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# NANOMAGNETIC SPONGE AGENT AND PHYSIOCHEMICAL ANALYSIS FOR REMOVAL AGED VARNISH FROM AN EGYPTIAN INLAID WOODEN ARTIFACT OF 18th CENTURY OTTOMAN PERIOD: CASE STUDY

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## ABSTRACT

This paper presents synthesis of a nanomagnetic sponge loaded with oil in water (O/W) microemulsion for removing aged varnish from an Egyptian inlaid wooden jewelry box artifact, Ottoman period, 18th century. It was displayed in the museum of faculty of applied arts, Helwan University, Giza, Egypt. The box had several deterioration aspects, one of them is damage of the varnish layer which deformed the box appearance. Magnetic nanoparticles of $CoFe_2O_4$ were incorporated into a copolymer based network of polyethylene glycol and acrylamide to obtain nanomagnetic sponge. It was loaded with two (O/W) microemulsions: the first one is based on poly (HEMA): Poly (methyl methacrylate/2hydroxyethyl 1 methacrylate); and, the second is based on Texapon-P (ammonium lauryl sulphate). Portable USB microscope, scanning electron microscope attached with energy dispersive X-ray analysis (SEM-EDX) unit, x-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) were used to characterize the inlaid wooden artifact and to evaluate the efficiency of the nanomagnetic sponge. The data confirmed that the box was fabricated from *pinus pinea* wood, was inlaid with ivory of different colors, brass alloy, and wooden veneer. Nanomagnetic sponge loaded with poly (HEMA) succeeded in removing the aged varnish layer without leaving any residues due to its new magnetic ability, neither penetrating the surface, nor swelling of the binding material used in adhesion of inlay pieces.

**KEYWORDS**: Nanomagnetic sponge, nanomaterials, (O/W) microemulsions, aged varnish, inlaid, wooden artifacts

## 1. INTRODUCTION

Inlaid wooden artifacts are one of the most important precious work of art in Egypt through ancient Egyptian periods. They consist of wood as a panel, different inlay materials such as ivory, bone, mother of pearl, and tortoiseshell (Blair et al., 2009; Serageldin et al., 2001; Abdelmoniem et al., 2020; Salama et al., 2017; 2018). In Ottoman period, manufacturers used veneer inlay more as walnut or another fruitwood (Brend et al., 1991). Usually, a coating varnish layer was utilized to protect their surfaces from moisture, dust, climatic changes, mechanical damage, and to enhance their appearance (Ozgence et al., 2012; Sonmez et al., 2009; Weththmuni, 2016).

Unfortunately, the application of varnish (polymer) coating induces sever modification of the main physiochemical properties of wooden artifacts (Horie, 1987). Also, natural aging of varnish was occurred, mostly due to photo and thermal oxidation, produced yellowing of its color, opacity, and cracks (Meijer, 2001; Demirci et al., 2013). So, the removal of the varnish layer is urgent for conservation and protection of these artifacts. It must be carried out without affecting the original artistic materials either chemically or physically (Baglioni et al., 2015).

The use of conventional pure organic solvents for removal of hydrophobic layers such as varnish is not suitable because most of them are toxic and do not allow a controlled cleaning. They can quickly diffuse into inner layers (Domingues et al., 2013; Stolow, 1963; Phenix, 2001). Dissolving of these hydrophobic materials through none-confined pure solvents can cause their penetration within artifacts porous matrix. After solvent evaporation, polymer residues may remain within the substrate porosity (Domingues et al., 2013).

Also it was found, that the chemical composition of two major wooden artifact components is affected by organic used solvents for cleaning (Darwish et al., 2008).

Recently, oil in water (O/W) microemulsions and micellar solutions were used as cleaning tools to remove hydrophobic materials such as aged organic varnish, and acrylic paints as alternative to traditional methods, (Carretti et al., 2007). But, there is a problem with limited lifting residues on the treated surfaces (O/W), because microemulsions may be associated with nanomagnetic sponges to obtain a gel like system for the cleaning of archaeological surface without undesired residuals on the works of art (Bonini et al., 2007).

The aim of the present work is the assessment of a nanomagnetic sponge for removal the aged varnish layer from an inlaid wooden jewelry box artifact, Ottoman period. This is a novel approach, the agent is new, and it is the first time to approve its success after a practical application.

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

#### 2.1.1. Inlaid wooden jewelry box artifact and manufactured wooden samples

The box was inlayed with ivory of different colors, metal, and wooden veneer. Its dimension is 35x 24x 28 cm$^3$. It has number 88/7 at the museum of applied arts faculty, Helwan University, see Fig.1.

Inlaid wooden samples 4x4x2cm$^3$ were fabricated to carry out the experimental study. Samples were covered with a thick layer of varnish according to ASTM D 358, and were exposed to artificial aging according to ASTM D 2366-86, as shown in Fig. 2.


*Figure 1 Egyptian inlaid wooden jewelry box, Ottoman period, displayed in the museum of the faculty of Applied Arts, Helwan University, Egypt. (A)Top side, (B) Front side, (C) Back side, (D) Underside, (E) Right side, (F) Left side.*


*Figure 2 (A)& (B) Manufactured wooden samples after inlay and coating by shellac varnish, (C) Reference sample without coating.*

### 2.1.2. Nanomagnetic sponge and microemulsions (O/W)

It was obtained by cross linking magnetic nanoparticles ($CoFe_2O_4$) through a polymer network based on polyethylene glycol (PEG) and acrylamide.

Two (O/W) microemulsions were prepared for loading on the nanomagnetic sponge. The 1st (A) is based on Poly (HEMA): poly (methyl methacrylate/ 2 hydroxyethyl 1 methacrylate), (Table 1), and the 2nd (B) is based on Texapon-P: ammonium lauryl sulphate (Table 2), see Figs 3&4.

*Table 1: Composition in weight % of (O/W) Poly (HEMA) microemulsion (A), prepared for the removal test.*

| Micro-Emulsion | Water in initial reactor charge | Methyl Methacrylate | HydroxyEthyl Methacrylate | Water in pre-emulsion | polyvinyl pyrrolidone | Ammonium persulfate |
|---|---|---|---|---|---|---|
| A | 47.5% | 20% | 5% | 25% | 2.0% | 0.5% |

*Table 2: Composition in weight % of (O/W) Texapon-P microemulsion (B), prepared for the removal test*

| Micro-Emulsion | Solvent ($H_2O$) | Texapon P Surfactant | Co-Surfactant (PeOH) | ND | Solvent (PC) |
|---|---|---|---|---|---|
| B | 74.8% | 3.4% | 7.2% | 2.8% | 11.8% |

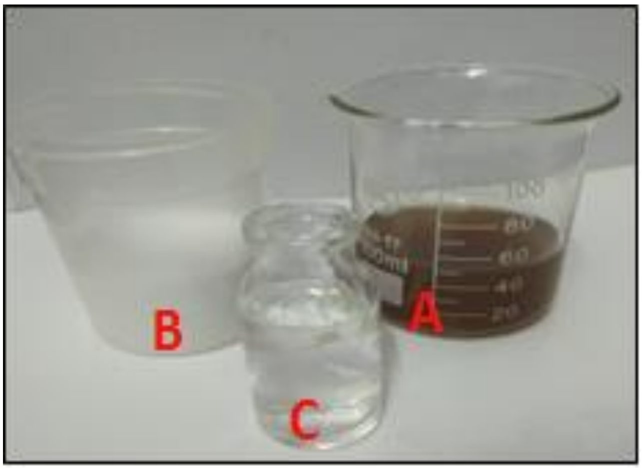



*Figure 3 (A) Nano Magnetic Solution , (B) Poly (HEMA) microemulsion, (C) Texapon- P microemulsion.*

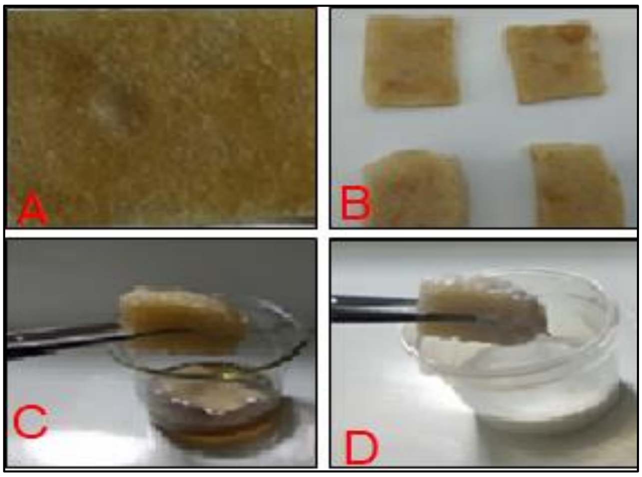



*Figure 4 Nano magnetic sponge: (A) Before using in removal (B) After cutting into shapes(C) After soaking in microemulsion for 10 min (D) Soaking in microemulsion.*

## 2.2. METHODS

### Optical microscope

Type M1 Imager microscope, Zeiss production, attached with Axiocam MRCS was used to identify the type of the wooden box. Java digital USB microscope, resolution *690 was used for examination of the varnish layer and its distortions.

### Scanning electron microscope SEM attached with EDX unit and portable digital USB microscope

Quanta 250 SEM, FEL Netherland, was utilized for examination of the wooden box and its deterioration aspects. EDX analysis was carried out to determine the sizes of CoO and $Fe_2O_3$ nanoparticles, as well as evaluation of the nanomagnetic sponge.

### X-ray diffraction analysis XRD

Phillips XRD equipment, model PW/1840 was utilized. The operating conditions are: 40Kv, 25mA, Cu Kα radiation, λ: 1.5418 Angstrom, Ni filter, 2θ scanning from 10-70, for characterization of metallic inlay in the box artifact.

### Fourier transformation infrared analysis FTIR

Bruker FTIR apparatus Verex 70 was used to determine the type of varnish on the wooden box, to characterize the binding material applied for fixing inlay pieces, and to evaluate the nanomagnetic sponge after loading with two (O/W) microemulsions.

### Application of nanomagnetic sponge loaded with (O/W) microemulsions

The nanomagnetic sponge was immersed in nanomagnetic ferro fluid which consists of $CoFe_2O_4$ nanoparticles to apply largest available magnetic field. Then the sponge was immersed in (O/W) microemulsion surfactants for 10 minutes. So, the sponge was ready to be applied directly on the surface of the wooden box for (30-40 minutes. An external magnet was used to remove any residues of nanomagnetic particles at the surface, as shown in Fig 5.

*(A)* *(B)* *(C)*

*Figure 5 Application of nanomagnetic sponge loaded with (O/W) microemulsions. (A) poly (HEMA) Microemulsion (B) Texapon-p, Microemulsion (C) External magnet for removal residues of nano gel.*

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of Inlaid box artifact

In the present study, examination of the inlaid wooden box artifact by each of optical and SEM microscopes proved that it consists of *Pinus pinea* wood as shown in Figs 6 & 7. Portable digital USB microscope declared that the varnish layer had several deterioration aspects such as opacity, change in color, fine cracks, and heterogeneity distribution (See Fig.8). Analyses of inlay materials by attached EDX unit with SEM microscope, confirmed that they constitute of ivory (Figs 9 & 10).

X-ray diffraction pattern (Fig.11) proved the existence of brass alloy (CuZn) card No. 52-0322. FTIR analysis (Fig.12) declared that the binding material used for fixing inlay materials is gelatin, due to the presence N-H absorption band at 3432cm$^{-1}$, C-H absorption band at 2921cm$^{-1}$, C=O band at 1622cm$^{-1}$, C-N-H band at 1528cm$^{-1}$ and C-H band at 1407cm$^{-1}$. FTIR pattern of varnish (Fig.13) declared that it is composed of shellac, due to the presence of absorption band O-H at 3432cm$^{-1}$, C-H stretching band at 2921cm$^{-1}$ C=O band at 1622cm$^{-1}$ and C-H band at 1407 cm$^{-1}$.

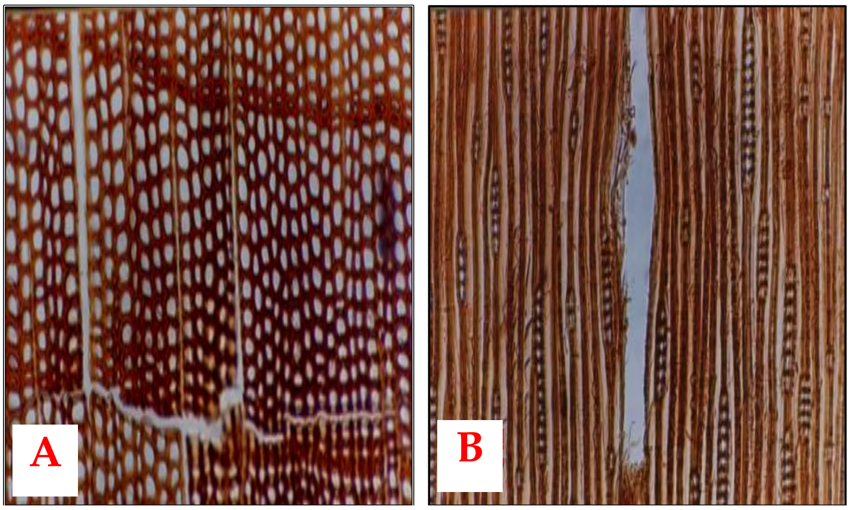



*Figure 6 Optical microscope micrographs of archaeological wooden sample, (A) Cross section, (B) Tangential section (63X).*

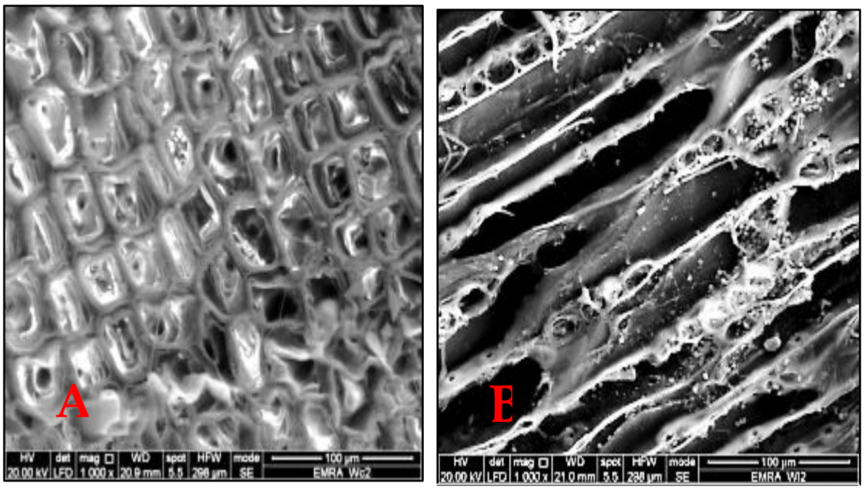



*Figure 7 SEM micrographs of archaeological wooden samples (A) Cross section, (B) Tangential section, (1000X).*


*Figure 8 Portable digital USB microscopic examination, showing deterioration of varnish layer: (A) Discoloration (B) Congregation of varnish and cracks (C) Micro cracks, 1000X.*

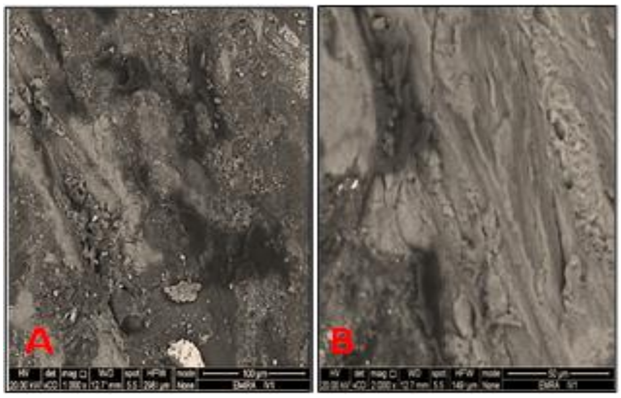



***Figure 9 SEM micrographs of archaeological wooden box, (A) Ivory inlay unit was completely covered with shellac layer, 1000 X, scale: 50 µm, (B) Ivory inlay unit was partially covered with shellac, 2000 X, scale: 100µm.***

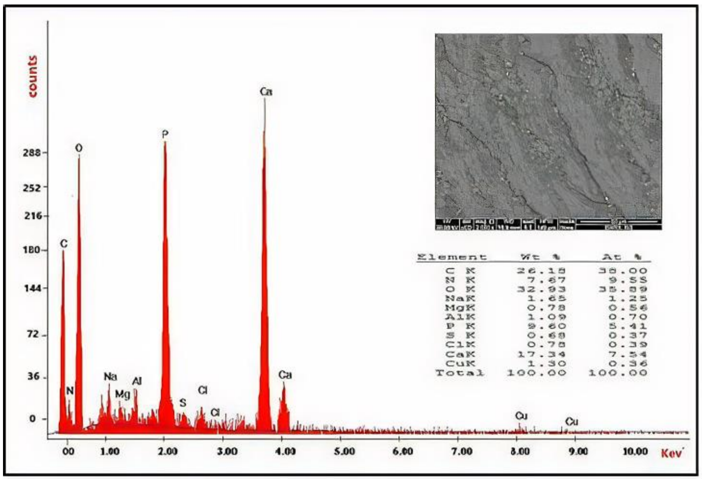



***Figure 10 SEM micrograph and EDX analysis of white inlay unit from the artifact, 2000 X. (KeV vs intensity) Fig. 10 : 50um & 200um***

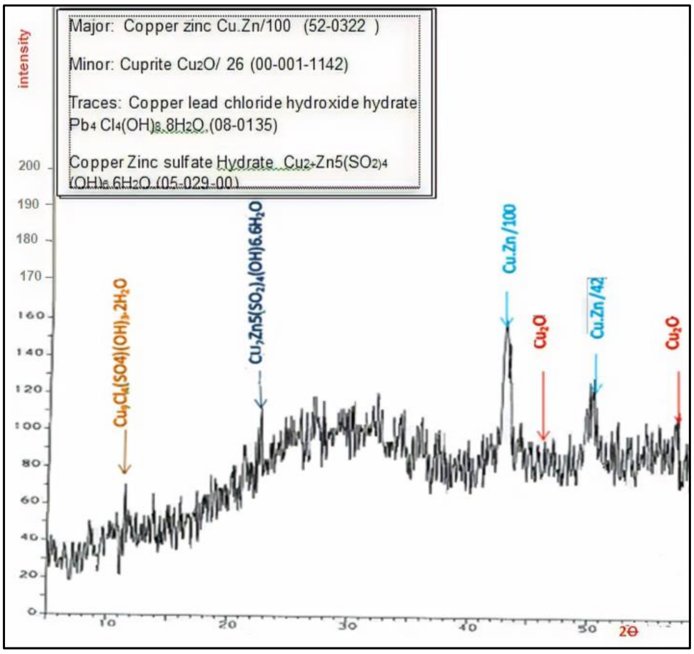



***Figure 11 XRD pattern of metallic wire used to define inlay shapes.***

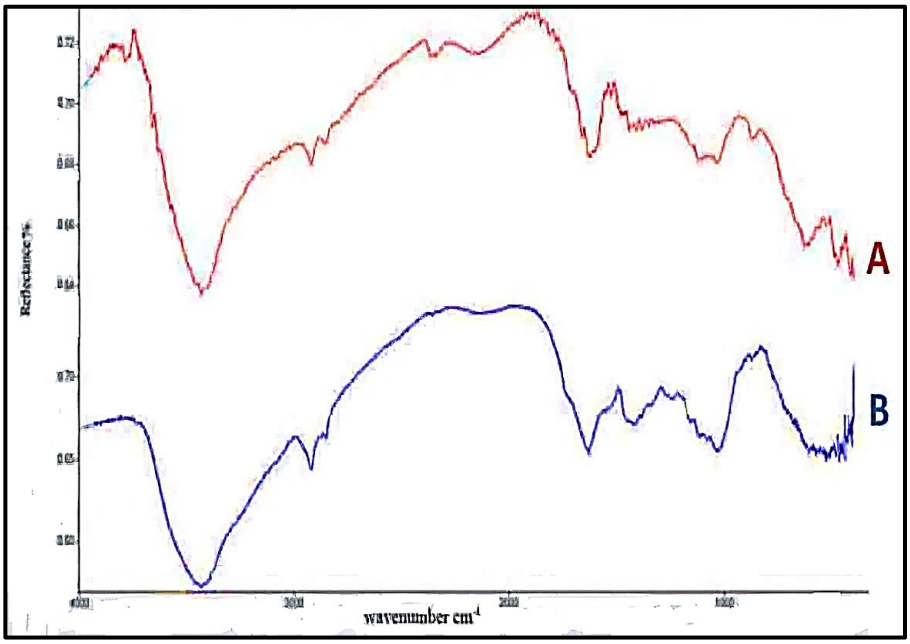



*Figure 12 FTIR spectra, (A) Adhesive material from artifact, (B) Reference gelatin sample*

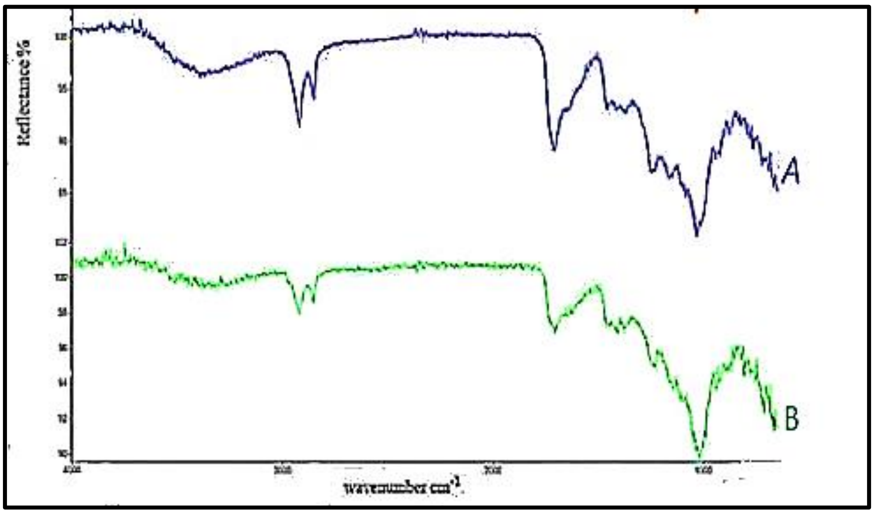



*Figure 13 FTIR spectra: (A) Varnish layer from artifact. (B) Shellac reference sam.*

### 3.2. ASSESSMENT OF NANOMAGNETIC SPONGE

The removal of the varnish layer from the surface of the box artifact is very sensitive and necessary for its treatment and conservation. It was completely degraded which distorted and hided the subsurface original colors. In this work, it is the first time to synthesize a nanomagnetic sponge loaded with (O/W) microemulsions for this purpose, to exclude the disadvantages of traditional mechanical and chemical cleaning methods. Examination and analysis of the nanomaterials used for preparation of nanomagnetic sponge were carried out by SEM attached with EDX unit. It confirmed that nano cobalt oxide CoO particles are less than 75 nm (Fig.14), and nano magnetic iron oxide $Fe_3O_4$ particles are less than 70 nm (Fig.15). The sponge was evaluated by SEM attached with EDX unit, and Fourier transform infrared analysis FTIR. The SEM micrographs data proved the success of nanomagnetic sponge loaded with poly (HEMA): poly (methyl methacrylate/2 hydroxyethyl 1 methacrylate) (O/W) microemulsion without leaving any residues on the surface, nor swelling of the binding material as shown in (Figs.16, 18, 19). On the other hand, texapon-p microemulsion was partially removed the aged varnish layer (Figs.17, 18, 19). FTIR analysis confirmed these data, whereas in case of poly (HEMA) microemulsion, the characteristic absorption bands assigned to C-H group at 2900 $cm^{-1}$ and -OH group at 3400 $cm^{-1}$ of the varnish were completely disappeared. On Contrary, in case of Texapon-p microemulsion, the above absorption bands were still existed which indicate that there are traces of the varnish layer on the surface, as shown in (Fig.20). In both two microemulsions there was no any trace presence of nanoparticles from the nanomagnetic sponge on the surface, which assured capability of the nanomagnetic sponge in the removal process. The nanomagnetic sponge loaded with poly (HEMA) (O/W) microemulsion was applied for removal the aged varnish layer from the box artifact as shown in Figs. 21& 22.

The superfacial aged varnish layer coating the box artifact is a hydrophobic material. Nanostructured fluids such as (O/W) microemulsions can dissolve it without surface penetration.

A microemulsion is a high performing removal tool, since it can remove hydrophobic layers using a small amount of organic solvents. The microemulsion droplets contain the appropriate solvent able to solubilize the polymeric layers, while water in the dispersing phase can penetrate within the porous substrate, avoiding the risk of redeposition of the dissolved polymers, because of its affinity within the hydrophilic pores of the surface.

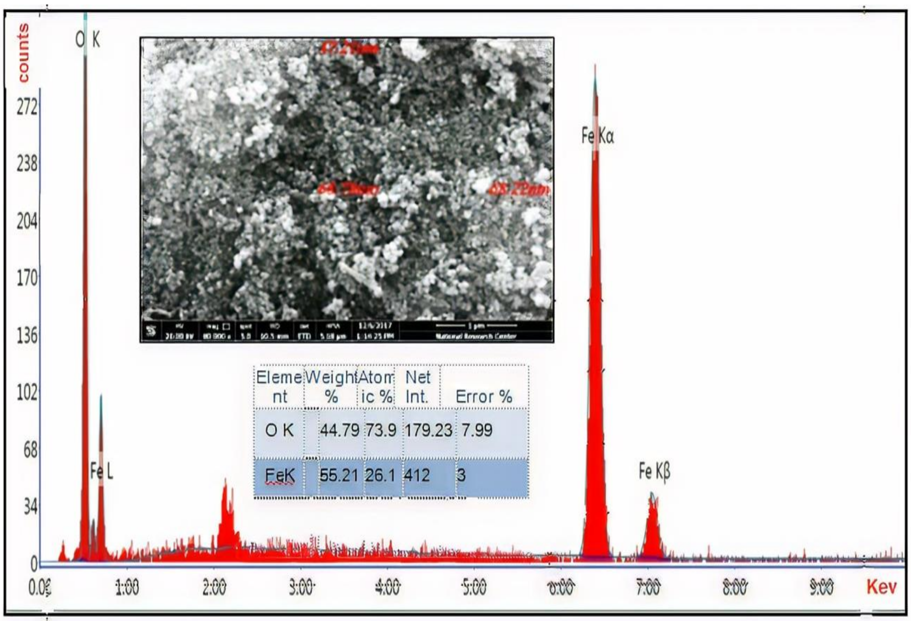



*Figure 14 SEM micrograph and EDX analysis for Fe2O3 nano particles, 8000X.*

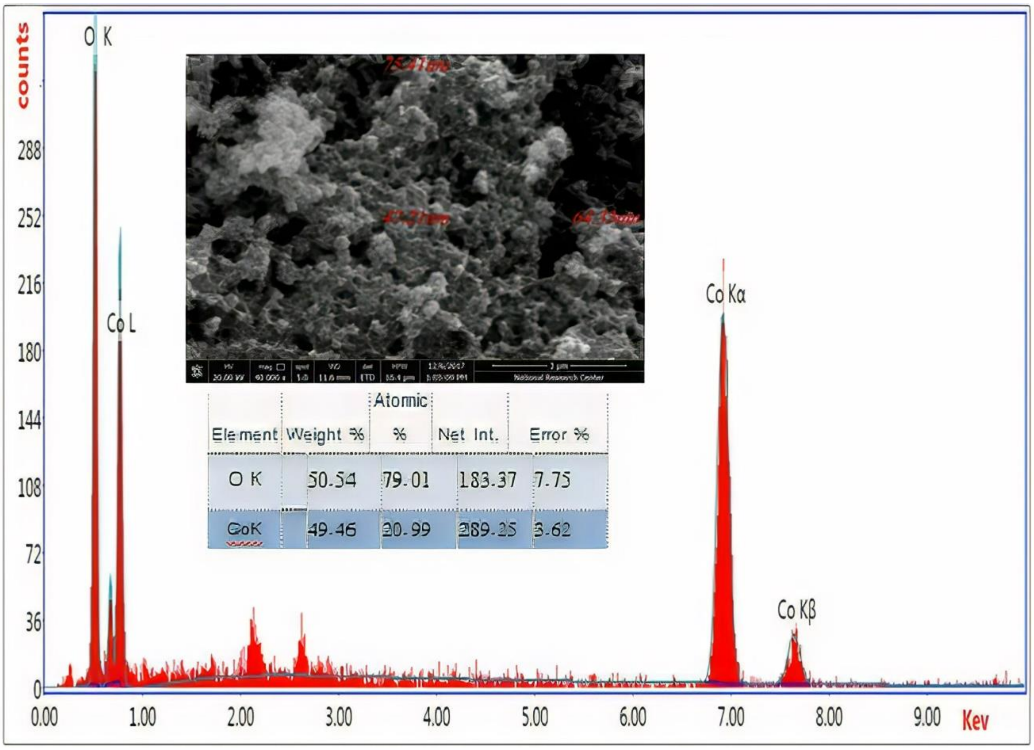
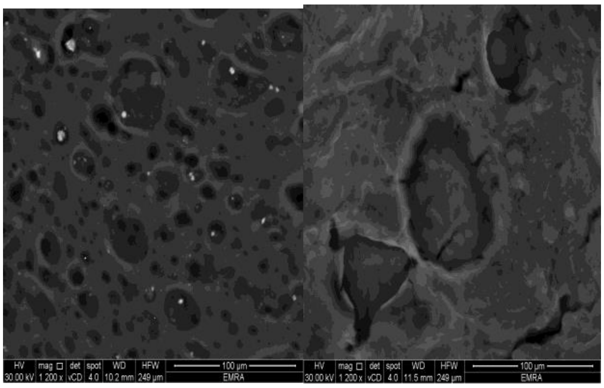



*Figure 15 SEM micrograph and EDX analysis for CoO nano particles, 4000X.*



(A) (B)

***Figure 16 SEM micrographs for nanomagnetic sponge: (A) Before loading with Poly (HEMA) microemulsion, scale: 100 µm, (B) After loading with Poly (HEMA) micro emulsion, 1200 X, scale: 100 µm.***

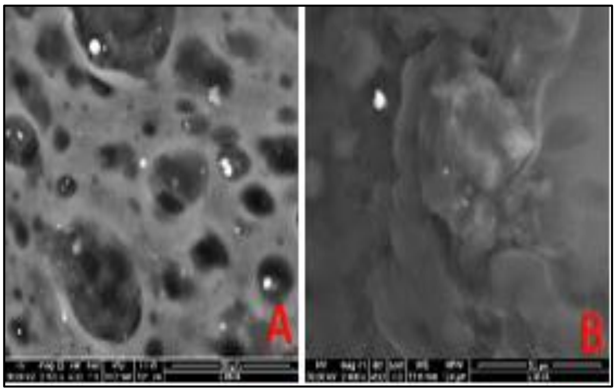



***Figure 17 SEM micrographs of nanomagnetic sponge: (A) Before loading with Texapon-P microemulsion, scale: 50 µm, (B) After loading with Texapon-P micro emulsion, 2400 X. scale: 50 µm.***

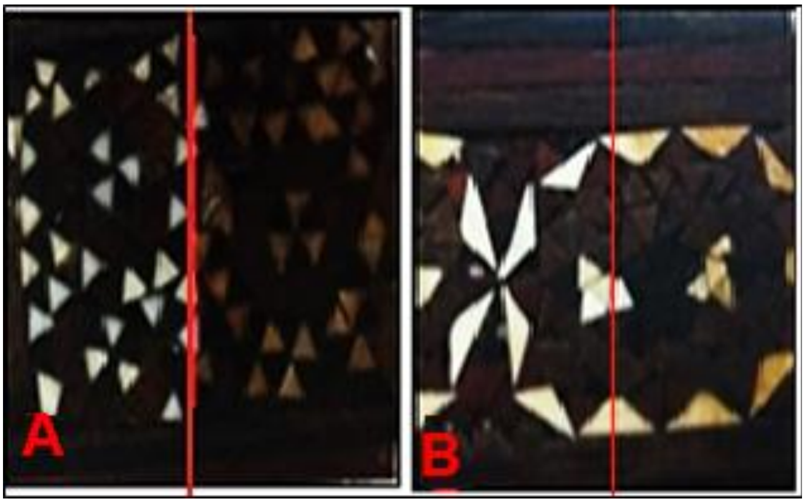



***Figure 18 Cleaning with nanomagnetic sponge (before and after) (A) Loaded with poly (HEMA) microemulsion. (B) Loaded with Texapon-P microemulsion.***

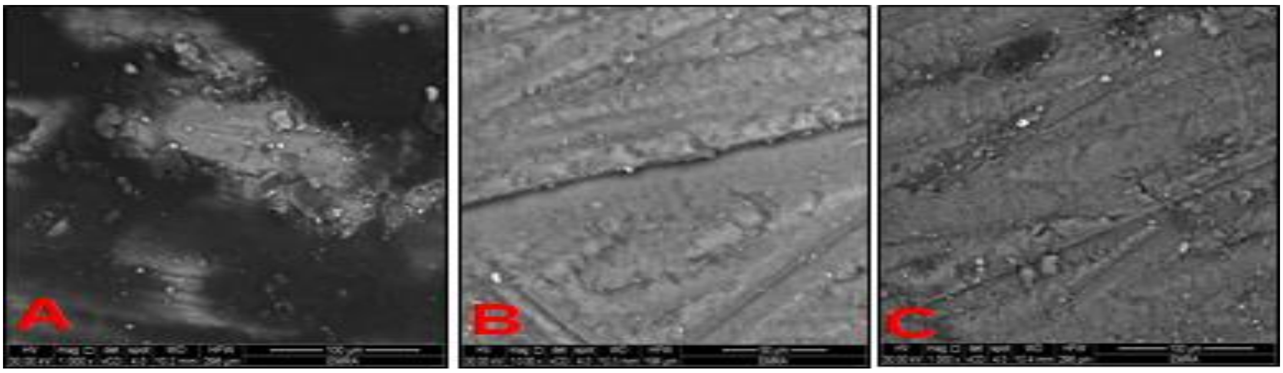



***Figure 19 SEM micrographs of manufactured ivory sample (A) Coated by varnish before cleaning, scale: 100µm, (B) After removal by nanomagnetic sponge loaded with poly (HEMA) microemulsion, scale: 50 µm, (C) After cleaning by nanomagnetic sponge loaded with Texapon-P microemulsion, 1000 X. scale: 100µm.***

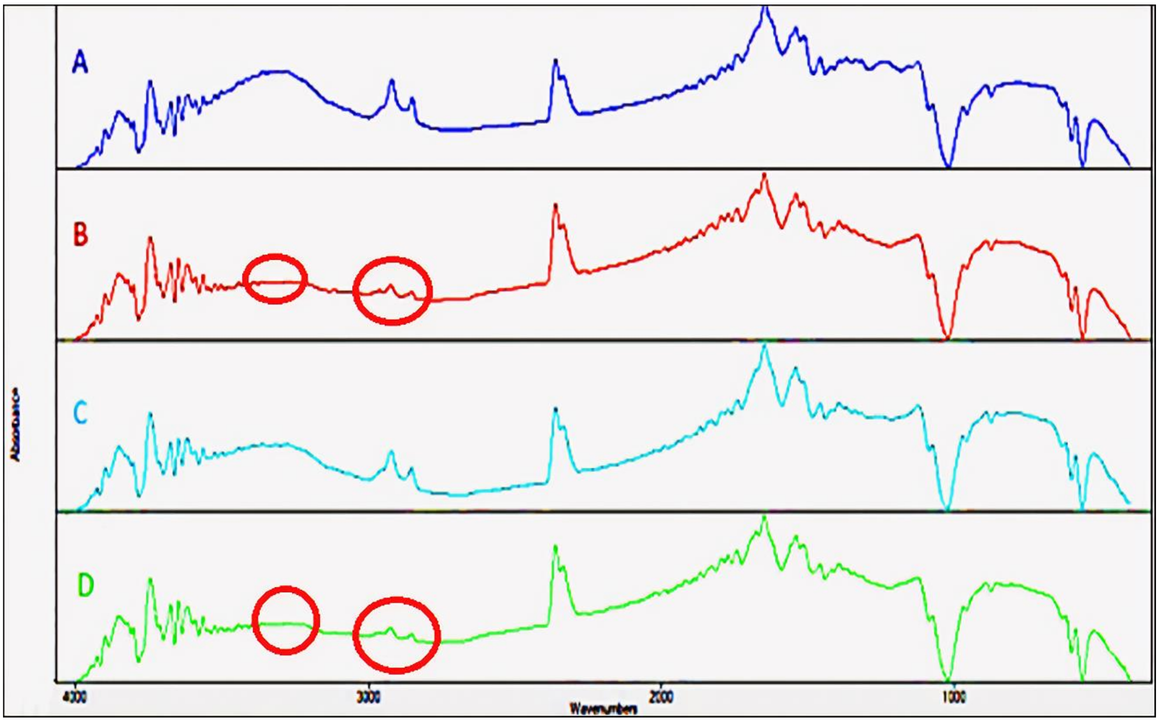



***Figure 20** FTIR spectra, (A) Manufactured ivory sample coated with shellac varnish, (B) After removal by nanomagnetic sponge loaded with Poly(HEMA) microemulsion, shows no existence of groups at 2900 cm$^{-1}$ and 3400 cm$^{-1}$ characteristic to shellac varnish (C) After removal by nanomagnetic sponge loaded with (Texapon-P) microemulsion, (D) Manufactured reference ivory sample without any coating. The red circles declared the positions of characteristic bands of shellac varnish after removal by Nanomagnetic sponge in case of poly(HEMA), and non-completely removal in case of Texapon-p.*

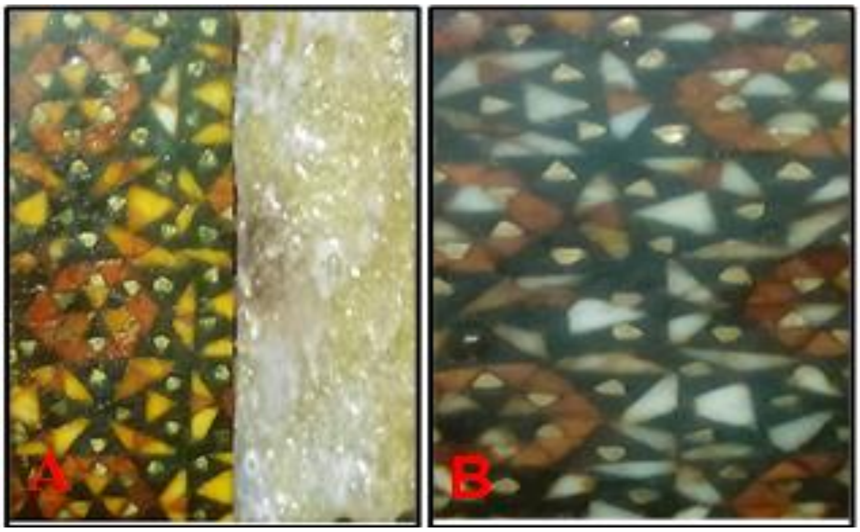



***Figure 21** Removal of varnish layer from the box artifact (A) During using nanomagnetic sponge loaded with Poly (HEMA) microemulsion, (B) After removal of varnish from the box.*


***Figure 22 (A) The box artifact before removal of shellac varnish layer, (B) Two parts: before and after removal, (C) After complete removal of varnish layer with nanomagnetic sponge loaded with Poly(HEMA) microemulsion and conservation.***

In ternary systems such as microemulsions where two immiscible phases (oil and water) are present with surfactant molecules may form a monolayer at the interface between the oil and water with the hydrophobic tails of the surfactant molecules dissolved in the oil phase and the hydrophilic head groups in the **aqueous** phase. One explanation for their thermodynamics stability is that oil/water dispersion is stabilized by the surfactant present and their formation involves the elastic properties of the surfactant film at the oil/ water interface, which involves as parameters, the curvature and the rigidity of the film.

Magnetic nanoparticles $CoFe_2O_4$ which are associated with acrylamide ethylene oxide polymer produce a sponge which loaded with oil in water microemulsions, forming a magnetically response gel-like and acting as a permanent hydrogel. This magnetic gel-like system was used in the release of the varnish (loaded) material, can be magnetically manipulated and removed from the loaded material (Bonini, M., et al., 2007).

## 4. CONCLUSIONS

In the present study nanomagnetic sponge loaded with poly (HEMA) poly (methyl methacrylate/2 hydroxyethyl 1 methacrylate) (O/W) microemulsion approved its success for completely removal of aged varnish layer from the surface of inlay wooden jewellery box artifact. Nanomagnetic sponge loaded with Texapon-p (ammonium lauryl sulphate) (O/W) microemulsion did not succeeded to completely remove the varnish layer. Yet the use of nanomagnetic sponge loaded with (O/W) microemulsions has limited the penetration of surfactant materials through the archaeological surface, and it supplied protection of both inlay pieces and the binding material used for fixing them. This sponge is characterized by magnetic properties which facilitate removal of residual surfactant material with an external magnet without applying any mechanical friction. It could be cut into pieces suitable for the desired survey of cleaning area, which gives elasticity and facility during application. Moreover, this sponge could also be dried, then grinded into powder, to be utilized another time in a gel form with the surfactant materials.

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