INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 7, Issue 2, April-June 2016: 443-458 www.ijcs.uaic.ro

THE CLEANING OF THE ISIS TEMPLE`S MURAL PAINTINGS IN UPPER EGYPT USING ZINC OXIDE NANOPARTICLES AND NON-IONIC DETERGENT

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Abstract

The Greek-Roman Isis temple is located on the west bank of Luxor; Upper Egypt was made of sandstone and decorated with different kinds of wall paintings. It suffers from many causes of deterioration and degradation mainly ground water, salt weathering, and different types of dirt accumulations on the relives and paint surface such as soot, grease, wax, biodeteriorated colored patches, bat patches, waste of birds and even house fly specks. All these lead to the gradual disappearance of paintings. In the present article we report a study on some Nanoparticles Materials synthesized by sol-gel process to set up a cleaning system to remove a wide range of different types of organic and inorganic materials from the surface of the wall paintings of the Isis temple. In order to verify the effectiveness of this method, different mural painting samples were collected from the temple for analytical characterization. The materials were characterized by optical microscopy, polarizing microscope, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD) and FTIR. According to the results, a number of wall painting samples were selected with paint layers that were composed of different pigments and covered with different patches. The experimental tests indicated the efficacy of mixture of ZnO nanoparticles (NP) + Vulpex $K5P_3O_{10}$ (potassium methyl cyclohexyl) (1:1) in the removing of wax, stains and blood patches. The results were supported by detailed photographic documentation, Fourier transforms infrared (FTIR) spectra and color change parameters.

Keywords: *Nanoparticles; Isis Temple; Mural Painting; Cleaning; Nonionic Detergent Cleaning; Color Stability*

Introduction

Isis temple stands on the West bank of the Nile at Luxor, 1km from Malqata and about 4 km south of Medinet Habu. Many emperors made additions to the temple over a period of 100 years. Today all that remains of the temple is its small main building and ruins of the propylon, along with its brick enclosure wall and the well. The temple precinct had an area of 74×51 meters; the temple itself is much smaller - 13×16m. Its entrance faces east. The outer walls don't have much decoration but on the inside the reliefs are well preserved and some have pigments. According to inscriptions on the propylon, construction of the Isis temple started around the beginning of 1st century CE [1]. According to one theory the temple's construction started under the reign of Nectanebo II and reached its finished form during the Greek-Roman era. The Isis temple of Deir Chelouit is important because Greco-Roman era religious buildings are rare in

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this area, and this is the only one not associated with the Theban Triad but with Isis. The temple was first examined by Karl Richard Lepsius in the mid-19th century, but he did not make a detailed description of it. A French expedition led by Christiane Zivie studied the inscriptions on the propylon and published their studies in 1992 [2]. Between 1971 and 1979 archaeologists from the Waseda University of Japan worked on the site. Remains found in the well prove that the well (and the temple itself) was already abandoned and used as a trash deposit in the Coptic era [3]. The reliefs of the temple are dated to the Greek-Roman era and are similar to the ones in Dendera and Philae [1]. Isis temple murals were carved on stone and the ancient artist used sunken relief in the murals of facades, which are exposed to sunlight and wind with sand and a combination of sunk/raised relief in the internal murals (Fig. 1). In some cases, the artist covered these reliefs with a thin layer of white plaster to receive pigments, while in others he did not. This clearly appears in the chapels and the *wabet* (place of cleansing). Two different types of sandstone were used: one was darker brown and the other was of a light yellowish color. Both varieties suffered the same forms of decay.

Conservation state

Visual examination inside the Isis temple revealed that all the surfaces of relieves present visible discoloration, generally grey/black, but occasionally brown, orange, red or green in appearance (fig. 2a) due to the prolonged action of microorganisms. The atmospheric conditions of the Isis tomb have favored the growth of microorganism, in particular where higher humidity values were present. Among the macroorganisms, bats had a critical importance in the mural paintings deterioration of Isis temple. They had more destructive tools than other macroorganisms through their excretions. These excretions which contain guano, blood and urine (Fig. 2b) cause not only aesthetic damages but also physicochemical changes of the substrate that lead to irreversible loss of valuable historical stone surfaces [4]. Concentrated layer from birds dropping, bees' nests and spider web nests were noticed clearly (Fig. 2c). Also, the wall is completely covered with concentrated layer from soot and patches of waxes (Fig. 2d), resulting from burnt candles by visitors in Coptic era which caused irreversible disfigurations, changing and reducing the surface permeability. The extensive observations of the zones with ground moisture and stone shows crumbling, scaling, and the most salt efflorescences appearances (Fig. 2e). Analyses showed that chlorides and gypsum are locally concentrated and accumulated. The presence of salts had led to the detachment and flaking of the paint layer (Fig. 2f). The aim of this research is to evaluate new analytical strategies using Nano micelles assembled with ZnO nanoP and dispersed in non-ionic detergent as cleaning agent and to compare to Ethomeen C_25 (Polyoxyethylene15), Vulpex (potassium methyl cyclohexy, (Triton X-114) Polyethylene Glycol Octylphenyl Ethers used here in removal of wax, soot and blood of bats (bats dropping) from the surface of wall painting in Isis temple at Luxor.

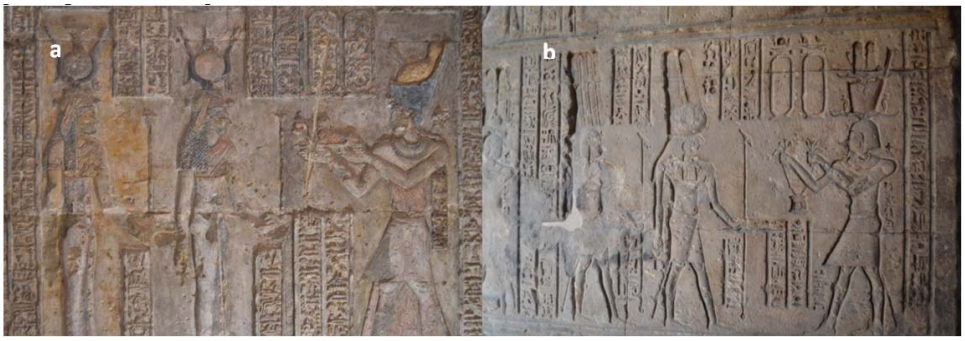

Fig.1. Mural painting at the Isis Monastery at Deir Chelouit **a-** raised relief; **b-**sunken relief in the internal wall of Isis temple with some pigments on whitewash.

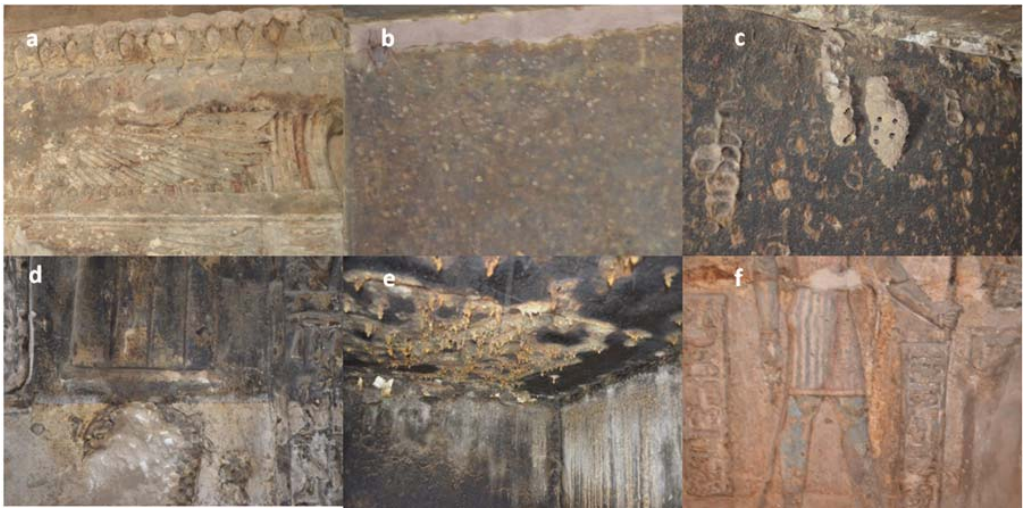

Fig. 2. Conservation state of the Isis Monastery, showing the high degree of decay of the sandstone: discoloration of the surface, bats dropping, concentrated layer from dust, wax and birds, bee nests, spider web nests, soot, oil soot layer and losses of pigments.

Nanoparticles for Cleaning: Principles and Practice

Cleaning is very often one of the first steps in the work of wall painting conservation. This process should be easily applicable, the action of the cleaning agent on the original surface should be totally controlled and it should be fast and economical [5]. The deterioration of wall paintings in Isis temple exposed to deterioration factors is a complex process in which chemical, physical and biological mechanisms are involved and a deep layer of oil soot, airborne particles and the formation of microbial biofilms in the surface layers (of the order of 1 mm thickness) of degenerated material, represents the final and most significant step of the degenerative cycle of wall paintings in the temple. All these aspects are very important to consider in order to find the suitable analytical strategies for cleaning the historical surfaces, affected by several deterioration events. The conservators in the temple have failed to remove these layers from the surface of the wall painting by traditional methods such as mechanical and chemical treatment. The mechanical methods were unable to remove internal wax without causing strong erosion of the reliefs itself. On the other hand, chemical methods (organic solvents, EDTA and nonionic detergent alone) do not always reach a completely satisfactory result as far as the aesthetic aspect is concerned (whitish veils, discoloring etc., are sometimes observed). Instead of using pure or mixed organic solvents, that can cause the spreading of the solubilized materials into the porous matrix, recently micro heterogeneous nanostructured dispersed system as oil-in-water microemulsions in which the dispersed phase is constituted by a solvent (called oil) effective in the solubilisation of the dark patina to be removed, and aqueous micellar solutions with a suitable co-solvent have been developed **[6]**. The novel properties of nanoP have been exploited in a wide range of archaeology conservation applications in cleaning, self-cleaning, consolidation and protection [7]. Nanoscience involves the study of materials on the nanoscale level between approximately 1 and 100 nm and involves study of how to control the formation of two- and three-dimensional assemblies of molecular scale building blocks into well-defined nanostructures or nanomaterials. Certain nanomaterials are attractive probe candidates because of their small size (1-100 nm) and correspondingly large surface-to-volume ratio [8]. In the recent years innovative formulation based on nanostructure fluids have been developed and successfully used for the removal of both grime/dirt and detrimental synthetics or natural coatings [9].

Materials and Methods

Some degraded and biodegraded small fragments sandstone samples, which contain some pigments, ground layer, paint layer and coating layer (colored patches - crusts layers - soot - blood) were sampled by using scalpel and forceps and analyzed through various investigation techniques.

Instrumentation

The mineralogical, petrographical and physical properties of the samples were studied. The samples were identified with means of:

Stereomicroscope (LEICA DM500) with (LEICA ICC50) camera was used to study the stratigraphic structure used in the temple and detect the alterations of stone surfaces. Polished cross sections have been prepared. This preparation requires the samples embedding in Araldit 1092 followed by abrasion and polishing of the specimen, trying to obtain plain surface to be observed at reflected light microscopy. The photomicrographs were recorded with various magnification degrees, up to maximum 40X.

SEM-EDX: The samples were investigated by means of scanning electron microscope using JEOL JSM 6400 with EDX micro analytical system which identifies the elemental composition of a sample.

PM: The mineralogy and texture of sandstone samples were further examined using a polarized optical microscope (Olympus BX51 TF Japan) with an attached digital camera, under magnification of 20X to 40X.

XRD: X-Ray diffraction was employed for the analysis of powdered samples in order to identify the mineralogical composition of the sandstone. A Philips PW 1840 diffractometer equipped with an automatic slit was used. The following conditions were applied: Cu Kα radiation (λ = 1.54056Å) at 40kv and 25mA, divergence and detector slits of 1.54056°, 1.54439° - 2 step size, and time for step of 1s. The XRD profiles were measured in 2θ goniometer steps for 0.300s.

FTIR analysis: Fourier transform infrared spectroscopy (FTIR) was used to identify the type of paint media. The samples were analyzed as KBr pellets by JASCO FT-IR–460 plus spectrometer in the 4000 to 370cm^{-1} range, at a resolution of 4cm^{-1}. The collected spectra have been expressed by absorbance units and baseline has been corrected.

In order to analyze morphology and particles dimension, the preparations ZnO nanoP were characterized by X-ray diffraction (XRD) and profile analysis, by transmission electron microscopy (TEM) JEOL JSM 6400 with an acceleration voltage of 100kV.

Color stability: The color stability of the pigment samples was determined after treatment with Konika Minolta spectrophotometer CM-700d (Japan).

Synthesis and Characterization of the ZnO nanoP and Nonionic Surfactant Detergents

In this paper a pure aqueous Nano zinc oxide suspension synthesized by sol-gel method was compared with a mixing of nanozincoxide and deferent non-ionic surfactant agent in order to examine their influence on cleaning the surface of mural painting from dirt, blood, soot and wax. Zinc oxide nanoP were prepared in laboratory using sol-gel method according to T. Butler et al (1998) [10] and M. Haase (1988) [11]. For synthesis of ZnO nanoP 1mg solution of zinc chloride was prepared by dissolving dry purified powder zinc chloride ($ZnCl_2$) in 50mL of Ethanol, 1mg Sodium hydroxide which was prepared by dissolving in 50mL of Ethanol and was added to it by dropping from burette. The mixture was continuously stirred in a magnetic stirrer at 80º C till complete precipitation. The dried precipitate was crushed, milled and then sieved to get uniform sized particles. After sieving the precipitate was calcined in a muffle furn ace at 350ºC for 3h by keeping the heating rate at 5ºC.

Results and discussions

Preliminary Sample Characterization

The Support

Texture: The quartz crystals are angular to sub-rounded in shape. They are surrounded by feldspars (partially altered to sericite); wavy extinction and concave convex of quartz were observed. Iron coating, staining and phosphate grains were also observed (fig. 3a-d).

XRD (Fig. 4) results indicate that the most abundant element in the sandstone samples is quartz (65.40%); white feldspars, (10.25%), calcite (5.10%), clay minerals (5% montomorillanite) appear in smaller amounts. Also XRD analysis showed NaCl concentration levels of 2% whereas samples from the lower parts from the temple ranged from 5.44 to 6.12%; these ratios indicate that an amount of NaCl has accumulated in certain areas of the building. So, salt crystallization is a direct cause of damage.

SEM: It is possible to observe variable sizes of angular and sub-rounded particles of quartz grains (fig. 5a). SEM photomicrograph shows that even quartz, which is one of the most durable minerals, showed susceptibility to mechanical deformation, it showed micro exfoliation, micro pitting appears clearly and dissolution of cements occurs of the sandstone which leads to an increasing in porosity and loss of cohesion of the stone and the disintegration of crystals is seen clearly (fig. 5b). The scanning examine also shows the presence of sodium chloride crystals in some phases of crystal and traces of crystalline salts mixed with crypto-salts accumulated in the pores (Fig. 5c). Also, the SEM photomicrograph showed crystals of gypsum (Fig. 5d). The observations revealed significant presence of shells and shell fragments (Fig. 5e). SEM micrographs showed the biodeteriorated stone surface beneath the microbiota (Fig. 5f). Extensive penetrations of fungal hyphae inside the stone were clearly established in some samples. Fungi are capable through a range of etching and chelating processes, to bore and burrow their way into mineral surfaces producing distinctive boreholes pits and channels.

EDX microanalysis of various sandstone samples listed in (Fig.6 & Table 1) showed that, the samples essentially consist of silicon (Si) (11.70 - 35.63%), (Calcium (Ca) (5.52 - 38.69%), Potassium (K) (4.35 - 30.58%), alumina (0.84 - 4.44%) sodium (Na) (3.20%) and sulfates (4.56-19.18%). Considering these results, it can be concluded that, the main building materials used in the temple is sandstone containing Si as the major cemented by calcite. The high amount of potassium (K) and Aluminum (Al) is attributed to feldspar content of the rock. A high concentration of sulfate (S) ions may be attributed to the crystallization of gypsum salts. The high concentration of sodium can perhaps be attributed to sodic or plagioclase feldspar or the high concentration of chlorine (Cl) (6.68 - 8.47%) and sodium (Na) (3.20%) can be attributed to the crystallization of halite salt. Iron (Fe) was identified in darker brown samples which is present as cement. In addition, the chemical analyses of sandstone samples from Isis temple reveal interesting points. Phosphate (P) elements are generally found in the all samples. The P content varies widely. It was generally a minor constituent (5.26 - 6.23%) but in exceptional sample it represents a major component (10.69 - 20.60%). It occurs mainly as phosphatic shell dirties and probably to a lesser extent as detrital apatite and probably also replaces silicon in silicate minerals [12]. Titanium (Ti) appeared to be correlated with the content of alumina. High manganese (2.00%) was noted in some samples which attributed to shale or phyllite. The presence of magnesium (Mg) with high concentration, suggests a somewhat dolomitic carbonate in the cement.

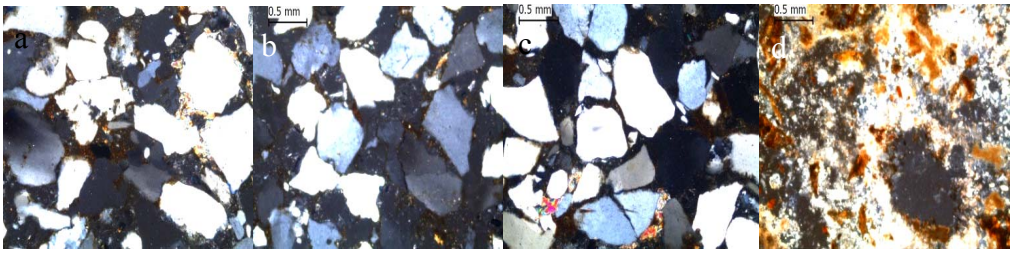

Fig. 3. Petrography micrograph of sandstone samples; **a-** subrounded and wavy extinction of quartz grains resulted of deterioration aspects and ferrous oxide, **b-** concave convex boundaries, dark and altered of quartz grains coated with clay minerals; **c-**angular grains of quartz and altered feldspar **d-** phosphate, Iron coating and staining.

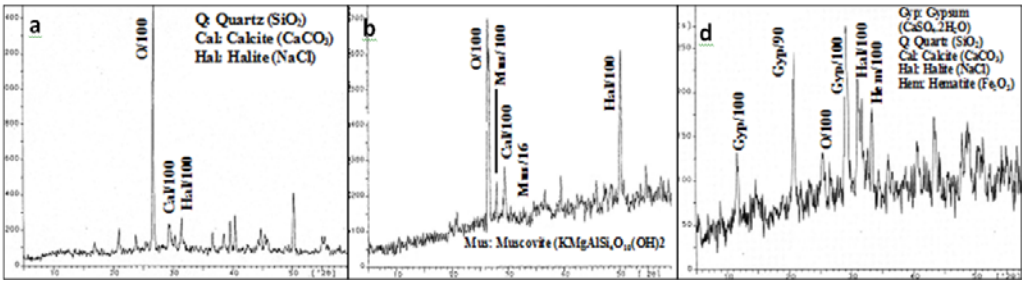

Fig. 4. XRD patterns of mural painting at Isis temple; **a-** Sandstone samples; **b-** salt sample; **c-** plaster samples.

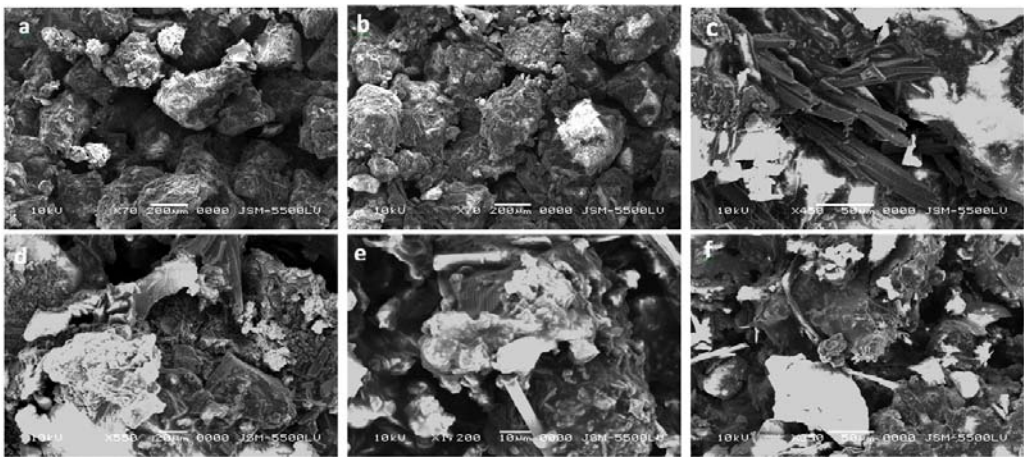

Fig. 5. SEM photomicrographs of the sandstone samples; **a-** deformation of subangular quartz grans; **b-** micro exfoliation; c- sodium chloride crystals; **d-** crystal of gypsum; **e-** shell and shell fragments; **f-** Extensive penetrations of fungal hyphae.

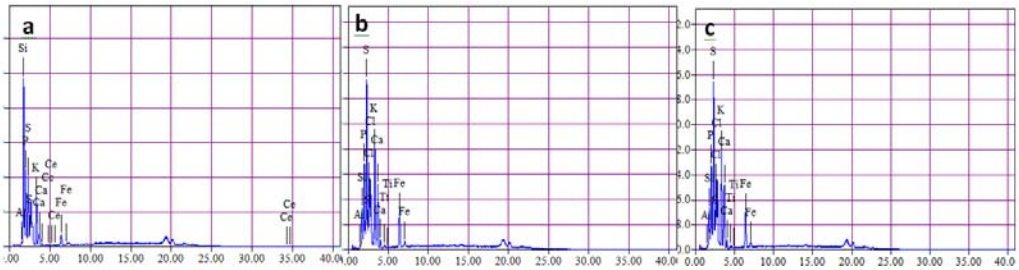

Fig. 6. EDX pattern of sandstone samples from Isis temple at Luxor.

The Ground Layer

The sample obtained from the degraded plaster from the temple of Isis under stereomicroscope shows a non-homogeneous surface layer and the grains are covered with thick layer of dirt, small fissures and smoke in outer surface of gypsum grains. EDX analysis reveals that the plaster sample taken from external relief contains Ca, S and K as the main elements with the contribution of Si, Fe, P, Cl and Na in small percentages (Fig. 7a). XRD patterns of the thin plaster (Fig.7b and c) indicated that it was mainly consists Gypsum ($CaSO_4 \cdot 2H_2O$), Anhydrite $CaSO_4$ (Transformation of gypsum $CaSO_4 \cdot 2H_2O$ to Anhydrite $CaSO_4$ by thermal weathering), Calcite $CaCO_3$, Quartz SiO_2 and a small amount of Halite NaCl. Calcite originates from limestone powder, quartz from aggregates and Halite from salts.

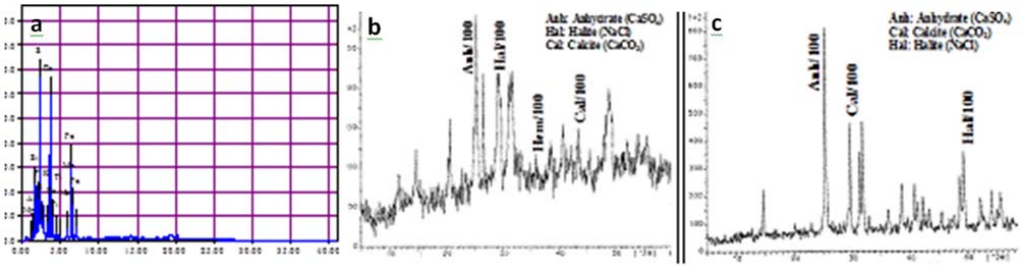

Fig. 7. Analysis results of plaster samples,
a- EDX pattern of plaster; **b-** external plaster sample; **c-** XRD pattern of internal plaster.

Table 1. Elemental content (%) of sandstone and pigment samples from Isis temple.

Sample no/ Element	Sandstone 1	Sandstone 2	Sandstone 3	External Plaster	Inner Plaster	Yellow pigment	Brown pigment	Red pigment	Blue pigment
Al	0.8460	4.4490	3.1807	0.7152	-	3.6280	0.6925	3.4107	1.6706
Si	35.6356	16.9366	11.7036	5.8973	1.2680	14.6503	3.3690	14.7468	7.5849
S	13.1355	4.5686	19.1873	15.9600	30.8316	19.9183	2.4962	13.7177	23.5308
K	22.0340	18.7551	4.3590	30.5837	-	-	-	1.7035	-
Ca	5.5221	19.6951	38.6993	21.4946	62.1488	40.5560	19.5886	23.7244	56.8062
Fe	1.4821	15.28	12.6590	5.3688	2.1629	15.2496	60.5426	35.1181	6.4779
Na	-	3.2930	-	-	-	-	-	-	-
Mg	-	2.6061	0.8396	-	-	1.7444	-	-	1.4223
Cl	-	6.6934	-	8.4790	-	-	-	-	-
P	20.6004	6.0364	6.6388	10.9066	-	-	-	-	-
Ti	-	1.9216	1.7603	0.5950	-	1.8895	-	0.5966	0.6108
Ce	0.7443	-	-	-	-	-	-	-	-
Mn	-	0.5314	2.0068	-	-	-	3.8712	-	-
Cu	-	-	-	-	-	2.2951	-	-	1.2777
As	-	-	-	-	-	0.0689	-	6.9822	-
Sr	-	-	-	-	-	-	-	-	0.6187
Zn	-	-	-	-	-	-	8.7424	-	-
Ba	-	-	-	-	-	-	0.6976	-	-

Paint Layer

X-ray diffraction (XRD) measurements were used to verify the crystal structures of the pigments, but the mineralogical composition of the pigments was not determined by XRD due to their low concentration in the thin films over priming layers. Hence, LOM and EDX analyses were carried out to find the elements which were present in the paint layers.

Yellow pigment: On careful observation under the stereomicroscope, the yellow pigment appeared to have different shades of yellow that can be described qualitatively as bright-yellow and orange-yellow. The examination showed the particles are polygonal in shape and coarse morphology of the surface (Fig. 8a). These large particle sizes suggest the

pigment was grounded after production. Also, subtle color differences may also be seen among the particles. Some of the particles appear red-yellow, while others are more intensely red. The elemental composition analysis of the yellow pigment indicates that it is mainly composed of Fe, Ca, S, Si, Al and As (Fig. 9a). The presence of Iron may be responsible for yellow pigment, Ca and S may be from ground layer. The less amounts of arsenic (As) and Cu may attribute to heavy metals in sandstone. The observation of aluminum in the paint layer can be explained as impurity found in the iron compounds. The most common yellow pigment in ancient and prehistoric Egyptian art is goethite, iron (III) oxhydroxide, commonly known as yellow ochre [13].

Brown pigment: The brown pigment appears to be homogeneous with regard to color and indeed only one shade of reddish-brown was observed. The observation revealed a net of micro-cracks at the surface of the color (Fig. 8b). In the EDX analyses of the brown pigment an important amount of Iron (60.54%) was observed (Fig. 9b). Brown color may be produced by iron oxide.

Red pigment: The image of the red paint sample showed an uneven thin layer which tends to be dark red (Fig. 8c). In the SEM-EDS analyses of the red pigment sample, Fe, S, Ca and Si were detected as major elements and As, Al, K, and Ti, as minor elements (Fig. 9c). The presence of iron was confirmed by using SEM-EDX on samples taken from red colored areas. There was a clear evidence of hydroxides (mainly hematite) that colored the pictorial film to vary degrees.

***Blue pigment*:** According to LOM indications, the blue pigment has irregular particle shapes, coarse grain and uneven thin layer. It is composed by small black inclusions of whitewash (Fig. 8d). The sample of blue pigment from Isis temple in this study was composed primarily of calcium (Ca), sulphur (S), silicon (Si), with cupper (Cu), iron (Fe), aluminum (Al), magnesium (Mg), titanium (Ti) and tin (Sn), present in different concentrations. The present analysis and the SEM-EDX information (Fig. 9d) confirms that Cu and Ca are correlated within cuprorivaite (Egyptian blue) domains identified based on their Cu. The presence of Mg, Ti and Sn, suggests an ultrabasic geochemical origin of the copper ore. The observation of aluminum (Al) in the paint layer can be explained as impurity found in the iron compounds. Egyptian blue was manufactured by heating silica sand, copper alloy filings or ores and potash or Natron, and was commonly found in artefacts from the 4th Dynasty onwards [14].

Binding Media Analysis

Fourier transform infrared (FTIR) spectrometry was employed with the aim of establishing the possible existence of an organic medium that acts as a binder in the paintings studied. FTIR analysis was carried out by scraping samples from the areas that were expected to be rich in binder material, that is, the pictorial film areas from red and blue pigment. The results of FTIR analysis of the samples listed in (Table 2, Fig.10) showed that, this high percentage is reflected in an important band in the IR spectrum, caused by the carbonate bands like stretching vibration of CO_3^{2-} (1430cm^{-1}). This strong band could be overlapping others in the 1300–1600cm^{-1} range and the bending vibration for calcium carbonate occurs at 875cm^{-1}. FTIR spectra revealed the presence of gypsum ($CaSO_4 \cdot 2H_2O$) due to the anti-symmetric and symmetric O-H stretching, 1144cm^{-1} due to asymmetric S-O stretching and 600 and 700cm^{-1} due to S-O bending. This indicates that the ground layer at Isis temple was made by mixture of calcium carbonate and gypsum. The organic binders show spectral features in the whole middle infrared spectral range. Animal glue is hydrolyzed collagen and therefore shows typical protein vibrations like the so called amide I (1620, 1640cm^{-1}, mainly C=O stretching) [15] and amide II (3400–3200cm^{-1} CH stretching and 2900–2800 cm^{-1}, NH stretching) band. The FT-IR spectrum of the binding media was similar with the stander animal glue [6].

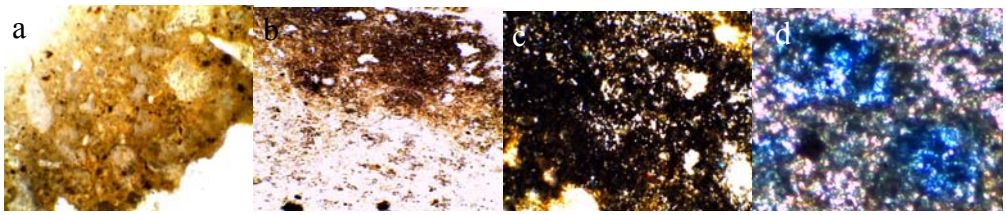

Fig. 8. LOM photomicrograph of paint layer:
a- yellow pigment, **b-** brown pigment, **c-** red pigment, **d-** blue pigment (X40).

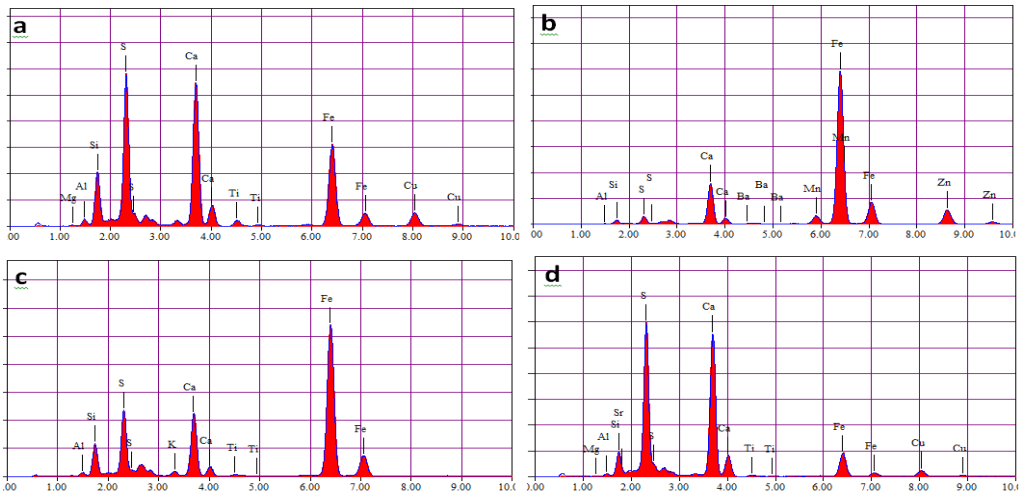

Fig. 9. EDX pattern of pigment samples; **a-** yellow pigment; b-brown pigment; **c-**red pigment; **d-** blue pigment

Table 2. FTIR results of binding medium paint layer in Isis temple.

Wave Number		Characteristic IR Absorption Bands
Blue pigment	Brown Pigment	
3407.6	3409.53	N-H stretching band 3400-3200 cm·'
2923.56	2924.52	C-H stretching bands 31 00-2800 cm·'
1622.8	1640.16	C=O stretching band 1 660-1 600 cm·'
-	-	C-N-H bending band of amid 1 565-1500cm·'
1446.35	1428.99	C-H bending band 1 480-1300 cm·'
857.524	857.524	O-C-O bending band of carbonate group of calcite. 900-650 cm·'
676.892	712.569	SO42- bending band of gypsum. 700-600cm·'

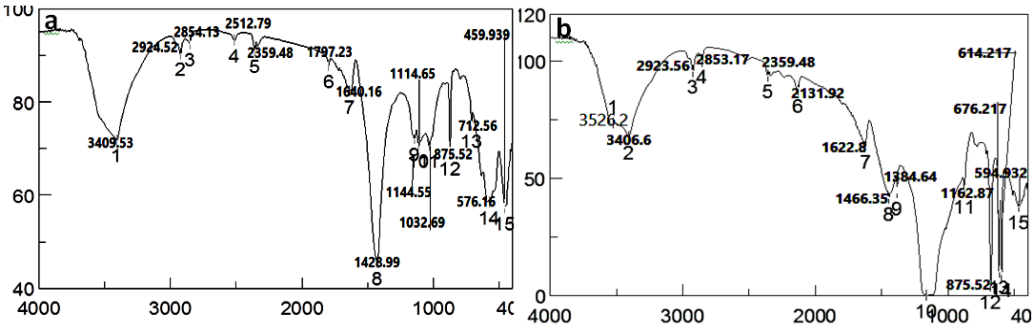

Fig. 10. FTIR spectra for the paint layer samples, **a-** Blue pigment; **b-** brown pigment.

Use of ZnO nanoparticles (NanoP)

Experimental samples Preparation

A typical wall painting, belonging to the classic tradition in Pharaonic Egypt, consists of sandstone used as a support and roughly three layers (Fig. 11a and b) whose main structural component is gypsum, calcium carbonate, and sand with ratio 2:1:0.5. The inner layer, which is laid on the wall, is called arriccio. Moving towards the surface, the intonaco layer is found, consisting of a plaster that often contains an equal amount of gypsum and calcium carbonate with little fine sand. The third and outer one is the paint layer, which is a thin film (50µm thick) made by a mixture of common pigments and animal glue as organic binders (which used in Isis temple) in the so-called tempera technique which is applied on the dried intonaco by using organic binder. On the other hand three kind of the most common pigment, brown (Hematite Fe_2O_3 + carbon black), red (Hematite), yellow (goethite FeOOH) and black (carbon black C) were used in the Egyptian wall painting. After the models preparation, an artificial and concentrated layer of the most common deterioration, dirt, which was obtained from the accumulated dust on the outer surface of the temple mixed with water supplemented with glue to increase cohesion with the model surface, bats blood obtained from dead bats, soot obtained from metal surface which has been exposed to soot rising from the burning of organic materials, scraped and mixed with oil and then put on the surface of the model using the brush and wax obtained from candles were added on the experimental models surfaces (Fig. 11c and d).

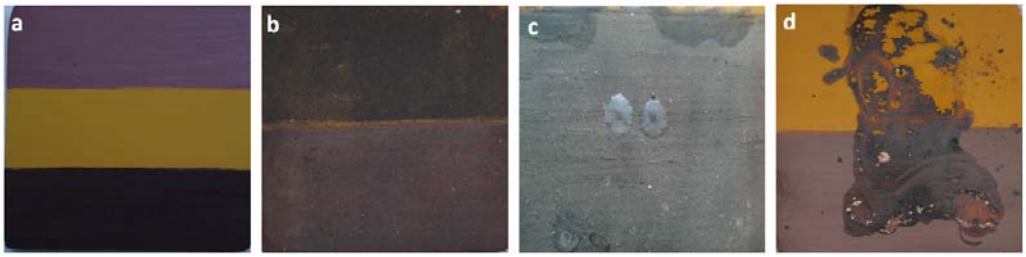

Fig. 11. Wall painting models before and after adding the deterioration aspects**:**
a,b- models before adding; **c-** soot, dirt and wax; **d-** bats blood.

ZnO nanoP cleaning study

The remarkable properties of zinc oxide have attracted the interest of many researchers in the past few years. ZnO nanoP have been used in the last years for solving a wide range of different conservation case studies, including the preservation of many mural painting in the world. One of the most remarkable commercial applications is their use in the self-cleaning effect on the surfaces, due to their property of blocking broad UV-A and UV-B rays, [16]. ZnO nanoP are believed to be non-toxic, bio safe and biocompatible nanomaterial [17]. The cleaning method by ZnO nanoP allows the accurate control of the areas to be cleaned without effects on the rest of the surface. The new method does not require long experience or special training [18]. TEM image and XRD measurements (Fig. 12a and b) showed that particles with such a small size are highly rich with ZnO. For the experimental work, five solutions were examined:

ZnO nanoparticles are dispersed in distilled water 5% and sonicated in an ultrasonic bath for 15 min to obtain a homogeneous and stable dispersion (1).

ZnO NPs are dispersed in Ethomeen C_25 (Polyoxyethylene15) 5% and sonicated in an ultrasonic bath for 15 min, to obtain a homogeneous and stable dispersion (2).

ZnO NPs + Vulpex ($K_5P_3O_{10}$) (potassium methyl cyclohexy (1:1) (3).

ZnO NPs + Polyethylene Glycol Octylphenyl Ethers (Triton X-114) $C_8H_{17}C_6H_4O(CH_2CH_2O)_7$(4).

Triton X100 (iso-octy) phenoxy poly ethoxy ethanol - $C_{14}H_{22}O(C_2H_4O)_n$ was previously added to ZnO NPs initial aqueous solution (5).

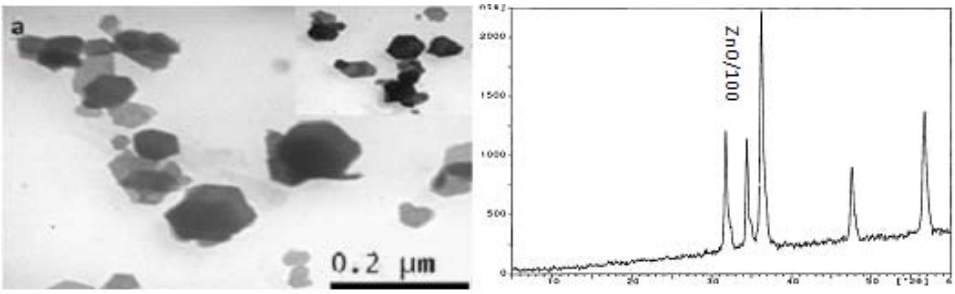

Fig. 12. TEM image (with size about 150-210nm) and XRD patterns of the prepared zinc oxide nanoparticles.

Evaluation of the cleaning treatment performances

To clean the surface of mural painting samples from different dirt, soot, wax and blood patches, two techniques were carried out: the 1st. is cotton swab technique, consisted of small cotton-wool compresses, wetted with the cleaning mixture solution, placed on an intervention layer of Japanese tissue, and left in contact with the paint surface for ten seconds (Fig. 13a). The 2nd was applied using an Arbocel compress. The application consists in the following procedures: the mixture was mixed with Arbocel (ARBOCEL is a powdery to fibrous cellulose additive) and applied over the paint surface (Fig. 13b). The application time ranged approximately from 30 to 60min. The poultice remained wet. Eventually, the poultice was removed and the remaining materials (blood and wax) were removed using a cotton swab embedded with distilled water (Fig. 13c). After cleaning, the slaps were subjected to artificial weathering cycles (AWC) by UV radiation at 254nm for 210 minutes using a UV lamp (125W Philips Hpk lamp. OSRAM L15W/20) placed at 50cm distance. We report here the major results obtained per cleaning procedure.

The nanoparticles solution cleaning was very effective in cleaning the models. On the other hand some different effects were noticed for the five mixtures used during cleaning. Through the records obtained from the previous experiments that had been done for evaluating the effect of ZnO NPs + Nonionic detergents on different pigments applied on mural painting sample, the following points could be conclude:

- Composite (1): It was observed that the different types of oil soot and blood start to disintegrate after 40 minutes of the suspension application. However, it was not easy to remove wax completely and thus the solution was left until the complete removal could be easily performed with a cotton swab. The wax and dirt started to disintegrate after about 50 minutes and completely disintegrated after 3hours. Figure 13d illustrates the cleaning procedure of different types of oil soot and wax. LOM confirmed the efficacy of ZnO nanoparticles for removing the deep layer of oil soot from the ground layer. Therefore, the purpose of ZnO nanoparticles use is to achieve a penetration between layers to do a deep clean of the soot and dirt, which is difficult to remove by traditional methods without causing negative impact on the layers.
- The optical images reveal that the cleaning proceeded by composite (2) gave good results, removing the soot after 30 minutes while the layer of dirt started to disintegrate after about 45 minutes and wax and blood were completely removed after 2 hours.
- From fig.14e it can be observed that the soot layer and blood batches crust of sample were successfully removed from the surface upon treatment with the composite 3.
- Composite (4) gave very good results for soot, dirt and good results of wax (Fig. 13e).
- Composite (5) was very effective in cleaning the models but had a discoloration effect and removed pigments (Fig. 13f).

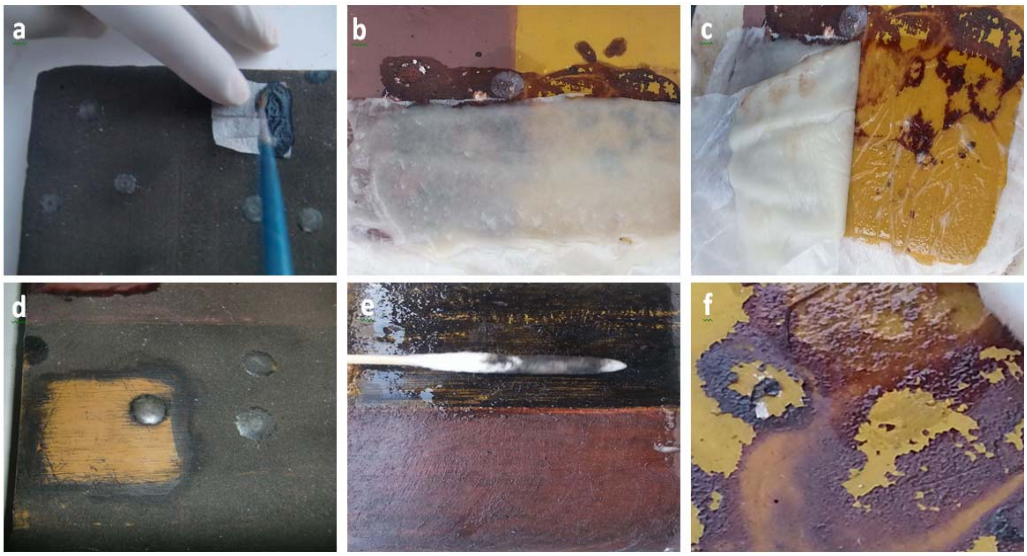

Fig. 13. Results of application of NPs for removal the deterioration aspects from the surface of mural painting; **a-** cotton swab technique; **b-** ZnO + Nonionic detergent in carbojel, **c-** removing of the poultice and the remaining materials; **d-** good affects for soot and dirties and none affects wax and blood; **e-** excellent affects for wax and blood batches; f- discoloration and removing pigments by composite (5).

Change of Color

The color stability was determined for the pigment samples which were treated by nanoparticle solution (NPs) mixing with nonionic detergent. Qualitatively, the nature of the color can be understood by examining the visible reflectance spectrum before and after the samples have been treated [19]. The changes in the color parameters L*, a*, and b* were measured, the results were showed in (table 3);

ΔL* (+ = lighter, – = darker), - Δa* (+ = shift to red; – = greener) and Δb* (+ = yellower; – = bluer) represent the differences between the values measured on treated and untreated (control sample for comparison) samples. The magnitude of the global color variation is given by $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2$ [20-27]: $\Delta E = (\Delta L^2) + (\Delta a^2) + (\Delta b^2)$, where ΔL*, Δa*, and Δb* are the differences between the values of the color indices before and after aging. For the lightness color (L* value), it can show that the pigments treated with ZnO nanoparticles dispersed in distilled water 5% turned a bit dark, while the pigments treated with ZnO NPs dispersed in Ethomeen C_25 gave good colors and were similar with the control sample; also, the pigments treated with ZnO NPs + Vulpex turned a bit dark especially in yellow pigment. The pigments treated with ZnO NPs + Triton X-114 gain little light especially in black and yellow pigments. The mixture of ZnO NPs + Triton X100 gave poor results; all pigments were tending to lighten up the color. For the red color (a* value), the best results were obtained from the treated samples with ZnO NPs dispersed in Ethomeen C_25 and ZnO NPs + Vulpex and the poor result were obtained from ZnO NPs + Triton X-114. For the yellow color (b* value), the treated pigment with ZnO NPs dispersed in Ethomeen C_25 and ZnO NPs + Vulpex were good and better than the other. The results confirmed that the treated samples with ZnO NPs dispersed in Ethomeen C_25 and ZnO NPs + Vulpex alcohol were good after cleaning because they gave good color stability. The colorimetric measurements reported in Table 2 confirmed that the ZnO NPs assembled with the Vulpex ($K_5P_3O_{10}$) induces the best recovery of the initial chromatic parameters, considering the smallest values of ΔE*.

Table 3. Change of color parameters of treated pigment before and after cleaning

Solution samples	Red pigment				Brown pigment			
	l*	a*	b*	ΔE	l*	a*	b*	ΔE
Control	52.64	13.02	11.93		53.64	3.24	3.40	
Composite(1)	52.85	15.87	12.92	3.02	51.36	4.09	4.44	2.64
Composite(2)	53.36	14.68	11.23	1.94	55.02	5.08	5.74	3.09
Composite(3)	53.72	15.23	13.14	2.74	54.38	3.96	6.14	2.92
Composite(4)	51.56	9.45	10.48	4.00	55.02	5.08	5.74	3.28
Composite(5)	54.67	10.02	7.28	5.85	48.93	3.72	4.60	4.69
Solution samples	**Yellow pigment**				**Black pigment**			
	l*	a*	b*	ΔE	l*	a*	b*	ΔE
Control	68.69	13.02	35.66		47.42	1.24	3.87	
Composite(1)	68.36	12.64	33.38	2.33	48.35	0.76	3.68	1.06
Composite(2)	61.83	9.67	19.34	18.01	49.28	0.87	3.46	1.94
Composite(3)	69.77	12.48	34.38	5.65	48.79	0.56	4.50	1.65
Composite(4)	60.60	10.22	21.46	14.19	50.23	1.22	6.59	3.70
Composite(5)	61.37	7.36	15.14	22.44	51.72	2.68	7.54	5.90

Cleaning of Isis Wall Painting Surface by Selected NPs and Nonionic Detergent

The surface of mural painting in Isis contains several disfiguring overlapping stains as blood batches, wax, soot and dirt. The cross section and optical microscope examination images shows, the soot impregnated into porous and covering the grains of the sandstone and plaster. For that reason, the use of nanoparticle solution (NPs) mixing with nonionic detergent was required. Results of the experimental study suggested that the ZnO NPs dispersed in Ethomeen C25 5% mixed with Vulpex ($K_5P_3O_{10}$) (potassium methyl cyclohexyl (1:1) was the best composite for removing the deterioration aspects. The cleaning of the surfaces is an irreversible process; therefore, the methodology chosen to remove batches must allow full control of all steps in order to ensure the complete solubilization/swelling and removal of the undesired materials while avoiding their penetration within the painting pores, so that the physiochemical properties of the mural are fully re-established [20].Treatment tests using these materials were undertaken at three different sites: the wall painting outside the temple, (which are affected by blood patches and remains of nests); the wall painting inside the temple (which are affected by soot, remain of waxes and blood patches) and finally for removal of oil-soot made by vandals to deface at Coptic era. The simple preparatory work to test the sensitiveness of pigments and binding media present in the painting stability of the painting was carried out on top using small amounts of the microemulsions on small areas with soaked in a swab, checking for possible negative effects. Composite (3) solution was applied using the two techniques (soaked in a swab or Arbocel compress poultice). The application consists in the following procedures: Composite (3) was mixed with Arbocel and applied over a thin sheet of Japanese paper, whose role is to avoid the adhesion of the poultice to the partially solubilized coatings. The contact time for each application was two hours and the temperature was 28ºC. Finally, the poultice was removed and the remaining materials were removed with a gentle mechanical action and then cleaned many times with cotton swab embedded with distilled water to remove any residual surfactant (Fig. 14).

Micro-samples were taken with scalpel from the painting surfaces before and after cleaning, and analyzed by LOM. The purpose of this was to determine the efficacy of the cleaning agents used. LOM confirmed the efficacy of ZnO NPs dispersed in Ethomeen C25 5% mixed with Vulpex ($K_5P_3O_{10}$) in cleaning. LOM micrograph shows the layer of deterioration aspects were completely removed (Fig.15). Also the FT-IR spectra, reported in (Fig. 16), show that no etching damages or changing was introduced on the wall painting substrata after the cleaning. FTIR results confirmed the stability of the pigments before and after cleaning of different kind of organic patches. A FTIR comparative study for the untreated samples (a) and treated sample with ZnO NPs assembled with the Vulpex was conducted. FTIR spectral assignment, there are typical frequencies of the two sample.

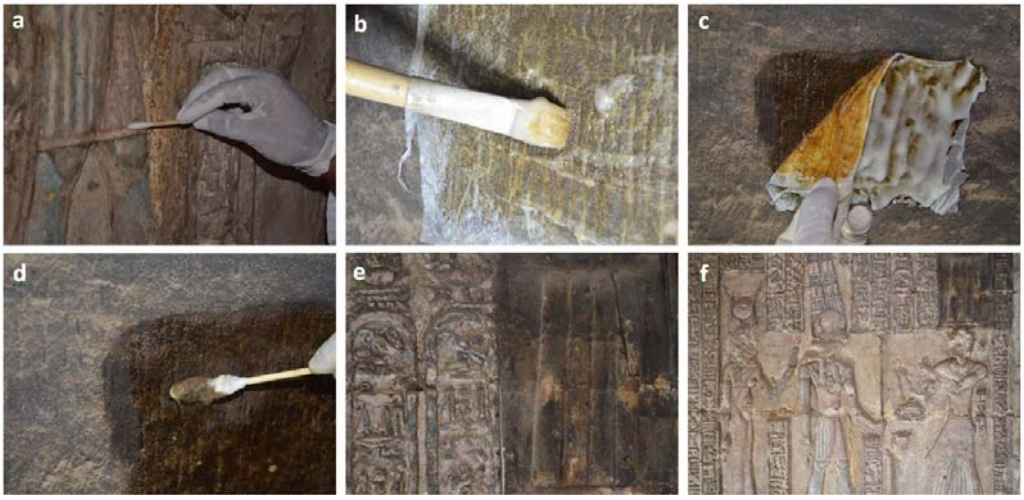

Fig. 14. Application of ZnO NPs on mural painting in the temple of Isis: **a**-cleaning by ZnO NPs with soaked in a swab; **b-** The wet pulp is manually distributed over the Japanese paper layer; **c-** Composite (3); **d-** removing of poultice; **e-** removing of remaining materials with cotton swab embedded with distilled water; **f-** the results of mechanical and chemical cleaning**.**

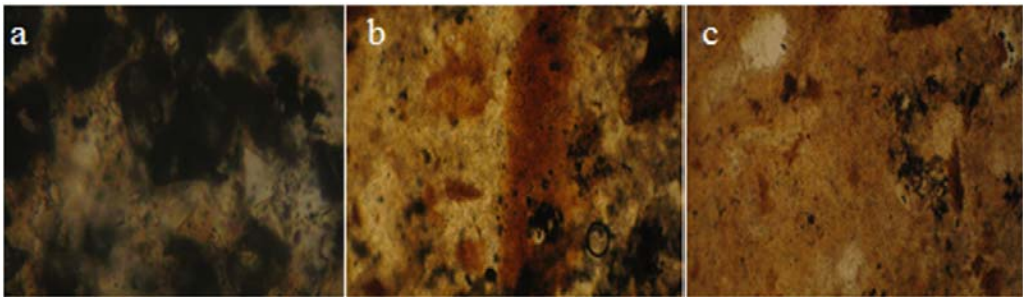

Fig. 15a, b, c. Optical microscopy results of application of ZnO nanoparticles dispersed in Ethomeen C25 5% mixed with Vulpex for removal blood and soot batches from sample from Isis wall painting, **a-** before application**, b-** during cleaning. **c-** After cleaning

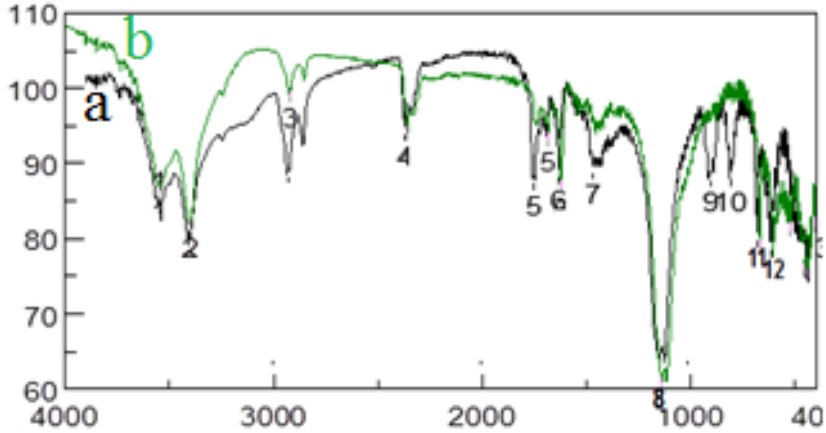

Fig. 16. FTIR patterns of untreated samples (a) and treated sample with ZnO NPs assembled with the Vulpex (b)

Conclusion

Visual examination of the wall painting at Isis temple reveals different kinds of alterations and degradation phenomena, such as structural damages (failures, erosion), biological attacks and effects of human exploitations. The examination with SEM and LOM reveals that the samples suffer from several deterioration of their structural coherence: extensive penetrations of fungal hyphae, black superficial crust covered the quartz grains and red areas attributed to metabolically active autotrophs which prevent us to see the pigments. XRD and XRF analysis lead to the conclusion that the red pigment is hematite, the yellow pigment is limonite, the brown pigment is hematite and the blue pigment is Egyptian Blue. FT-IR spectrum of the binding media revealed that the binder used was similar with the animal glue. The lab analysis revealed that, the mixture of ZnO NPs + nonionic detergent [Vulpex ($K_5P_3O_{10}$) (potassium methyl cyclohexy] (1:1) mixed with Arbocel and applied over a thin sheet of Japanese paper are the most effective in removing the batches (blood, soot, dirt and waxes) from the surfaces of wall paintings. The results of the color stability tests confirmed that the sample cleaned with mixture of ZnO NPs + nonionic detergent [Vulpex ($K_5P_3O_{10}$)] was good after cleaning because they gave a good color change stability and was similar to the control color. These mixtures were applied at Isis temple to clean the wall painting surface from the patches and gave excellent results. FTIR results showed that no significant differences can be seen in the FTIR spectra of pigments before and after cleaning.

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Received: December, 08, 2015
Accepted: April, 15, 2016