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EFFECT OF THE MORPHOLOGY OF NANO-MAGNETIC MATERIALS IN CONSOLIDATION OF EGYPTIAN COPTIC FRESCO PAINTING

Kholod K. Salama*[1], Mona F. Ali [2], Said M. El-Sheikh[3]

[1]National museum of Egyptian civilization, Cairo, Egypt
[2]Conservation Department, Faculty of Archaeology, Cairo University
[3]Nano- Structured Materials and Nanotechnology Division, Advanced Materials Department
Central Metallurgical Research & Development (CMRDI), 1142, 1Cairo, Egypt

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**Corresponding author: Kholod K. Salama (kholodkhairy@yahoo.com*

ABSTRACT

The magnetic nano particles (MNP's) presented in cobalt ferrite $CoFe_2O_3$ and magnetic nano wires (MNW's) presented in spinel nickel zinc ferrite magnetic nanowires $NiZnFe_2O_3$ are popularly used in medicine field and in electronics. In present work they have been used in conservation field for consolidation of 2 models (one for application of MNP and other for MNW) of an Egyptian fresco painting (3rd to 7th c. AD) kept in Coptic museum. They are filling the gaps inside the structure and improve the way of penetration of the magnetic nano materials through surface. The two treated models were studied by Fourier transform infrared(FTIR), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Spectrophotometer to determine the visual properties, and morphological and physical properties of the treated two models. The effect of different morphology of magnetic nano wires and magnetic nano particles on the mechanical characteristics of treated models using means of mechanical tests was evaluated. Both the two models proved that there is an improvement in mechanical properties occurring in both, but the magnetic nanowires act as nano wire in combaining the interior structure, thus, the model treated with MNW exhibited high resistanceto in bursting and hardness tests.

KEYWORDS: Nano magnetic, Morphology, Coptic fresco, consolidation, Hardness

1. INTRODUCTION

Since the discovery of carbon nano-tubes (CNTs) scientific and technological community have shown unprecedented enthusiasms in the studies on one dimensional nano-materials such as nano-tubes NTs, nanowires (NWs) and nano-rods (NRs) (Abinayaa, 2014, Liritzis et al., 2020). It has been elaborated above that the successful applications of magnetic nanoparticles in various field depends on particle size, surface area and morphology besides to their intrinsic magnetic moment and magneto crystalline anisotropy characteristics (Blee and Matisons, 2007). A precise control of these various factors (Size, Shape, Composition, And Structure) can control the magnetic characteristics of the material (Kholod, 2017; Khan, 2012). Antiferromagnetic materials (such as MnO, CoO, NiO, and $CuCl_2$) are compounds of two different atoms that occupy different lattice positions. (Missa, 2013) In this paper we discuss some of the main features of MNPs & MNWs. This paper is not meant to cover all aspects of magnetic nanoparticles. Only shedding light on selected nanomaterials and its role in consolidation of the models of Coptic fresco painting and the magnetic property helps or not in connecting the structure and improve the depth of penetration inside the treated models by using an external magnetic to control the magnetic nano particles inside the structure of the mural paintings. The scanning electron microscope (SEM) and X-Ray diffraction (XRD) were used to characterize the influences of magnetic nanoparticles for consolidation of an Egyptian Coptic fresco painting (3^{rd} - 7^{th} c AD).

2. MATERIALS AND METHODS

Magnetic nano particles and nano wires were synthesized according to (El-Sheikh, 2013, 2010) and Absolute Ethanol 99 % from ADWIC Company.

2.1. PREPARATION OF NANO-MAGNETIC SUSPENSION

For obtaining homogeneous dispersion and stable suspension of the of magnetic nano particles and nano wire in ethanol, a 20 gm /L the amount of magnetic nano material was sonicated in an ultrasonic bath power 100 watt for 2 h to obtain an homogeneous and stable dispersion can be used in consolidation the models of fresco paintings .

Table 1. The composition of the obtained mixed system for consolidation

Component	MNP	MNW
Magnetic nano material	2 gm	2 gm
Ethanol	98ml	98 ml

Figure 1: The Egyptian Coptic fresco painting

2.2. THE FRESCO PAINTING CONDITION

The surface of current fresco painting has a gypsum spots and a black crust as shown in (Fig.1) (Casadio, 2000) and the whole fresco painting suffered from weakness as a vital crack are obvious. The models of Egyptian Coptic fresco were exposed to artificial aging to create similar circumstances for the original fresco painting which kept in the Coptic Museum with registration number 8245. Then the surfaces were treated with systems described in Table 1 by use of immersion coating procedure.

2.3. THE PREPARATION OF THE MODELS

The models were prepared according to the original mural painting (Fig. 1) in three layers: a first layer of rough coating, this mortar is a mixture of hydrated lime-calcium hydroxide and coarse sand, (Lucas, 1962). The second layer consists of hydrated lime and well-filtered fine sand, The third layer is the pictorial layer made of pigments and pure water applied in several coatings with a brush (Merrifield, 1992) The calcified layer results from the carbonation of the lime mortar, while drying, produces a transparent protective crust (outer membrane that forms as a result of carbonation of lime) (Kholod, 2019; Bratitsi, 2018, 2019).

Figure 2: (a, b) The application of the suspension of nano-magnetic material using brush through Japanese paper, (c) The appearance after application

Figure 3: The magnetic nano materials don't affect by the external magnet as it penetrates the porous of the mural painting being connected with it's structure.

2.4. THE CONSOLIDATION WITH MAGNETIC NANO-MATERIALS

For consolidation, the model of Coptic fresco paintings was treated with magnetic nano material in ethanol using brushes through Japanese paper (Fig.2) as all applications of nano-materials (Baglioni, 2012; Kholod, 2017). The choice of magnetic nano wires or magnetic nano particles because of the magnetic property of the magnetic materials but unfortunately after the application the magnetic property is disappeared (Fig.3) due to the interactions of the magnetic nano-materials with the structure of the models. The models were subjected to different accelerated ageing test to simulate the most common outdoor heritage deterioration processes due to weathering agents. So, they were exposed to temperature 25^{o}C for 12 h then up gradually to 60^{o}C for 8 h and then left them in room temperature for 24 h, this round repeated 10 times to define the state of models after exposing for changing in temperature. (Batterham, 2008).

2.5. CHARACTERIZATION OF MAGNETIC NANO-MATERIALS

The morphology was examined by scanning electron microscope model Quanta 250 FEG Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n FEI company, Netherlands). Sample preparation consisted of application of a superficial gold film by sputtering to prevent electro-static charge. X-ray diffraction were obtained using PAN analytical X-Ray Diffraction equipment model X 'Pert PRO with Monochromatic, Cu-radiation (θ1.542Å) at 50 K.V., 40 M.A. and scanning speed 0.02^{o}/sec. were used. The reflection peaks between 2θ=2^{o} and 60^{o}, corresponding spacing (d, Å) and relative intensities (I/I^{o}) were obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files. FTIR analysis were obtained using a FT-IR Thermos Nicolet 760. The resolution is 4 cm^{-1} (Region 4000: 400 / Absolute threshold 0.002/Sensitivity: 50).

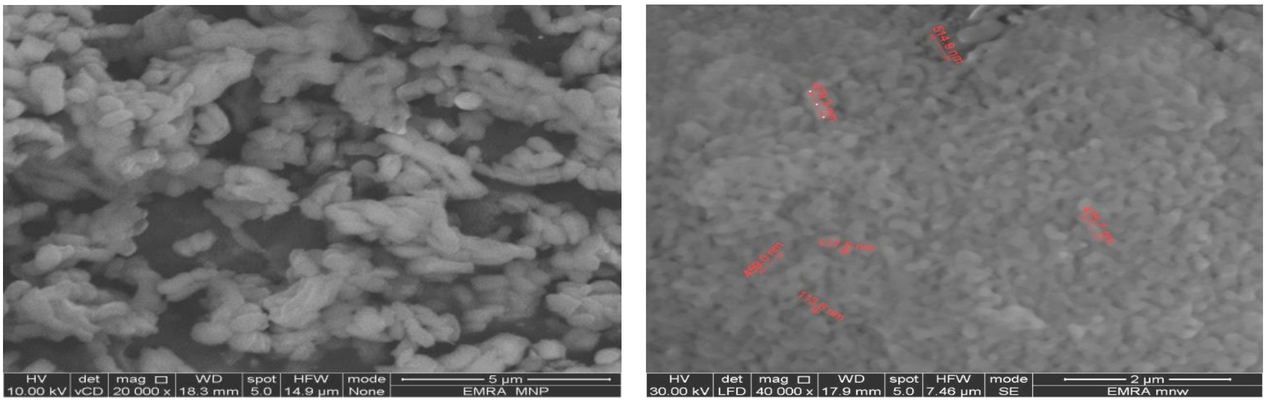

Figure 4: The characterization of magnetic Nano particles and Nano wires with their nano size using Scanning electron microscope, The left one shows the MNP in size range 117-170 nm, and right one expresses the MNW in size range 164-250 nm.

2.6. COLORIMETRIC MEASUREMENTS

Color changes induced by protective products and samples degradation were evaluated by spectrophotometer Optimatch 3100® from the SDL Company (Kholod, 2018) The dimension of the measured area of each sample equals to (1X1) cm^2. Colors standard L* corresponding to the brightness (100 = white, 0 = black), a* to the red–green coordinate (positive sign = red, negative sign = green), and b* to the yellow–blue coordinate (positive sign = yellow, negative sign = blue). The total color difference ΔE* between two color stimuli $\Delta E^* = \{(\Delta L^*)_2 + (\Delta a^*)_2 + (\Delta b^*)_2\}$ (Darwish, 2013; Bratitsi, 2018).

2.7. HARDNESS AND BURSTING

The details of hardness and bursting methods used are as follows:

The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 mm - 1.4 mm diameter, with a 30° conical point, 0.1 mm radius tip. This exerts 44.64 N of force (Briffa et al., 2012) The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54 mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to Newton to be 44.45 N (Kopeliovich, 2016).

Tinuis Olsen H5KT machine was designed for using in Research and Quality Control to measure material's strength and performance. All tests are designed and implemented by Tinius Olsen in accordance with key international testing standards including ISO, ASTM, EN and other industrial standards. The load measurement accuracy: +/- 0.5% of applied load from 2% to 100%, and position measurement accuracy: +/- 0.01% of reading or 0.001 mm (www.tiniusolsens.com)

3. RESULTS AND DISCUSSION

Magnetic nano particles and nano wires dispersed by sonication in ethanol for 1 h led to obtain the MNP suspension after the application of suspension on the model by brush through the Japanese paper (Baglioni, 2012) The MNW & MNP lost their magnet property as they don't affected by the external magnet as shown in Fig. 3. On other hand, they only filled the gaps as evidenced from SEM observations but there is a visual properties, such as, changes in colors of the treated model which can be tested by using spectrophotometer.

3.1. THE VISUAL PROPERTIES AND THE CHANGES OF COLORS AFTER TREATMENT

The purpose of comparison the changes of visual colors before (5a) and after treatment (5b) to detect the wide change of colors which caused by treatment. The color of the models after treatment with magnetic nano-particles and nano-wire a transparent membrane appeared on the surfaces as shown in (Fig.5c).

Through SEM it was documented that the magnetic nano particles and magnetic nano wires acted as filler to the interior structure (Fig.6) as the magnetic materials appeared inside the interior structure of the models.

***Figure 5:** (a) the model before the treatment of magnetic nano- materials, (b) and (c) the model after the treatment of magnetic nano materials.*

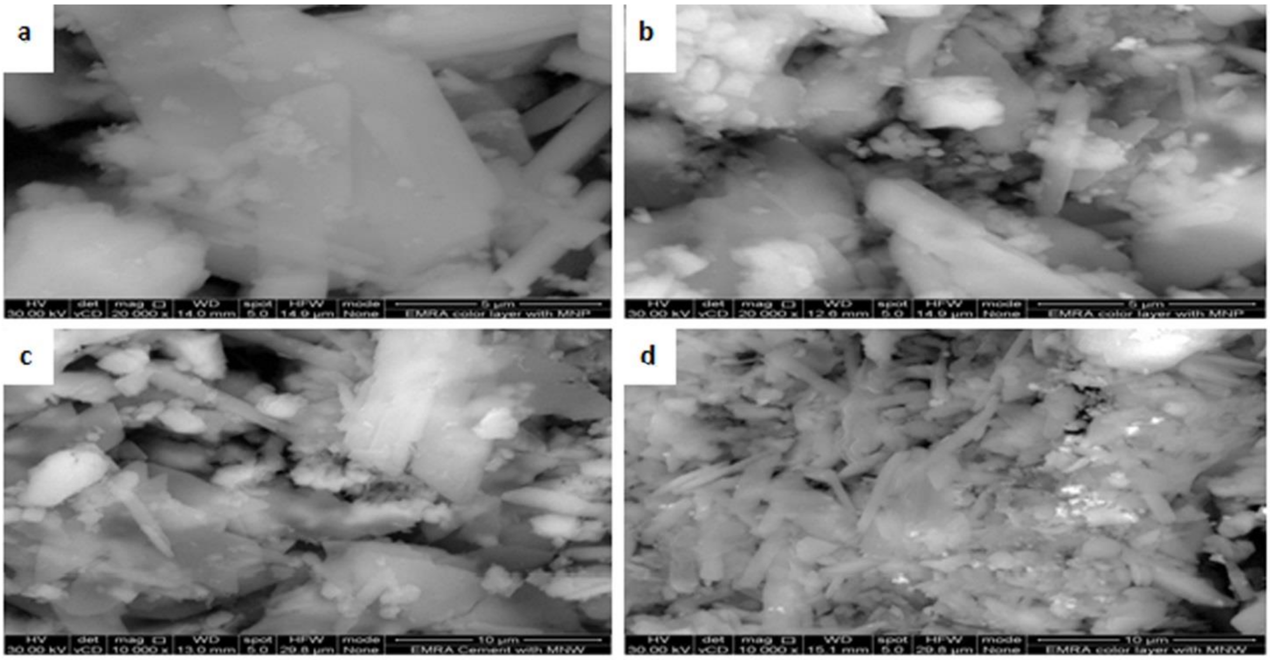

***Figure 6:** (a,b) The SEM image show MNW which filled the gaps inside the structure of models & (c,d) MNP filling the gaps inside the structure of the models.*

3.2. X-RAY DIFFRACTION

Fig.7 shows the XRD patterns of the treated models before and after treatment revealed that the calcite and gypsum are more major components in samples from model treated with magnetic nanoparticles and nano-wires in addition to compounds Taenite (Ni,Fe), ZnO, and SiO_2 in percentage 38% in the treated model with magnetic nano wire but in case of the treated model with magnetic nano particles the compounds $CoFe_2O_3$ and SiO_2 were found beside the original structure of the untreated model (calcite and gypsum) Orthoclase 44% with percentages of iron, nickel and silica 35%. The compounds in the charts assured the addition of magnetic nano wires and magnetic nano particles besides the original structures (calcium carbonate) of the models.

3.3. FTIR SPECTROSCOPY

Fig.8 shows FTIR spectra of A) untreated paint layer B) spectra of MNP C) spectra of MNW D) a comparison between MNW and paint layer after treatment and E) a comparison between MNP and paint layer after treatment.

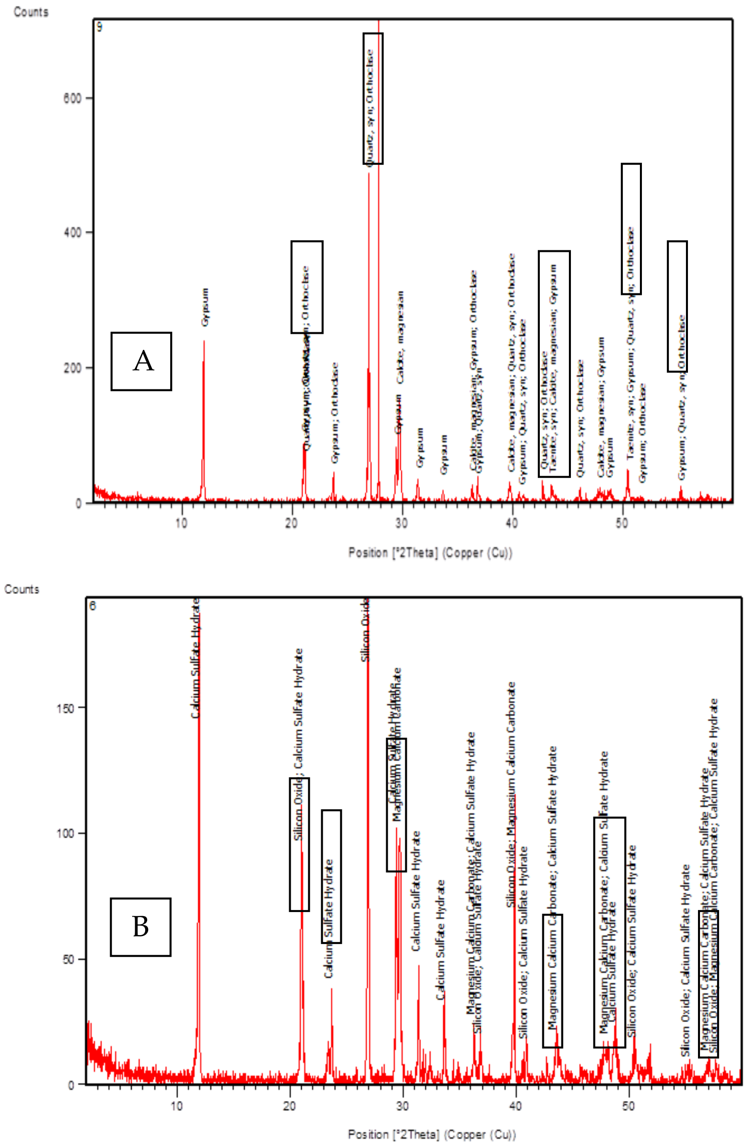

***Figure 7:** (A) the sample of model treated with magnetic nano-wire revealed the peaks of original structure of model beside that the silica and magnesium (B) the XRD pattern of sample of the treated models with magnetic nano-particles revealed the peaks of original structure of model beside that Taenite (Ni,Fe) and silica.*

The FTIR of untreated sample (Fig.8A) revealed that at least one strong absorption band from C-O stretching at 1415 cm^{-1} calcite, carbonate bending CO_3 vibrations produce sharp bands in the region of 900-650cm^{-1}. SO_4 bending and stretching band at 667, 1107 cm^{-1}, anti-symmetric and symmetric O-H stretching bands of gypsum at 3522, 3399 cm^{-1}.(B)The FTIR spectra of MNP revealed 1085 cm^{-1} finger print region bending rocking Fe-O, Co-O500-700cm^{-1} ,Fe^{+3}-O^{-2} 593-581cm^{-1} ,Stretching Si-O-Si 3427-3441 cm^{-1},and week band on 966-981cm^{-1} (C) The FTIR spectra of MNW revealed finger print region bending at 1058 cm^{-1} of aliphatic C-H, stretching 2851cm^{-1}, stretching C=C 2920 cm^{-1}, Si-OH 981-966 cm^{-1}, Fe^{+3} vibrations 425 cm^{-1} and Ni, Fe (D)and (E). The spectrum of sample before treatment is similar to the spectrum after treatment with magnetic Nano particles and magnetic Nano wires. Hence, the magnetic Nano particles and magnetic Nano wires don't affect the paint layer peaks as the same peaks of calcium carbonate and gypsum appeared on their ordinal absorption areas.

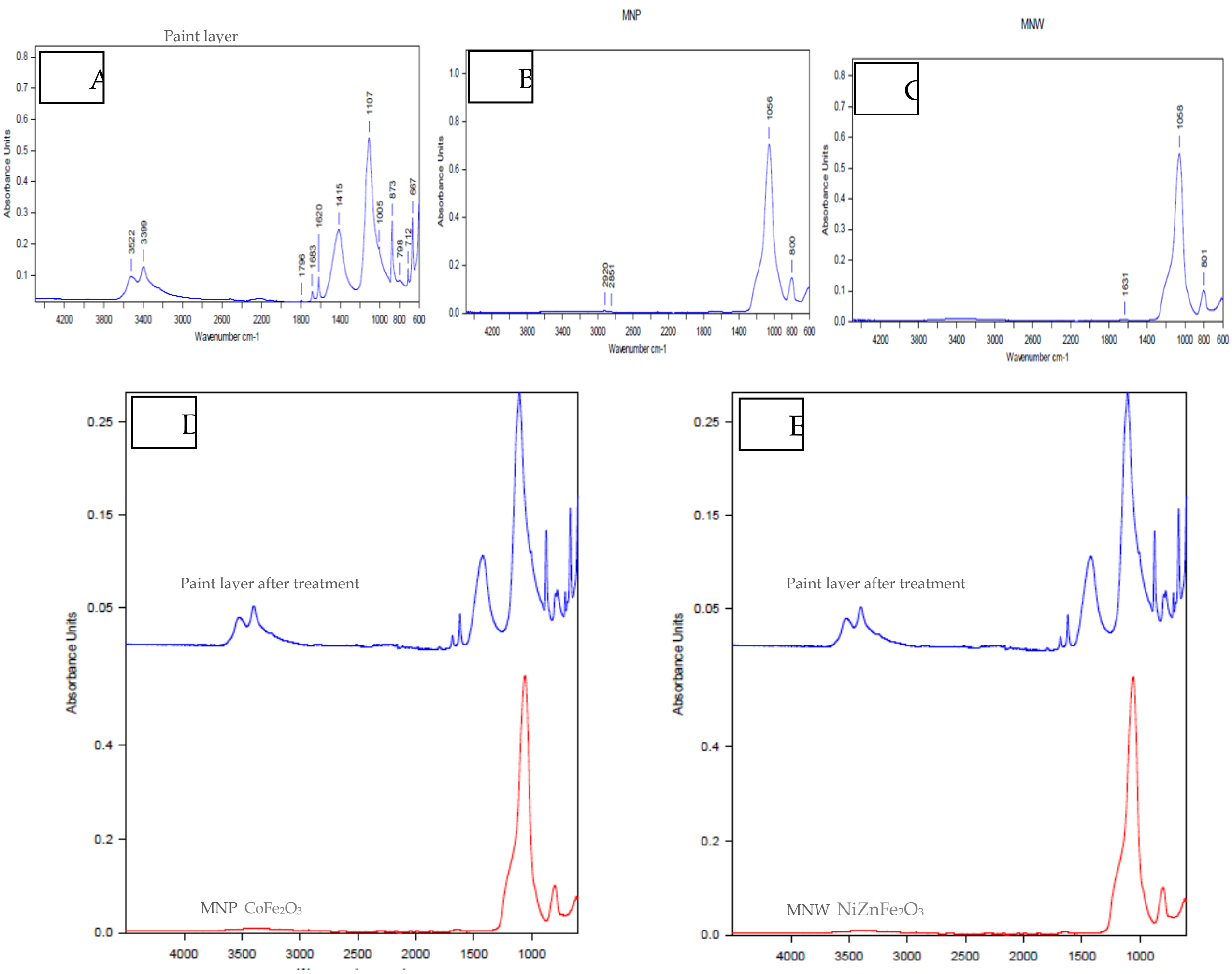

Figure 8: FTIR spectra of (A), (B)MNP, (C)untreated paint layer (D) a comparison between MNP after paint layer treatment and (E) a comparison between MNW after paint layer treatment

3.4. SPECTROPHOTOMETER

Table 2 shows the color variation promoted on the models after treatment with magnetic nano particles and magnetic nano wires ΔL* is the variation in luminosity, Δa* is the variation in the red–green parameter, Δb* is the variation in the blue–yellow parameter and ΔE* is the total color difference. Displays the color variations of the treated models for the tested treatments, the most important contribution came from L* a* b* where L* represents lightness (0% black, 100% white), a* redness-greenness, and b* yellow-blueness. For this work the values of a* > 0 and b* > 0 which represent the colors red and yellow, respectively. The yellow color of untreated models falls within the range: L* -9.88, a* 3.24 and b* 0.062. In general, treatments of magnetic nanomaterials led to yellowness of the model surfaces (Kholod, 2018).

- 2< Δ*E* < 3: fairly perceptible difference
- 3< Δ*E* < 6: perceptible difference
- 6< Δ*E* < 12: strong difference
- Δ*E* > 12: different colors

There were a small color variations expected on red an increased depth and brightness and small increase of the parameters generating slight yellowing probably due to residues of the solvent or accumulation of magnetic nano-materials (Darwih, 2013).

Table 2: coordinate of color obtained by using spectrophotometer

Color	ΔL*	Δa*	Δb*	ΔE*	Observations
YellowUntreated	-9.88	3.24	0.0062	10.42	**10 > Δ*E* > 5 In0the0untreat ed samples.**
Black untreated	-0.76	-	2.22	2.35	
Red untreated	1.60	0.08 0.87	1.09	2.12	
Yellow MNW	-35.60	-0.72	-13.75	38.17	**The results showed Δ*E* >12 This value Increased because of MNW & MNP**
black MNW	-2.48	0.54	-8.62	**11.03**	
Red MNW	-2.08	1.48	6.22	6.72	
Yellow MNP	-19.99	-0.14	-8.78	**21.83**	
black MNP	-2.80	0.22	-10.67	**2.52**	
Red MNP	-37.29	-1.08	-6.37	**37.85**	

3.5. HARDNESS AND BURSTING

a. The hardness tests using Shore D

The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 mm - 1.4 mm diameter, with a 30° conical point, 0.1 mm radius tip. This exerts 44.64 N of force (Fig.6) (Briffa et al., 2012). The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54 mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to Newton to be 44.45 N. (Kopehie,2016). Hardness tests for untreated model and treated models with nano-magnetic materials presented in Table 3. The hardness results of treated models increased over the untreated model. The improvement happened due to the application of nano-magnetic materials which fill the gaps.

b. the bursting strength tests or compressive strength using Tinuis Olsen

The Bursting strength or compressive strength expresses the ability of samples to bear compressive strength to be broken (Briffa et al.,, 2012) Bursting strength for untreated model and treated models with nano-magnetic materials presented in Table 4. The results proved that there is a little improvement happened in the presence of due to the application of nano-magnetic materials which fill the gaps and the morphology of magnetic nano wire is more effective as they were like wires but in case of magnetic nanoparticles the improvement in bursting strength of models was 306 N/mm², un like the bursting strength for the treated model with MNW'S was 383 N/mm² so the morphology of MNW'S more effective than MNP'S in consolidation.

Table 3: shore D models surfaces hardness results

Sample	Average hardness shore D	Shore D (Newtons)
Untreated model	19 ± 0.5	13 N
Magnetic nano wire	35 ± 0.5	18 N
Magnetic nano particles	35 ± 0.5	18 N

Table 4: Bursting strength of models results

Sample	Bursting strength (Newton /mm²)
Untreated model	224 N/mm²
Magnetic nano wire	383 N/mm²
Magnetic nano particles	306 N/mm²

4. CONCLUSIONS

It was reported the use of nano-magnetic materials for consolidation models of an Egyptian Coptic fresco and their magnetic properties in penetration. The results of treatment revealed that the magnetic property has been removed after the application as the MNP & MNW penetrated the structure and filled the gaps. In the hardness and bursting tests there was a little improvement because of filling the gaps and the morphology of magnetic nano wire is more effective as they were like wires but in case of magnetic nanoparticles the improvement in bursting strength is obvious, thus the morphology of MNW'S is more effective than MNP'S in consolidation. However, they caused an obvious change in colors according to the spectrophotometer results so they can be used in consolidation of fresco paintings as filler.

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