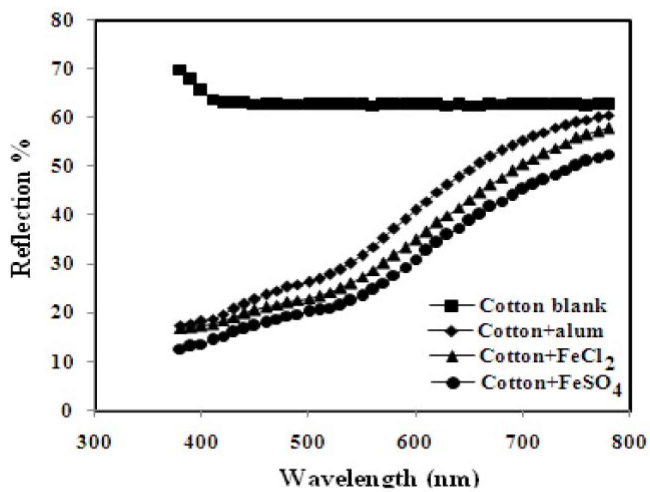


Figure 2 : The change in reflection (%) value for different cotton fabrics with wavelength.

The color parameters: L (brightness), a and b (color components), c (chroma), h (hue) and ΔE (color difference), of the same dyed cotton fabrics under test, mordanted by the three mentioned mordants are tabaluated in TABLE 2, L parameter measures the lightness of the sample and varies from 100 for perfect white to zero for black. It is clear that the cotton samples dyed by this natural dye and mordanted by $FeSO_4$ are darker in color than the other mordants. The increase in L represents lighter colors.

TABLE 2 : Values of color parameters: L, a, b, h, c and the color difference, ΔE, for cotton samples

Samples	L	a	b	H	c	ΔE
Blank	83.26	0.03	-0.21	278.45	0.21	0.00
Dyed	55.67	12.08	21.16	60.27	24.37	36.92
Dyed + alum	64.39	9.48	16.29	59.81	18.85	26.79
Dyed + $FeCl_2$	60.54	9.30	13.86	55.86	17.86	28.29
Dyed + $FeSO_4$	57.12	9.43	14.20	56.13	16.69	31.29

The parameter 'a' varies from green for negative value and red for positive value. It is noticed from TABLE 2 that its value increases in case of cotton samples dyed by Calligonium comosum and mordanted by alum i.e. these samples gained more red coloration. In considering the color component 'b', it found that a considerable increase in b values for the dyed cotton fabrics mordanted by alum which indicates the tendering of these samples towards blue color. By following the color difference (ΔE) between the investigated dyed cotton samples and those dyed and mordanted by different mordanted, it is clear that there is a large difference when mordnting the cotton samples by $FeSo_4$ mordant.

From TABLE 2, in considering h values of the cotton dyed mordanted fabrics, it is noticed that the sample mordanted with alum is little higher in h than the other two samples mordanted by $FeCl_2$ and $FeSO_4$ which take nearly the same value. By following the chroma (c) of these cotton fabrics, the sample mordanted by alum is also little higher in c and both cotton fabrics mordanted with $FeCl_2$ and $FeSO_4$ have nearly the same value of c.

Optical absorption measurements

From Figure 2 the absorption coefficient (α) of cotton fabrics was calculated from its reflection spectra and the results are shown in Figure 4 as a function of wavelength range 400-700 nm. It is clear from Figure 3 that the initial point of the absorption coefficient of blank cotton has the highest value. The absorption coefficient value of dyes and mordanted cotton follows the order: mordanted with alum > with $FeCl_2$ > with $FeSO_4$.

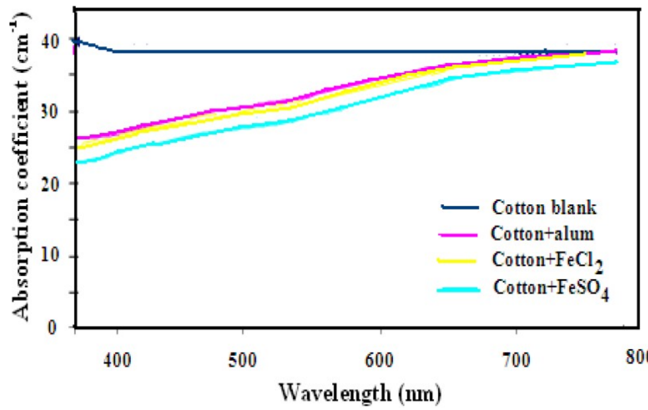


Figure 3 : The change in absorption coefficient values of different cotton fabrics with wavelength

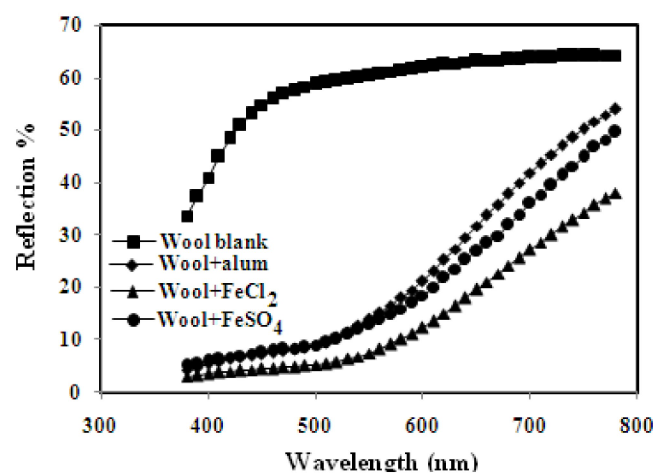


Figure 4 : The change in reflection (%) value for different wool fabrics with wavelength

The change in the absorption coefficient value may be due to the change in the chemical bonds between the natural dye and fabric samples which occur due to the formation of active free radicals which may combine and form other molecular species[23,24]. This in turn leads to the formation of new color centers i.e., prefential light absorption at particular wavelength this process is enhanced in the presence of a mordant, depending on the mordant type. Mordant role is to strength the linkage formed between the reactive species of the cellulosic fabrics chemical groups and the dye polar group's. Besides; hydrogen bonds are formed between hydroxyl group of the dye used and the chemical groups in the

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fabric[25]. Thus, as the number of these polar groups in the dye and the substrate increase, the chance for linkage increase, i.e., dye-up take increase and this in turn improve the light fastness.

Reflection measurements of wool fabrics

The reflectance percent (R%) as a function of wavelength in the visible range 380-7800 nm for wool fabrics samples dyed with Calligonium comosum mordanted by the three previous used mordants, is shown as Figure 4. It is noticed that there is a steady color variation as a function of wavelength, since the behavior with respect to the wavelength is the same for each individual sample.

It is noticed that the reflectance percentage for samples dyed and mordanted with alum and ferrous chloride at the beginning of the visible range from 380 to 540 nm nearly have the same value and their lines coincides with each other in the curve but after 540 nm they separated in value till the end of the visible range. The percentage decrease in R% for the three wool samples than the blank one take the order $FeCl_2$ (40.77%) > $FeSO_4$ (22.75 %) > Alum (6%) This means that the wool samples dyed and mordanted with alum have the highest absorptivity of calligonum Comosum dye, while those dyed and mordanted with $FeCl_2$ have the lowest absorptivity.

TABLE 3 records the variation in the brightness (L), the color parameters (a, b, c, and h) and the color difference (ΔE) of the blank, dyed mordanted wool fabrics by alum, Ferrous chloride and ferrous sulfate. The value of L decreases when using $FeCl_2$ as a mordant and has nearly the same higher value in case of the two other mordants. Also the value of the color parameter 'a' increase when using alum as a mordant. The drop in case of using $FeSO_4$ as a momrdant means decreases in red component instead of green one. From the same table the value of 'b' shows its highest value in case of mordanting the dyed wool fabrics by alum. This means that the yellow component increase instead of the blue one.

From the table, all the values of the hue (h) for the mordanted dyed wool samples are higher than the wool fabrics dyed with Calligonum Comosum and take the order: samples mordanted with alum > with $FeSO_4$ > with $FeCl_2$. It is noticed that the hue value of the blank undyed wool sample is nearly equal the double of all the dyed mordanted wool fabrics. Also, the chromaticity (c) increases to its highest value in using alum as a mordant.

TABLE 3 : Values of color parameters: L, a, b, h, c and the color difference, ΔE, for wool samples

samples	L	a	b	h	c	ΔE
Blank	81.95	-0.38	5.86	93.72	5.8700	0.00
Dyed	30.04	19.08	14.41	37.06	23.9100	56.09
dyed + alum	45.77	15.33	22.45	55.67	27.1800	42.79
dyed + $FeCl_2$	35.10	14.60	17.29	49.81	22.6300	50.50
dyed + $FeSO_4$	44.03	12.64	18.35	55.44	22.2800	41.99

Optical absorption measurements

From Figure 4 relating the reflectance % (R%) and wavelength (λ), the absotption coefficient (α) of all the wool fabrics under investigation was calculated and represented in Figure 5. The absorption coefficient value of dyed and mordanted wool fabric has the order alum > $FeSO_4$ > $FeCl_2$. All of these values are higher than that of dyed unmordanted wool fabric.

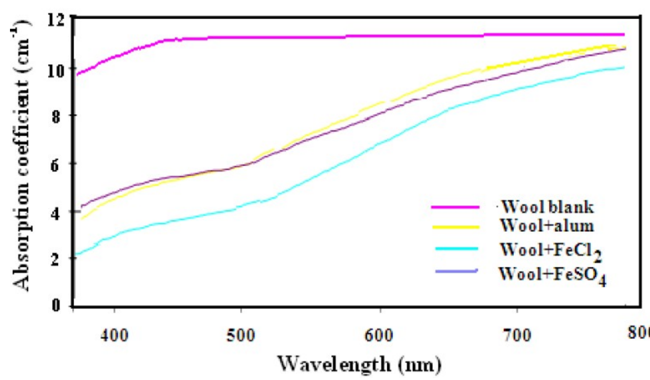

Figure 5 : The change in absorption coefficient values of different wool fabrics with wavelength

CONCLUSION

Calligonum comosum extract used in wool and cotton fabrics dyeing has shown as a source of natural, non-toxic dye which cause an increase in the exhaustion rate due to the presence of –OH groups in the dye extract. This –OH groups have high polarity which enhance the absorption and color intensity, The quantity of extracted dye is considerably small to reach the same desired dyeing results.

The procedures of dyeing and mordanting were applied easily in the limits of legal environmental conditions with low costs.

The application of spectroscopic analysis on wool and cotton fabric can be considered as an effective tool and may be commercialized, and can be used to determine the optical conditions for improving fabrics characteristics.

A wide range of soft lustrous colors were obtained on wool and cotton fabrics when the dyed fabrics were mordanted by using alum, ferrous chloride, ferrous sulfate each applied separately.

The decrease in transmission, increase in absorption coefficient and the observed changes in color parameters with the change of the mordant type is due to the change in the molecular configuration as a result of the change in the chemical bonds in the fabric, dye and the mordant, which may lead to formation of new color centers.

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