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Original article

NEW MATERIALS FOR ENHANCING THE DURABILITY OF MURAL PAINTINGS OF THE TOMB OF QEN-AMUN TT 93, LUXOR, EGYPT

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Abstract:
The aim of this research is to study the main deterioration aspects and evaluate the treatment of mural painting at the Tomb of Qen-Amun TT93 dating back to the 18^{th} dynasty, New Kingdom (c. 1550-1069 BC.), in the Theban Necropolis, on the west bank of the Nile in Luxor. In this study, the surface of deteriorated mural paintings were investigated using PLM, TEM investigation of the eggshell nano-particles, XRD analysis, FTIR spectroscopy, and SEM-EDX. To our knowledge, it is the first report on the mixture of the ethyl silicate and the egg shell nano-particles application of mixture for the treatment of deteriorated mural painting surfaces in the Tomb of Qen-Amun TT93.The samples were collected from the fragment of wall painting, painted with the depiction of two women, Tomb of Qen-Amun (TT93). The obtained results showed that the structures fragment of wall painting included three layers from the top to bottom: yellow pigment, fine plaster, coarse plaster composed of quartz, clay minerals, iron oxides, and plant fibers. The results illustrated that the mixture was highly effective at consolidating cracks, and the appearance of the treated surfaces was

1. Introduction

n the Sheikh Abd el-Qurna, the Theban Necropolis, on the west bank of the Nile in Luxor, Tomb of Qen-Amun TT93 dates back to the 18^{th} dynasty. More than three hundred tombs can be found there, all belonging to the New Kingdom (c. 1550-1069 BC). The tomb of Qen-Amun TT93 is located in ancient Thebes. It is at the top of the mountain called today the Tombs of the Nobles, in Sheikh Abd elQurna, across the river Nile from the city of Luxor. This palace-like tomb, that is approximately 3.400 years old, is full of mural paintings. TT93 stands for Theban Tomb number 93. A designation given to it in much more recent times to record and locate many tombs of many sizes, from very small to large tombs in Luxor (ancient Thebes), built in antiquity into the bedrock by digging and carving out stone from the mountain to sculpt the desired architectural design into it. The tomb has never been thoroughly excavated or studied but has been visited by scholars in the XIX^{th} and XX^{th} centuries. Jean-François Champollion (the first to decipher Egyptian hieroglyphs) and Ippolito Rossellini (the founder of Italian Egyptology) made a 2-year French Tuscan expedition together to Egypt in 1828, and they visited the tomb of Qen-Amun. In the early nineteenth century, Champollion, Lepsius, Wilkinson, and Prisse d'Avennes visited the tomb, but until the Metropolitan Museum of Art published the tomb of Qen-Amun at Thebes in the late 1920_s, which details its exploration and documents its contents, it was largely neglected [1-5], fig. (1).

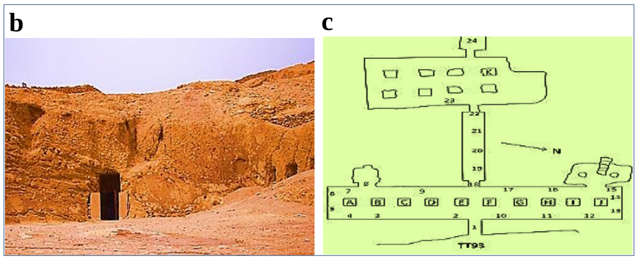

Figure (1) **a.** the location of the tomb of Qen-Amun-TT93 in Luxor (*After: https://www.kena-mun.com/gallery-miscellaneous*) **b.** plan of the tomb (*After: https://en.wikipedia.org/wiki/TT93*), **c.** the main entrance of the Qen-Amun Tomb - TT93

1.1. *Geological structure of the Theban necropolis*

A geological study found that the west bank of Luxor consists of three main formations, fig. (2) which are >350 m thick:

1) *The base is Tarawan chalk*
2) *The middle is Esna shale*
3) *The top is Thebes limestone*.

In the Theban Mountains, which rise approximately 462 meters above sea level, marine limestone (lower Eocene) and marls more than 350 meters thick dominate. Nobles tombs were cut into the bedrock of the Theban mountains. The tomb of QenAmun - TT93, cut into Esna shale formation, can be found sporadically with a thickness of about 55 meters. The geology of the studied area plays an important role in defining the conservation state of the tombs The Theban Mountains are mostly composed of clay minerals and carbonates, with small amounts of quartz, gypsum, halite, and anhydrite. When clay minerals and soluble salts are present in the geological structure, deterioration is more effective [6-11].

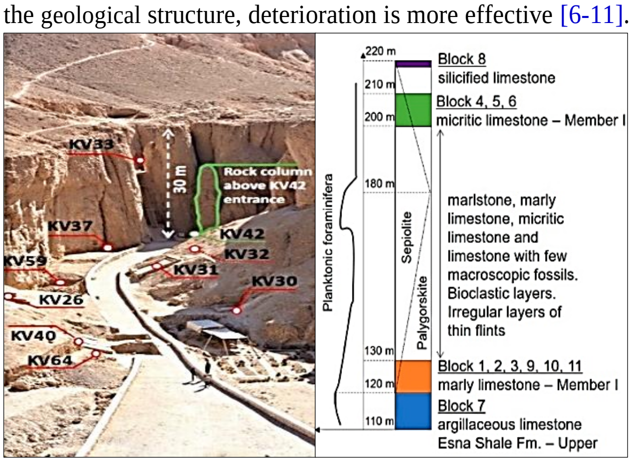

Figure (2) geological map of the study area

1.2. *Condition assessment of the tomb*

Stone quality in Thebes is poor (impurities contained in the rock, such as halite), so most tomb chapels were plastered and painted rather than decorated with reliefs. The tomb of QenAmun - TT93 suffer from different weathering forms, such as cracks, strength loss, and detachment of plaster due to the harsh weather conditions in Luxor. The wall paintings are exposed to high values of temperature (41-46 °C) in summer and temperatures (7 °C) in winter [9-16]. Based on the visual observations of the Tomb of Qen-Amun - TT93, many vertical and horizontal cracks were observed in the wall paintings, as well as crack networks in the mural painting surfaces due to deterioration factors, fig_s. (3).

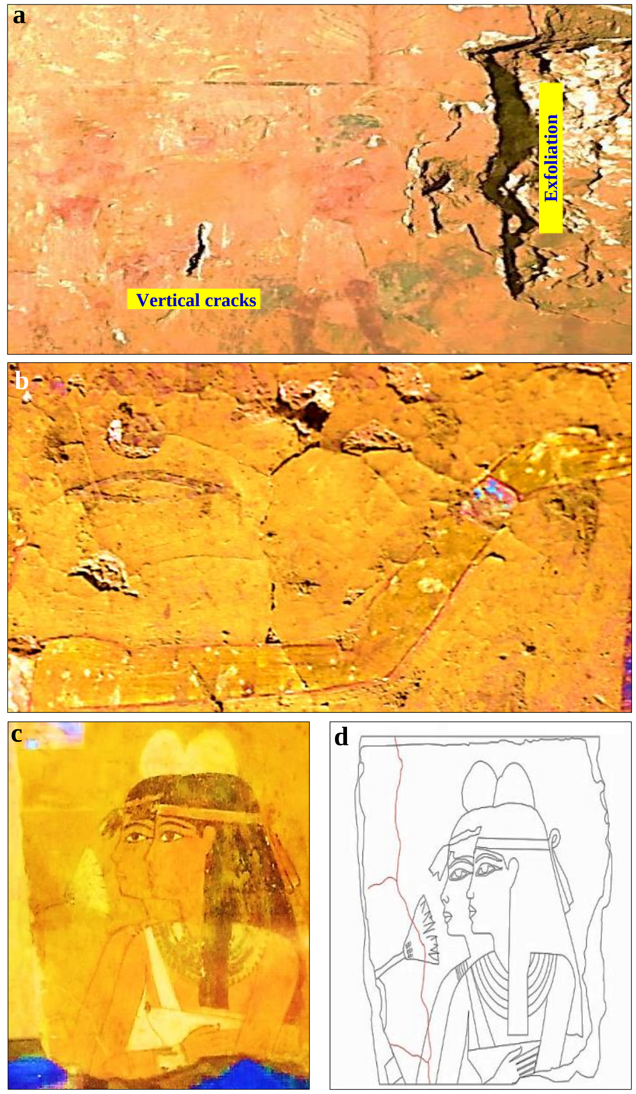

Figure (3) **a.** vertical cracks, gaps and exfoliation, **b.** the horizontal crack networks in the mural painting surfaces due to deterioration factors, **c.** fragment of wall painting, painted with depiction of two women, Tomb of QenAmun (TT93) Luxor Museum, **d.** mapping of the fragment of wall painting condition and place the crack via AutoCAD

2. Materials and Methods

2.1. *Materials*

Some samples (average size 1cm) were chosen from damaged areas of the wall painting including yellow color. They were collected to characterize the wall paintings at the tomb of QenAmun (TT93) to provide the information about the cross section of the paint layers of the fragment of wall painting. Epoxy type 27-751 and its hardener, in addition to sandpaper sizes (800:4000) were used for sample preparation. In addition, two treatment products were applied to inject the cracks:

1) *Eggshell nanoparticles product*
2) *Ethyl silicate 3% in ethanol that can be used to injection the crack networks in the mural painting surfaces.*

To our knowledge, it is the first report on the application of eggshell nanoparticles for the injection of cracks mural painting surfaces eggshell is a natural bio-ceramic composite that has a unique chemical make-up of inorganic and organic compounds. It consists of an inorganic shell and an organic membrane. The shell with its membrane weighs approx. 11% of the egg weight. The inorganic constituent of eggshells is mainly calcium carbonates (95% in the form of calcite), whereas its organic compounds are a matrix of proteins, glycoprotein, proteoglycan, and type X collagen sulphated polysaccharides (5%) [17-20]. Owing to this unique chemical composition, eggshell has extensively gained attention among researchers for its medical and dental benefits. For example, Khandelwal and Prakash [21,22] demonstrated how calcium carbonate derived from eggshells could be used to produce hydroxyapatite, which is mainly used in bone and dental treatments. Abdulrahman, et al. [23] reported that eggshell-based hydroxyapatite and nano-hydroxyapatite could reduce the cost of treatment in bone repair or replacement

2.1.1. Eggshell nanoparticles preparation method

Chicken eggshell powder was prepared by the calcination protocol given by World Property Intellectual Organization (*WO/2004/105912: Method of Producing egg shell powder*) [24]. Chicken egg shell contains about 95% of calcium carbonate which on conversion to basic calcium oxide due to calcination is responsible for an increase in alkalinity [25]. Twelve chicken eggs used were cleaned with distilled water and kept in hot boiling water for 10 mints at 100 °C to facilitate the removal of membranes. The eggshells were crushed and powdered to small particles with sterile mortar and pestle. The tiny, crushed particles obtained were then kept in a muffle furnace (Neycraft Model JFF 2000) at 1200 °C to make sure the resulting powder was pathogen-free. Then the dried powder was milled by using milled by ball mill machine (planetary-ball-mill-pm-400) for 10 h, speed 350 rpm and 3 min intervals.

2.1.2. Preparing of nanocomposite

The nano mixture was prepared using the sonication technique by dispersing 20 gm wt% of eggshell nanoparticles powder (average size 50 nm) in 1000 mL of ethanol for 30 min using an ultrasonic mixture and magnetic stirrer. The eggshell nanoparticles was mixed with ethyl silicate in 1:1 ratio. After that, an ultrasonic mixture and magnetic stirrer were used for 25 min for homogeneous textures

2.2. *Investigation and analytical methods*

Different investigation and analytical techniques were adapted for characterizing and studying then collecting samples. The sample was investigated using PLM (*Model OlympusBX3*). HR-Transmission Electron Microscope model *JOEL JEM-2100*, with operating at 200 kV equipped with Gatan digital camera Erlangshen ES500. The surfaces of the samples were observed using SEM-EDX (*Model JEOL-JSM/ 6010LA*). The voltage of acceleration was 15-20 kV and the size of spot was 50. It was used in South Valley Univ., Qena, Furthermore, X-ray diffraction pattern has been performed using *XPERT-PRO* Powder Diffractometer system, with 2 theta (20^{o}-80^{o}), with Minimum step size 2 Theta: 0.001, and at wavelength (Kα) = 1.54614^{o}. XRD ana-lysis was used in Nanogate Lab., Cairo. Finally, *JASCO (FT/IR- 4100)* FT-IR in Nanogate Lab Cairo, Egypt was used to measure of nanoeggshells.

3. Results

Cross-section samples to be used for were divided into small pieces, then embedded in epoxy after the completely drying the epoxy, they were polished by using sand-paper different sizes with wet-type sandpaper to get smooth, fig. (4).

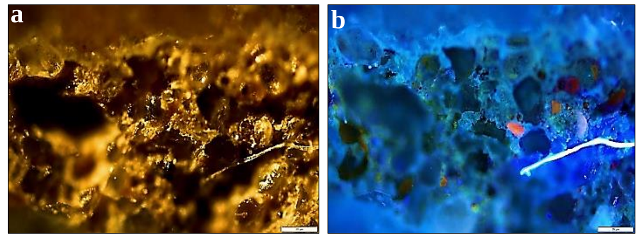

Figure (4) cross-section image of mud mortar structures; mainly clay minerals, lime, sand, aggregates and animals dung addition to chopped straw as binding materials; **a.** under PLM (BMM), **b.** under UV light to get more details about mud plaster.

3.1. *PLM observation (BMM)*

The cross-section is useful for the investigation of materials. Examination by PLM was used to examine fragment of wall decoration and identify its three layers. The structures fragment of wall decoration from the top to bottom composed of three layers: **a)** *color layer* (yellow pigment) with 0.1 cm thickness, **b)** *fine plaster* with 0.3 cm thickness, and **c)** *coarse plaster*1.2 cm thickness. Furthermore, the cross-sectional also attested that the studied sample is composed of quartz, clay minerals, iron oxides, and organic fibers. Moreover, PLM investigation revealed that the yellow pigment formed of very homogeneous and fine grains has many vertical and horizontal cracks and had a loos surface as a result of shrinkage of the clay minerals in the preparatory layers, cracks appear in the painting layer. This suggested that yellow pigment was produced using iron oxides. It also showed that the fine plaster layer composed formed of homogenous fine grains, fig. (4).

Figure (4) **a.** fragment of wall decoration, painted with depiction of two women, tomb of *Qen-Amun* (TT93), it was returned to Egypt as a gift from the clos foundation, Spain, on 30/1/ 2009 Luxor**, b.** cross-section image of the fragment with three layers from top to bottom (yellow pigment, fine plaster, coarse plaster) under PLM

2.2.1. TEM investigation

Electron Microscope proved that the size and shape of nano-particles were 48.25 and 72.20, as shown in fig. (5)

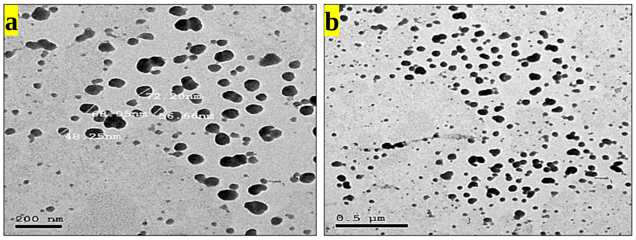

Figure (5) Shows TEM photomicrographs of **a.** the eggshells nano-particles with high-resolution (ave. size 50 nm) **b.** $CaCO_3$ nanoparticles

2.2.2. SEM-EDX observation and analysis

The investigation structure of the wall decoration fragment showed that the identified three layers were applied on the surface of the wall, fig. (6-a). The structures fragment of wall composed essentially of three layers from the bottom to top as argued with PLM observation (*coarse plaster, fine plaster and yellow pigment*). The coarse plaster composed of clay, quartz, and straw; a bonding material was added to the mud mixture, fig. (6-b). Furthermore, it showed some deterioration features, such as *granular disintegration* and *cracking*. Additionally, these layers were weak in the internal structure, which led to many cracks. In the same context, EDX analysis proved that the yellow pigment was based on (Fe) (probably goethite) α-FeO(OH). It was related to the present spectrum (goethite). Furthermore, EDX analysis showed a mixture of Fe and As-based pigments, probably orpiment As_2S_3 mixed with goethite, figs. (6-c). The coarse and fine plaster consisted of calcium (Ca), sulfur (S), silicon (Si), aluminum (Al), and magnesium (Mg), figs. (6- d).

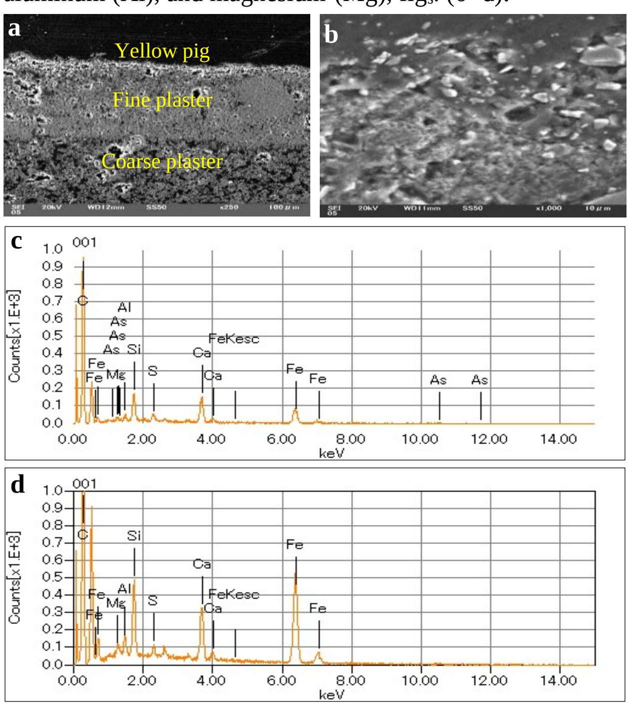

Figure (6) SEM photomicrograph of **a.** three structure layers of the wall decoration fragment, **b.** deterioration features and EDX patterns of **c.** yellow pigment, **d.** coarse plaster

2.2.3. XRD analysis

X-ray diffraction pattern was been performed using XPERT-PRO Powder Diffractometer system, with 2-theta (20°-80°), with minimum step size 2 Theta: 0.001, and at wavelength (Kα) = 1.54614°, fig. (7).

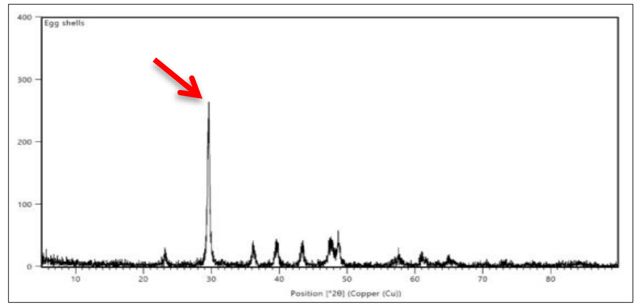

Figure (7) XRD pattern of major peak at 2θ= 29.49 indicating that the major phase of the eggshell is calcite ($CaCO_3$) after thermal treatment at 1200 °C and milling

2.2.4. FTIR spectroscopy

FT-IR vertex 70 RAM II, Bruker Spectrometer was used to measure nano-eggshells, fig. (8).

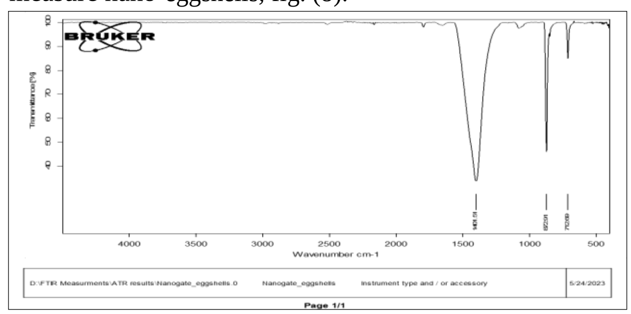

Figure (8) FTIR spectrum of nano eggshells; the functional groups are carboxylic and carbonyl groups with hydroxyl and carbonyl groups

2.2.5. Morphological results of nano-composite

The surface morphology of the treated samples was differed after treatment process, where, granular disintegration affected the samples was disappeared due to positive effects of mixed, treated material (ethyl silicate and the Egg shell nano-particles), fig. (9).

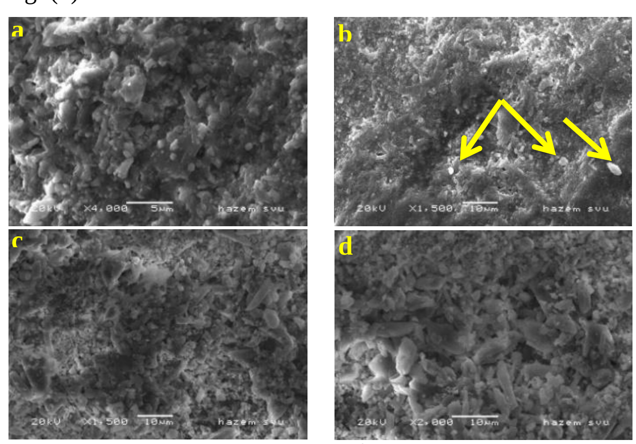

Figure (9) **a.** SEM photomicrograph of painted layer treated samples by ethyl silicate and the eggshell nanoparticles, **b.** distribution of the egg shell nanoparticles on the surface, compared to **c.** & **d.** untreated samples of the painted layer

4. Discussion

Based on the findings of the above analyses and examinations, at the tomb of Qen-Amun, Theban tomb TT93, in Luxor it is apparent that ancient Egyptian artists used the traditional method used inside rock tombs at the Theban tombs. From top to bottom, the structure's fragmented wall decoration was made up of three layers: Yellow pigment, fine plaster, and coarse plaster, which was made up of quartz and clay minerals with high concentrations of O, Al, Mg, and Si. Together with organic fibers and iron oxides. calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), and quartz (SiO_2) made up the fine plaster. From the predynastic era to the Roman era, Egyptian artists employed yellow pigment, or goethite, extensively to paint women's skin. The goethite sample's yellow pigment was found near Aswan and the western desert oasis [25,26]. The findings of the examinations indicated that the severe weather and deteriorating elements in Luxor caused the tomb of Qen-Amun - tomb TT93 - to suffer from many weathering forms, including plaster separation, strength loss, and fissures. It is worth mentioning that the cracks were injected with two different treatment products: The first was eggshell nanoparticles product; the second was 3% ethanol-dissolved ethyl silicate, which can be utilized to inject crack networks into mural painting surfaces. This is the first report on the use of eggshell nanoparticles to introduce fractures into mural painting surfaces. With a distinct chemical composition of inorganic and organic components, eggshell is a naturally occurring bioceramic composite. It is made up of an organic membrane and an inorganic shell. About 11% of the weight of the egg is made up of the shell and membrane. Eggshells are mostly composed of inorganic materials, such as calcium carbonates (95% of which are in the form of calcite), while their organic components include a protein matrix, glycoprotein, proteoglycan, and type X collagen sulphated polysaccharides (5%).

5. Laboratory Conservation Procedures

As a result of the above studies, a laboratory wall painting, fig. (10-a) was subjected to experiment conservation steps to evaluated the efficiency of tested material using the following criteria:

5.1. *Pre-consolidation*

The 1st step was to apply temporary strips of tissue paper saturated by ethyl silicate 3%, in order to prevent weak parts of the plaster from collapsing, fig. (10-b)

5.2. *Mechanical cleaning*

After the mural paintings had been pre-consolidated, the 2nd step was began, where, the surface deposits and dust were carefully removed using an air pump and soft brushes, and the egg shell nanoparticles was prepared using vortex and ultrasonic fig. (10-c).

5.3. *Re-adhesion of detachment and cracks*

The 3rd is the step was injection and re-adhesion; its main goal was to prevent the remaining parts of mural paintings and conserve them against collapsing in the long term. The application method of the treatment was as follows:

1) Applying syringe of alcohol in the injection hole to prepare the cracks for the nano composite.

2) Starting the injection process from the lower to the higher level, and then, injecting the nano composite composed of eggshell nano-particles and ethyl silicate 3% through the crack networks spread in the painting surfaces and the voids between the painting layers using a thin syringe, fig. (10-d).

3) Cleaning the surface by suitable organic solvent to remove any harmful materials after treatment, fig. (10-e & f).

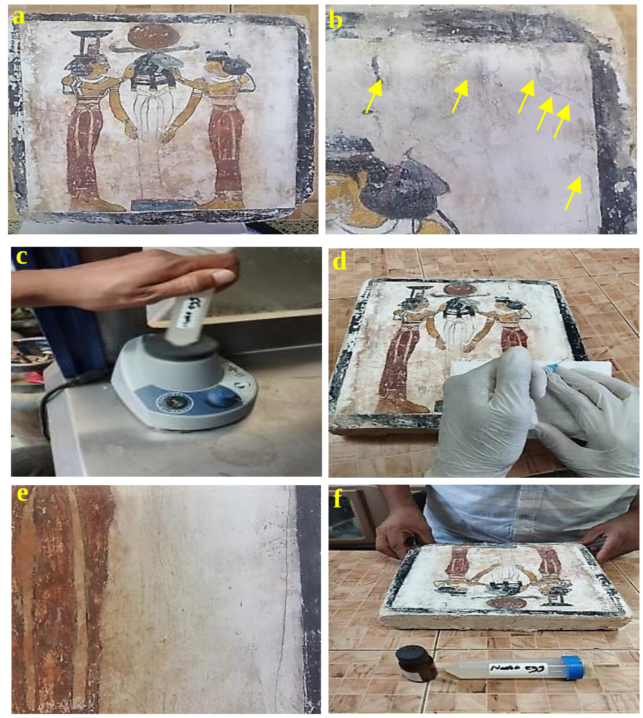

Figure (10) **a.** Experimental samples prepared with the same characteristics as the mural paintings in the tomb of Qen-Amun (TT93), **b.** horizontal and vertical cracks before, **c.** preparation of the eggshell nanoparticles by vortex and ultrasonic, **d.** cracks injection, **e.** Cracks after treatment, **f.** teated sample

6. Conclusions

Microscopic investigation and analytical study indicated that the ancient Egyptian artist prepared the mural paintings using traditional techniques. The result of investigating fragments of wall decoration by SEM-EDX showed the cross-section observation identified three layers were applied on the surface of the wall from top to bottom: Yellow pigment (probably goethite), fine plaster that composed of calcite ($CaCO_3$), gypsum ($CaSO_4.2H_2O$), and quartz (SiO_2), and coarse plaster that was composed of quartz, clay minerals, and organic fibers. Due to the harsh weather conditions in Luxor, Qen-Amun's tomb - TT93 had different forms of weathering, such as cracks, strength losses, and detachment of plaster. Consolidating and filling gaps and cracks posed the greatest challenge to treating the studied mural paintings because of their fragility. The results of the experimental study showed that the mixture of the eggshell nano-particles and ethyl silicate 3% could be used to inject the crack networks in the mural painting surfaces. This mixture was highly effective in consolidating cracks, and the appearance of the treated surfaces was preserved and not any changes. On the other hand, the mixture of eggshells nanoparticles *and ethyl silicate 3% was suitable for the treatment of cracks and more matching in color. The SEM posttreatment images showed that the nanocomposite successfully interacted with the wall painting grains and clogged the surface pores. EDX was able to identify the major and minor compositions of the wall painting. More specifically, silicon (Si), calcium (Ca), sulfur (S) were identified as the main element and iron oxide (Fe) aluminum (Al), and magnesium (Mg)as a minor element*

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