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Characterization of artificially dyed aged stained cotton carpets to simulate the archeological model samples

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ABSTRACT

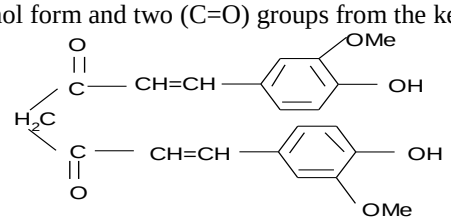
In order to success in removing stains from historical dyed samples, it is necessary to understand the nature and type of these stains. This research work aimed to study in detail the different changes occurring on mimic cotton carpet samples dyed with natural yellow dye turmeric and subjecting to different stains (blood, mud and wax). All the stained samples were subjected to light ageing followed by cleaning with different detergents according to the nature of the stain. The examined samples were characterized and evaluated using FTIR-ATR analysis to examine the change in the chemical structure after each treatment process and studying the effect of such processes on the crystallinity/amorphousity of the samples. Also, the color measurement in the CIELAB system was used to quantify the change in samples' colors through the different treatments. The obtained results indicated that: there was an obvious change in the transmission peak intensities of the different functional groups after each treatment, a variation in both the crystalline index (C.I) and % crystallinity of the examined samples and the cleaning process greatly depends on both the type of stain and the cleaning material.

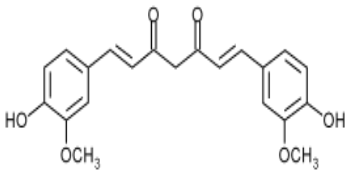
Introduction

Growing awareness of the value of archeological materials for many different areas of science has resulted in increasing interest in these archeological textiles. Environmental factors namely, fluctuation of relative humidity and temperature, dust and dirt, atmospheric pollution, insects and human negligence usually cause deterioration of textile and their colors. In addition, deterioration in textiles may be due to internal factors results in stains [(1)].

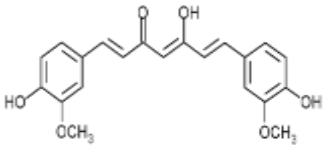
Light is the major cause, which contributes to the deterioration of the artwork materials leading to the color fading, discoloration or other deterioration in organic materials such as paper, textiles and leather. The change in art objects color caused by ageing are major problems encountered by artists, conservators and museum curators [(2)].

Turmeric is a bright yellow powdered root and relative of the ginger plant. It is popular in Middle Eastern foods and is often used as a natural yellow dye. The powerful element in Turmeric is Curcumin (bis (4- hydroxyl-3-methoxyphenyl)-1, 6-heptadiene- 3, 5- dione), has a conjugated symmetrical structure with single (C-C-) and double (C=C) bonds alternately .Its chemical structural formula indicated in figure 1[(3,4)]. Curcumin can exist in at least two tautomeric forms: enol and keto. In the central part of the molecule it has a (C=O) and a (C-OH) group from the enol form and two (C=O) groups from the keto form.





Keto form



Enol form

Figure 1: Curcumin structure

In order to success in removing stains from historical dyed textiles or carpets, it is necessary to understand the nature and causes of these stains. Accidental staining is due to contact with substances such as food, dyes, dust, blood …etc. Some stains can be removed with the normal washing process, but stubborn stains may require special treatments. Nearly, all synthetic detergents have similar molecular structures and properties; it consists of a long hydrocarbon chain and a water-soluble ionic group [(5)].

Oils, waxes greases, tars, resins and varnishes may be removed by using organic solvents. There are many different solvents, each having a different effect on a stain, and each varying in toxicity. Greasy stains are removed with the use of surfactant. A surfactant decreases the surface tension or attraction between the molecules of the water. This allows the water to approach the fiber and the soil particles more closely, and is called wetting [(6,7)].

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Fourier Transform Infra-red (FTIR-ATR) spectroscopy technique provides information about the change in the different functional groups and the chemical bonding of fabrics because of different treatments conducted to the fabric such as finishing, dyeing, staining and cleaning using different detergents [8].

This research work was carried out using cotton carpet samples dyed with natural turmeric yellow dye and stained with the different stains separately, i.e. blood, mud and wax. All the stained samples were subjected to light ageing followed by cleaning using different detergents according to the nature of the stain as reported elsewhere [9]. The results of the dyed aged cleaned samples were evaluated and compared via measuring FTIR-ATR spectra in the range 4000-650 cm^{-1} and color difference (ΔE) values.

Experimental Work:

I- Materials and chemicals:

1. Samples of cotton carpets having dimensions 10x10 cm^2 with 16 knots/cm^2 and pile height 4 mm premordanted with alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$] using 50g alum/100 g fibers at 80 ºC for one hour. The mordanted samples were dyed with turmeric (C.I. Natural Yellow 3) dye solution having concentration 20g\L at 80 ºC for one hour with liquor ratio 1:30 using the conventional exhaustion dyeing method [10].
2. different stains: blood, mud and wax
3. Chemicals and Detergents: 1% ammonia solution, 0.5% acetic acid, 15% NaCl solution, neutral soap and benzene.

II- Staining Methods, Cleaning and Measurements:

Staining:

Fixed volume of each stain was applied on the mordanted dyed carpet samples separately and left to dry at ambient conditions followed by light ageing according to AATCC standard method 16-1998

Cleaning Process:

It was carried out using the mechanical method (rubbing) whereas the recommended detergents were used for each stain as follows:

For blood stain: Three different detergent media were used separately: acidic (0.5% acetic acid), alkaline (1% ammonia solution) and neutral (15% NaCl).

For mud stain: Different concentrations of neutral soap (0.5%, 1% and 2%) were used separately.

For wax stain: A white paper towel was put over the stained area and the tip of warm iron was pressed gently over the waxy area until it melts and adhere to the towel then lift the towel from the carper sample. Finally, the residue stained area was sponged with benzene solvent [9].

Finally, all the cleaned samples were left to dry at ambient conditions for 24 hours.

Measurements:

FTIR-ATR transmission spectra of all the above mentioned samples were recorded by means of Nicolet 380 Spectrometer using a zinc selenid crystal, in the wavelength range 650-4000cm^{-1} with an average scan rate 128 and resolution of 4 cm^{-1}. To ensure reproducible contact between the crystal face and the sample, a pressure of about 18 Kpa was applied to the crystal holder. .

Color measurements for all the samples under test were carried out according to the CIELAB system using Optimatch 3100 ® SDL spectrophotometer. Due to the change in the color and hue as a result of staining and cleaning ΔE was taken as a measure of the color difference in the visible range of spectra (400- 700 nm) between the standard and the sample, whereas, the dyed sample was taken as the standard and the stained aged or cleaned samples were taken as the samples [11].

Results and Discussion:

Fourier-Transform Infrared spectroscopy with attenuated total reflection (FTIR-ATR) can give high light on the chemical changes that occurred in cotton samples as a result of the different treatment processes, i.e. dyeing, staining ,ageing and cleaning with different detergents, by evaluating the variation in peak intensity values of structural functional groups as illustrated in figure 2 and clarified in table 1. In considering the different functional groups in cotton samples, the following bands were obtained : hydrogen-bonded O-H stretching at $\upsilon \approx 3500\ cm^{-1}$, the C-H stretching at $\upsilon \approx 2900\ cm^{-1}$, the C-H wagging at $\upsilon \approx 1395\ cm^{-1}$, peak around 1163 cm^{-1} related to C-O-C and the CH=CH at $\upsilon \approx 666\ cm^{-1}$ [12,13] . The data in table 1 showed that the changes in the peak intensity values of these characteristic bands.

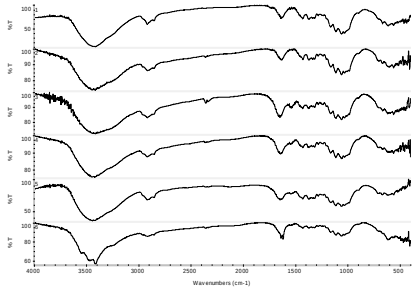

Figure 2: FTIR –ATR transmission spectra of the dyed blood stained aged and cleaned samples under

Test where:

1- Undyed cotton samples
2-Dyed cotton samples with turmeric dye
3- Dyed blood stained aged
4- Dyed stained aged and cleaned by basic medium (1%ammonia sol.)
5- Dyed stained aged and cleaned by acidic medium (0.5% acetic acid)
6- Dyed aged stained and cleaned by neutral medium (15% sodium chloride)

Figure (1) confirms the chemical structure of turmeric dye, it contains the following groups: phenolic OH group at $\upsilon \approx 3500\ cm^{-1}$, aliphatic CH group at $\upsilon \approx 2900\ cm^{-1}$, a very strong band at around 1600 cm^{-1} showing a mixing between C=C and C=O of benzene ring, and a prominent band at $\upsilon \approx 1163\ cm^{-1}$ assigned to C-O-C vibration and a band at $\upsilon \approx 666 cm^{-1}$ assigned to out of plane vibration OH groups. It is obvious that, all the above mentioned bands are common between both cotton fabric and turmeric dye except that band at $\approx 1395\ cm^{-1}$ which is related to C-H bending in cotton only [14]. In spite of this, most of bands show a decrease in intensity after dyeing (table 1).

The chemical structure of blood shows the following bands [15,16]: $\upsilon \approx 2900\ cm^{-1}$ contributed to anti-asymmetric stretching vibration of CH_2 and CH_3 from fatty acids in phospholipids, a sharp band at $\approx 1600\ cm^{-1}$ referred to C=O resulting from (CONH) amide I of fibrous tissue. These two bands are common between the three materials, blood, cotton and turmeric. The band at $\approx 1163\ cm^{-1}$ represents symmetric and anti-asymmetric stretching vibration from the phosphate (PO_4^{-3}) group in case of blood stain, while in turmeric and cotton this band refer to C-O-C stretching vibration [14,15]. The band at $\approx 1540\ cm^{-1}$ which contributes to N-H bending of fibrous tissue present only in blood, so it appeared after staining the dyed cotton samples with blood. Table 1 showed that almost of the bands showed an

increase in intensity after staining the dyed samples except the two bands at υ ≈ 3500 cm^{-1} and υ ≈ 1600 cm^{-1} showed a decrease in intensity.

When the dyed stained aged samples were cleaned using three different pH media of detergents (basic; 1%NH_3, acidic; 0.5% CH_3COOH and neutral; 15% NaCl), generally the peak intensity values of the different function groups showed the highest intensity at the neutral medium and the lowest intensity at the basic medium while the acidic lied in-between, except for the band at ≃ 2900 cm^{-1} which showed the reverse trend and the intensity of O-H stretching at ≃ 3500 cm^{-1}show a constant value. Besides, On comparing the effect of the cleaning process on the peak intensity values of the mentioned function groups with their corresponding in the dyed stained aged samples (table 1), it is clear that the intensity of the peaks at υ ≈ 1600 and 1540 cm^{-1} greatly increased with detergents, the peak intensity at υ ≈ 3500 cm^{-1} having constant value, and the peak intensity at υ ≈ 2900 cm^{-1} showing higher value in both acidic and basic medium, while the intensity values of the bands at υ ≈ 1395 cm^{-1} , υ ≈1163 cm^{-1} and υ ≈666 cm^{-1} were higher in the neutral medium.

FTIR-ATR technique can be used to monitoring the crystallinity of the samples via calculating the crystallinity index (C.I) which is taken as the ratio between the stretching and the bending mode for C-H group at ≈ 2900 cm^{-1} and 1395 cm^{-1} respectively , through the different treatment processes. The results are indicated in table 2. It is clear that the crystalline index increased with dyeing followed by a decrease with ageing the dyed stained aged samples. In addition, the crystalline index has the following order for the different detergent media: basic> acidic> neutral, both acidic and basic media having higher values than that of the dyed stained aged samples. The higher the C.I means that the higher is the crystallinity to amorphousity ratio, i.e. the lower is the amorphous region. The % crystallinity for the different treatment processes can be calculated using the following equation [17, 18]:

$$\%\text{crystallinity} = \frac{I_{t-}I_o}{I_o} \text{X100}$$

The results indicated that, the % crystallinity has a close relation and trend to the crystalline index. The increase in the crystalline index with dyeing means that the dye penetrated the fiber pores and aggregated inside it, while the decrease in the crystalline parameters after blood staining means that, both the dye and the stain were removed from the pores with ageing, so the amorphousity increased for some extent. Also, most of the cleaning processes showed a decrease in the C.I. which means more dye removal, i.e. increase the porosity and these results were manifested through the color difference measurements.

To evaluate the change in color as a result of the different treatments, i.e. dyeing, staining, ageing and cleaning, Spectrophotometic measurements were used. The most used color models are the perceptually uniform CIE L*a*b* because of its features as humans vision and underling the color components (color lightness L*, color coordinates ± a*- reddish/greenish and ± b*- yellowish/bluish). The color difference (ΔE) between a sample and standard in this system is given by [11]:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Where $\Delta L^* = L^*_{sample} - L^*_{standard}$, etc.

Since, in this research work, we have different colors on the samples, .i.e. yellow dye with red blood stain or with dark mud color stain or with the greasy wax stain, so ΔE values were taken as a measure of the color changes in the visible region (400-700 nm).

Table (2) shows the color difference ΔE whereas; the dyed sample was taken as the standard and the stained aged or cleaned as the sample. The results indicated that the ΔE values followed the order: dyed stained aged > acidic > basic > neutral. This means that, cleaning with neutral medium remove the dye color from the sample alongside with the stain.

Figure (3) shows FTIR-ATR transmission spectra of the dyed cotton samples stained with mud and cleaned with different concentrations of soap solutions , while the variation in the different functional groups were recorded in table (3). It is clear that, a new band at υ ≈ 3698 cm^{-1} assigned to O-H phenol stretching of mud appeared after staining [19] and disappeared after cleaning with the different soap concentrations. Besides, the following bands are common between mud stain and the dyed samples; υ ≈ 3500, υ = 2900, υ ≈ 1600 and υ ≈ 666 cm^{-1}. So, their intensities were obviously increased after staining.

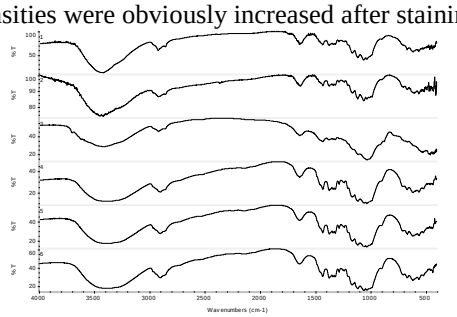

Figure 3: FTIR –ATR transmission spectra of the dyed mud stained aged samples under

Test where:

1- Undyed cotton samples 2-Dyed cotton samples with turmeric dye

2- Dyed mud stained aged

3- Dyed stained aged and cleaned by 0.5 % soap concentration.

4- Dyed stained aged and cleaned by, 1.0 % soap concentration.

5- Dyed aged stained and cleaned by 2.0 % soap concentration

In considering the effect of different soap concentrations, it was found that all the peaks showed a large decrease in their intensity values compared to the stained samples and these intensity values were nearly comparable to that of the dyed samples, which means that, the cleaning with soap may remove the stain and this result was manifested by the appearance of the phenol band of mud at 3698 cm^{-1} after staining and disappeared with cleaning.

Regarding to the crystallinity of the samples in view of the crystalline index (C.I) values (table 4), it was noticed that both the C.I. and % crystallinity increased for the stained aged samples followed by decreasing with cleaning and the lowest value was obtained at 0.5% soap concentration.

In concerning the color removal of the stain in terms of color difference, the lowest ΔE was obtained on using 0.5 % soap concentration, which means that, cleaning with soap, specially with the lowest concentration greatly remove the satin.

FTIR-ATR transmission spectra of the wax stain as illustrated in figure 4 and listed in table 5 showed nearly all the peaks common between cotton, turmeric and wax stain. Also, the band at υ ≈ 2900 cm^{-1} was splitted into two sharp bands at 2914 cm^{-1} and at 2848 cm^{-1} assigned to the asymmetric and symmetric CH_2 starching vibrations respectively account for most of the aliphatic absorption of waxes. The higher frequency region of carbonyl absorption at υ ≈ 1600 cm^{-1} can be assigned to the wax esters. Some attention was also paid to the C-O stretching

vibration of esters in the region υ ≈ 1163 cm^{-1} [20,21]. It is clear that, nearly most of the bands showed increase in their intensity values with the staining than that with dyeing, this can be attributed to the structural characteristics of the stain.

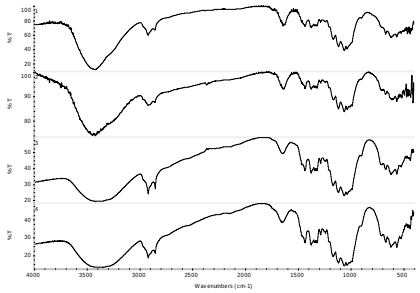

Figure 4: FTIR –ATR transmission spectra of the dyed wax stained aged samples under

1- Undyed cotton samples
2-Dyed cotton samples
3- Dyed wax stained aged
4- Dyed stained aged and cleaned by the conventional method.

On considering the cleaning process on the intensity of the function groups (table 5) , it was noticed that, the O-H stretching at υ ≈ 3500 cm^{-1} had nearly a constant value, while both the asymmetric and symmetric C-H stretching bands at υ ≈ 2917 and 2848 cm^{-1} were increased after cleaning. On the other hand the other obtained bands ,i.e. at υ ≈ 1600, 1395, 1163 and 666 cm^{-1} were all decreased after cleaning comparing to their intensities after staining but their intensities were higher than that of their dyed corresponding ones.

Regarding to the change in crystallinity of the samples with the different treatment processes, i.e. the crystalline index and % crystallinity (C.I) values (table 6), it was found that, there is a large decreased in both C.I and % crystallinity values after staining and after cleaning .

In concerning the color removal of the stain in terms of the color difference, it was noticed that ΔE was decreased after cleaning comparing to that after staining indicating a stain removal moderately (table 6).

Conclusion:

Detailed analysis of FTIR-ATR spectra of the treated cotton carpet samples throughout different treatment processes (dyeing, staining and cleaning) have shown the presence of common functional groups between cotton fabric, turmeric dye and the stain (blood, mud and wax) varying in their intensities with the different treatments. In addition, the obtained spectral data clarified that there are significant differences between the spectral features of the examined samples before and after staining, whereas, a new band, each corresponding to a stain type, was appeared after staining and vanished or varied in intensity after cleaning. Regarding to the effect of cleaning on the different stains it was found that:

For blood stain: the convenient media for cleaning was the neutral medium (15% NaCl),

For the mud stain: the lowest soap concentration (0.5% neutral soap) was good enough to remove the satin

Finally, for wax stain: the traditional method of cleaning wax was adequate to remove the stain.

The crystallinity parameters (C.I. and % crystallinity) shown that there is a close relation and trend between the C.I. and % crystallinity.

However, the analysis of the color difference (ΔE) has demonstrated that, the higher the color removal, the higher the ΔE values. It was noticed that, ΔE values varied significantly with the variation of the detergent pH media for blood stain (basic, acidic and neutral) or with the soap concentration for the mud stain (0.55, 1% and 2%) and take the order: For blood stain: acidic > basic > neutral and for mud stain: 2% > 1% > 0.5%

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Table 1: FTIR-ATR transmission (%T) bands intensities of dyed samples stained with blood and cleaned using different media

Detergents Media			Stained Aged	Dyed	Undyed	Peak position cm^{-1}
15% NaCl (neutral	0.5% CH_3COOH (acidic)	1% NH_3 (basic)				
9.99	9.99	9.99	9.99	12.12	9.99	3500 O-H str.
42.22	47.10	49.09	44.25	42.95	58.21	2900 C-H str.
60.51	53.28	47.49	39.23	65.83	71.23	1600 C=O, C=C
83.72	71.42	66.63	57.45	------	------	1540 N-H bend.
66.37	51.26	47.98	51.84	40.61	68.53	1395 C-H bend.
47.97	38.15	34.65	40.76	23.52	52.54	1163 PO_4^{-3} & C-O-C
64.06	45.21	40.09	46.11	38.08	59.16	666 O-H Out of plane

Table 2: The crystalline parameters and ΔE values of the examined samples stained with blood

Treatment		Crystalline index	%crystallinity	Color difference (ΔE)
Undyed		0.85	-----	-----
Dyed		1.06	24.70	-----
Blood Stain Aged		0.95	Zero	4.3
Different Detergents Media	Basic	1.02	20.00	0.6
	Acidic	0.92	8.23	3.8
	Neutral	0.63	-25.88	-11.67

Table 3: FTIR transmission (% T) bands intensities of dyed samples stained with mud and cleaned with different soap concentrations:

Cleaning With Different Soap Concentration			Stained aged	Dyed	Undyed	Peak Position cm^{-1}
2%	1%	0.5%				
------	------	------	67.88	------	------	3698 O-H phenol str.
14.05	15.05	17.18	37.98	12.12	9.99	3500 O-H str.
37.22	37.58	37.32	71.18	42.95	58.21	2900 C-H str.
66.47	66.69	66.25	66.17	65.83	71.23	1600 C=O, C=C
36.37	36.60	37.57	52.57	40.61	68.53	1395 C-H bend.
21.49	22.32	23.17	54.94	23.52	52.54	1163 C-O-C
36.79	37.51	38.84	48..18	38.08	59.16	666 O-H Out of plane

Table 4: The crystalline parameters and ΔE values of the examined samples stained with mud

Treatment		Crystalline index	%crystallinity	Color difference (ΔE)
Undyed		0.85	-----	-----
Dyed		1.06	24.70	-----
Mud Stain Aged		1.35	58.82	6.00
Different soap concentrations	0.5%	0.91	7.06	1.46
	1 %	1.03	21.17	1.95
	2%	1.02	20.00	2.02

Table 5: FTIR-ATR transmission (% T) bands intensities of dyed samples stained with wax and cleaned with the traditional method:

After Cleaning	Stained aged		dyed	undyed	Peak position cm^{-1}
10.00	9.99		12.12	9.99	3500 O-H str.
23.22	20.35	2917 Assym. Str. CH_2	42.95	58.21	2900 C-H str.
29.52	27.76	2849 sym. Str. CH_2			
72.91	77.24		65.83	71.23	1600 C=O, C=C
41.08	49.99		40.61	68.53	1395 C-H bend.
25.13	32.39		23.52	52.54	1163 C-O-C
45.49	54.75		38.08	59.16	666 O-H Out of plane

Table 6: The crystalline parameters and ΔE values of the samples stained with wax:

Treatment	Crystalline index	%crystallinity	Color difference (ΔE)
Undyed	0.85	-----	-----
Dyed	1.06	24.70	-----
Wax Stain Aged	0.48	-43.54	37.47
After Cleaning	0.64	-37.41	34.42