Analytical Characterization of Some Historic Stucco Busts from Muhammad Ali Family, Egypt

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The stucco busts of Muhammed Ali family had not received any adequate researches concerning the methods of implementation and conservation. Thus, this research will try to shed more light on them through studying three stucco busts kept in Prince Mohammed Ali's Museum in El Manial by USB digital microscope, photographing under UV light, X-ray diffraction, the Fourier transform infrared, and scanning electron microscopy–energy dispersive X-ray analysis. The physicochemical study of the three stucco busts indicates that they are hollow cast stucco busts. Gypsum is the main component of these busts, in addition to traces of quartz and calcite. Zincite was used as a pigment in the white painting layer of Khedive Ismail stucco bust. The detection of greenalite, zincite, and barite testifies the whitish green painting layer of Khedive Tawfiq stucco bust. At the same time, the occurrence of hematite in Khedive Ismail stucco bust testifies the effect of iron nails corrosion. The Fourier transform infrared results indicate that the used organic media of pigments is glue.

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1. Introduction

Stucco casting had played an important role in the history of art, especially in the execution of monuments. The role of stucco casting can be divided into three categories. Firstly, using casts as a preparatory stage for the production of a more durable material such as marble and bronze. Secondly, utilizing them as copies for transferring three-dimensional images from one place to another. Finally, using them as artworks in their own right [1].

The reasons behind the popularity of stucco as a material for casting, carving, and modelling lie in its cheapness and easiness of manipulation, as well as the execution of finer details when casting, requiring low calcination temperatures and the validity of its application on variable substrates [2–5].

The stucco statues of Aïn Ghazal in Jordan, neolithic seventh-millennium BC, constitute the earliest survival stucco statues in the world [1]. These statues were made from Ain Ghazal marl, as the chemical analysis revealed the detection of clay, calcium carbonate powder and about 10% of lime made from marl. These statues were made by plastering the armatures made of reed bundles tied together with cordage by the previous mix [6, 7].

It is worth mentioning that the stucco was known in ancient Egypt as a sculptural medium in combination with other materials. The stucco had been used on the well-known bust of the prince Ankhhaf, Fourth Dynasty, and the queen Nefertiti, Eighteenth Dynasty. At the same context, the death masks played a significant role in Egyptian art from the Old Kingdom to the Roman period. The oldest cast statues were started in the Greek period by Lysistratos of Sikyon [1]. In modern Egypt, stucco busts flourished as a casting art in the period of Muhammad Ali family, influenced by the European renaissance art (Fig. 1).

Fig. 1. The studied stucco busts: (a) Muhammad Ali Pasha, (b) Khedive Ismail, (c) Khedive Tawfiq.

Despite the widespread of stucco castings, they have a tendency of deterioration. This is because of the solubility of their gypsum component [4], the high porosity of stuccos [4, 8–10], and the differential properties of their components, as they may contain variable materials such as wooden and metal armatures used as supports. As well, they may contain animal hair, burlap, or plant materials such as excelsior, hemp, and jute for reinforcement [4].

The variable composition of dispersed dust on stucco surfaces disfiguring them. As well, the hygroscopic properties of dust layer facilitate the growth of microorganism, salt damage, and the corrosion of iron armatures [2, 11, 12] (Fig. 3a).

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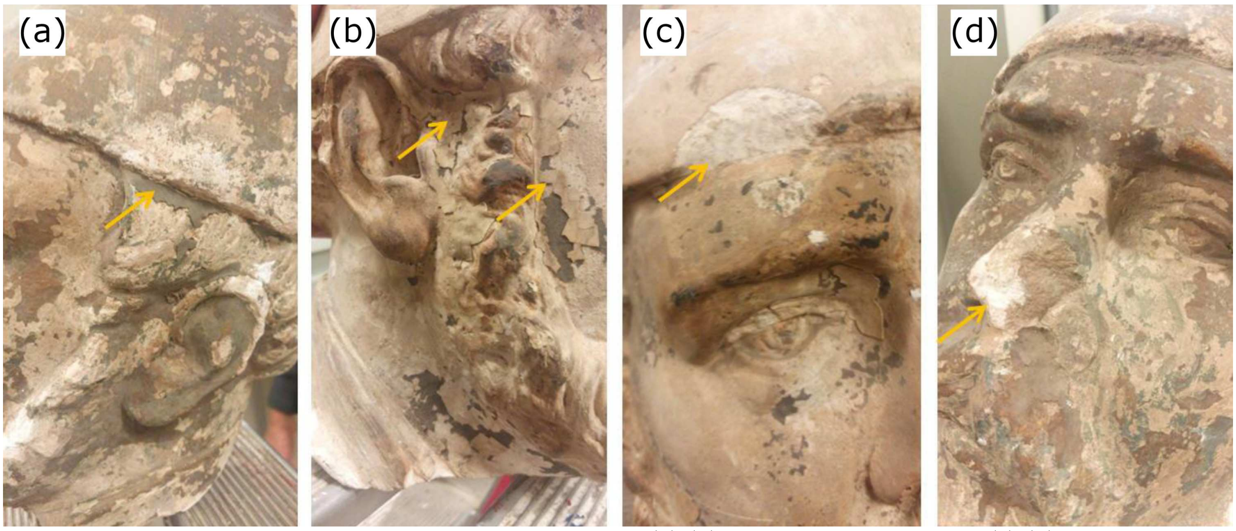

Fig. 2. Some deterioration aspects of the studied stucco busts: (a),(b) losses in painting layers, (c),(d) superficial losses and scratches.

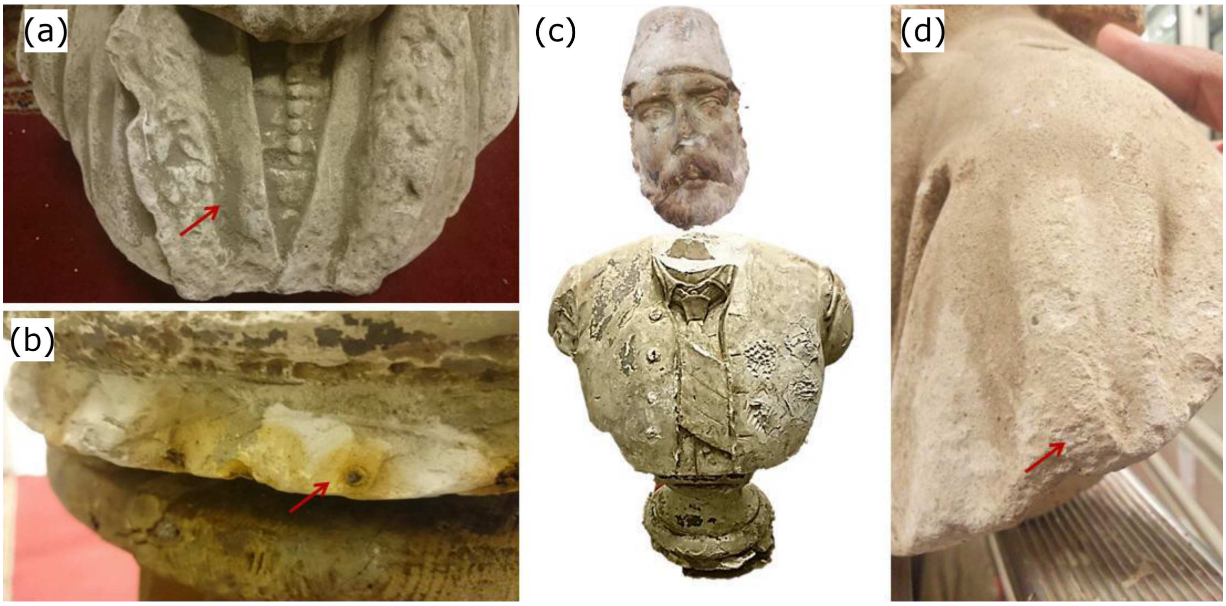

Fig. 3. Some deterioration aspects of the studied stucco busts: (a) dusts deposits, (b) the effect of iron armatures corrosion, (c) breaking of Khedive Ismail stucco bust into two pieces, (d) disintegration of the edges of Muhammad Ali Pasha stucco bust.

In humid environments, iron armatures can be attacked very strongly by gypsum. The rust of these armatures causes the cracking of the surrounding stuccos as well as their surface discoloration (yellow color appearance) [13–15] (Fig. 3b).

As well, the exposure of gypsum stuccos to these environments helps in the increasing of gypsum solubility which causes their surface disintegration [4] (Fig. 3d).

The stucco busts of the current research belong to Muhammad Ali Pasha, Khedive Ismail, and Khedive Tawfiq from Muhammad Ali family. The family had been founded by Muhammad Ali Pasha and had ruled Egypt for more than one hundred and fifty years (1805–1952). These stucco busts are now kept in the Prince Mohammed Ali Museum in El Manial.

This research aims to make a physicochemical study of the stucco busts to identify their deterioration aspects and to figure out a proposal for the conservation of the three stucco busts.

2. Deterioration aspects of the stucco busts

A close up visual inspection helped in the determination of the deterioration aspects, as what will be referred to in the following items:

- Several parts of the painting layers were lost from the surfaces of the three stucco busts, especially on the stucco surface of Khedive Tawfiq bust. Sometimes, the painting layer consists only of white layer, other times it consists of several layers (Figs. 2a, b).

- The wide spreading of superficial damages e.g. scratches that may be resulted from mishandling and poor storage (Figs. 2c, d). Casting air bubbles were observed inside the busts due to casting process.
- Dust is highly dispersed on the surface of the busts. It is a potential source of damage.
- The corrosion of iron nails (Fig. 3b).
- The Khedive Ismail stucco bust was broken in two pieces and four medals that were on the chest have disappeared (Figs. 3c, 4c). A probable cause for these damages might have been inadequate handling and storage procedures.
- The disintegration of the edges of the stucco busts (especially, Muhammad Ali Pasha) may have resulted from the slight solubility of the gypsum component (Fig. 3d).
- Incomplete interventions can be detected in the back of Khedive Ismail bust, namely the incomplete application of a protection layer.

3. Execution methods of the stucco busts

Two possible execution methods for casting of these stucco busts:

Firstly, they were cast directly as shown in detail by Millar [16] and Badde [2], Figs. 4a, b: the hollow casts are made by pouring a portion of gauged stucco mortar into the mould, which can be shaken and rolled in order to let the stucco mortar flow into every part of the mould. Then the surplus stucco mortar is poured into a basin while turning the mould over until the stucco mortar shows signs of becoming firm. This process can be repeated many times until the cast is sufficiently thick.

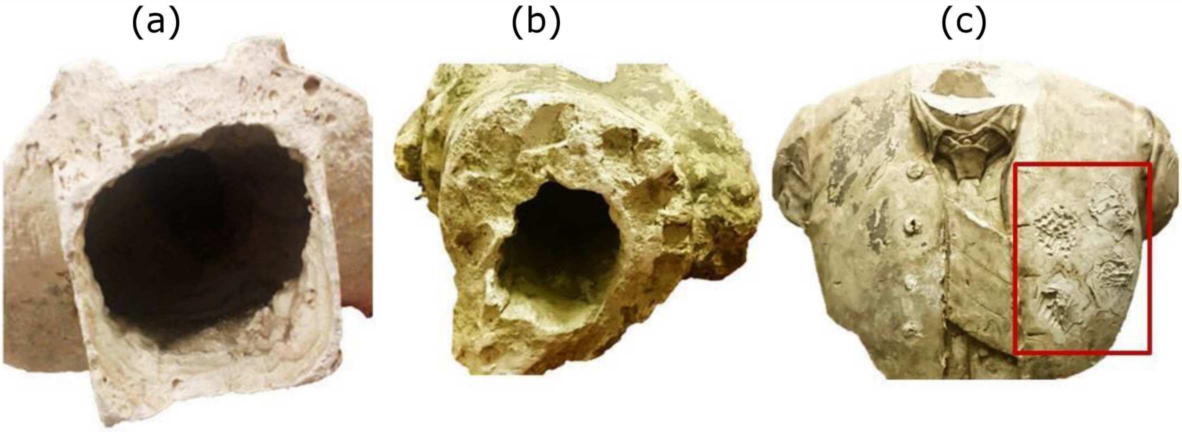

Fig. 4. The hollow casting of the studied stucco busts which justifies the use of plaster piece mould or gelatin mould in their execution.

Secondly, the stucco busts were cast with a gelatin mould. Before silicone was introduced into the casting procedure as a flexible material for mould production, gelatin was applied onto a model isolated with shellac or wax. The gelatin was treated with alum to be more durable. Then two or more pieced "mothermould" or gypsum case was fitted onto it, which in turn was treated with shellac. The gelatin mould could be cut accurately to pull out the model and more than four casts could be produced with it. In the case of the stucco bust of Khedive Ismail, which is characterized by the existence of its base, the bust and the base may have been moulded and cast separately, then fixed together. This method decreases the weight of the mould, gives a greater opening for filling in and more freedom when casting [16, 2]. The four lost medals (at the chest area of Khedive Ismail stucco bust) indicated that these medals were added after casting of the stucco bust by scratching their areas of fixation. Then they have been executed by the addition of a layer of fresh plaster to the scratched areas to fix the cast medals (Fig. 4c).

4. Materials and methods

4.1. Sampling

Seven representative samples were collected carefully by a micro scalpel from deteriorated, separated, and unseen parts (the internal hollow parts) from the stucco busts to identify the chemical composition and deterioration aspects. All of the analysed and investigated samples were collected from areas with less historic and aesthetic values and sometimes the same sample was used for more than one analysis (see Table I and Fig. 1). As well, two dust samples were collected to be examined by USB digital microscope.

4.2. Examination by USB digital microscope and photographing with the help of UV lamps

Some samples of stucco and paint layers were observed using a handheld USB digital microscope (model PZ01 — made by Shenzhen Supereyes Co. Ltd, China) with the following technical specification: image sensor

TABLE I

Description of the analyzed samples collected from the studied stucco busts.

Sample no.	Sample description (the samples location is shown in Fig. 5)
(1)	Dark painting layers from the surface of Khedive Ismail stucco bust.
(2a)	Stucco sample taken from the core of Khedive Ismail bust (the chest) to identify its mineralogical components.
(2b)	Stucco sample affected by iron corrosion (Khedive Ismail bust).
(3)	Dark painting layers from the surface of Khedive Tawfiq stucco bust.
(4)	Stucco sample taken from the core of Khedive Tawfiq bust to identify its mineralogical components.
(5)	Stucco sample taken from the core of Khedive Ismail bust (the head) to identify its mineralogical components.
(7)	Stucco sample taken from the internal hollow parts of Muhammad Ali Pasha bust to identify its mineralogical components.

0.3 megapixels, magnification factor 10–500 times, photo capture resolution 640 × 480, 320 × 240 and LED illumination light resource adjustable by control wheel. This microscope was used to examine the cross-sections of stucco busts, their painting layers stratigraphic composition and collected dust samples. Surface layers and cross-section of Khedive Ismail stucco bust (the two parts) were examined by digital camera under UV light to collect information about the casting procedures.

4.3. X-ray powder diffraction

The X-ray powder diffraction (XRPD) technique was used in order to determine the mineralogical composition of the seven samples which were obtained using a diffractometer type (XPERT PRO PANalytical, Netherlands), operated at 45 kV, using a Cu K_{alpha} radiation wavelength of 1.54060 Å. Generator current is 30 mA. The measurements were made at room temperature. The reference data base used for matching is PDF-4+2015RDB. Preparation of each sample consisted of grinding the dry samples on one direction, by using a mortar and pestle to obtain a fine powder. The XRPD analysis was done at XRD Unit in Nanotechnology and Advanced Material Central Lab (NAMCL), Agriculture of Research Center (ARC), but the matching was done at Faculty of Archaeology, Cairo University.

4.4. Scanning electron microscopy with energy dispersive X-ray analysis

The microstructure and morphology of the mineral constituents in the stuccos were recorded with a scanning electron microscope (SEM), model Quanta FEG 250 attached with EDX unit (energy dispersive X-ray analyses), with accelerating voltage 20 kV, without coating the samples. The SEM-EDX was done at the National Research Center, Giza, Egypt.

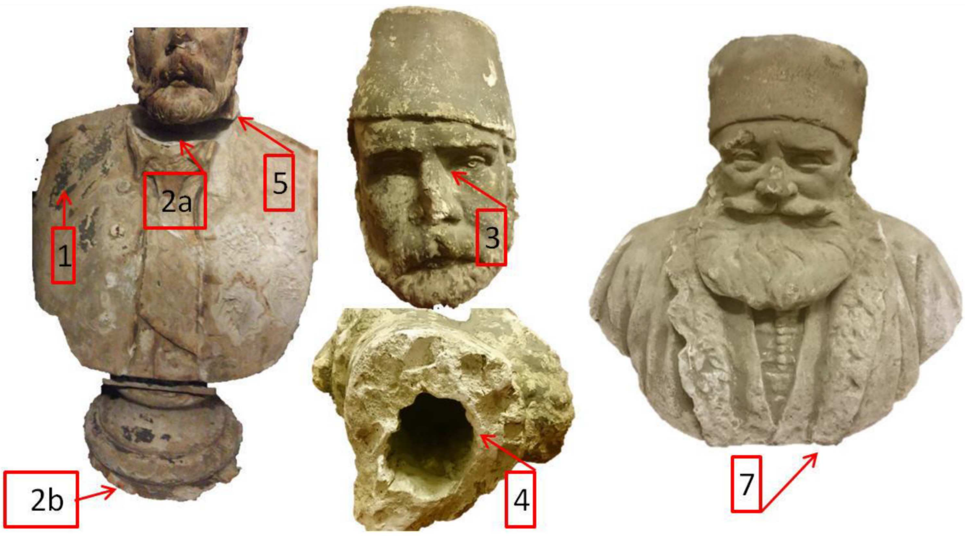

Fig. 5. The locations of samples taken from the studied stucco busts.

4.5. Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra were obtained using a spectrophotometer (JASCO FT/IR-4100 type A, measurement range 4000–450 cm^{-1}, resolution of 4 cm^{-1} and drive speed AUTO, 2 mm/s). The sample preparation process consisted of grinding it to obtain a fine powder which was then mixed with KBr powder (in the ratio 1:15). The FTIR quantitative analysis was done at the micro-analytical center of Cairo University.

5. Results and discussion

5.1. Investigation by USB digital microscope and photographing with the help of UV lamps

The observations done by USB digital microscope of some detached samples of paint layers, stucco, and dust revealed the following results (Fig. 6).

- The appearance of wooden chopsticks and parts of hair, Figs. 6a, b.
- The cross-section investigation of the paint layer proved that sometimes it was applied directly on the stucco surface, Fig. 6d, other times it was applied on a white layer (Fig. 6c). According to XRD analysis the white layer consists of zincite and barite (Fig. 9).
- The wide spreading of fine sand particles in gypsum stucco, as well as the yellowish appearance of the surface layer of Khedive Ismail stucco bust (that appearance may be related to the application of glue varnish layer or the natural ageing of stucco surface) (Fig. 6e).
- Also, the examination of surface layers and cross-section of Khedive Ismail stucco bust by digital camera under UV light shows the presence of some parts of thick paint layers, especially in the under-cut parts of head and chest. In addition the examination of the chest cross-section reveals the appearance of many layers of cast stucco mortar used to execute the stucco bust which confirms what was proposed by the authors (Fig. 7).

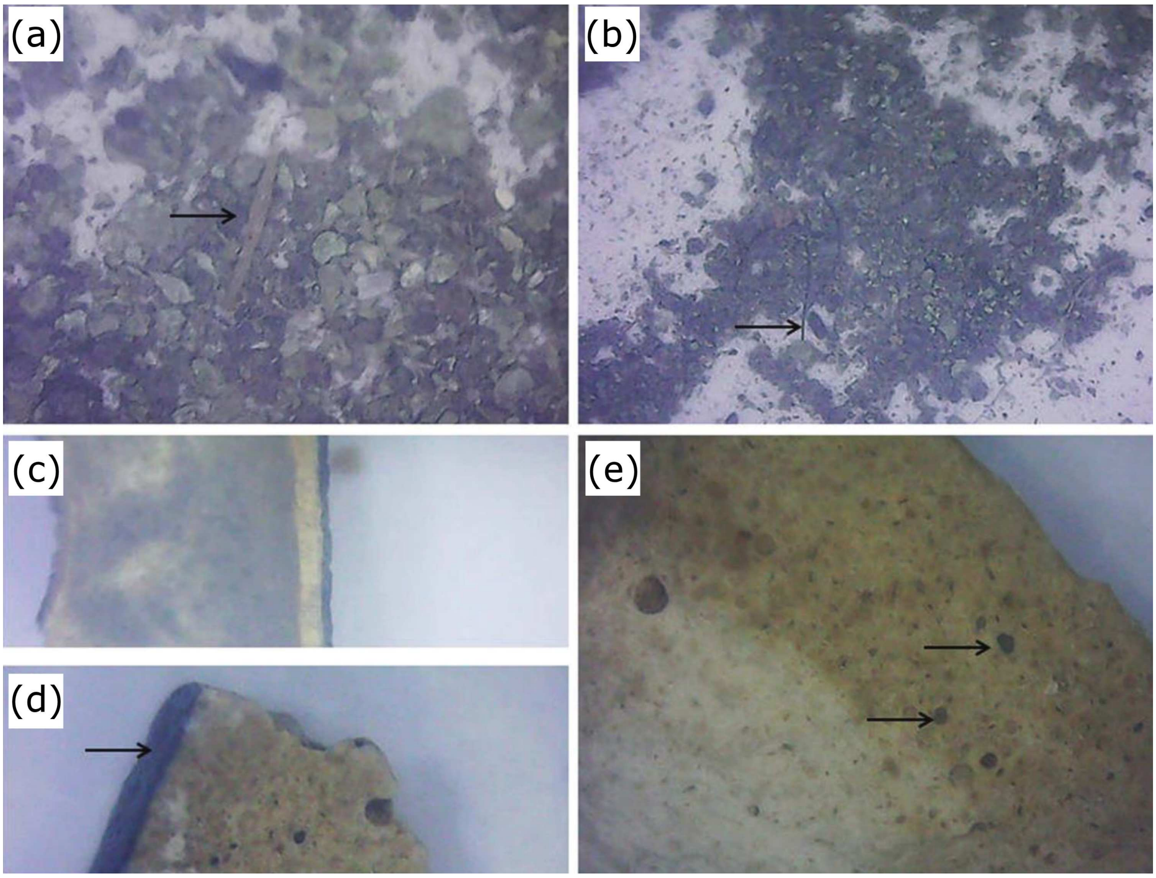

Fig. 6. (a)–(e) USB digital microscope images of some detached samples of paint layer, stucco and dust.

5.2. X-ray powder diffraction

The XRPD patterns of the analysed samples are shown in Fig. 8 and the semiquantitative analysis of the mineralogical composition is summarized in Table II. The results obtained indicate the following:

- Gypsum is the main component of samples 2a, 2b, 5, 4, and 7. Calcite in sample 2a and quartz in samples 2b and 4 are minor constituents, which may be related to impurities in the raw materials. When quartz appears in medium quantities as in samples 1 and 3, it means it was probably added as filler to facilitate casting and to increase strength or may related to the two possibilities [17–19] (Fig. 8).
- The XRD analysis of dark painting layer from the surface of Khedive Ismail stucco bust (sample 1) revealed that it contains mainly zincite (ZnO).

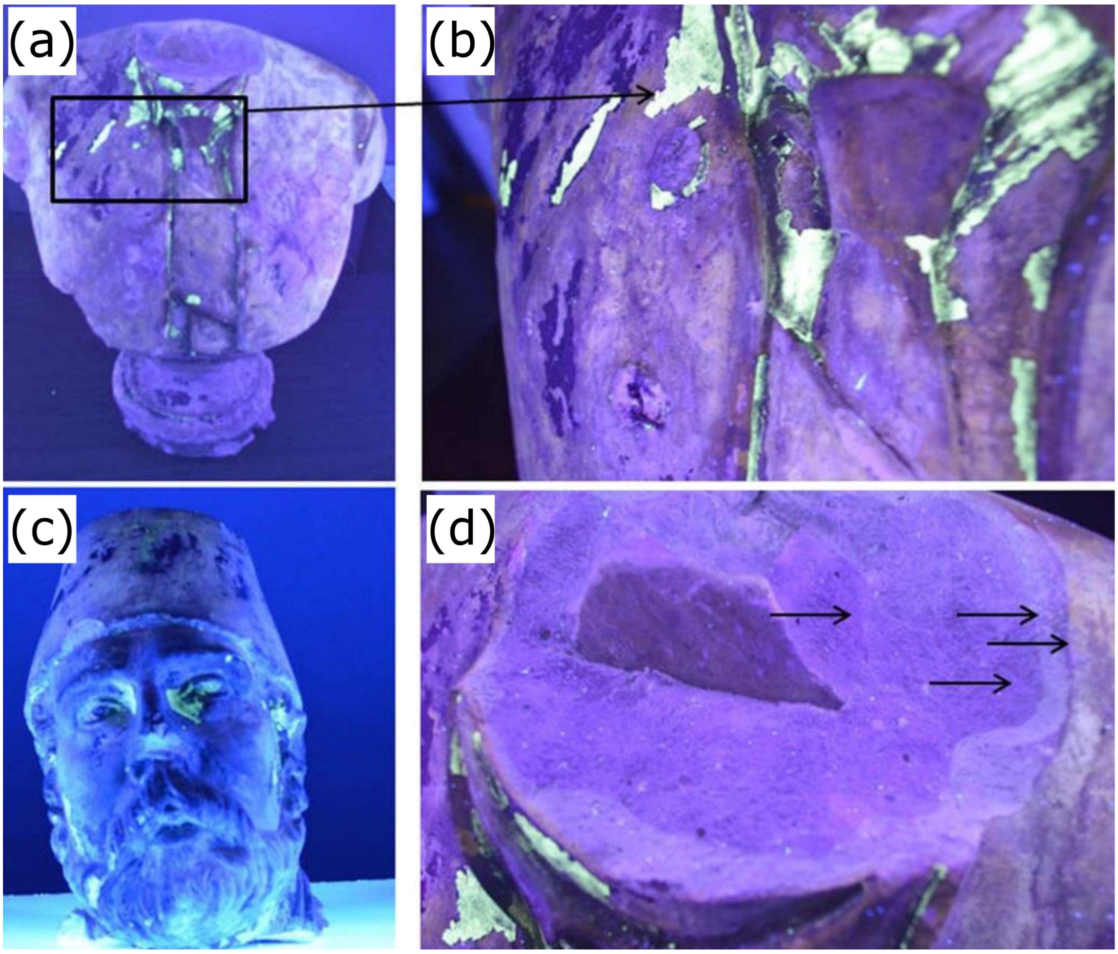

Fig. 7. Surface layers and section view of the chest of Khedive Ismail stucco bust recorded by digital camera under UV light.

The use of the white pigment of ZnO had been started at about 1845 [20]. As for the darkened color, it may be related to the discoloration of glue used as a binding media for the white pigment because of the reactivity of zinc oxide with the organic components of glue, degradation of the organic media, dust deposition or all of these factors (Fig. 9a) [21, 22].

- The sample of the darkened paint layers taken from the surface of Khedive Tawfiq stucco bust (sample 3) contains gypsum, quartz, zincite, barite, and greenalite. The presence of barite may be related to its usage as a white pigment (barite is a pigment that can have many colors mainly the white color as well as the yellowish white, the grayish white, the brownish white and the dark brown [23]). Greenalite is responsible for the light green color of Khedive Tawfiq stucco bust (it can have many colors such as blue green, light yellow green, and dark green [24]). The period of Khedive Tawfiq was characterized by the spread of this degree of green color (Fig. 9b).

- The presence of hematite in sample (2b) in Khedive Ismail bust confirms its responsibility for the discoloration of stucco bust pedestal which had occurred because of corrosion of iron armatures (Fig. 9c).

TABLE II

The approximate XRD analysis results of the studied stucco busts.

Sample	Component									
	Ca	Qu	Gy	An	He	Zi	Por	Gr	Mag	Ba
(1)	−	++	++	−	−	+++	−	−	−	−
(2a)	+	−	+++	−	−	−	−	−	−	−
(2b)	−	+	+++	−	+	−	−	−	−	−
(3)	−	++	+	−	−	++	−	+	−	++
(4)	−	+	+++	−	−	−	−	−	−	−
(5)	−	−	+++	−	−	−	−	−	−	−
(7)	−	−	+++	−	−	−	−	−	−	−

Ca = calcite, Qu = quartz, Gy = gypsum, An = anhydrite, He = hematite, Zi = zincite, Orth = orthoclase, Por = portlandite, Gr = greenalite, Mag = magnetite, Ba = barite, − = not detected, + = traces, ++ = minor constituent, +++ = major constituent

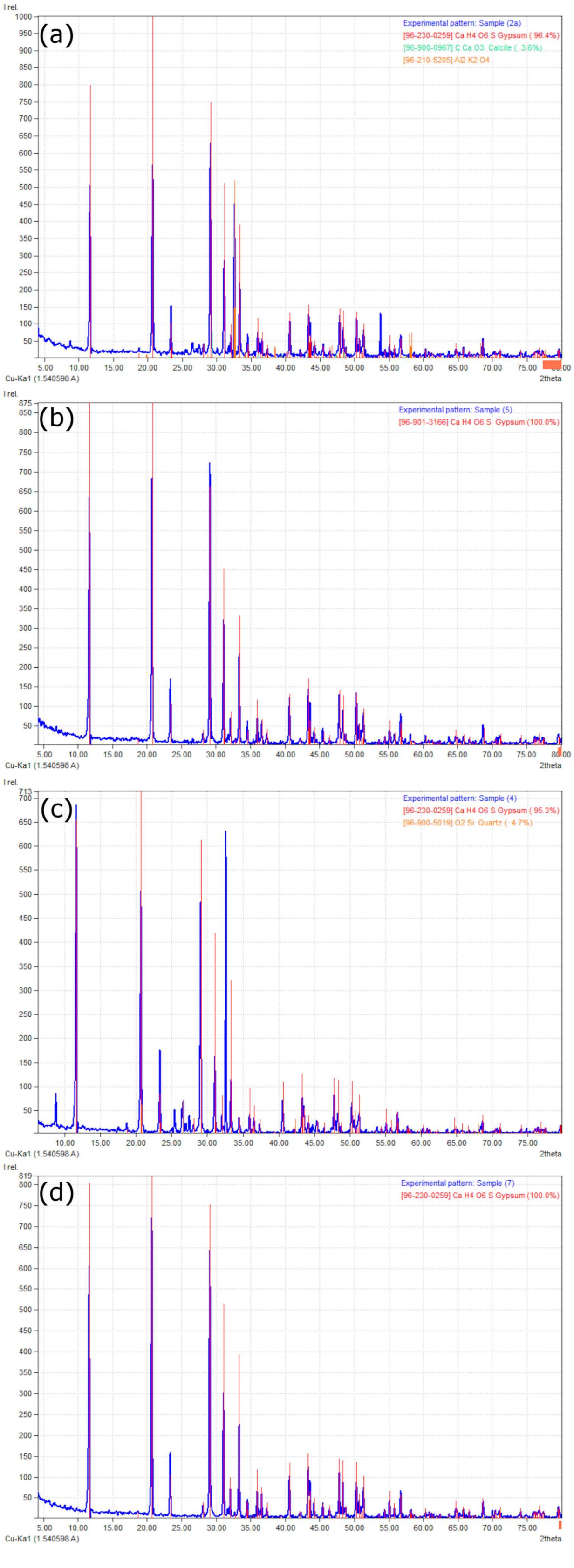

Fig. 8. (a)–(d) X-ray diffraction patterns of the samples taken from the three studied stucco busts showing they are mainly composed of gypsum.

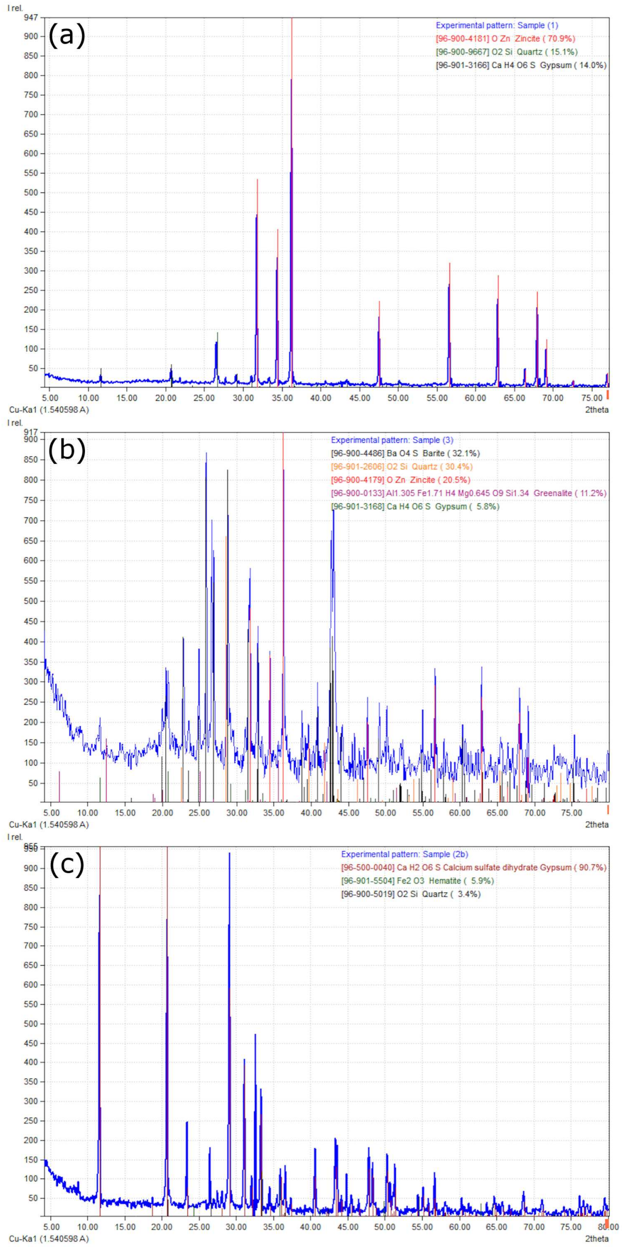

Fig. 9. (a) and (b) show the XRD profiles of the painting layers taken from the surface of Khedive Ismail and Khedive Tawfiq stucco busts, respectively (c) corresponds to the sample taken from the parts affected by iron corrosion in the Khedive Ismail bust.

5.3. Scanning electron microscopy with energy dispersive X-ray analysis

The observations made by scanning electron microscope for the three representative samples of the components of stucco busts (2a, 4, and 7) showed the presence of interlocked needle-like crystals of gypsum. That was confirmed by the presence of Ca, S, and O elements in EDX analysis while the presence of Ca, C, Si elements testifies the existence of calcite and quartz, also detected by XRPD analysis, Figs. 10–12. The EDX analysis results

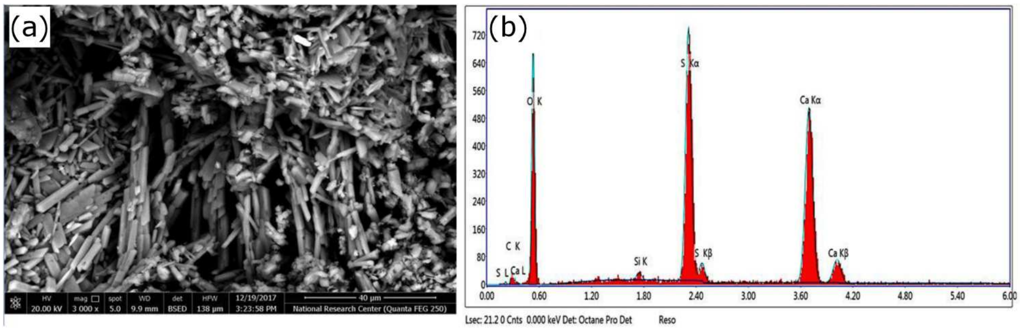

Fig. 10. Scanning electron micrograph (a) and EDX analysis (b) of the chest of Khedive Ismail stucco bust.

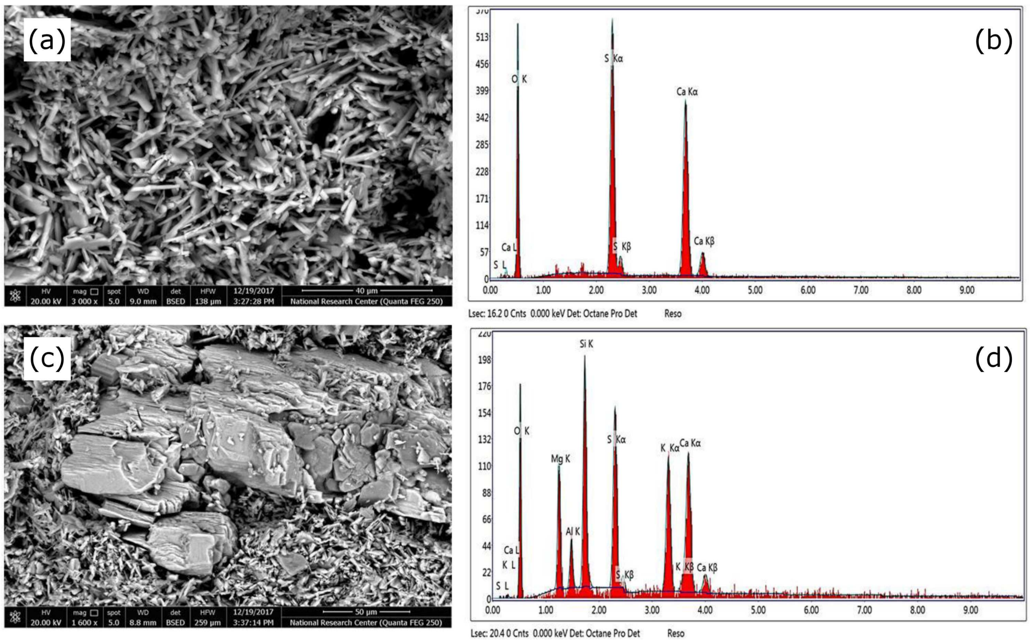

Fig. 11. Scanning electron micrograph (a)and EDX analysis (b) of Khedive Tawfiq stucco bust sample.

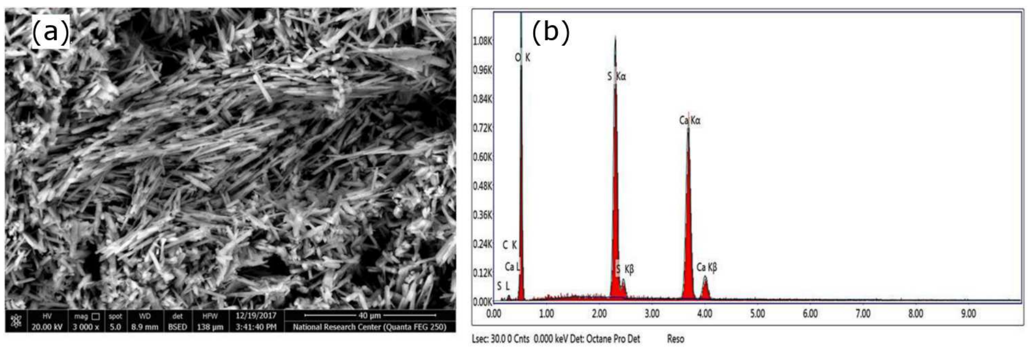

Fig. 12. Scanning electron micrograph (a) and EDX analysis (b) of Muhammad Ali Pasha stucco bust.

of Khedive Tawfiq stucco bust sample 4 revealed the appearance of Ca, Al, Si, Mg, and K elements which may be related to traces or contaminations of clay minerals (Fig. 11).

5.4. Fourier transform infrared spectroscopy

With the help of FTIR standard analyses of glue and gypsum, the following results were obtained in the FTIR analyses of samples 2a, 3, and 4:

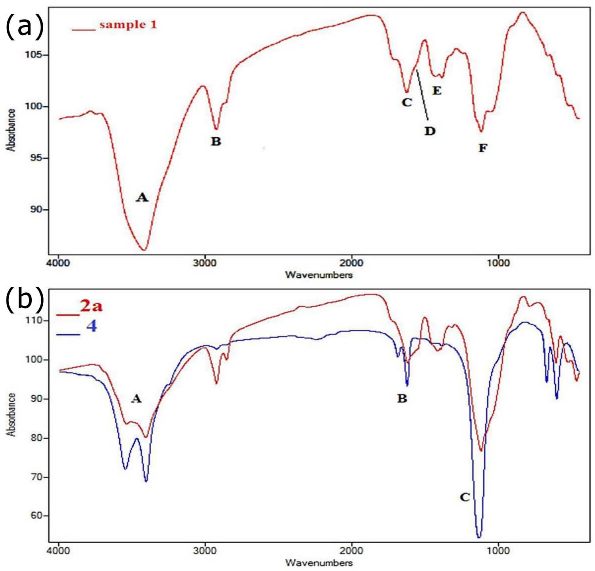

Fig. 13. (a) Infrared spectra of the dark painting layer sample taken from the surface of Khedive Ismail stucco bust (1), (b) Infrared spectra of the two stucco samples of Khedive Ismail and Khedive Tawfiq busts (2a and 4).

TABLE III

The FTIR analysis results of the dark painting layer sample taken from the surface of Khedive Ismail stucco bust (1) and the two stucco samples of Khedive Ismail and Khedive Tawfiq busts (2a and 4).

Code	Function groups	Wave numbers [cm^{-1}]
	Sample (1) glue	
A	O–H stretching	3420
B	C–H asymmetric stretching	2874–2927
C	C=O conjugated stretching (amide I)	1624
D	N–H bending + C–N stretching (amide II)	1562
E	C–H bending	1381–1443
F	C–N stretching (amide III)	1115
	Samples (2a and 4) gypsum	
A	O–H antisymmetric and symmetric stretching	3552–3401
B	$(SO_4)^2$ stretching	1624
C	C–O stretching + asymmetric $(SO_4)^2$ stretching	1131

- In the dark painting layer taken from the surface of Khedive Ismail stucco bust (sample 1) glue can be identified according to the wave numbers shown in Table III (Fig. 13a).
- In the samples of Khedive Ismail and Khedive Tawfiq stucco busts (2a and 4) gypsum was confirmed as the main binding component, Table III (Fig. 13b).

6. Conclusions

The scientific study of the three stucco busts of the current research provides quite interesting information concerning their execution methods and physicochemical characteristics. The naked eye examination, alongside photographing under UV lamps, revealed cast directly as a hollow cast by using plaster piece mould or gelatin mould.

The used analytical methods proved that gypsum is the main binding component of the stucco busts; quartz and calcite appear as minor constituents and may be related to impurities in the raw materials. When quartz appears in medium quantities, it means it was probably added as filler to facilitate casting and to increase strength. SEM results confirmed the XRD results by the clear presence of the interlocked needle-like crystals of gypsum as well as the presence of Ca, S, and O elements in the EDX analysis. XRD analyses results indicated that zincite was used as a white pigment in the white painting layer of Khedive Ismail stucco bust. Greenalite, zincite, and barite were used in the light green painting layer of Khedive Tawfiq stucco bust. The detection of hematite in Khedive Ismail stucco bust proved the effect of iron nails corrosion. FTIR results indicated that glue was the organic binding media of pigments and confirmed the results obtained with the other techniques.

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