



Volume 9, Issue 2, Spring2015

Evaluating Study of Ultrafast Laser-assisted Cleaning of Historical Textiles Conservation

Harby E. Ahmed ^{1,2}, Amal A. El-Ebissy ³, Ilya Mingareev², Martin Richardson² harbyezzeldeen@yahoo.com.

¹Department of Conservation, Faculty of Archaeology, Cairo University, Egypt
²Townes Laser Institute, The College of Optics & Photonics, University of Central Florida, USA
³Textile Metrology Lab, National Institute for Standards, Alharam, Giza, Egypt

ABSTRACT

Museums contain a high number of historical textiles were made from silk dyed fabric that decorated with metallic threads. Pulsed laser radiation was used in order to remove dirt, corrosion and small particles from a substrate in different historical objects such as textiles. this study presents the experimental results on laser irradiation of silk dyed with natural dyes using ultrafast laser radiation (pulse duration <100 fs) with different pulse energies, in order to evaluate and to better understand the effect of laser interaction on historical textiles. Silk fabric has been prepared and dyed with natural dyes to be similar to the Egyptian Historical textiles. The resulting surface morphology was studied by using SEM and optical microscopy. In addition, color parameters (CIE Lab) and chemical properties of irradiated samples were studied for silk dyed with safflower or cochineal dyes, and alum, CuSO4 or ferric citrate mordants. Furthermore, determination of samples thickness and degree of crystallinity were performed before and after laser irradiation.

Keywords: Laser, cleaning, textiles, dyes, SEM, FTIR, Color change

1. Introduction.

Archeological textiles found in excavation sites are often characterized by the presence of natural sediments (for example, soil, insects and dust) deposited on the material during centuries. Moreover, conservators frequently cover the finds with consolidate material in order to preserve them from the detrimental action of external agents. Furthermore, many of these textiles contain metal threads as decorations. Metal threads deteriorate over time and corrode due to

chemical action of different corrosion favoring conditions such as high and fluctuating relative humidity, air pollutants and elevated temperatures (Balazsy and Eastop 1998; Hacke et. Al, 2005; Landi, 1992). Removing these undesired layers without damaging the historical objects can permit one to restore the original aesthetics (restoration) (Belli et al, 2006). Pulsed laser radiation has been utilizes to remove dirt, soil and corrosion from historical objects to cultural heritage restoration and conservation (Bloisi et al, 2004; Belli et al,

2008; Astillejoa et al, 2003; Abdel-Kareem and Harith, 2008). A small number of articles studied the effect of the laser irradiation on various type of natural fibers (Simileanu and Striber, 2008). The use of ultrafast laser radiation (pulse duration <100 fs) offers a new processing regime that is characterized by the minimum heat induced to the material, high spatial selectivity, and allows "gentle" processing of brittle, thinwall, micro-scale-sized, and thermally and structurally sensitive materials. In addition no studied have been reported on the effects of laser irradiation on silk dyed with natural dyes mordated with different type of mordants that are similar for textiles archaeological. In this article we examined the behavior of 'clean' silk fabrics dyed with natural dyes with respect to mechanical (bulk) and colorimetric (surface) properties before and after ultrafast laser irradiation. In contrast to the previously reported laser cleaning studies, we utilize tightly focused laser radiation produced by a commercial femtosecond laser system with the pulse duration tp = 100 fs to enable textile cleaning and modification processes with the minimum impact on structural, physical and chemical properties. In this first study we investigate mainly the effects of laser processing on the physical and chemical properties of textiles.

2. Materials

A silk fabric was degummed by a double treatment in a nonionic detergent (7g/L) at 95°C for 30 min, washed twice with distilled water and extracted with petroleum ether. All sericin, representing 34% of the silk samples weight was removed by this treatment.

 Greek silk fabrics were supplied by TSIAKIRIS Co., Soufli—Greece. www.tsiakiris.gr.

- Alum, iron (III) chloride FeCl₃ and copper (II) sulfate pentahydrate CuSO₄.5H₂O were purchased from Fluka.
- Safflower and Cochineal dyes were obtained from Wild Colors, Birmingham, UK. www.wildcolours.co.uk.

3. Dyeing3.1. Extraction of Dye

The dyeing with madder dye 10% (w/v) was carried out according to the following procedure:

- Grinding dye to a fine powder.
- Soaking the powder in distilled water for 24 h to extract the color from the powder.
- Heating and boiling temperature the extract for 2 h with continuous stirring. Water was added to compensate for the evaporation during the boiling process.
- The extract was cooled and then filtered many times to get a clear colored solution.

3.2. Dyeing Procedure

The dyeing procedure was performed by the exhaustion method according to Bechtold (Bechtold et al, 2003) using a liquor ratio (LR) of 1:20 (For 1 g of goods a dye bath volume of 20 ml is applied). Ten grams of degummed silk fabric were used as protein fiber substrate. In experiments with the addition of mordants, Alum, iron (III) chloride and copper (II) sulfate pentahydrate were added as a concentrated solution (50 g l⁻¹) to give a final dye bath concentration of 2.5 or 5 g l⁻¹ mordant. After dyeing, the unfixed dyestuff was removed by rinsing three times with cold water (5 min, room temperature, LR 1:20).

J

Α

Т

Table 1. Structure of silk fabrics used in the experiment

Samples	Color Coordinates					
	K\S	L	a	b		
Silk – Safflower- Alum	0.2359	72.10	-1.95	31.82		
Silk – Safflower- Iron	0.6218	63.74	0.10	27.21		
Silk – Safflower- Copper	0.5273	65.13	-3.17	27.47		
Silk – Safflower- no mordant	0.3933	68.45	-1.09	32.01		
Silk – Cochineal - Alum	2.2672	46.35	21.30	0.75		
Silk – Cochineal – Iron	1.2889	54.34	7.36	13.50		
Silk – Cochineal - Copper	4.2510	45.99	-0.74	6.59		
Silk – Cochineal- no mordant	1.3088	55.51	16.24	1.58		

4. Experimental 4.1. Laser irradiation procedure

Textile irradiations were performed using a SpectraPhysics Spitfire femtosecond CPA laser system operating at the wavelength λ =800 nm, pulse duration $t_p = 100$ fs, and pulse repetition rate $f_{rep} = 1$ - kHz. Samples were processed at different pulse energies E_D = 50, 100 and 200 μJ. Laser radiation was focused on the surface of samples using a microscope objective 5x/NA=0.1 resulting in a spot size of approximately 10 µm. Sample areas of 10 ×10 mm² were irradiated using Newport VP-25x linear 3D translation stages and by adopting line-scan approach with a distance of 200 µm between individual lines. The relatively high laser pulse energies typically used for processing of metals, semiconductors and other hard matter, as well as the large distance between the scanning lines were chosen in order to minimize direct interaction of laser radiation with textiles. In addition, high pulse energies are responsible for the creation of intense shockwaves in the material to be removed that is assumed to contribute to the effective and gentle processing.

5. Testing and analysis 5.1. Morphological study

The morphology of the surface of the fabrics was investigated using scanning electron microscopy (Merlin Compact, SEM) and optical microscope (Carl Zeiss, Germany). Small samples were taken from different parts the object and investigated under SEM

before and after laser application, to show the quality of the fibers as well as the damage induced to these fibers (Batcheller, 2005; Nicola, 1993).

5.2. Color Measurement

The dyeing properties of the dyed silk fabrics were examined studying two main parameters; dye ability expressed as color strength (K\S) and fastness to light which was evaluated instrumentally by measuring the color difference parameter (ΔE). This gives more accurate and precise value for the actual amount of faded dye. The CIE Lab values of the dyeing were measured using a double beam Color-Eye ® 3100 spectrophotometer in the spectral range 400-700 nm. The colors are given in CIE Lab coordinates, L* corresponding to the brightness (100 = white, 0 = black), a^* to the red-green coordinate (positive sign = red, negative sign = green), and b^* to the yellow-blue coordinate (positive sign = yellow, negative sign= blue). The total color difference is specified as $\Delta E^* = \{(\Delta L^*)^2 +$ $(\Delta b^*)^2 + (\Delta a^*)^2$ (Booth, 1984; Wyszecki and Stiles, 2000). The CIE-Lab values of the color changes were measured using a double beam Optimatch spectrophotometer (Datacolor Spectraflash SF 450, UK).

Measuring the thickness of the silk dved fabric with natural dyes before and after laser application was a challenging task. Determination of thickness of fabric samples

5.3. Textiles thickness measurement

in laboratory is usually carried out with precision thickness gauge (Stéphane, 2002). In our experiments, the thickness measurement was performed using a Digimatic outside micrometer, Japan.

5.4. Fourier Transform Infrared Spectral (FTIR) Analysis

FTIR spectroscopy analysis was performed using a Thermo Scientific, Nicolet 380 spectrophotometer in the spectral range 400-4000 cm⁻¹, resolution of 4 cm⁻¹ and the number of scans was 64. Fabrics were measured by "smart performer ATR" unit accessory with zinc selenide crystal. The vibrational bands that appear in the infrared spectra provide information about the secondary structure of silk fabrics and information about the chemical functional groups of a sample. This leads to a general characterization of the material or the identification of specific compounds (Michele, 1989; Thompson et al, 2009). An expanded spectrum in the 400-4000 cm ⁻¹ range was used for measuring several factors with a spectral resolution of 4 cm1. Each spectrum was the result of an average of 16 scans. We took small samples of different colors and investigated them before and after leaser irradiation.

5.5. X-ray diffraction analysis

Wide angle x-ray scattering (WAXS) measurements of unaged and aged samples were carried out with a SIEMENS X-Ray Diffractometer – D 5000, given 40 Kv CU Ka, radiation of 30 mA. The diffractograms were recorded over $2\theta = 50$ to 300 continuously at a scan rate of 20/min. Crystallinity index (crystalline to amorphous ratio) can be calculated using the following equation (Segal et al, 1959).

$$CrI = (I_{002} - I_{am}) \times 100$$
 I_{002}

Where I_{002} is the maximum intensity (in arbitrary units) of lattice diffraction, while I_{am} is the intensity of the lattic diffraction in the same units at $2\theta = 20$, the angle that represents the amorphous scatter of fiber.

6. Results and desiccation6.1. Morphological Study

Surface structural damage for textile samples after laser application can be determined by SEM images as shown in Fig.1. One can see the disruptive effects of laser irradiation on textiles pulse energies $50\mu J$, $100\mu J$ and $200\mu J$. There is a direct correlation between the degree of damage to the fibers, and the adopted laser pulse energy. It is a clear that the lowest damaging impact on fiber was achieved at the pulse energy at $50\mu J$.

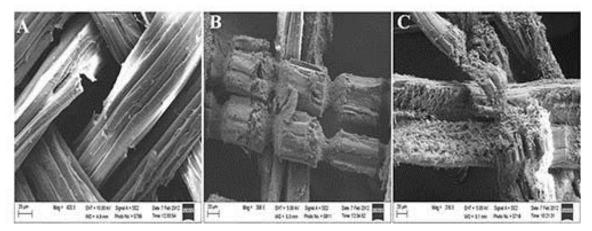


Figure 1. SEM images of silk dyed fabric after laser application, irradiated at different pulse energies with (A) 50 μJ, (B) 100 μJ, (C) 200 μJ,

6.2. Color Changes

The results of the change in optical parameters of silk dyed with safflower dye and cochineal dye after laser application are demonstrated o Table 2, Fig 4 and 5. The laser-induced color change is reflected in the modulation of color values in dependence on the pulse energy. For examples, the increase (ΔE) of silk dyed with safflower dye mordanted with alum was 4.9, 5.69 and 10.45 when irradiated with 50µJ,100 µJ and 200 µJ pulses, respectively. Also it is observed that there is increase in the K/S. It is clear that the L* corresponding to the brightness was changed as well. For example, brightness increase of silk dyed with Safflower dye mordanted with Alum, Iron and Copper. From table.2 it is observed a positive correlation between pulse energies and the degree of brightness change. Notes that the effect of the laser on the silk dyed with safflower dye mordant with alum greater than its effect on the rest of the samples. See Fig 4B. By other hand, it is clear that there is a slight increase in the redness with laser application with different pulse energies for silk dyed with safflower dye mordanted with alum and without mordant, while there is increase in greenness for silk dyed with safflower dye mordanted with iron and copper. Also one can see a slightly increase in blueness for all the silk dyed with safflower dye. As shown in Table 2 and Fig 4C and D.

5 Article Designation: Refereed **JTATM**

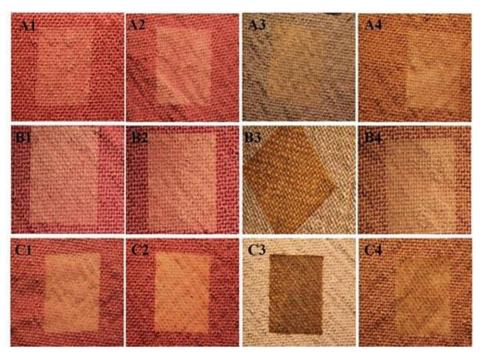


Figure 2. Effect of laser irradiation on color and surface morphology change of different samples. The index letters A, B and C correspond to different laser pulse energies applied, i.e. 50μ J, $100~\mu$ J and $200~\mu$ J, respectively. The index numbers represent different samples: (1) Silk dyed with cochineal without mordant (2) Silk dyed with cochineal mordant with alum (3) and Silk dyed with cochineal mordant with iron (4),

Furthermore, increasing value (ΔE) of silk dyed with cochineal dye mordanted alum was 0.54, 1.51 and 1.90 when irradiated with 50 μ J, 100 μ J and 200 μ J pulses, respectively. Also it is observed that there is increase in the K/S. By other hand, it is clear that there is a slight increase in the redness with laser application with different pulse

energies for silk dyed with cochineal dye mordanted with alum and copper, while there is increase in greenness for silk dyed with cochineal dye mordanted with iron and without mordant. Also one can see a slightly increase in yellowness for all the silk dyed with safflower dye. As shown in Table 2 and Fig 5C and D.

Table 2. Color change of samples after laser application

Pules	samples					
Energy		ΔK/S	ΔL^*	∆a*	Δb*	ΔΕ
50 μ J	Silk – Safflower- Alum	0.0877	3.18	0.14	-3.73	4.91
100 μ J	Silk – Safflower- Alum	0.184	5.07	0.46	-5.01	5.69
200 μ J	Silk – Safflower- Alum	0.276	6.09	0.96	-7.21	10.45
50 μ J	Silk – Safflower - Iron	0.1189	2.53	-0.33	-0.5	0.65
100 μ J	Silk – Safflower - Iron	0.17	3.62	-0.76	-0.63	1.21
200 μ J	Silk – Safflower - Iron	0.19	4.11	-1.11	-1.23	1.64
50 μ J	Silk – Safflower- Copper	0.1327	2.01	-0.31	-2.42	2.11
100 μ J	Silk – Safflower- Copper	0.212	2.2	-0.43	-3.43	3.46
200 μ J	Silk – Safflower- Copper	0.231	2.45	-1.01	-5.89	2.97

50 μ J	Silk – Saff- no mordant	0.0217	0.67	0.63	-1.0	1.86
100 μ J	Silk – Saff- no mordant	0.146	1.4	1.04	-1.59	2.01
200 μ J	Silk – Saff- no mordant	0.121	3.73	1.32	-4.44	2.54
50 μ J	Silk – Cochineal - Alum	0.3464	0.44	0.29	0.12	0.54
100 μ J	Silk – Cochineal - Alum	0.461	1.32	0.46	0.42	1.51
200 μ J	Silk – Cochineal - Alum	0.502	2.31	0.97	0.89	190
50 μ J	Silk – Cochineal - Iron	0.0698	3.54	-1.42	0.67	3.01
100 μ J	Silk – Cochineal - Iron	0.0779	4.49	-1.52	1.02	2.56
200 μ J	Silk – Cochineal - Iron	0.131	6.02	-2.04	1.3	4.43
50 μ J	Silk – Cochineal - Copper	0.469	1.43	0.94	1.56	2.41
100 μ J	Silk – Cochineal - Copper	0.639	3.1	2.1	2.58	1.99
200 μ J	Silk – Cochineal - Copper	0.702	4.78	3.6	3.57	4.31
50 μ J	Silk – Cochineal - no mord	0.124	7.05	-2.76	1.43	3.76
100 μ J	Silk – Cochineal - no mord	0.169	10.17	-3.1	3.13	2.65
200 μ J	Silk – Cochineal - no mord	0.217	12.45	-3.97	4.23	5.13

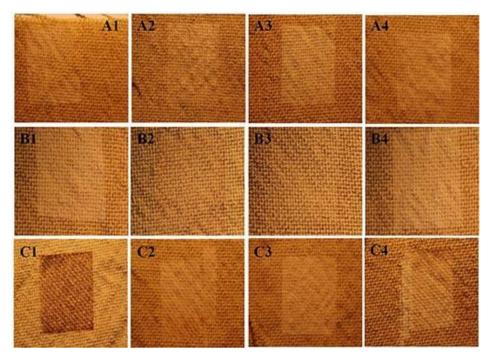


Figure 3. Effect of laser irradiation on the color and surface morphology change of different samples. The index letters A, B and C correspond to different laser pulse energies applied, i.e. 50μJ, 100 μJ and 200 μJ, respectively. The index numbers represent different samples: (1) Silk dyed with safflower without mordant, (2) silk dyed with safflower mordant with alum, (3) silk dyed with safflower mordant with iron and (4) silk dyed with safflower mordant with copper,

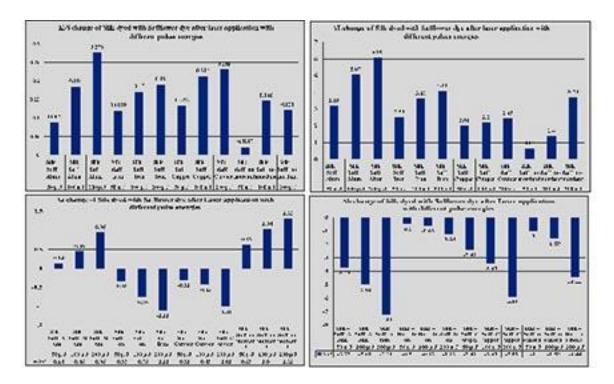


Figure 4. A, correspond to K/S change of silk dyed with safflower dye after laser application with different pulse energies. B correspond to ΔL change of silk dyed with safflower dye after laser application with different pulse energies. C correspond to Δa change of silk dyed with safflower dye after laser application with different pulse energies. D correspond to Δb change of silk dyed with safflower dye after laser application with different pulse energies,

Ί

M

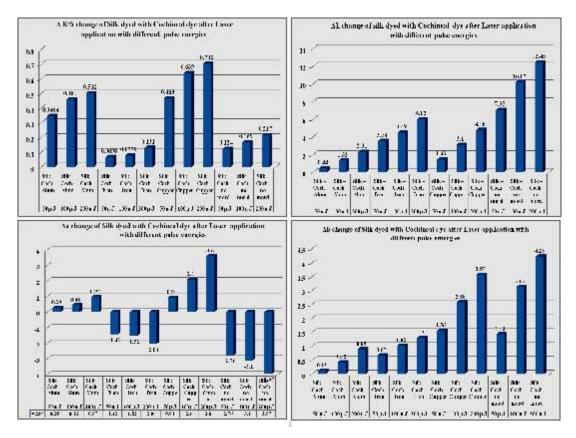


Figure 5. A correspond to K/S change of silk dyed with cochineal dye after laser application with different pulse energies. B correspond to ΔL change of silk dyed with cochineal dye after laser application with different pulse energies. . C correspond to Δa change of silk dyed with cochineal dye after laser application with different pulse energies. . D correspond to Δb change of silk dyed with cochineal dye after laser application with different pulse energies,

6.1. Thickness Changes

Table 3 presents the measured sample thickness. Thickness of samples before and after laser application can provide an indication for the behavior of silk fabric dyed with natural dyes after laser irradiation

at different pulse energies. One can see that all samples are affected by the laser irradiation. When the laser power increases, the thickness of the samples is decrease correspondingly.

Table 3. Thickness change of samples after laser application

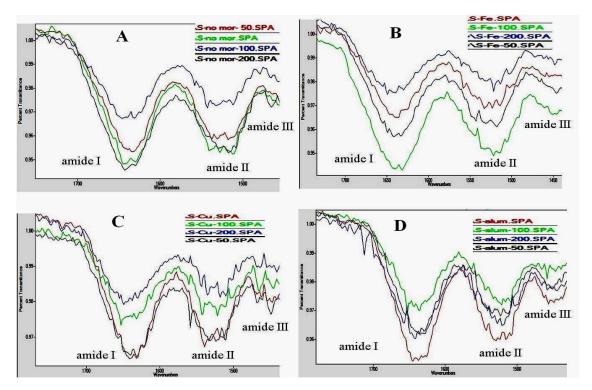
Samp	les	Samples Thickness [mm]			
		Before Laser irradiation	After laser irradiation	Change	
50	Silk – Safflower- Alum	0.306	0.285	0.021	
	Silk – Safflower- Iron	0.29	0.282	0.008	
	Silk – Safflower- Copper	0.304	0.295	0.009	
	Silk – Safflower- no mordant	0.291	0.285	0.006	
μJ	Silk – Cochineal - Alum	0.286	0.27	0.016	
	Silk – Cochineal – Iron	0.296	0.282	0.014	
	Silk – Cochineal - Copper	0.321	0.307	0.014	
	Silk – Cochineal- no mordant	0.307	0.3	0.007	
	Silk Safflower- Alum	0.29	0.262	0.028	
	Silk – Safflower- Iron	0.282	0.253	0.029	
	Silk – Safflower- Copper	0.314	0.275	0.039	
100 μ J	Silk – Safflower- no mordant	0.299	0.275	0.024	
μ,	Silk – Cochineal - Alum	0.309	0.282	0.027	
	Silk – Cochineal – Iron	0.296	0.271	0.025	
	Silk – Cochineal - Copper	0.32	0.284	0.036	
	Silk – Cochineal- no mordant	0.294	0.257	0.037	
	Silk - Safflower- Alum	0.3	0.254	0.046	
200 μ J	Silk – Safflower- Iron	0.284	0.244	0.04	
	Silk – Safflower- Copper	0.309	0.242	0.067	
	Silk – Safflower- no mordant	0.292	0.261	0.031	
	Silk – Cochineal - Alum	0.299	0.249	0.05	
J	Silk – Cochineal – Iron	0.299	0.254	0.045	
	Silk – Cochineal - Copper	0.34	0.28	0.06	
	Silk – Cochineal- no mordant	0.314	0.282	0.032	

6.2. Fourier Transform Infrared Spectral (FTIR) Analysis

Infrared absorption spectra of silk show characteristic absorption bands assigned to the peptide bonds (-CONH-) that are known as amide I, amide II, and amide III. Amide I is useful for the analysis of the secondary structure of the proteins and is mainly related with the C=O stretching, and it occurs in the range of 1,700–1,600 cm⁻¹. Amide II, which falls in 1,540–1,520 cm⁻¹ range, is related with the N–H bending and C–N stretching vibration. Amide III occurs in the range of 1,430–1,450 cm⁻¹ and it results from C–H bending vibration. In addition, the positions of these bands

indicate the conformations of the protein materials 1,650 cm⁻¹ (random coil) and 1,630 cm⁻¹ (β-sheet) for amide I, 1,540 cm⁻¹ (random coil) and 1,520 cm⁻¹ (β-sheet) for amide II (Ahmed and Sawsan 2012; Andrew, 1994). The results in Figs 5 and 6 showed that all the amide I and amide II appeared at 1,620 cm⁻¹ and 1,513 cm⁻¹ respectively indicating that all the silk samples present are mainly in β -sheet structure. Fig.6a showed the intensities of all bands of silk dyed with safflower without mordants after laser application with 50µJ, 100µJ decreased while increased after laser application with 200µJ compared with that of the control indicating the occurrence of hydrolysis and slight oxidation. Fig. 6b showed the intensities of all bands of silk dyed with safflower mordant with Iron after laser application with 50µJ decreased while increased after laser application with 100µJ and 200µJ compared with that of the control indicating the occurrence of hydrolysis and slight oxidation. Fig. 6c showed the intensities of all bands of silk dyed with safflower mordant with Copper after laser application with 100µJ and 200µJ decreased

while the same after laser application with 50µJ compared with that of the control indicating the occurrence of hydrolysis and slight oxidation. Fig. 6d showed the intensities of all bands of silk dyed with safflower mordant with alum after laser application with 50µJ, 100µJ and 200µJ decreased compared with that of the control indicating the occurrence of hydrolysis and slight oxidation.



N.B. All the samples are dyed with safflower using various mordants (A: without mordant, B: iron, C: Copper and D: alum),

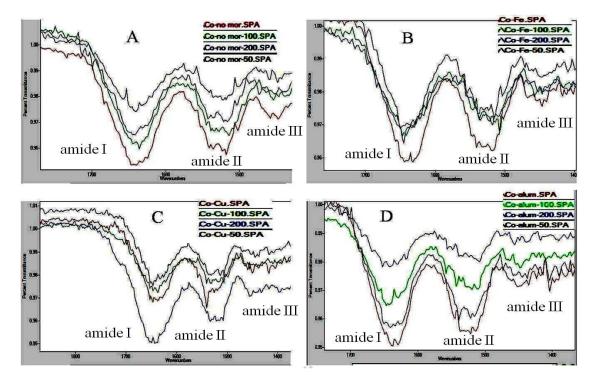
Figure 6. Effect of Laser application with 50µJ, 100µJ and 200µJ. A and B show the intensities of all the bands decreased compared with that of control. These results can be explained due to the as a result of hydrolysis and photo- oxidation.. C and D show the intensities of all the bands increased compared with that of control. These results can be explained due to the solubility of the products resulting from photo-oxidation,

Fig. 7a shows the intensities of all bands of silk dyed with cochineal without mordants after laser application with 50μJ, 100μJ and 200μJ decreased compared with that of the control indicating the occurrence of hydrolysis and slight oxidation. Fig.7b shows the intensities of all bands of silk dyed with cochineal mordant with Iron after laser application with 50μJ decreased while

increased after laser application with $100\mu J$ and $200\mu J$ compared with that of the control indicating the occurrence of hydrolysis and slight oxidation. Fig. 7c shows the intensities of all bands of silk dyed with cochineal mordant with Copper after laser application with $50\mu J$, $100\mu J$ and $200\mu J$ decreased compared with that of the control indicating the occurrence of hydrolysis and

slight oxidation. Fig. 7d shows the intensities of all bands of silk dyed with safflower mordant with alum after laser application with 50µJ, 100µJ and 200µJ

decreased compared with that of the control indicating the occurrence of hydrolysis and slight oxidation.



N.B. All the samples are dyed with Cochineal using various mordants (A: without mordant, B: iron, C: Copper and D: alum),

Figure 7. Effect of Laser application with 50μJ, 100μJ and 200μJ of silk dyed with cochineal dyed. The intensities of all the bands increased compared with that of control. These results can be explained due to the solubility of the products resulting from photo-oxidation,

6.3. Effect of ageing conditions on the crystallinity

It is clear that the silk is a semi-crystalline protein fiber therefore a study of its crystallinity may lead to a more detailed knowledge of the degradation process. Any treatment with the potential to change fiber morphology may sometimes lead to crystallization or decrystallization.

XRD results of silk samples after laser application are presented in two ways. The first way presents the percentage of the crystallinity index of unirradiated sample and those treated by laser irradiation. As shown in Table 4, there is a drastic decrease

of crystallinity index for irradiated silk samples these is may be due to thermal action of laser.

The second way is the Wide Angle X-ray (WAXS) diffractograms of unirradiated and irradiated silk samples. Fig.8 illustrates WAXS diffractograms of silk after laser irradiation with different pulse energies showing the effect of the laser application on the silk crystallinity. There is a difference between the diffractograms of the irradiated and unirradiated silk samples due to the action of laser irradiation process. There were changes on the size and shape of the crystalline area of the samples.

Table 4. Crystalline Index of aged silk with different aging methods (18 days thermal ageing, 154 h light ageing and acid ageing 4% Sulfuric acid)

Samples	Crystalline area		Amorphous area		Crystallinity	
	2θ	Counts	2θ	Counts	Index	
Silk - Original	20.613°	439	12.130°	134	77.45 %	
Silk irradiated with laser pule 50 µ J	20.550°	412	13.242°	127	69.05 %	
Silk irradiated with laser pule 100 µ J	20.466°	334	13.475°	123	64.99 %	
Silk irradiated with laser pule 200 µ J	20.527°	319	13.354°	119	62.04 %	

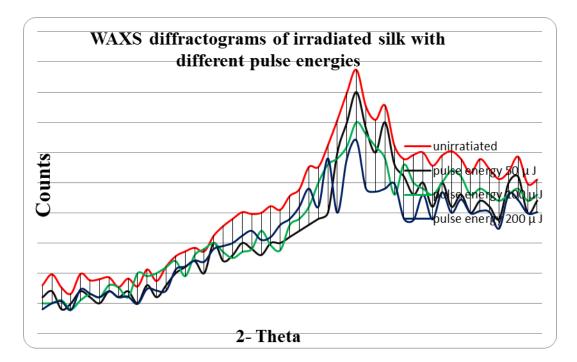


Figure 8. Show Wide Angle X-ray (WAXS) diffractograms of unirrdiated and irradiated silk with different pulse energies. One can see that the irradiated silk showed a reduction in the peak intensity (counts) in both the amorphous and crystalline regions for irradiated silk samples,

7. Conclusion

While laser processing is highly effective in cleaning historical surfaces such as stones and metals objects, the use of lasers in cleaning historical textiles needs more studies in order to investigate the effects of the laser on the physical and chemical properties of fabrics dyed with natural dyes. This paper is the first part of an extensive study of our team to study the effect of the laser on the characteristics of silk textiles

dyed with natural dyes. From SEM images we can see the destructive influence of the laser radiation on fiber under these conditions however we expect a very effective removal of dirt and clay. Also laser irradiation causes a considerable color change of the samples. There is a clear impact on the thickness of the samples after treatment, resulting in a decreasing thickness with increasing laser pulse energy. Investigation by FTIR shows the destructive

effect of laser on amide I, amide II, and amide III of silk fabric dyed with safflower or cochineal dyes. This study does not recommend using a femtosecond laser to clean the surface of historic silk textiles dyed with safflower or cochineal dyes mordanted with various mordants directly at least under the reported experimental conditions produced extensive damage to the textiles, further studies will be performed towards the minimization of the fiber damage. This can be achieved by a careful choice of processing parameters, the use of material-selective adaptive strategies. From our preliminary experiments we can conclude that ultrafast laser radiation can be used to remove the upper layers of heavy dirt and contaminations found on historical textiles and the subsequent cleaning can be competed either by traditional methods or with low-energy laser processing.

8. References

- Abdel-Kareem, O. and Harith, M.2008. Evaluating the use of laser radiation in cleaning of copper embroidery threads on archaeological Egyptian textiles. *Applied Surface Science*, Vol, 254, PP. 5854–5860.
- Ahmed, H. and Sawsan, D. 2012. Effect of Museum Conditions on Historical Dyed Silk Fabric with Madder Dye. *Journal of Polymer Environment*, Vol. 20, PP. 96–606.
- Andrew, S. 1994. Using ultraviolet and infrared techniques in the examination and documentation of historic textile. *Conservator*. Vol, 18, PP. 86–94.
- Astillejoa, M. Martína, M. Oujjaa, M. Rebollara, E. Domingob, C. García-Ramosb, J. and Sánchez-Cortésb, S. 2003. Effect of wavelength on the laser cleaning of polychromes on wood. *Journal of Cultural Heritage*, Vol. 4, PP. 243–249.
- Balazsy, A. and Eastop, D. 1998. *Chemical principles of textile conservation*, UK, 1998.

- Batcheller, J. 2005. Optical and scanning electron microscopy techniques for the identification of hair fibers from Romano-Egyptian textiles, in: R. Janaway, P. Wyeth Eds.), Scientific Analysis of Ancient and Historic Textiles: informing preservation, display and interpretation, AHRC Research Center for **Textile** Conservation and Textile Studies, First Annual Conference, UK, July, 13–15, pp.51-57.
- Bechtold, T. Turcanu, A. Ganglberger, E. and Geissler, S. 2003. Natural dyes in modern textile dyehouses- how to combine experiences of two centuries to meet the demands of the future? *Journal of Cleaner production*. Vol, 11, PP. 499–509
- Belli, R. Toniutti, I. Miotello, A. Mosaner, P. and Avi, D. 2008. Excimer laser irradiation at 248 nm of wooden archaeological objects and polymeric consolidants used in conservation: a study of cone formation and optimum cleaning parameters. *Applied Physics A*. Vol, 92, PP. 217–221.
- Belli, R. Miotello, A. Mosaner, P. and Toniutti, L. 2006. Laser cleaning of artificially aged textiles. *Applied Physics A*, Vol.83, PP. 651–655
- Bloisi, F. Vicari, I. Barone, A. Martuscelli, E. Gentile, G. and Polcaro, C. 2004. Effects of Nd:YAG (532 nm) laser radiation on 'clean' cotton. *Applied Physics A*, Vol. 79, PP. 331–333.
- Booth, J. 1984. *Principles of Textile Testing*. 3rd edition, Butterworth-Heinemann. USA.
- Hacke, A. Carr, C. and Brown, A. 2005.
 Characterisation of Metal Threads in
 Renaissance tapestries, In: Post print
 of the First Annual Conference,
 Scientific Analysis of ancient and
 Historic Textiles: Informing
 Preservation, Display and
 Interpretation, Archetype Publications
 Ltd, July 13-15, 2004, pp.71-78.

J.

Τ

Α

Τ

M

- Landi, S. 1992. *The Textile conservator's manual*, 2nd edition, London.
- Michele, D. 1989. Fourier Transform infrared spectral analysis of natural resins used in furniture finishes. *Journal of American Institute for Conservation*, Vol. 28, PP. 43–56.
- Nicola, G. 1993. The examination and conservation of tow Indian textile. *Conservator*, Vol. 17. PP. 102- 111.
- Segal, L. Creely, J. Martin, J. and Conrad, C. 1959. An Empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal*, Vol, 29. PP. 786–794.
- Simileanu, M. and Striber, J. 2008. Radvan, Aspects concerning laser conservation of organic art works. *Romanian Reports in Physics*, Vol, 60, PP.105–110.
- Stéphane, F. Durand, B. Freyburger, J. 2002. Fabric thickness dynamic measurement during a classic uniaxial tensile test. *Experimental Mechanics*, Vol. 42, PP. 84-92.
- Thompson, T. Gauthier, M. and Islam, M. 2009. The application of a new method of Fourier Transform Infrared Spectroscopy to the analysis of burned bone. *Journal of Archaeological Science*, Vol. 36, PP. 910–914.
- Wyszecki, G. and Stiles, W. 2000. Color science concepts and methods, 2nd edn. Quantitative data and formulae. New York. U.S.A.

M