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Research Article

STUDY OF THE EFFECT OF ENVIRONMENTAL CONDITIONS ON THE RED COLOR OF SAINT YEHNES CAMA ICON, MALLAWI, EGYPT

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ABSTRACT

Icon of Saint Yehnes Cama studied for identification of the components of icon painting and assessment the effect of environmental conditions. The obtained results revealed that linen fibers were used as flexible support, kermes carmine red was used as pigment and egg yolk was used as binder. Linen fibers are not affected with the environmental conditions, while organic pigment "kermes carmine red" shows degradation of its components with fading of the paint color and absence of varnish layer.

Keywords: Icon, Environmental Conditions, OM, ATR-FTIR, FESEM-EDX, XPS.

1. INTRODUCTION

The studied icon has been hold in monastery of Saint Yehnes Al-Kasir that locates a distance of 12 km from Mallawi.[1] Mallawi is located a distance of 45 km in south of Minya governorate and a distance of 270 km in south of Cairo.[2] This area is described as a desert area and characterized with hot climate and shining sunlight.

Basic layers of the icon painting are support, ground, paint (pigment and binder) and varnish layers.[3] There are many factors which can cause deterioration of the icon painting such as temperature, light, humidity, air pollution and insects.[4] Temperature and light are the most important factors to cause deterioration of the painting. Oxidation process through thermal or photochemical energy is called "Auto-oxidation Reaction" and it is initiated by action of metal oxides and other salts that present in the pigments. The oxidation process leads to degradation of the organic molecules and deterioration of the binder and varnish of the painting.[5]

Lake pigment is, a natural organic pigment, prepared when a dye has been precipitated on inorganic carrier. Aluminum hydroxide is a common carrier used to produce transparency. Barite can be added to the lake pigment to give its opacity. Other compounds can be used as carriers such as: chalk, gypsum, clay, tin oxide and zinc oxide. Often a mordant such as: tannic acid, lactic acid or sodium phosphate is used to fix the lakes to the substrate.Carmine lake is a generic name for two organic red lakes that are obtained from scale insects, cochineal "derived from the cochineal insect" and kermes "processed from the kermes insect". Carmine lakes are not resistant to light and weather.[6]

Spectroscopic techniques have been applied to give information about the painting materials to describe the general state of icon. Optical microscope (OM) is used for identification the fiber structure. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) gives characteristic bands of organic and inorganic materials. Field emission scanning electron microscope (FESEM) is used to examine the topography of the paint film.Energy dispersive spectroscopy (EDS) is used for elemental identification.X-ray photoelectron spectroscopy (XPS),also known as electron spectroscopy for chemical analysis

(ESCA), has been used to examine the surface of the painting and it has the advantage of determination of the oxidation state of an element.[7]

1.1. Historical Background
Icon of Saint Yehnes Cama has been hold in Church of Saint Yehnes Cama, Monastery of Saint Yehnes Al-Kasir. The monastery dates back to 6th century.

1.2. Icon Description
Saint Yehnes wears brown sticharion, black tailasan with golden cross in his right hand and blackstick in his left hand. There is yellow halo around his head. The saint stands with brownish-red background. The icon shows longitudinal fractures in the wood support and peeling of the paint surface. Two samples were carefully extracted from fibers of the canvas, and redcolor "damaged edge of the background layer".

2. MATERIALS AND METHODS
2.1. MATERIALS
2.1.1. Historical Samples
Two small samples were obtained from the damaged parts of icon. The samples were canvas fibers and red color.

2.1.2. Reference Samples
Four reference materials were assembled and analyzed by ATR-FTIR method. The reference samples are gypsum, lead white, chalk and egg yolk materials.

2.2. Instruments and Methods
2.2.1. Optical Microscope (OM)
Canvas fibers were analyzed by Leica motorized optical microscopesystem equipped witha digital camera Leica ICC50 HD (Leica DM750, Wetzlar, Germany).

2.2.2. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)
Spectra were recorded using Vertex 70 FTIR spectrometer (Bruker Optics, Billerica Inc., Massachusetts, USA) equipped with a diamond crystal and DLaTGSdetector accessories. The spectra were acquired with 16 scans in the range 4000-400 cm^{-1} and resolution of 4 cm^{-1}.

2.2.3. Field EmissionScanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (FESEM-EDX)
Quanta FEG-250 Field emission scanning electron microscope (FEI Company, Hillsboro, Oregon, USA) was used for imaging the paint surface under secondary and backscattered modes. EDX unit (Energy Dispersive X-ray Spectrophotometer, EDAX Apollo SDD, Mahwah, New Jersey, USA) was used to identify the chemical composition of paint sample. FESEM-EDX analysis was performed at low-vacuum conditions, accelerating voltage 20 kV, resolution 1 nm, and magnification 14× up to 1,000,000×.

2.2.4. X-ray photoelectron spectroscopy (XPS)
X-ray photoelectron spectroscopy study was performed using K-Alpha XPS (Thermo Scientific, East Grinstead, UK) utilizing monochromatic Al Kα X-ray source (hυ = 1486.6 eV). Survey spectra were collected for elemental quantification using a 400 µm spot of X-ray to define the analyzed area: 50 eV pass energy, 10 msdwell time and 0.1 eV step size.

3. RESULTS AND DISCUSSION
Study of the icon materials using OM, ATR-FTIR, FESEM-EDX, and XPS shows that the flexible support is linen fibers and the ground material are gypsum, lead white and the pigment is kermes carmen red, and the binder is egg yolk. Infrared results of historical samples (Table 1) will compare to those of reference samples (Table 2).
Linen fibers (Fig. 2) appear as flexible support and it is marked with cracks and nodes along the fibers.[9]Linen is characterized with good dimensional stability and coarse fabric fibers, and this illustrates the strength of canvas fibers with the environmental conditions.[10,11]
Gypsum is (Fig. 3) shows ATR-FTIR bands at 3398 cm^{-1} υ(O-H), 1622 δ(O-H), 1100 υ(SO_4^{-2}), and 671 cm^{-1} δ(SO_4^{-2}).[12-14] EDS microanalysis (Fig. 5) indicates the presence of Ca, C, S, and O elements which are characteristic of gypsum.[15]
ATR-FTIR spectrum of lead white (Fig. 3) exhibits characteristic bands at 3398 υ(O-H), 1622 δ(O-H), 1410 υ(CO_3^{-2}), and 873 cm^{-1} δ(CO_3^{-2}).[14,16] EDS microanalysis (Fig. 5) reveals the existence of Pb element of lead white.[15] FESEM micrograph (Fig. 4) demonstrates the presence of lead white with bright particles.
ATR-FTIR spectrum of the red color (Fig. 3) manifests characteristic bands at 3398 υ(O-H), 2920, 2851 υ(C-H), 1647, 1622, 1541 cm^{-1} υ(C=C)$_{Aromatic}$, and 1100 cm^{-1} υ(C-O) that refer to red lake (kermes carmine).[12,17] FESEM micrograph (Fig. 4)shows dark-gray appearance indicating its organic composition.[18] EDS microanalysis (Fig. 5) detects Ca, S, Si, Al, Mg and Fe elements of

clay as a carrier for the organic dye.[19] Also, appearance of ATR-FTIR bands of chalk at 1410, 875 and 712 cm^{-1} as a carrier for the kermes carmine dye.[13,14,16] Presence of Ba, S, and O elements within EDS microanalysis that may refer to use barium sulfate (barite) as additive to provide opacity of the pigment.[17] Salts of the pigment initiate the oxidative reactions in which heat and sunlight of the environment cause discolor of kermes carmine pigment to a faint sepia-like brown.[20] This assumption is confirmed by cracking of the paint film in FESEM micrograph and appearance infrared bands of oxalate at 1622 cm^{-1} with broad band at 1410 cm^{-1}.[21,22]

Egg yolk (Fig. 3) is identified by bands at 3398 υ(N-H), 2920, 2851 υ(C-H), 1647, 1622, 1541 υ(C=O), 1541, 671 δ(N-H), 1541 υ(C-N) and 1410 cm^{-1} δ(C-H).[23-25]

No characteristic ATR-FTIR bands were identified for varnish material.

These results are confirmed by XPS analysis (Tables 3 and Fig. 6) showing binding energy of (C1s) at 286.97 eV which is characteristic for benzene (anthracene ring of kermes carmine), carboxylic acid (kermesic acid of kermes carmine), and amine (amino acids of egg yolk). In addition to binding energy of (O1s) at 533.79 eV which is characteristic for hydroxyl organic group (hydroxyl group of kermes carmine), polymer (amino acids of egg yolk).[26]

4. CONCLUSION

A multi-method approach has been used to investigate the icon materials and study the state of icon. Spectroscopic techniques have been used for characterization the painting materials are OM, ATR-FTIR, FESEM-EDX and XPS. Visual observation shows that there are fractures in the wood support and peeling of the paint surface. Chemical analyses show that icon materials are linen fibers, gypsum, lead white, kermes carmine red and egg yolk. The obtained results manifest the effect of sunlight and heat of the desert area around the icon by fading of the red color of kermes carmine to resemble the brown color, and removal of the varnish layer.

Fig. 1**: Icon of Saint Yehnes Cama**

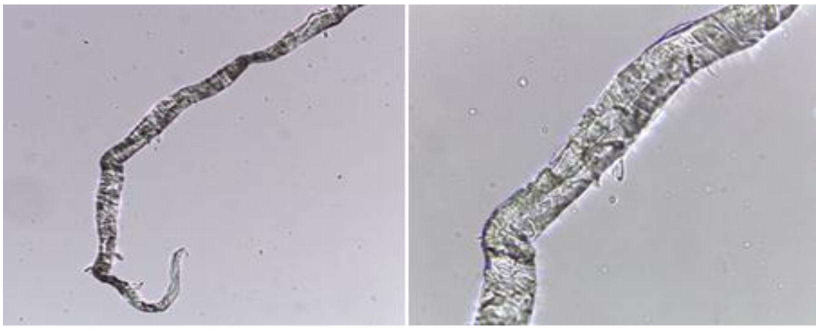


Fig. 2: Linen Fibers of Canvas Layer

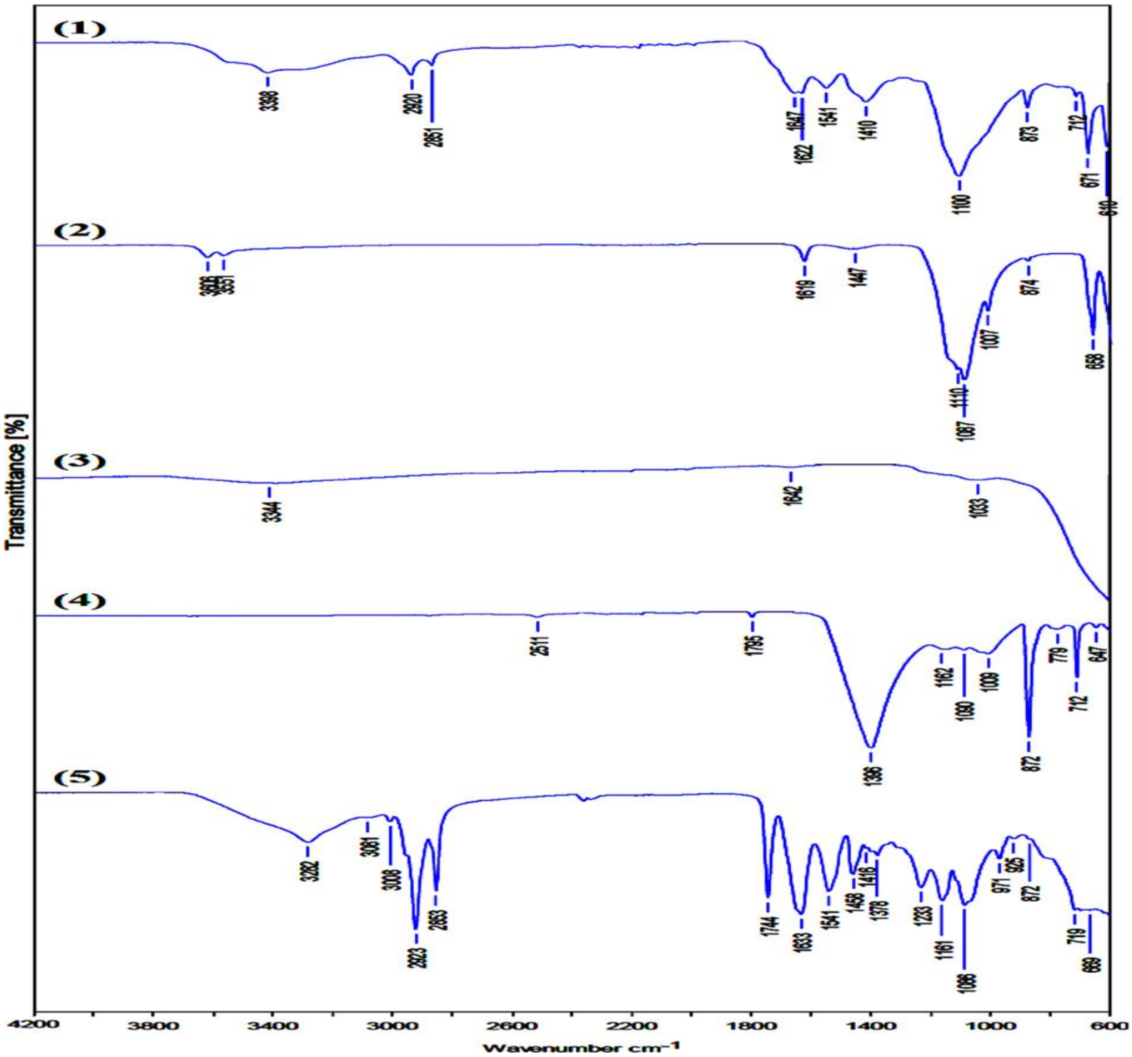


Fig. 3: ATR-FTIR Spectrum of: (1) Historical Sample "Red Color"; (2) Gypsum; (3) Lead White; (4) Chalk; (5) Egg Yolk

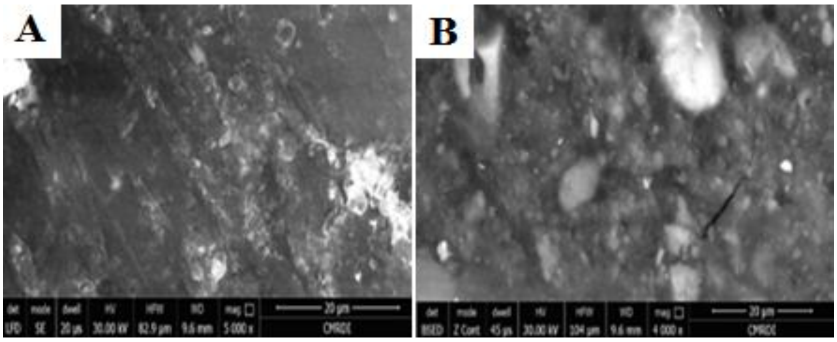
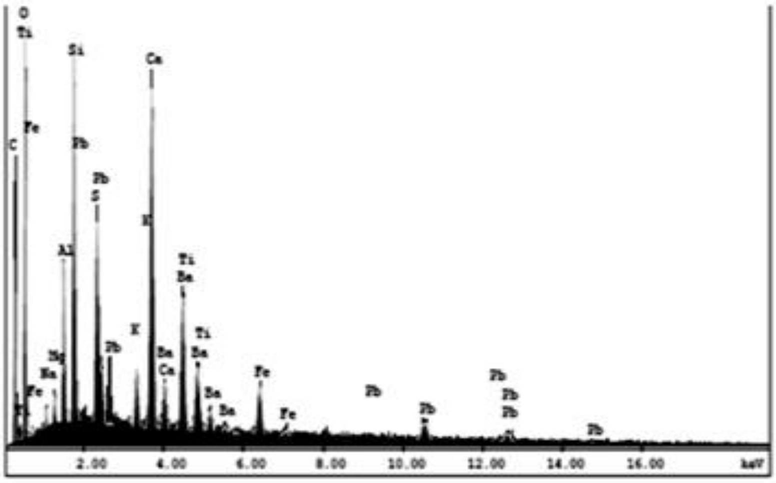


Fig. 4: FESEM of Red Color
(A)Secondary Electron Image (B) Backscattered Electron Image



EDS Quantitative Results

Element	Wt%	At%
CK	27.90	44.51
OK	31.57	37.81
NaK	0.92	0.76
MgK	0.85	0.67
AlK	4.08	2.90
SiK	8.50	5.80
SK	2.79	1.67
KK	1.06	0.52
CaK	6.16	2.94
BaL	8.73	1.22
TiK	0.22	0.09
FeK	1.81	0.62
PbL	5.43	0.50

Fig. 5: EDX Spectrum and Elemental Composition of Red Color

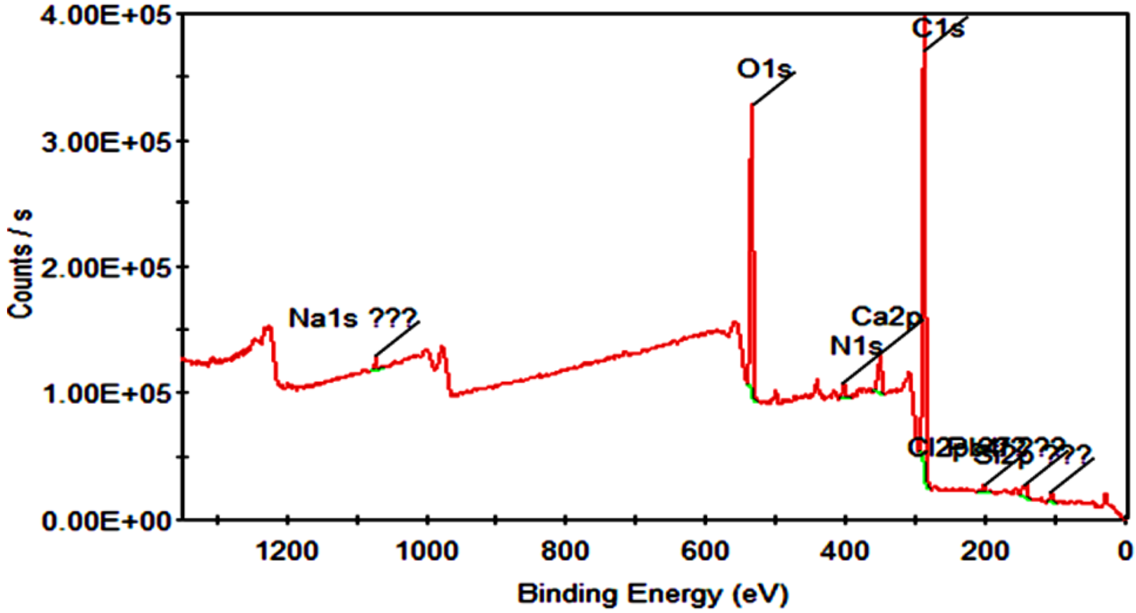


Fig. 6: XPS Spectrum of Red Color

Table 1: Characteristic Infrared Wavenumbers of Red Color

Color	Wave numbers (cm^{-1}) in IR Spectra	Material
Red	3398, 1622, 1100, 671	Gypsum
	3398, 1622, 1410, 873	Lead White
	1410, 875, 712	Chalk
	3398, 2920, 2851, 1647, 1622, 1541, 1410, 1100, 712	Kermes Carmine Red
	3398, 2920, 2851, 1647, 1622, 1541, 1410, 671	Egg Yolk

Table 2: Characteristic Infrared Wavenumbers of Reference Samples

Material	Wavenumbers (cm^{-1}) in IR Spectra
Gypsum[8]	3606, 3551 υ(O-H), 1110, 1087υ(SO_4^{-2}), 658 δ(SO_4^{-2})
Lead White	3344 υ(O-H), 1642 δ(O-H)
Chalk[8]	1396 υ(CO_3^{-2}), 872, 712 δ(CO_3^{-2})
Egg Yolk[8]	3282 υ(N-H), 2923, 2853 υ(C-H), 1744, 1633 υ(C=O), 1541, 669 δ(N-H), 1541 υ (C-N), 1458, 1416, 1378 δ(C-H)

Table 3: Elemental Binding Energy and Atomic Percentage of Red Color

Electron Orbital	Binding Energy	Atomic Percentage
C1s	286.97	75.16
O1s	533.79	18.41
Ca2p	349.46	1.79
N1s	401.85	1.60
Na1s	1073.08	0.45
Cl2p	201.15	0.73
Si2p	104.78	1.71
Pb4f	141.51	0.16

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