SCIENTIFIC CULTURE
www.sci-cult.com

SCIENTIFIC CULTURE, Vol. 7, No. 2, (2021), pp. 49-68
Open Access. Online & Print

DOI: 10.5281/zenodo.4465518

AN EXPERIMENTAL STUDY FOR CONSOLIDATION OF ARCHAEOLOGICAL CARTONNAGE USING KLUCEL G AND CHITOSAN, WITH NANOCALCIUM HYDROXIDE

Hala A.M. Afifi, Rushdya Rabee Ali Hassan*, and Shimaa M. Menofy

Restoration and Conservation Department, Faculty of Archaeology, Cairo University, 12613 Giza, Egypt

Received: 15/12/2020
Accepted: 03/02/2021

**Corresponding author: Ali Hassan Rabee (rushdyarabii@yahoo.com)*

ABSTRACT

The paper discusses using of Klucel G and chitosan loaded with nano-calcium hydroxide as consolidates for damaged Cartonnage extracted from dry excavations soil. Analytical methods used in these analyses included scanning electron microscopy (SEM), transmission electron microscopy (TEM), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and digital microscopy. The results proved the success of Klucel G in giving better results than Chitosan, and the performance of the two materials improved by adding nanomaterial, although the best one was Klucel G with nano-calcium hydroxide 3%.

KEYWORDS: nanotechnology concept, archaeological Cartonnage, Hydroxypropylcellulose, Chitosan, Nano calcium hydroxide

1. INTRODUCTION

Although dry burial environments are considered one of the best burial environments in general for most of discovered archaeological materials. Especially organic materials in ideal conservation conditions (Peacock, 1987), the level of the air's RH is the major affecting factors of the burial soil before extracted beside to the kind of burial environment and the type of archaeological material itself (Chemello and Davis, 2014; Afifi et al., 2011a). It is this which will bring deterioration or preserves the archaeological material; if the RH is low, organic materials are in general well preserved. At worst, if the air in a cavity is too dry, the damage will appear as a general weakness and cracks of the painting and preparation layer. On the other hand, in a moist environment, organic materials have a very high probability of being attacked by micro-organisms (bacteria, fungus, mould that will usually lead to the slow destruction of the object (Guichen,1995; Afifi et al., 2011b). As a result of the composite structure of the Cartonnage (organic inorganic porous materials) (see, Afifi et al., 2011a, 2020 a, b, c), the reactions and behaviour of each substance differ from the other, organic archaeological materials are hygroscopic, cellular in composition, and they increase in size or shrink according to the level of relative humidity and the difference in temperature rates. If it extracted from wet sediments it lose their water upon detection, while those extracted from dry sediments absorb water from the atmosphere when relative humidity is high and in the event of a low level of relative humidity, the substance loses the remaining internal content of water, leading cracks, crumbling, wrapping or shattering and so on. Also, organic materials like textile mainly degraded by oxygen and microorganisms such as Aspergillus Niger that is found in sandy burial environments (Nord et al., 2005). Both archaeological inorganic (porous) materials such as decorated surfaces are sensitive to immediate damage factors upon detection and exposure to the atmosphere, so the detection makes them in contact with drier air and the water filling the pores evaporates that was worked to end the stability state and caused difference in the rates of expansion and shrinkage of each layer. Lifting from sandy or very dry soils can be more challenging because of the difficulty in isolating the object from its burial context and ensuring that fragile and fragmented artifacts stay together (Chemello and Davis, 2014). If possible, the excavation restorer resort to postponing the resulting environmental shock by using some materials that keep the archaeological material from deteriorations, such as lifting a part of the soil and consolidate the pieces once they are extracted using one of the appropriate consolidation materials when artifacts are too fragile to be lifted without breakage or loss, as is often the case with severely embrittled organic material, consolidation in situ may be necessary (Ahmed, 2015). For the success of the consolidation process, the selected material must meet several conditions, such as restoration and reversibility, and it in any way it should not change the basic chemical and physical composition of the original material. They should provide a good aging stability, as well as being consistent against insect infestation or microbiological growth (Johnson, 2018; Afifi et al., 2011b).

From this point, the researchers used this technique in conducting an experimental study of the effect of using some traditional materials alone, which gave good results with similar materials, such as Hydroxypropyl cellulose (Klucel G) that was used widely as a good consolidation material of pigment material. Feller and Wilt (1993) study found that the higher molecular weight grades of Klucel (such as M and H) to be less stable than lower molecular weight grades (G and L).Conservators have frequently used Klucel G for the consolidation of matte paint, and other grades have been used in poultices, inpainting media, and infilling media.It has also been used by many researchers such as (Henry, Walter, et al.1993)who state that Klucel-g can be used successfully in water/alcohol solutions to consolidate pigmented ethnographic materials which have a matte surface quality, also it has been used in ethanol to consolidate darker colors like the blues and browns of water-based paints which are sensitive(i.e. darken) with aqueous consolidates. Mahony (2014) also refers that it gave good results when it was used to strengthen the organic protein substances by dissolving it in the organic solvents, it did not work to cause a major color change and helped to preserve the natural appearance of the archaeological material. Martínez et al., (2020) reported that Klucel G at a concentration of 1% gave the best results compared to other materials such as ethyl silicate (Estel1200, BE), ethyl silicate (Nanoestel, NE), acrylic resin (Paraloid® B72, PAB72), polyvinyl-butyral (Mowital® B60H, MW) and thermoplastic polymer (Aquazol®, AQ), when used in the restoration of the painting color as azurite, cinnabar and lead red, it gave very good results in reducing the rates of color change compared to other materials, that gave large rates of color change, Klucel G also gave less change in shape and scale and less effects on the color distributions of the samples and their colors homogeneity. Abdel Kader et al., (2018) and Hassan (2019a) also used Klucel G to consolidate Greco-Roman organic dedicatory Panels, Klucel-G was dissolved in 3% ethyl alcohol to consolidate the

painting layer. Ali et al., (2016) quotes the success of Klucel-G and Chitosan in restoring archaeological Cartonnage in the Egyptian Museum, the consolidation process start with consolidate the fragile parts, removing the cotton bandages which was used to maintain the shape of the mask. Japanese tissue adhered with Klucel G is used to support the mask and consolidate pigments surfaces and Linen textile ruptures were fixed and consolidated using Chitosan 5%. Salem et al (2016) also mentioned its good effect in restoring one of the painting wooden coffins extracted from the excavations with a concentration of 5%, as it gave good results in binding the painting layer with the preparation layer. Badr (2013) and Ali et al., (2016) also used it in fixing preparation layers and powdered painting and filling cracks at a concentration of 5%. Ali et al., (2016) used it to strengthen the surface of the Cartonnage facing by applying Japanese tissue stripes glued with Klucel G 5% in Ethyl Alcohol and pasting ruptures in layers of linen and ground layer using Chitosan 5% in Ethyl Alcohol. Studying its effect on organic matter that is mainly composed of cellulose (Zhang et al., 2020) it proved its good effect of using HPC in the coating treatment and could significantly and proved that HPC could enhance the photo durability of cellulose-based materials with different pigments under accelerated UV aging conditions.

Chitosan, another consolidation material that was used to consolidate organic archaeological material specifically and provided good results of protection of the objects from microbiological damage and a good strength and penetration. Christensen et al., (2015) used Chitosan in the restoration of one of the organic materials (wood), and it was found that Chitosan solution penetrated at least 1 cm along the grain over the span of 2 weeks. Depolymerizing the Chitosan only improved uptake slightly and left an open structure.

As restoration techniques have developed, the pure consolidation materials have been mixed with a nanomaterial. The dispersion of nanoparticles in the polymers used in the consolidation and protection processes lead to a significant enhancement of their physiochemical and mechanical properties and the minimizing of particles size into Nano scale, which results in better properties from the large grain size of the materials of the same chemical composition (Eloriby et al., 2019). It also can solve many problems found in the traditional interventions such as resistance to biological damage or isolation of the surface from external damage factors such as water and dust (Sierra-Fernandeza et al., 2017). Mostafa et al. (2019) presented the results of using hydroxypropyl cellulose on the painting samples painted with hematite, yellow ochre and black carbon the results showed its success in giving acceptable color change values at a concentration of 1% and by adding nano material (ZnO) the color change reduce. Also it helped in improve the stability and durability of the consolidation material. Abo Elgat et al., (2020), Hassan (2020), and Afifi et al., (2020c) mentioned the effect of mixing Chitosan with nanoparticles (NPs) of Ag, ZnO, or cellulose (NCL) and examined their effects on the mechanical, optical, and fungal inhibition properties of cellulose material (paper sheet), the tensile, tear, and burst indices were observed. Chitosan+ ZnO NP (1%) showed the highest fungal mycelial inhibition against *Aspergillusflavus* and Chitosan, Ag, NP (1%) exhibited the highest against A. terrus, Daehne and Herm (2013) studied and tested the effect of different groups of pure and nanoparticles calcium hydroxide dispersed in alcohols on the moral painting consisting of pigments and plaster. The results indicated that pure material is not suitable enough because of their low viscosity and insufficient and by adding it to Klucel (hydroxypropylcellulose) it achieved very promising results in consolidation the pigment layers, Reinforcement the preparing layer, filling cracks, and detachments (Afifi et al. 2019b).

The idea of the present experimental investigation came to using nanoparticles that match their nature with the original archaeological material and work to protect it in the future from the influence of damage factors with possibility of deep penetrate into damaged zones without limitations due to the particle size. Thus, nano calcium hydroxide was used mixed with HPC and Chitosan where the idea was to develop and test the effect of combining that material on the properties of the consolidation material and to know the effect of adding them on the study archaeological materials. Finally, it is the first study using Klucel G and chitosan loaded with Nano calcium hydroxide in conservation of Cartonnage, and in present study a bridge between the conservation of pigments, and the field of nanotechnology is discussed.

2. MATERIALS AND METHODS

2.1 PREPARATION OF EXPERIMENTAL SAMPLES

The experimental samples were prepared with the components and proportions of the archaeological Cartonnage according to the analytical and examination studies in this field by Mahmoud (2010) and Katsaros et al., (2010). The work steps were made as follows (Fig.1):

- ✓ linen samples measuring 5 x 5 cm were prepared the weaving pattern is (1/1), they were washed with deionized water to remove the contaminants then the samples left to dry at room temperature

- ✓ the gum Arabic solution (10% w/v): 50 g. gum Arabic was mixed with about 450 ml. water until the material is completely dissolved (about 15 min.).
- ✓ -the linen fabric was soaked with gum Arabic solution then left to dry in a clear air.
- ✓ preparation layer (ground layer): 250g of calcium carbonate was dissolved in aqueous solutionof gum Arabic (10% w/v),the layer was applied by casting method and left to dry .

The pigment materials (Egyptian blue and red ochre) were applied separately after dissolving it with gum Arabic and applied using a brush, then the samples were left to dry in the room air.

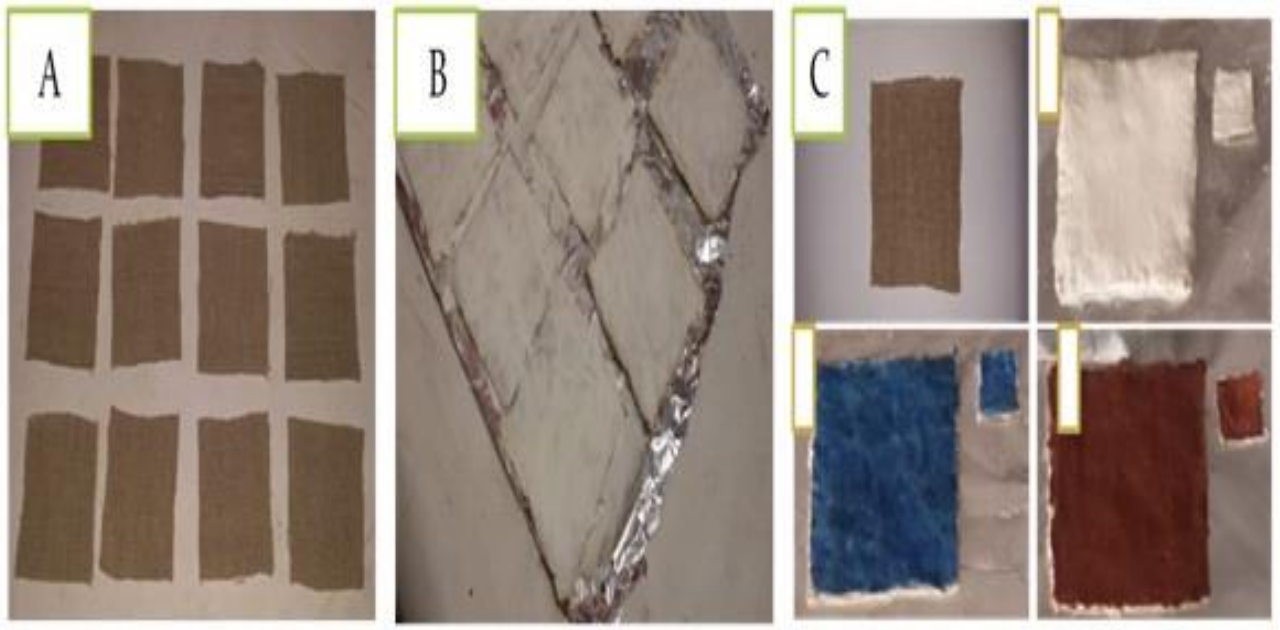

Figure 1. Preparation of the experimental samples. (A) the textile support, (B) the sample after application the ground layer (Calcium carbonate), and (C) after application the pigments (Egyptian blue and red ochre).

Accelerated aging

The samples were buried in a burial environment similar to Egyptian soil (sandy soil) then it subject to artificial ageing at a temperature of 80 °C and 65% RH for 264 hours (264 hours) according to the American specification the ageing was performed in CA See 0573 Large Environmental Chamber, National Institute of Standards NIS, Egypt. (Scott et al., 2009; Weatherhead and Buckley, 1988; AIC-BPG, 1989).

Polymers and nanoparticals

In the current study two polymers were used, Hydroxypropylcellulose (HPC) and Chitosan (1-4, 2-amino-2-deoxy-β-D-glucan) The polymers were supplied by Italian CTS Company.

Nanoparticles

TEM images (Fig.2) provided grain size of Nano-calcium hydroxide with particle diameter average < 50 nm between 12.09-24.25 nm, produced and characterized by Nanografi Nanotechnology company, Ankara, Turkey and the data sheet supplied by the company.

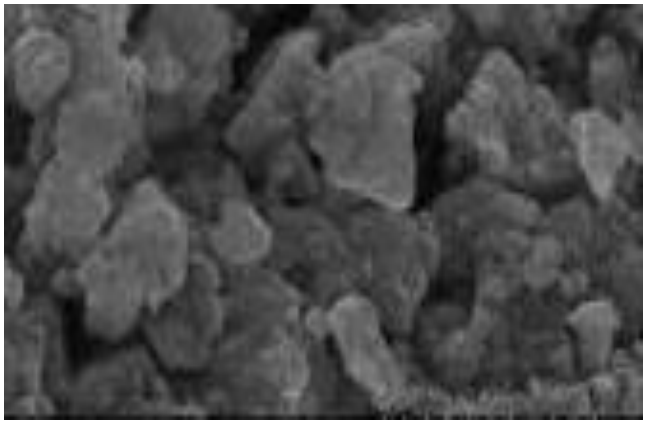

Figure 2. Calcium hydroxide nanoparticles used in the study using TEM.

2.2 PREPARATION OF THE NANO-COMPOSITES

The preparation includes:

A. amount of 98 ml of ethyl alcohol is added to (3g) of HPC to make concentration 3%, and 95 ml of ethyl alcohol added to (5g) of HPC to make concentration of 5% (5 g Klucel G) of ethyl alcohol by placing it on

an open flame with the thermal flask used with aluminum foil to prevent the volatilization of the alcohol and the heating is done at a temperature less than 40°C.

B. amount of 2 gm. dissolved in 1000ml of acetic acid used as a solvent of Chitosan, after preparing, 98 ml of it was add to 3g of Chitosan to make 3%, and 95 ml of it was add to 5g of Chitosan to make 5%, then the material was dissolved using an open flame with the use of the thermal flask used with aluminium paper to prevent the volatilization of the alcohol and the heating is done At a temperature less than 40 degrees Celsius with The obtained Nano-composites were prepared directly by blend-mixing of dissolved polymers 3%, 5% w/v, with nanoparticles 0.09, 0.25 g), To complete dissolution, the mixture was placed in an airtight bottle and placed in a wave machine for 5 days to ensure the completion of the of Suspend nanoparticles on the solution.

Visual assessment and photography

The authors performed visual assessment to determine the aspects of changes occurred in the samples before and after treatment. This method is very effective because the changes can easily identifiable.

Change of colour

The colour change meter device, Shenzhen Wave Optoelectronics Technology Co., Ltd. Co., Ltd with the model WR-10QC was used to determine the changes resulting the effect of consolidation process.

Digital microscope

The samples were investigated by using Dino Capture 2.0 optical portable digital microscope version 1.5.12 and were recorded with digital camera under 50-200X magnification to study their surface. LOM can provide information of the surface stains, the degree of transparency, and the material filling of the cracks.

Scanning Electron Microscope

The surfaces were imaged with a Quanta 200 scanning electron microscope manufactured by FIE and equipped with the (EDS) decoding system Model 6587, Mag 2400, 124.4 volts, acceleration of voltage of 25 kV, and the microscope was used in the effect consolidation material on the Cartonnage layers and its role in linking the granules.

ATR-FTIR

The samples were analysed using an ATR-FTIR device in the projects sector of the Ministry of Antiquities Model FT- IR- 4100 type A made by JASCO in order to identify the effect of consolidates on the binding media.

3. RESULTS AND DISCUSSION

3.1 VISUAL EXAMINATION

It was noted that the treated samples with Chitosan have had a dramatic colour change (clear yellowing) and this effect increase by increasing the concentration, while the samples treated with Klucel at concentrations of 3% and 5% recorded good results in terms of transparency compared to the control sample (aged one). Moreover, using Chitosan with addition of Nano-calcium hydroxide, it gave better results, but not the best at all. Klucel gave better results in terms of transparency and non-change of the surface appearance of the samples, which was improved by adding nanomaterial at a concentration of 5% and a concentration of 3%, as it is noted that they are the closest and best treated samples in terms of surface appearance. We can also observe that the visual color change of the experimental samples is depended on the pigment types.

Hence, the results of the visual examination can be discussed according to the type of pigment s as follows: 1) red pigment: red pigment recorded a slight change colour after treatment as compared to others pigments especially after the addition NPS. From Fig. 3 we can observe that Concentration of 3% of Klucel G with calcium hydroxide (NPS) gave the best results, followed by the Chitosan at a concentration of 5% then Klucel G at a concentration of 3% for red pigment, 2) Blue pigment: we can observe that the Klucel G at a concentration of 3% gave the best results followed by Chitosan at a concentration of 5%, then Klucel G 3% with NPS and finally Klucel at a concentration of 5%, 3) Ground layer (white): Klucel G + NPS at a concentration of 3% gave the best results, followed by the use of Klucel G at a concentration of 5% and Klucel G at a concentration of 3%.

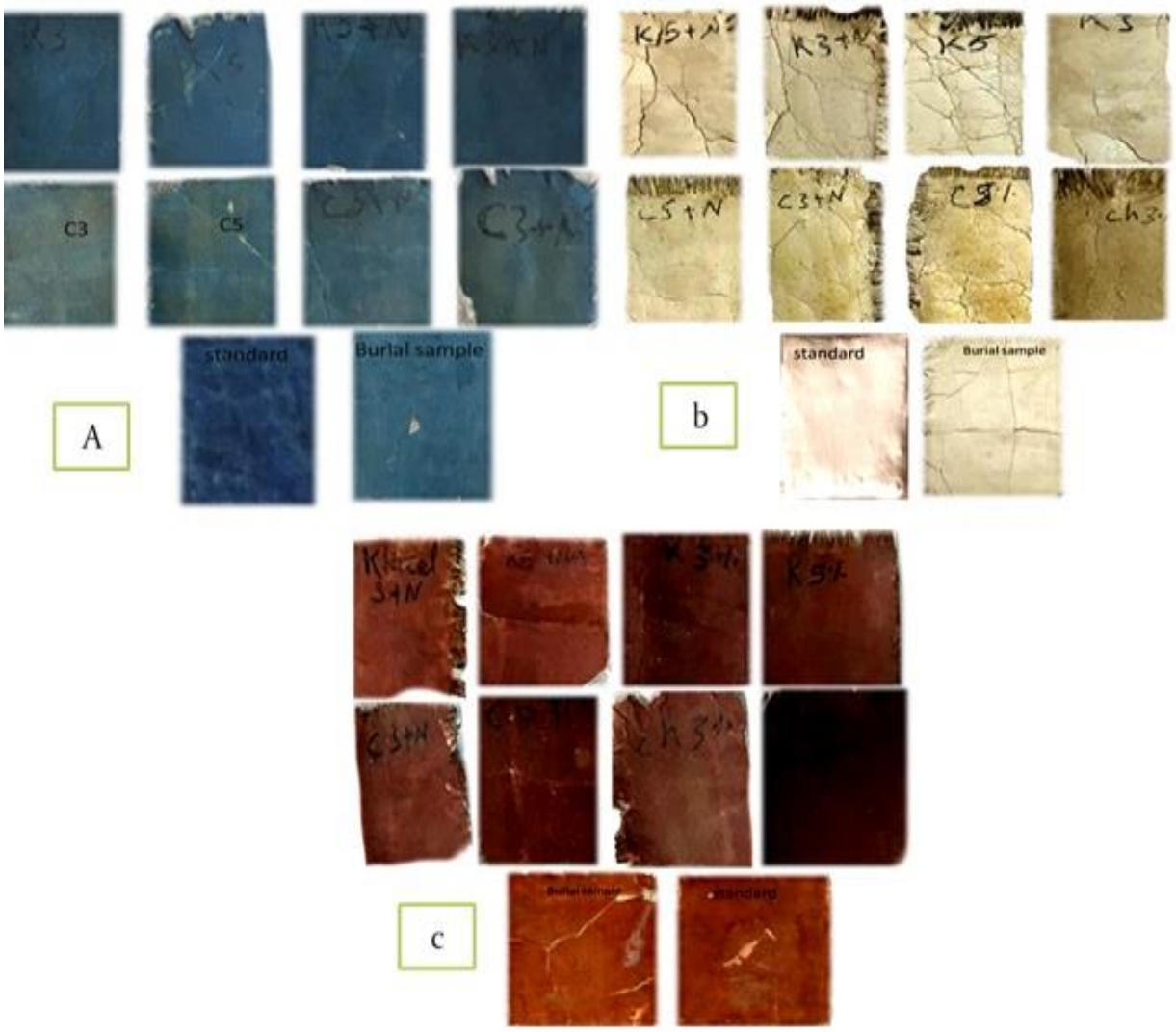

Figure 3. Visual examination of the blue (A), white (B), red (C) samples treated with Klucel and Chitosan compared to the extracted sample from the soil, showing the yellowing resulting from the use of Chitosan, whereas, the Klucel gave a transparent colour appearance.

3.2 The colour change of the treated samples.

Red ocher pigment sample

Table 1 shows the effect of the used consolidates in improving the optical properties of aged sample, where, Klucel G / Nano calcium hydroxide at a concentration of 3% recorded ΔE = 3.07 followed by Chitosan 5% (ΔE = 3.77), then by Chitosan at a concentration of 3% with values of (ΔE = 4.53), then Klucel 3% (E = 4.73), all acceptable ΔE values which ranges between 3.07 and 4.73 for treated samples. While the rest of the concentrations gave results of changing visible to the naked eye; such as Chitosan 3% + Nano which gave values of colour change (ΔE = 5.81), followed by Klucel 5% (ΔE = 14.30) and Chitosan 5% + Nano (ΔE = 14.62), which shows the effect of those poor concentrations and severe distortion of the optical properties of the sample. According to literature, the ΔE value must be < 5 (James et al.2001; Zou et al.1994). According to reported values the ΔE scale in color are as follows: 1) ΔE < 0.2: not perceptible difference, 2) 0.2 < ΔE < 0.5: very small difference, 3) 0.5 < ΔE < 2: small difference, 4) 2< ΔE < 3: fairly perceptible difference, 5) 3<ΔE < 6: perceptible difference, 6) 6< ΔE < 12: strong difference, 7) ΔE > 12: different colors (Sham, et al., 2004; Raghavan et al., 2008; Hassan 2019a, b).

Egyptian blue

The results of ΔE of Egyptian blue showed that Klucel 3% gave ΔE about 3.63 followed by the Chitosan at a concentration of 5% (ΔE E = 4.57), then Klucel 3%, + nanocalcium hydroxide with a value of (ΔE = 4.67) and Klucel 5% with a value of (ΔE = 4.92), while the rest of the concentrations for the same ma-

terials gave results caused an increase in the ΔE values such as 3% Chitosan + Nano (ΔE = 5.28), 5% Chitosan + Nano (ΔE = 5.42), 3% Chitosan (E = 6.37) and Klucel 5 + calcium hydroxide which gave values of total color change (ΔE). = 8.14).

Ground layer

While the results of the ΔE of ground layer (calcium carbonate) showed that the best treatment was Klucel / Nano calcium hydroxide with a total color change value (ΔE= 3.3), followed by the use of the pure Klucel G at a concentration of 5%, which gave colour change values (ΔE = 3.4), while the rest of the concentrations gave results ranging from satisfactory to bad, although they did not help in reducing the values of color change resulting from the soil, because Klucel at a concentration of 3% gave color change values (ΔE = 4.77). Klucel was followed by 5% calcium hydroxide nanomaterial with colour change values (ΔE = 5.48) see Table 1.

Table 1. The results of the colour change of the red (A), blue (B), and white calcite (C) consolidated samples compared to the sample extracted from the soil (aged samples).

A

Sample	L	A	B	L	A	B	ΔL	ΔA	ΔB	ΔE
	buried sample			Consolidation samples			Color changes			
k3 red	49.98	5.54	6.5	53.6	8.22	7.96	3.62	2.68	1.46	4.77
k5	49.98	5.54	6.5	59.3	14.04	13.25	9.32	8.5	6.75	3.40
k3+n	49.98	5.54	6.5	51.55	7.9	7.69	1.57	2.36	1.19	3.03
k5+n	49.98	5.54	6.5	55.42	11.33	10.92	5.44	5.79	4.42	5.48
ch3	49.98	5.54	6.5	53.5	7.19	8.83	3.52	1.65	2.33	13.24
ch5	49.98	5.54	6.5	47.17	3.56	4.95	-2.81	-1.98	-1.55	11.24
ch3+n	49.98	5.54	6.5	54.14	8.75	9	4.16	3.21	2.5	13.71
ch5+n	49.98	5.54	6.5	55.61	-7.07	1.7	5.63	-12.61	-4.8	7.04

B

Sample	L	A	B	L	A	B	ΔL	ΔA	ΔB	ΔE
	Buried samples			Consolidation samples			Color changes			
k3 Blue	56.07	-5.22	-3.38	56.09	-8.21	-5.45	0.02	-2.99	-2.07	3.63
k5	56.07	-5.22	-3.38	57.93	-8.03	-6.97	1.86	-2.81	-3.59	4.92
k3+n	56.07	-5.22	-3.38	54.08	-7.57	-6.9	-1.99	-2.35	-3.52	4.67
k5+n	56.07	-5.22	-3.38	58.75	-9.98	-9.42	2.68	-4.76	-6.04	8.14
ch3	56.07	-5.22	-3.38	59.86	-6.35	1.62	3.79	-1.13	5	6.37
ch5	56.07	-5.22	-3.38	55.69	-7.43	0.61	-0.38	-2.21	3.99	4.57
ch3+n	56.07	-5.22	-3.38	51.8	-5.44	-0.27	-4.27	-0.22	3.11	5.28
ch5+n	56.07	-5.22	-3.38	55.61	-7.07	1.7	-0.46	-1.85	5.08	5.42

C

Sample	L	A	B	L	A	B	ΔL	ΔA	ΔB	ΔE
	buried sample			Consolidation samples			Color changes			
k3 white	84.59	1.62	11.05	80.39	2.16	13.25	-4.2	0.54	2.2	4.77
k5	84.59	1.62	11.05	85.4	2.21	14.3	0.81	0.59	3.25	3.40
k3+n	84.59	1.62	11.05	84.1	2.01	14.02	-0.49	0.39	2.97	3.03
k5+n	84.59	1.62	11.05	79.84	2.47	13.65	-4.75	0.85	2.6	5.48
ch3	84.59	1.62	11.05	72.23	2.04	15.8	-12.36	0.42	4.75	14.04
ch5	84.59	1.62	11.05	80.01	2.4	21.29	-4.58	0.78	10.24	11.24
ch3+n	84.59	1.62	11.05	71.62	1.16	15.47	-12.97	-0.46	4.42	13.71
ch5+n	84.59	1.62	11.05	79.1	2.03	15.45	-5.49	0.41	4.4	7.04

3.3 THE OPTICAL AND MICROSCOPIC EXAMINATION BEFORE AND AFTER TREATMENT

Klucel G (3%, 5%) with nano calcium hydroxide

The optical microscope showed good effect of Klucel (3% and 5%) on the surface appearance of treated samples (Figs.4-7) no yellowing of the surface of the treated sample was observed as compared to the sample extracted from the soil. The red pigment layer showed a brightness on the surface of the consolidation sample compared to the sample extracted from the soil, and the image of the treated blue samples showed a slight glossiness compared to the aged control one, but the treatment did not help in filling the cracks. The image of the textile sample showed good result on the surface appearance of the sample, also it did not result in surface shine compared to the sample extracted from the soil. After adding nano calcium hydroxide; the examination revealed that the

surface became shinier, especially the linen sample furthermore the cracks have disappeared.

From SEM photomicrographs (see Figs 8-11), it is clear that the untreated samples are completely separated from each other, whereas in case of polymer treated samples, full pores can be noticed which may be due to the formation of the hydrogen ponds between pigments structure and polymer matrix. Also, some aggregates of the polymer can be noticed on treated samples which is a good evidence for the success of the polymer treatment process. Furthermore, SEM images, reported in Figs 5 &7, clearly indicate that the nanocomposite treatment is homogenously distributed over the samples surfaces. The adhesion of small clusters of nano calcium hydroxideto cellulose fibers in linen textile is clearly seen.

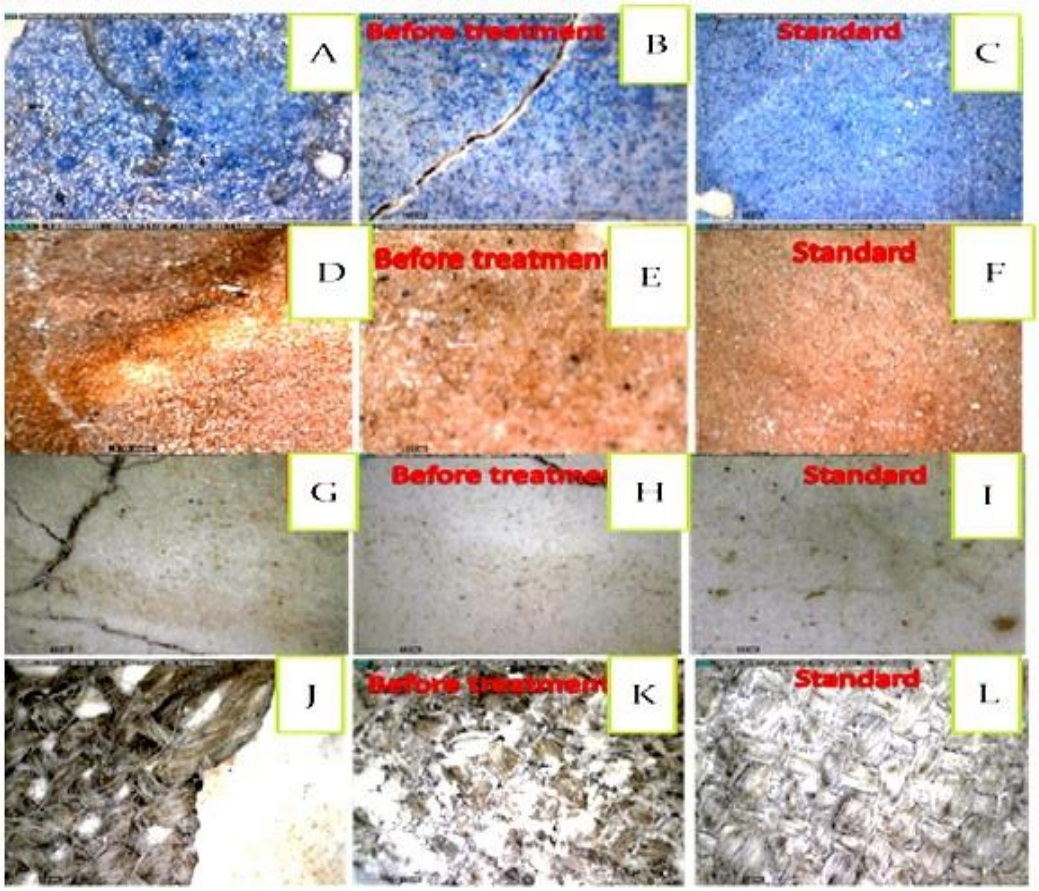

Figure 4. Optical microscopy images of samples before and after cosolidation process using klucel G 3% , A-C blue pigment, D—F red pigment, G-I ground layer and J-L textile layer. Dramatic shine was observed in the treated samples.

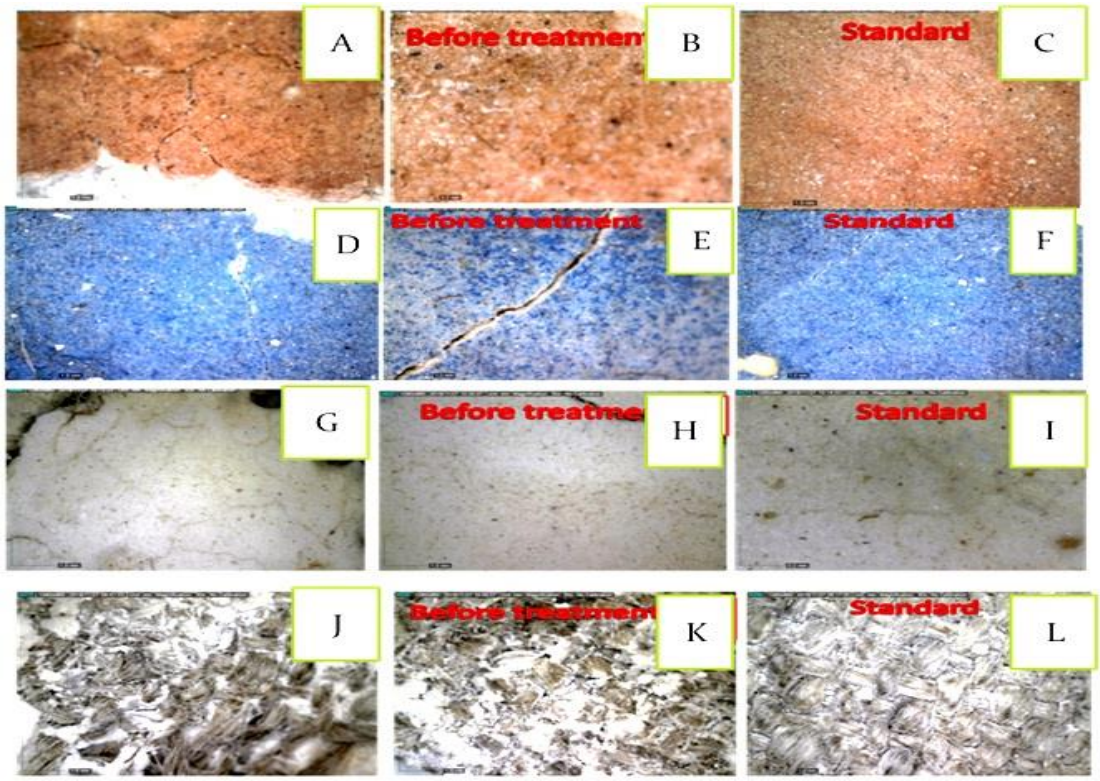

Figure 5. Optical microgrphs of samples (red ,blue, ground layer and textilesupport before and after cosolidation process using klucel G 3%+ nano calcium hudroxide.

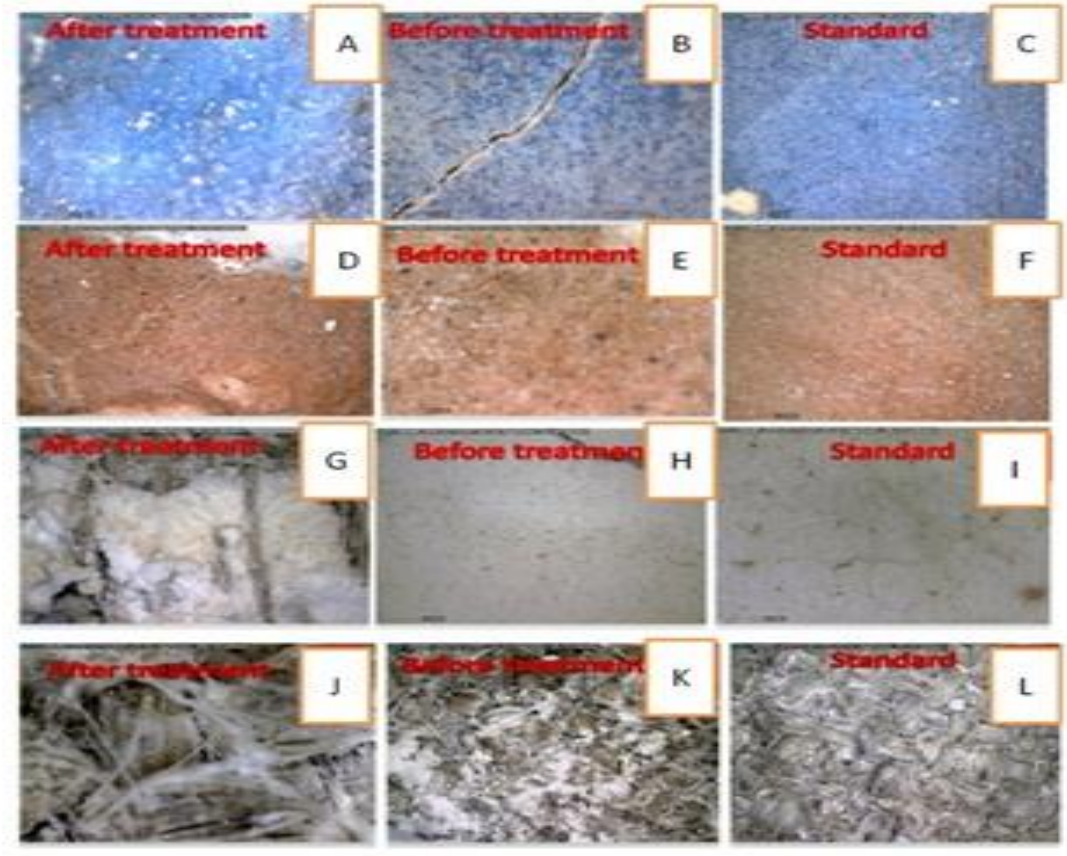

Figure 6. optical microscopy micrographes of samples before and after cosolidation process using Klucel g 5%.

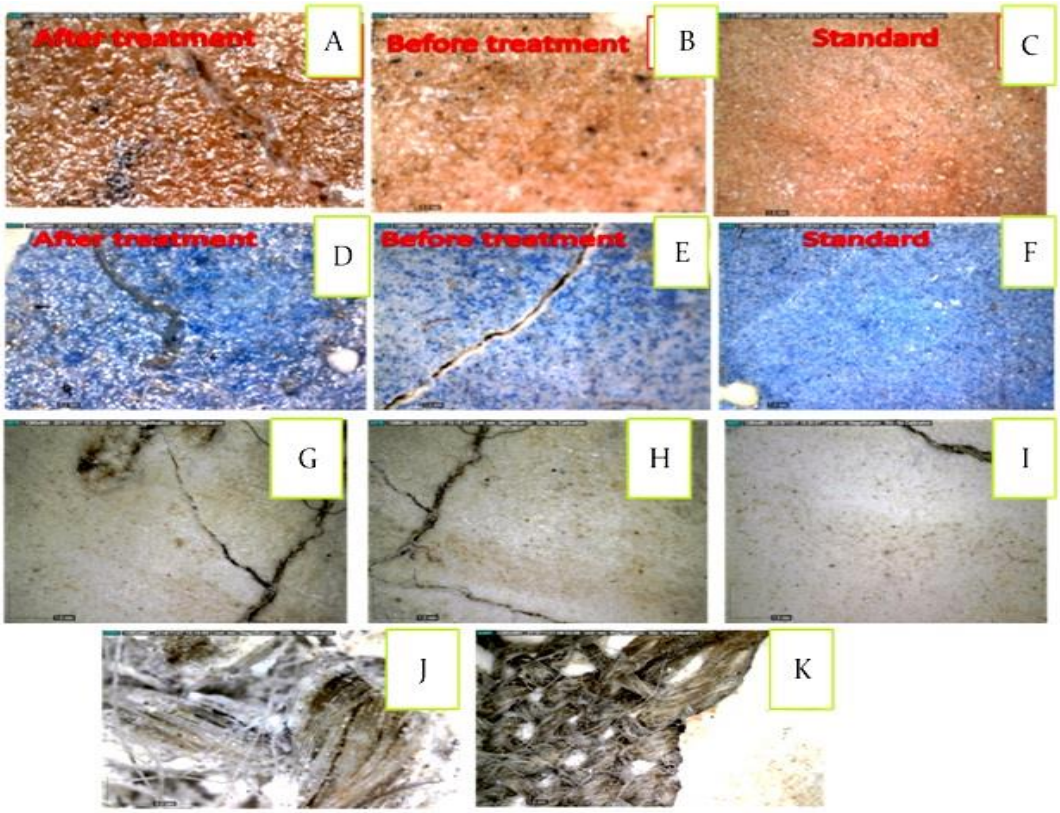

Figure 7. Optical microscopy micrographes of samples before and after cosolidation process using klucel g 5%/ nano calcium hydroxide,the reult showed that it gave better results in reducing the gloss resulting from the consolidation material and also helped in fillingthhe cracks.

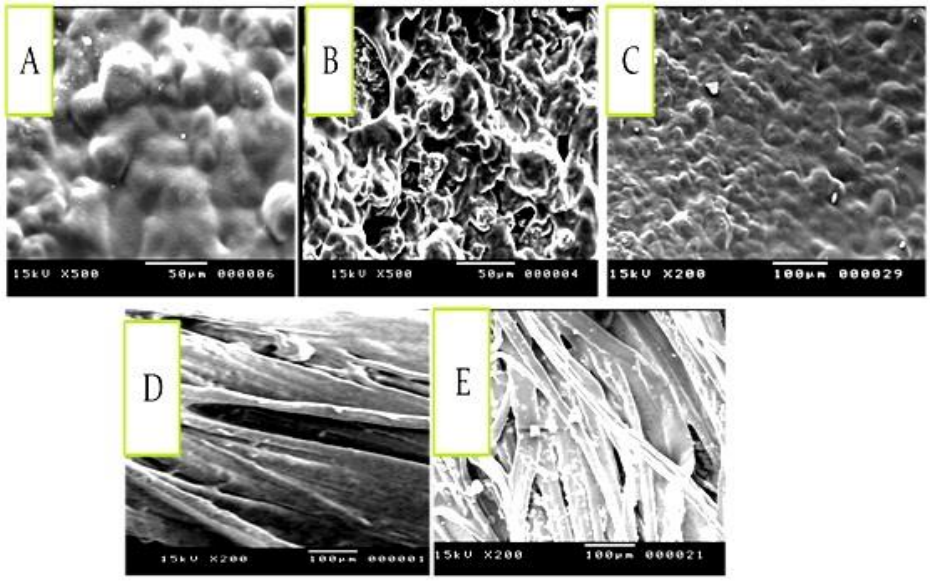

Figure 8. SEM photomicrographs of samples before and after cosolidation process using klucel G 3%, (A) control, (B) blue pigment, (C) red pigment, (D) ground layer, and (E) textile layer. The results verify a homogeneous between consiobate and sturcture of Cartonnage.

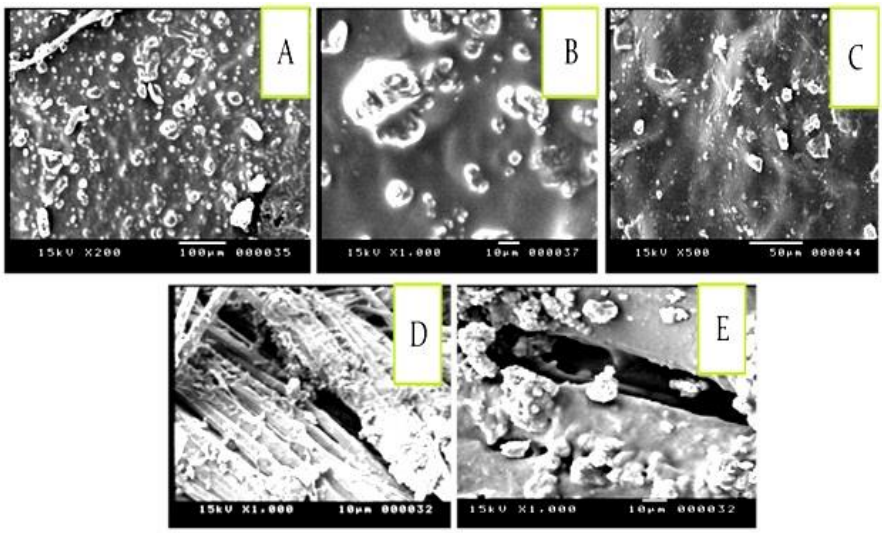

Figure 9. SEM photomicrographsof samples before and after cosolidation process using klucel 3%/ nano calcium hydroxide, (A) control, (B) blue pigment, (C) red pigment, (D) ground layer, and (E) textile layer. It proves the good diffusion of the nanomaterial and its formation of a cohesive layer with the consolidation material.

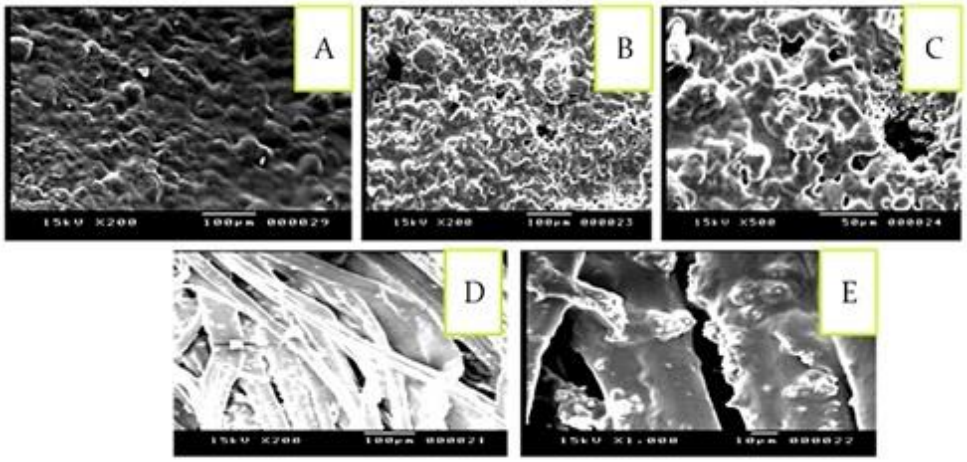

Figure 10. SEM photomicrographsof samples before and after cosolidation process using klucel G 5%, (A) control, (B) blue pigment, (C) red pigment, (D) ground layer, and (E) textile layer. The results verified the fine spread of the consolidation material and its penetration and homogeneity to obtain a homogeneous and orderly distributed layer

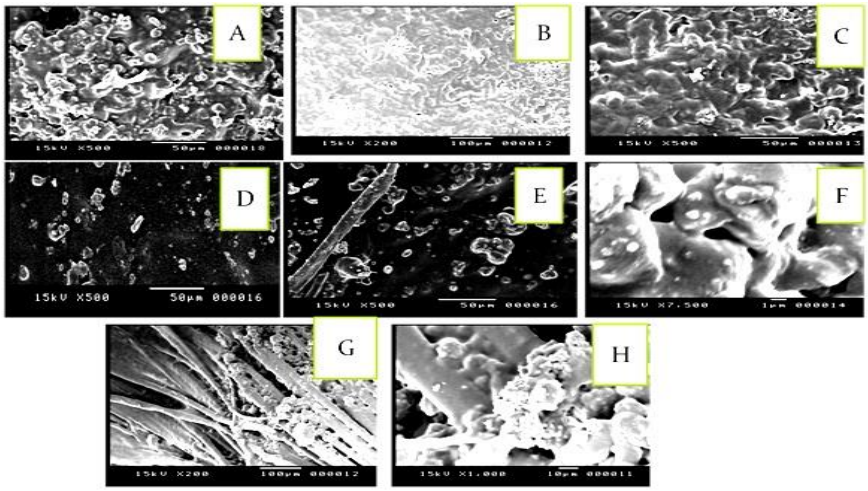

Figure 11. SEM photomicrographs of samples before and after cosolidation process using klucel G 5%/ nano calcium hydroxide,(A) control, (B) blue pigment, (C) red pigment (D), ground layer, and (E) & (H) textile layer. The data justify the good result of the consolidation spread. However, it is noticed that some lumps appear with nano material.

Chitosan 3%, 5% and 3,5% with Nano calcium hydroxide

Figs 12- 15 confirmed that Chitosan 3% and 5% caused yellowing on the surface of treated samples therefore, with the addition of Nano calcium hydroxide, the yellowing significantly decreased furthermore, some stains on the surface was observed as compared to the sample extracted from the soil (aged sample). We noticed the difference in the degree of yellowing according to the nature of the pigments, as chitosan recorded the lowest yellowing value with the red pigment. Furthermore, we can observed that in spite of the reduced yellowing, the samples treated with nano-calcium hydroxide were covered with a white semi-transparent layer on the surface, which gave a slight change in the brightness of the samples.

By examining by SEM (Figs.16-19) we note an irregular surface in some region of the textile layer. Furthermore, the preparation layer have shown the poor distribution and irregularity of the material, where some granules appeared with wide intermediate distances, while not performing their role in binding, as micrographs reveal the deep cracks occurred in all samples.

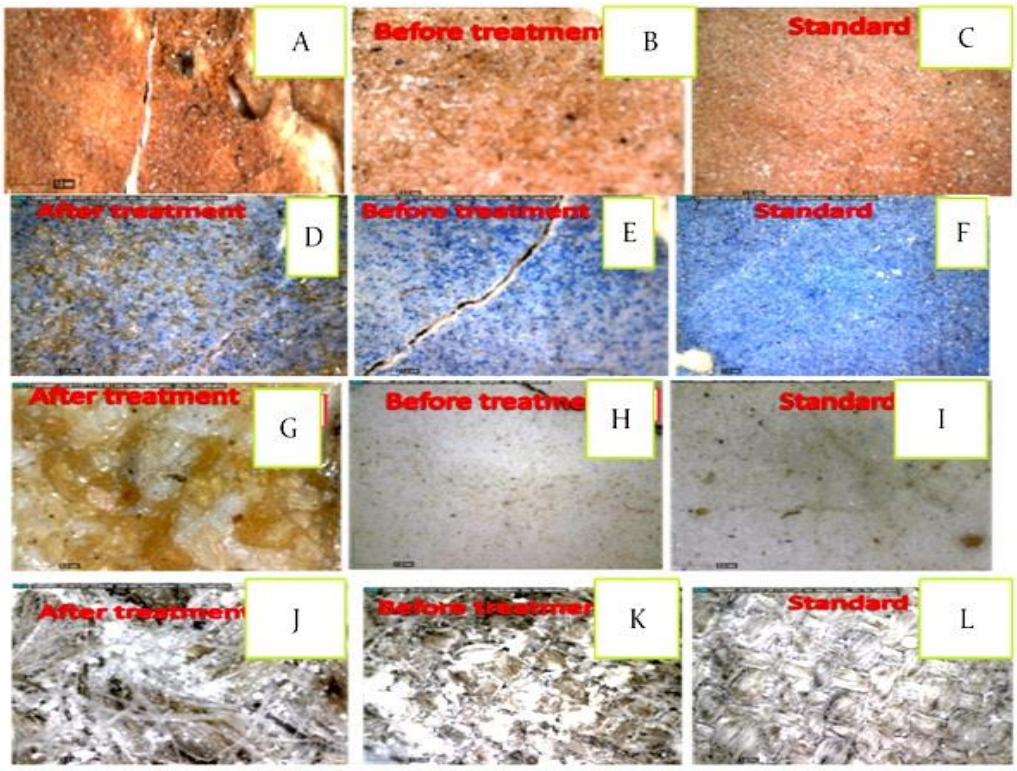

Figure 12. Optical microscopy photo of samples before and after cosolidation process using chitosan 3%. The results have shown that it caused severe yellowing with its deposition on the surface, and severe surface stains on the surface.

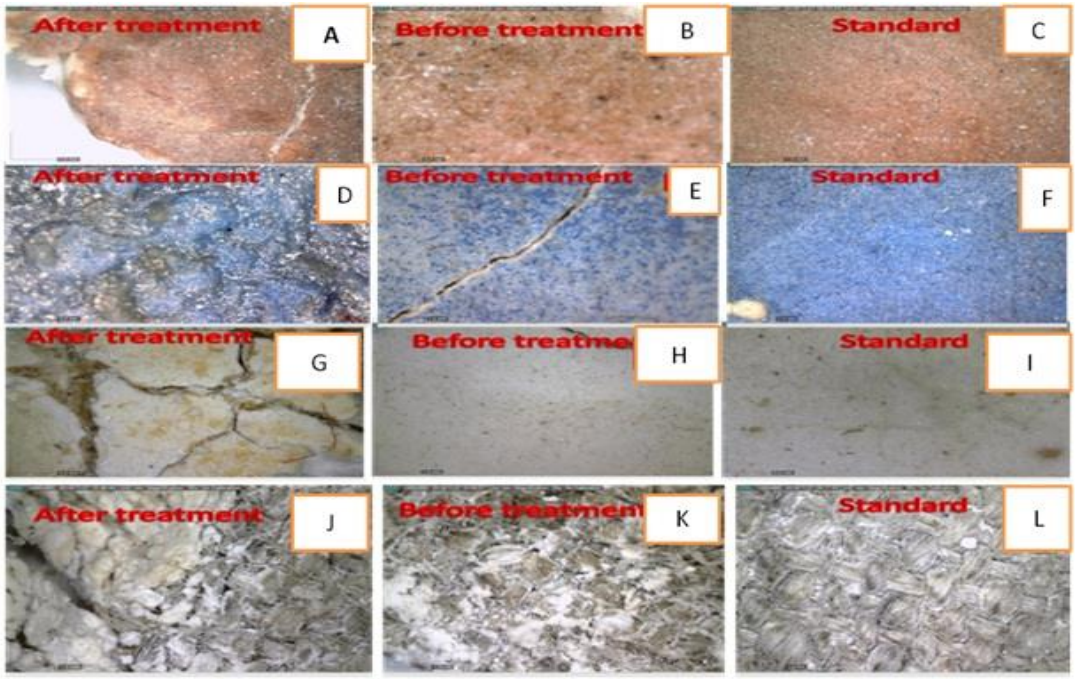

Figure 13. Optical micrographs of samples before and after cosolidation process using chitosan 3%/ nano calcium hydroxide. The results have shown that it caused severe yellowing, brightness and surface stains.

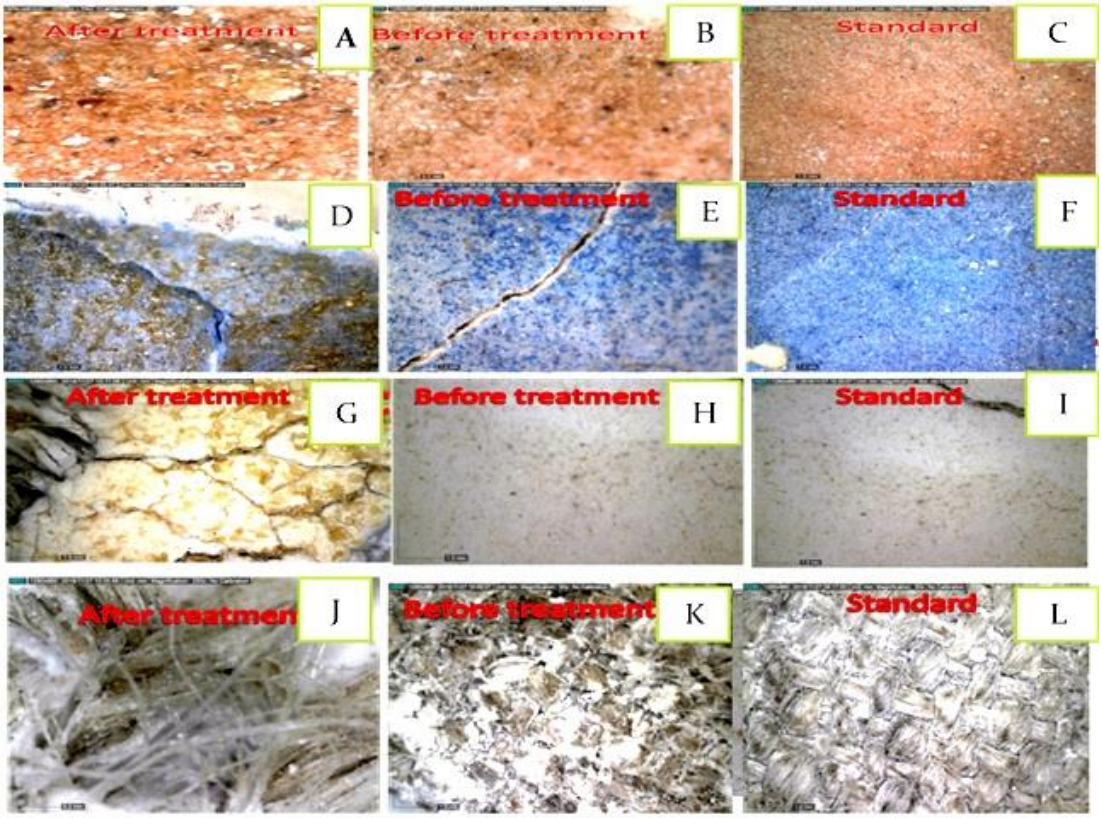

Figure 14. Optical microscopy photo of samples before and after cosolidation process using chitosan5%. The result revealed that it caused severe yellowing, brightness and surface stains.

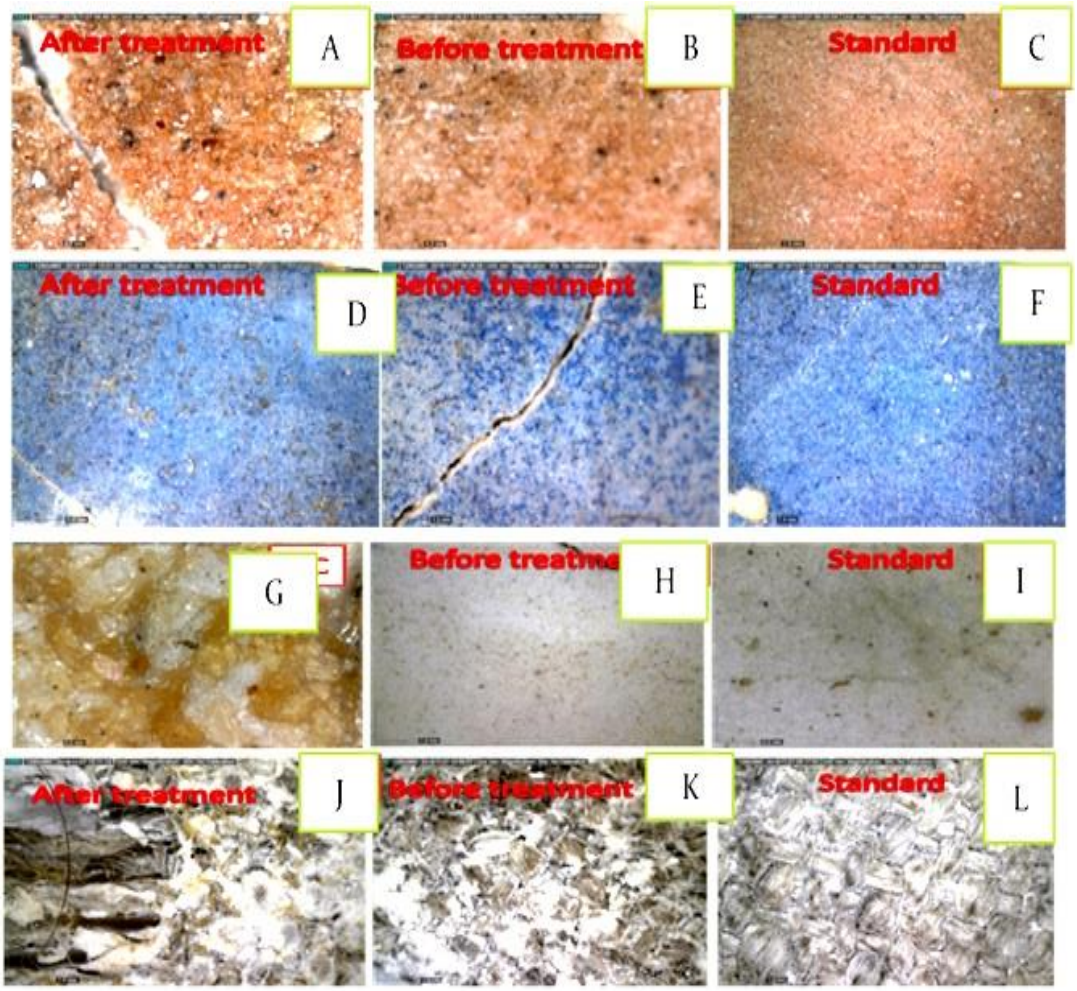

Figure 15. Optical micrographes of samples before and after cosolidation process using chitosan/ nano calcium hydroxide, the results have shown that it caused severe yellowing, brightness and surface stains.

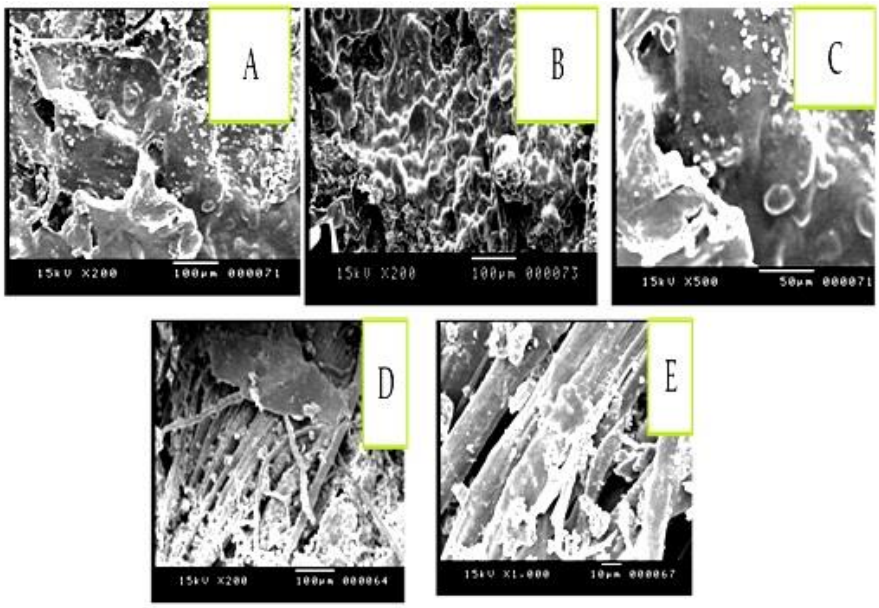

Figure 16. Scanning microscopy photo of samples before and after cosolidation process using chitosan 3%.(A) control , (B) blue pigment, (C) red pigment, (D) ground layer, and (E) textile layer. It gave an irregular surface, which indicates its bad effect on strengthening the material under study.

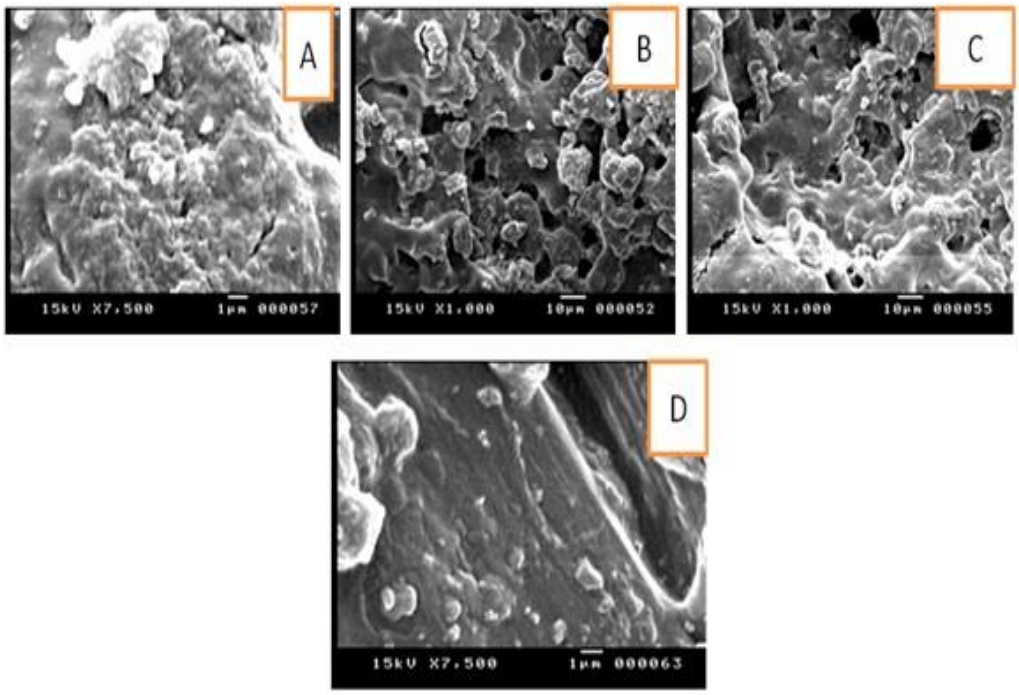

Figure 17. Micrographs of samples before and after cosolidation process using chitosan3%/ nano calcium hydroxide, (A) blue pigment, (B) red pigment, (C) ground layerand, (D) textile .

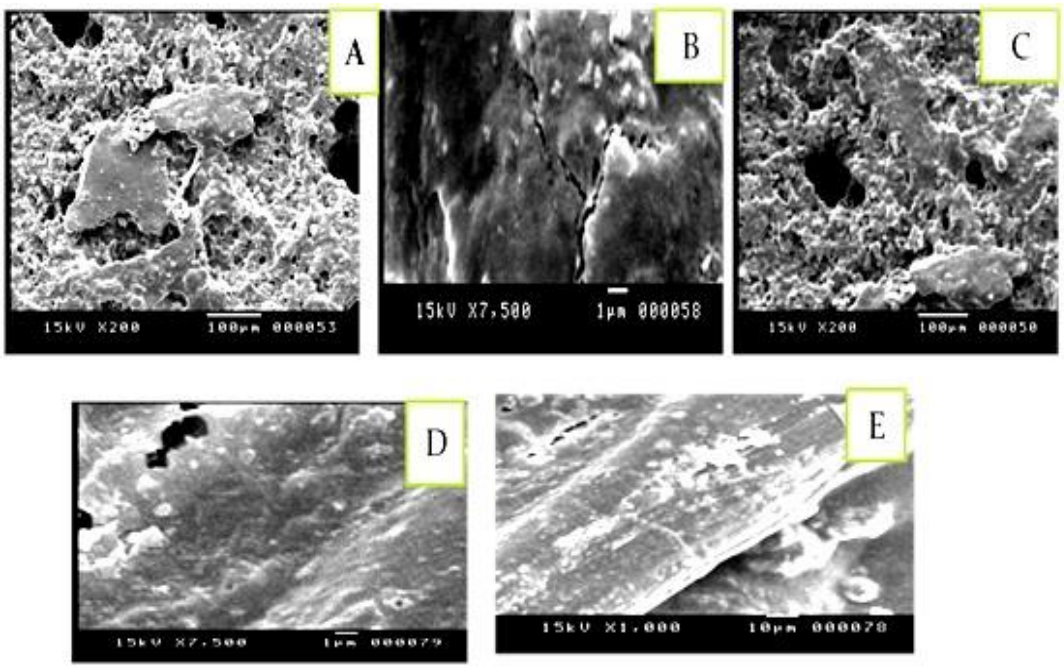

Figure 18. Scanning microscopy photo of samples before and after cosolidation process using Chitosan5%, (A) control , (B) blue pigment, (C) red pigment, (D) ground layer and (E) textile layer. The examination revealed the formation of an irregular layer with many cracks.

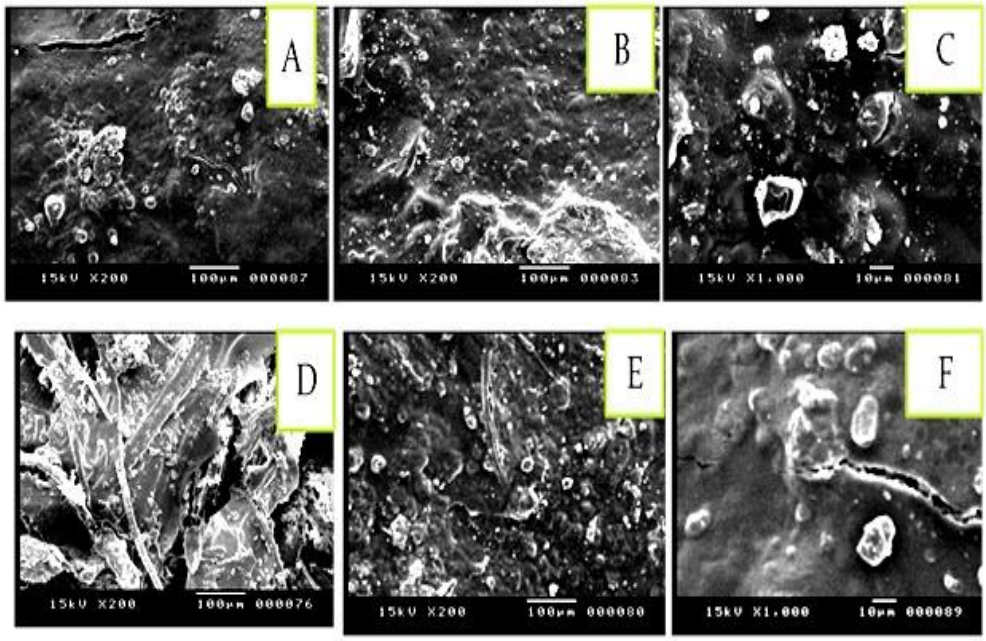

Figure 19. Scanning microscopy photo of samples before and after cosolidation process using chitosan 5% / nano calcium hydroxide, (A) control, (B) blue pigment, (C) red pigment, (D) ground layer and (E, F) textile layer. The examination revealed the formation of an irregular layer with many cracks.

3.4 FTIR

KLUCEL G

The results (Figs. 20-22) show the success of *Klucel* G and Klucel G with calcium hydroxide (NP) in preserving the properties of the binding media (Arabic gum) without changing them. After treatment with Klucel G 5% and 3%, a dramatic increase in bands around 1416 and 1320 cm^{-1} are assigned to -CH2 scissoring and -OH bending vibration, respectively. The band at 1043 cm^{-1} is due to OCH-O-CH 2 stretching (Hassan, 2021), and GA 3321 cm^{-1} O-H stretching, characteristic of glucosidic ring, 1605cm^{-1} COO-symmetric stretching, 1437 cm^{-1} COO-asymmetric stretching, 1200-900 cm^{-1} fingerprint of carbohydrates. Also, the short peaks around 2900 cm^{-1} are due C-H stretching of aliphatic group. Furthermore, the carbonyl groups that may be formed because of further oxidation of C-OH groups of carbohydrates decrease.

CHITOSAN

FTIR spectra show sharp peaks at 564 cm^{-1} (out-of-plane bending NH, out-of-plane bending C–O), 711 cm^{-1} (out-of-plane bending NH), 1174 cm^{-1} (C–O–C stretching), 2865 cm^{-1} (CH2 stretching), and 3594 cm^{-1} which attributed to chitosan components. Furthermore, hydroxyl groups are centered at about 3400 cm^{-1} which can be assigned to the stretching vibrations of bonded acid OH groups and the decreasing of the intensity and broadening of the carbonyl peak (1733cm^{-1}) on both sides resulting from the generation of ketone and acid groups. In addition we observe the disappearance of the band at 1080cm^{-1} corresponding to C-O vibration with growing of a small absorption at ca. 1547cm^{-1}. These changes may result from bond scission of main-chain and elimination of side groups. The results proved that concentration 3% of Klucel G and Chitosan gave the best results as compared to the standard sample and these results dramatic increase by adding Nano calcium hydroxide.

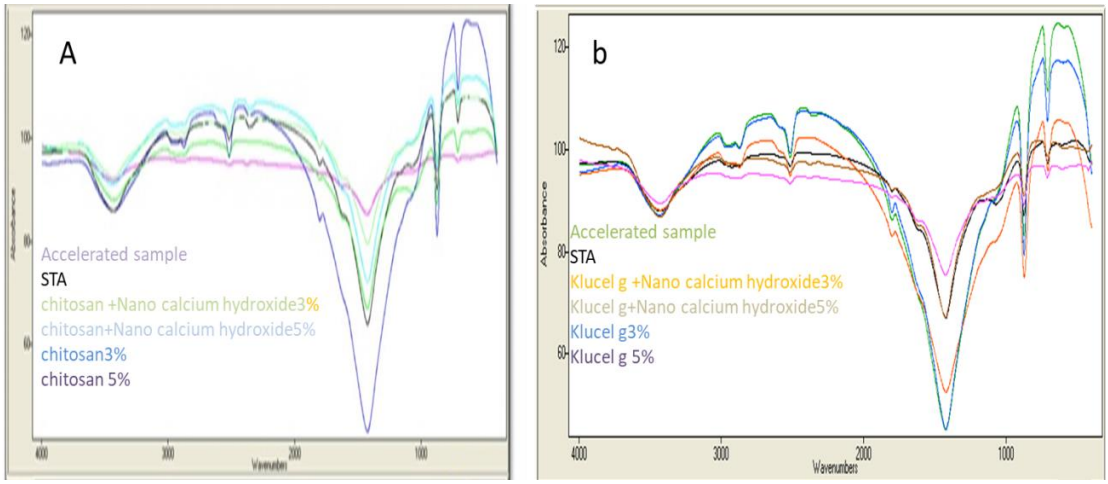

Figure 20. FTIR results of the consolidated blue samples comparing to the sample extracted from the soil.

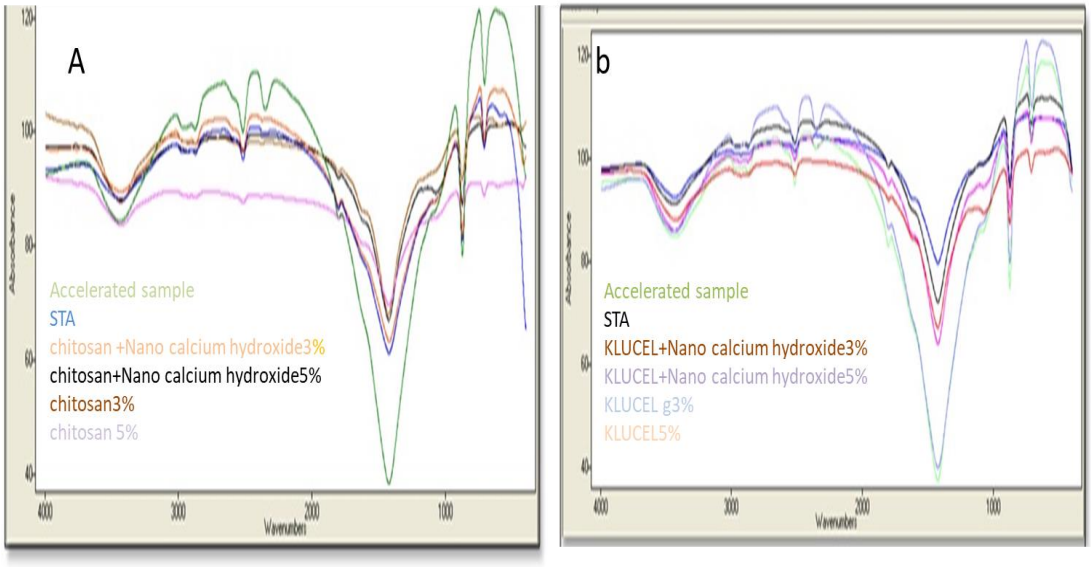

Figure 21. FTIR results of the consolidated red samples (A) chitosan, and (B) Klucel G compared to the sample extracted from the soil.

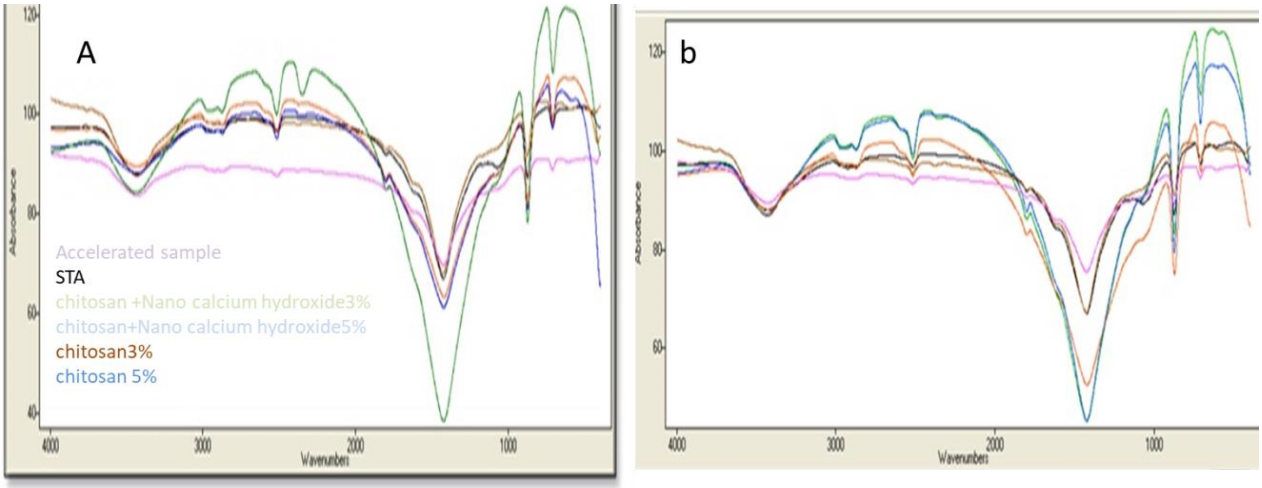

Figure 22. FTIR results of the consolidated white samples (A) compared to the sample extracted from the soil (B).

3. DISCUSSION

When photographing the surfaces of the treated samples using the optical microscope, the photos showed the effect of the previous materials on the surface appearance of the samples, Klucel G with the addition of nanomaterial at a concentration of 3% gave the best results when photographing all the experimental samples and did not cause yellowing or brightness of the surface, followed by the use of the same concentration of Klucel without the presence. The nanomaterial did not cause yellowing of the surface, followed by Klucel at a concentration of 5%, and Klucel at a concentration of 5%, and the addition of Nano-calcium hydroxide, which gave acceptable results but caused the surface to shine. Also, the results of examining the materials treated with the selected using a scanning electronic microscope proved that Chitosan was not given in its different concentrations good results, it's appeared in the form of clusters with higher concentrations, as well as cracking appears in many samples, while the Klucel material with all its concentrations gave very good results in terms of distribution and giving a surface. The level and non-cracking of all samples, in addition to the above, the results of the study of the physical properties of the samples treated with Chitosan showed that they did not achieve good results compared to Klucel, which gave better results when adding to the nanomaterial. From this standpoint, Klucel has proven its success in preserving the surface appearance of the samples, as it gave very good results in terms of the degree of transparency and also gave good results when measuring the amount of the resulting color change, which is the most important characteristic of any strengthening material used to strengthen the colored materials. The microscopic examination also proved well its success in encapsulating the color granules, but it is noticed that some flashing occurs when photographing samples with a higher concentration, which did not happen in samples with a lower concentration, which gave very good results in all tests. Especially when adding nanocalcium hydroxide at a concentration of 3%, this gave both a good degree of encapsulation for the color grains and also a good encapsulation of the tissue wafers. Without the occurrence of Nano composition in one of the regions, which filters it, it is the best concentrations for use in cases similar to the materials used in the present study.

4. CONCLUSION

The experimental study for consolidation of archaeological cartonnage using Klucel G and chitosan, with nano-calcium hydroxide have shown that the buried object suffered from severe deterioration phenomena, including dust, stains, cracks, macro-cracks, ruptures, missing parts in the painting and the ground layers, as well as fragility, brittleness and incorrect treatments. These are attributed to main three deterioration factors and related mechanisms: the first one is fluctuations in temperature and humidity due to the lack of environmental systems control; the second factor is dust from the burial soil; the third factor is attributed to the structure of Cartonnage (composite material). This composite structure usually leads to variation in the ratio of extension and shrinkage of all mentioned components. Furthermore, these variants exhibited cracks, macro-cracks, cleavage, flaking, separation of layer and the missing parts in both the paint and ground layers.

The archaeological cartonnage samples were treated with pure polymers and Nano- particles/polymer. The methodology has proved that the addition of nanoparticles to the acrylic-based polymers improved the ability of polymers to consolidate and protect the samples that were tested under artificial aging. The experimental section asserted that Klucel G with Nano calcium hydroxide is more suitable than Chitosan in the conservation of our samples. The Chitosan was not acceptable when applied in all concentrations used in the study, it gave bad results when applied to all pigments, which worsened by increasing the concentration, and decreased by the addition of nanoparticles, but it did not give the required results compared to Klucel. It appears in the form of clumps on the surface and gave unorganized surfaces containing many cracks when examined using SEM. To the contrary the Klucel G achieved good results in causing unnoticeable color changes, which were improved by adding nanomaterial, especially at a concentration of 3%, and did not cause clumps. The concentration also helped to give good strength and bonding, and by adding nanomaterial, the cohesion between the color layer and the layer was restored, giving also good results when evaluated using SEM.

The methodological investigation has been satisfactory, but the monitoring is essential to secure if other changes occur to the rest of the archaeological materials and the strengthening materials used to treat them, because any treatment needs to be further verified to offer a possible basis for future research in this area.

REFERENCES

Ali, M. F, El Sheikha, A.M, Ali, A.F (2016) Analytical study and conservation of gilded mummy form cartonnage from the Greco-Roman period in Cairo museum. *Mediterranean Archaeology and Archaeometry,* Vol. 16, No 2, pp. 127-137. DOI: 10.5281/zenodo.53070.

Afifi, H. A.M. (2011a) Analytical investigation of pigments, ground layers and media of Cartonnage fragments from Greek-Roman period. *Mediterranean Archaeology and Archaeometry*, Vol. 11, No. 2, pp. 91-98.

Afifi, H.A.M. (2011b) Comparative efficacy of some plant extracts against fungal deterioration of stucco ornaments in the Mihrab of Mostafa Pasha Ribate, Cairo, Egypt. *American Journal of Biochemistry and Molecular Biology*, Vol.2, No 1, 40-47.

Afifi, H.A.M., Abd El-Kader, S., Hamed, M., Mohamedy, S. & Dawod, M. (2019) A dating approach of a refundable wooden Egyptian coffin lid, *Scientific Culture*, Vol.5, No. 1. pp. 15-22.

Afifi, H.A.M., Afifi, M.A., Etman, H., Abdrabbo, A.M. & Kamal, H.M. (2020a) Typological Study and Non-Destructive Analytical Approaches Used for Dating a Polychrome Gilded Wooden Statuette at The Grand Egyptian Museum. *Scientific Culture*, Vol. 6, No. 3, pp. 69-83.

Afifi, H.A.M., Galal, H.S., Hassan R.R.A. (2020b) Characterization of pharaonic cartonnage from a late period, Saqqara excavations. *Pigment & Resin Technology*, Vol. 49, No. 4, pp. 255-264.

Afifi, H.A.M., Hassan R.R.A., Abd-EL-Fattah M.A. & Menofy S.M. (2020c) Spectroscopic characterization of preparation, pigment and binding media of archaeological Cartonnage from Lisht, Egypt. *Scientific Culture*, Vol. 6, No 1, pp. 9-23.

Ahmed, H. (2015) Restoration of Historical artifacts and made available for exhibition in museums. *Journal of Life Science. Vol.* 12, No 5, pp. 183-192.

AIC-BPG (American Institute for Conservation of Historic and Artistic Works) (1989) *Adhesives, paper conservation catalogue, book and paper group*, 6th edit, AIC: Washington DC.

Ali, M.F., Mansour, M., Badr, N.M.& Salem, M.Z.M. (2017) Study of biodeterioration and Chromatic alterations of painted and gilded mummy Cartonnage at the Saqqara Museum storeroom, Egypt, *Archaeometry*, Vol.60, No 4, pp. 854-858.

Bader, N and Al-Gharib (2013) Assessment of deterioration and conservation of a polychrome wooden coffin, from Al-Arish Museum, Egypt. *International Journal of Conservation Science,* Vol.4 No 4, pp. 397-412

Chemello C. & Davis S. (2014) Dry/Desert conditions: Preservation and conservation. In: Smith C. (eds) *Encyclopedia of Global Archaeology*. Springer, New York. https://doi.org/10.1007/978-1-4419-0465-2_493.

Christensen, M., Kutzke, H & Hansen, F.K. (2015) New materials used for the consolidation of archaeological wood–past attempts, present struggles, and future requirements, *Journal of Cultural Heritage,* Vol.13, No 3, pp. 183–190.

Eloriby, R., Dawi1, S & Mustafa, M. (2019) Consolidation and protection of glass artifacts using Nano composites. *Applied Sciences.* Vol. 4, No 18, pp. 222-239.

Essayed, Y. (2019) Conservation of The Flowers Canvas Painting (1) at The Egyptian Agricultural Museum. *Journal of Archaeological and Restoration Studies*, Vol.9, No 1, pp.39-51. DOI: 10.21608/ejars.2019.38436.

Hamed, S. and Hassan, M.L. (2019) A new mixture of hydroxypropyl cellulose and nanocellulose for wood consolidation. *Journal of Cultural Heritage*. Vol. 35, pp.140-144.

Hamilton, D.L (1998) *Methods of Conserving Underwater Archaeological Material Culture.* Conservation Files: ANTH 605, Conservation of Cultural Resources I. Nautical Archaeology Program, Texas A&M University, World Wide Web, http:// nautarch.tamu.edu / class/ANTH605.

Hassan, R.R.A. (2019a) The restoration of two historic leather bindings according to a new strategy. *Journal of the Institute of Conservation,* Vol.42, No 3, pp. 210-225. DOI: 10.1080/19455224.2019.1654532.

Hassan, R.R.A. (2019b) Fourier transform infrared spectroscopy to detect thermal degradation of vegetable and chrome-tanned leather. *Spectroscopy Letters,* Vol .52, No 5, pp.288-296. DOI: 10.1080/00387010.2019.1623262

Hassan, R.R.A. (2020) Using polaroid zinc oxide nanocomposites in strengthening a historical printed paper: application to "Annales Agricoles" – 1829AD. *Pigment & Resin Technology,* Vol. 49, No.5, pp.369-375. https://doi.org/10.1108/PRT-02-2020-0012.

Hassan.R.R.A. (2021) Sodium dodecyl sulfate micro-emulsion as a smart cleaning agent for archeological manuscripts: surface investigations. *The European Physical Journal Plus*, Vol. 136, 37. https://doi.org/10.1140/epjp/s13360-020-00973-w

Feller, F.L and Wilt, M. (1993) *Evaluation of cellulose ethers for conservation,* The Getty conservation institute. United States of America. Second printing.

James, A. R., Priya, S., Uchino, K., & Srinivas, K. (2001). Dielectric spectroscopy of Pb(Mg1/3Nb2/3)O3-PbTiO3 single crystals. *Journal of Applied Physics*, 90, pp. 3504-3508. https://doi.org/10.1063/1.1401802.

Johnson, J.S. (2018) Consolidation of archaeological bone: A conservation perspective, *Journal of Field Archaeology*, Vol. 21, No 2, pp. 221-231. https://doi.org/10.1179/009346994791547661.

Katsaros, T., Liritzis, L., Laskaris, N. (2010) Identification of Theophrastus' pigments Egyptian Kyanos and psimythion from an archaeological excavation: A case study, *ArchéoSciences (Revue d'Archéométrie),* Vol.34, pp. 69-79.

Mahmoud, M.H.H. (2010) Preliminary Investigation of Ancient Pigments from The Mortuary Temple of Seti I, El- Qurna (Luxor, Egypt). *Mediterranean Archaeology and Archaeometry*, Vol. 11, No. 1, pp. 99-106.

Mostafa, A.M., Abd El Kader, S.M., Afifi, H.M. and Mohamady, S. (2019). A Comparative study on the colour change of pigments due to the consolidation of conventional spectroscopic techniques and laser-induced breakdown spectroscopy. *Applied Physics A: Materials Science and Processing,* Vol. 125, No 8, pp. 312-3120.

Nord, A., Tronner, K. &Mattsson, E. (2005) Environmental threats to buried archaeological remains, *AMBIO,* Vol.34, No 3, pp. 256-62.

Salem, R., Owais, A. and Salama, R. (2016) The conservation of an Egyptian polychrome wood coffin from late period. *Egyptian Journal of Archaeological and Restoration Studies,* 6, pp. 23-37. 10.21608/ejars.2016.6845.

Scott, D.A., Warmlander, S., Mazurek, J. and Quirke, S. (2009) Examination of some pigments, grounds and media from Egyptian Cartonnage fragments in the Petrie Museum, University College London. *Journal of Archaeological Science,* Vol.36, pp.923–932.

Sierra-Fernandez, A., Gomez-Villalba, L., Rabanal, M. & Fort, R. (2017) New nanomaterials for applications in conservation and restoration of stony materials: A review. *Materiales de Construcción*. 67, 107. 10.3989/mc.2017.07616.

Weatherhead, F., and Buckley, A. (1988) *Artist's pigments from Amarna, Reports V,* Egypt Exploration Society, London, pp.202- 240.

Zhang, P., Wan, J., Wang, K. & Li, Q. (2017). Influence of nano-SiO_2 on properties of fresh and hardened high performance concrete: A state-of-the-art review. *Construction and Building Materials*, 148, pp. 648-658. 10.1016/j.conbuildmat.2017.05.059.

Zou, X. N. Gurnagul, T. Uesaka, J. Bouchard, (1994) Accelerated aging of papers of purecellulose: mechanism of cellulose degradation and paper embrittlement. *Polymer Degradation and Stability,* Vol. 43, No 3, pp. 393-402.