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A NEW WAY IN SYNTHESIZING MAGNETIC NANO GEL FOR CLEANING AN EGYPTIAN COPTIC FRESCO PAINTING

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ABSTRACT

Cleaning artworks is a very difficult process as the usage of pure organic solvents increases the toxicity and environmental impact of the cleaning techniques. Magnetic gels are very promising materials for cleaning movable and immovable artwork surfaces. The synthesis of a well-known magnetic nanoparticle gel was initiated by esterifying polyethylene glycol with anhydride concurrently. The new magnetic gel, made by cross-linking magnetic nanoparticles of $CoFe_2O_4$ into a copolymer based network of 3-octadecyl -1-vinyl imidazolium bromide ($C_{18}VIBr$) and N,N'-Methylenebis acrylamide, was used in cleaning Coptic fresco painting models. The Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope, polarized microscope and the Optical microscope were used to monitor the success of synthesis of the new gel with the magnetic nanoparticles in cleaning the artwork surfaces.

KEYWORDS: Nano gel, Magnetic nano particles, Magnetic nanogel, Cleaning, Fresco, Microemulsion.

1. INTRODUCTION

Organic solvents have been used in the cleaning of art works. The direct use of pure organic solvents on artworks has resulted in the swelling of the original binding media and varnish layers, they are also difficult to control in the cleaning process (Baglioni, 2013) resulting in the dispersion of solvent in unwanted areas (Brajer, 2007) and possible solvent diffusion into the internal layers of the painting (Giorgi, 2009) Usually, a cleaning process is carried out to remove superficial layers that may induce further degradation to the artifact. These layers can be hydrophilic (e.g. superficial grime) or hydrophobic (e.g. aged varnishes and adhesives). While the removal of hydrophilic layers is easily performed with aqueous methods, the removal of hydrophobic layers is commonly carried out through the use of pure organic solvents. Most organic solvents are toxic and do not allow a controlled cleaning since they can quickly diffuse into inner layers (Andresson, 2014) For this reason, pure organic solvents are rarely used in conservation treatments today .Since 1980, gel technology has been used to successfully clean artworks, as it assures a great control over the liquid cleaning agent's contact with the surface (Domingues, 2013) Gels can be divided into two major categories, depending on the nature of their bonds: physical and chemical gels. Physical gels are formed by electrostatic interactions between polymeric chains, so they are usually viscous systems that can respond to heat or be disrupted by mechanical forces. Polysaccharide based gels (e.g. agar-agar or gellan gum) are an example of physical gels and are, at present, one of the most promising tools used by conservators with the intent of retaining the cleaning agent (Baglioni, 2015) These gels, however, are fragile and do not have the suitable retention features. Using physical gel has a very bad side effect which leaving residues of the gel on the treated surface which in the future attract the dust and the cleaned place turned in to a black area because of the gel residues so the treated area must be treated with organic solvents to remove the residues of the gel (Baglioni, 2009), Chemical gels are, on the other hand, characterized by the presence of covalent bonds. They have a specific shape given during synthesis and have strong gel cohesion, so no gel residues are expected after treatment using chemical gels. Chemical gels are more versatile because depending on the components (monomer, cross-linker, liquid medium, etc.) and the quantitative proportions it is possible to obtain gels with different chemical-mechanical properties (Domingues, 2013) In the specific case of cleaning water-sensitive artifacts, the ideal container would be a highly retentive soft hydrogel. the nanotechnology produce a great new way in controlling of the gel by adding magnetic nanoparticles so the surface became clean without leaving any residues by using an external magnet (Blee, 2008), or without touching the art work surface (Baglioni, 2013) In this paper we present the potential application of new synthesize nano gel to be used in cleaning artwork surface.

2.MATERIALS AND METHODS

2.1 Materials

The materials used are 1-vinylimidazole (10.0 g; 106.26 mmol), 1-Bromooctadecane (35.67 g; 107 mmol), 20.0 mL of ethyl acetate, N,N'-Methylenebis acrylamide (0.5 g), acrylamide (30 g), potassium persulfate (0.2 g), $Fe(NO_3)_3 \bullet 6H_2O$, $Co(NO_3)_2 \bullet 6H_2O$ (99%, Aldrich) and urea (99, Merck). Water was purified by a Millipore Elix 3 apparatus: the resistance of the ultra pure water was 18 MΩcm.

2.2 Synthesis of polyacrylamide nanogel through the synthesis of 3-octadecyl -1-vinyl imidazolium bromide (c_{18}vibr)

A round bottom flask equipped with stirrer and thermo pocket was charged with 1-vinylimidazole (10.0 g; 106.26 mmol), 1-Bromooctadecane (35.67 g; 107 mmol) and 20.0 mL of ethyl acetate. The mixture was stirred at room temperature for 3 h in an inert atmosphere and the temperature was raised gradually to 50 °C for 24 h. After cooling, white precipitate of 3-octadecyl -1-vinyl imidazolium bromide is obtained. The obtained material was filtered off and recrystalline with warm ethyl acetate and finally dried under vacuum at 40 °C, giving rise to a yield of 78.5%. Then C_{18}VIBr (2.5 g), N,N'-Methylenebis acrylamide (0.5 g) and acrylamide (30 g) were dissolved in distilled water (100 mL) under nitrogen atmosphere. After complete desolvation, The temperature rose to 45 °C for 30 min and potassium persulfate (0.2 g) was added. The mixture was allowed under mechanical stirring for 12 h to complete polymerization.

2.3 Synthesis of magnetic nanoparticles

$Fe(NO_3)_3 \bullet 6H_2O$, $Co(NO_3)_2 \bullet 6H_2O$ (99%, Aldrich) and urea (99, Merck) were weighed to obtain their molar ratio of 2:1:4. The mixture were stirring to make a clear solution. The sol was treated in a domestic microwave working at 850 W, 2.45 GHz for 3–5 min.

2.4 Synthesis of magnetic polyacrylamide

Nanogel under inter atmosphere, $CoFe_2O_4$ (4.0 g) was added stepwise to pre-dissolved C_{18}VIBr (2.5 g), N,N'-Methylenebis Acrylamide (0.5 g) in100 ml distilled water under external sonication at temperature of 0°c. After 30 min 0.15 g of potassium persufate pre-dissolved in 20 mL water is added. The temperature was raised to 35°C for 24 h to complete polymerization process.

2.5 The application of nano gel and magnetic nano gel

The usage of nano gel in cleaning and removing undesired layers from surfaces was successful but with lifting residues can be ignored (as shown in Fig. 1) to avoid lifting any residues on the treated surfaces the magnetic nano particles were added to the nano gel. The color of nano gel turned in to black color because of the cobalt ferrite magnetic nano particles the removing of the gel can be done with an external magnet without touching the surface (as shown in Fig. 2).

Figure 1 the nano gel before and during using it in cleaning surface of the fresco Coptic model

3. CHARACTERIZATION DATA FOR 3-OCTADECYL-1-VINYL IMIDAZOLIUM BROMIDE

Analytical data was obtained from the Microanalytical Center at Cairo University and proton magnetic resonance spectra was recorded on a Varian EM-390 90 MHz. The molecular weight of $C_{23}H_{43}BrN_2$ is 427.51. The elemntal analysis are Calcd. C, 64.62; H, 10.14; Br, 18.69; N, 6.55; Found C,64.7; H, 10.31; Br, 18.34; N, 6.65. m.p. =71.7 °C. From this data itcan noticed that the presence of Br beside C, H and nitrogen and the calculate values are similar to the practical vales. The NMR analysis for chracterization of bonds between elements gave the following results:

^{1}H NMR (DMSO): δ = 0.96 (t, 3H; CH_3), 1.22 (m, 30H; $-CH_2-$), 1.4 (m, 2H; $-CH_2-CH_2-N$), 3.9 (m, 2H; $-CH_2-N$), 5.14 (dd, 1H; **CH_2**=CH), 5.4 (dd, 1H; **CH_2**=CH), 5.6 (dd, 1H; CH_2=C**H**), 7.26 (s, 1H; N-**CH**=CH-N), 7.29 (s, 1H; N-CH=C**H**-N-CH=CH_2), 8.23 (s, 1H; N=CH-N). All bonds found in the compound are present in proton magnetic resonance spectra such as CH_3, $-CH_2-CH_2-N$, N=CH-N and CH_2=C**H.**

Figure 2 The nanogel with magnetic nano particles colored black , with magnetic properties as the gel became controlled with an external magnet.

3.1 FTIR Spectroscopy

The mixture of nanogel with the microemulsion change the spectra in (2854, 2927,2027 cm^{-1}) and magnetic nano gel with the microemulsion change the spectra in (1378, 1477, 1501, 1636 cm^{-1}) To confirm this statement, ATR-FTIR spectra, shown in (as shown in Fig. 3).

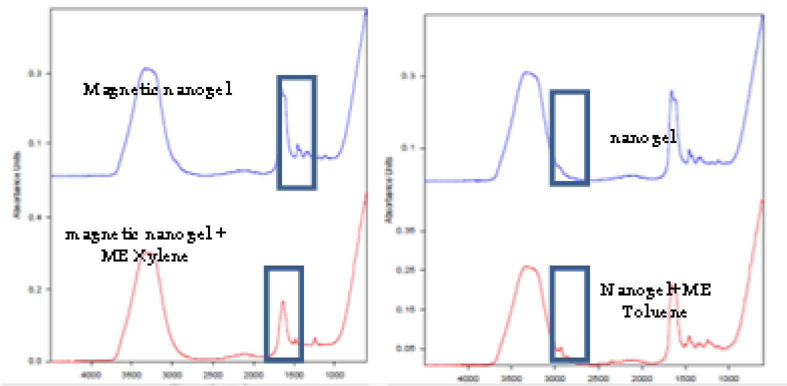

Figure 3 The spectra of nano gel and nano gel with ME Toluene and the magnetic nano gel and the magnetic nano gel with ME Xylene.

3.2 X-Ray diffraction to the magnetic nanoparticles

The combusted powders were characterized by X-ray diffraction (XRD) on a Shimadzu XD-1 Diffract meter using Cu-target & Ni-filtered radiation. High resolution transmission electron microscope (HRTEM) is a JEOL 2100F TEM at an accelerating voltage of 200 kV with Electron Diffraction (SAED) (as shown in Fig. 4).

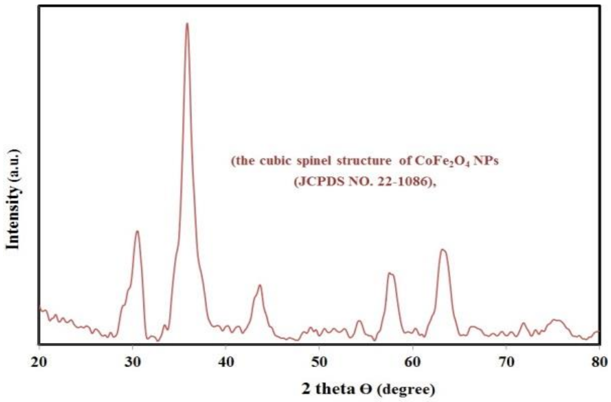

Figure 4 XRD of $CoFe_2O_3$NPS

3.3 Scanning electron microscope

Using SEM 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 for Gun. 1n FEI company, Netherlands. Sample preparation consisted of application of a superficial gold film by sputtering to prevent electro-static (as shown in Fig. 5).

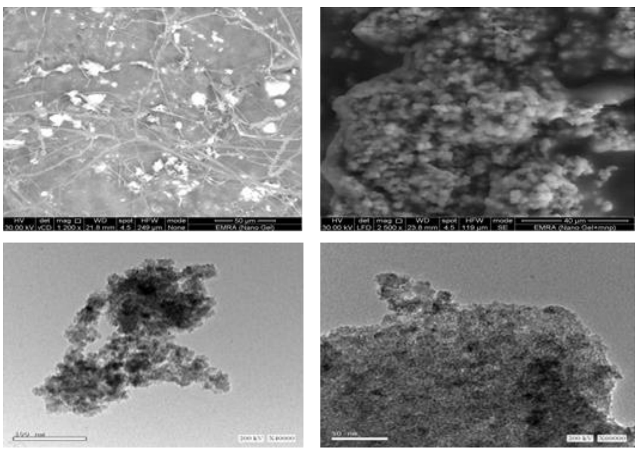

Figure 5 (Upper) SEM to the MNPS, Lower left shows the fibers of nano gel before adding magnetic nano particles , Lower right the magnetic gel.

3.4 Optical Microscope

The samples were examined after mounting gel on a glass slide, and they were examined by the optical microscope with power magnification 500 X (as shown in Fig. 6).

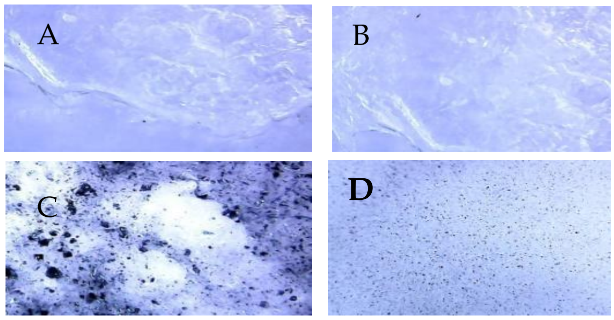

Figure 6 (A) the nano gel, (B) the nano gel mixed with ME Toluene , (c) the magnetic nano gel, (D) the magnetic nano particles inside the magnetic nano gel mixed with ME Xylene.

3.5 Polarized Microscope

Nano gel has been studied using microscopic examination of the polarizer, as this depends on the light microscope into force on the sample and reflected from the sample surface and given optical properties. Thus, samples can be tested by any polarized light vibrates in one direction and it gives more accurate than ordinary light details. The samples were examined polarized microscopy to identify the distribution of magnetic nanoparticles in nano gel before and after mixing with microemulsions. Samples were prepared by mounting them on a glass slide (as shown in Fig. 7).

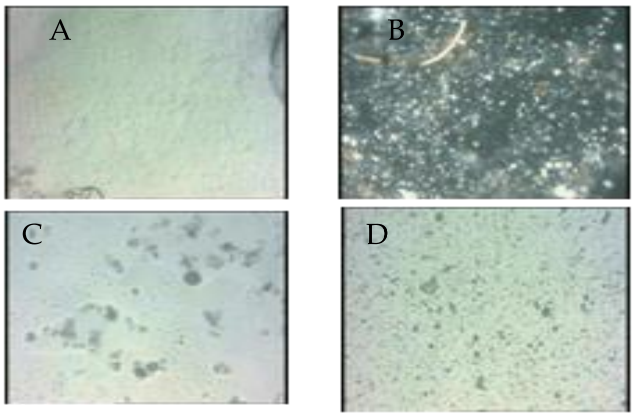

Figure 7. (A) The nano gel power magnification X-63_{PPL}, (B) the nano gel mixed with ME Toluene power magnification X-63_{PPL}, (C) show the magnetic nano particles inside the magnetic nano gel power magnification X-400_{PPL}, (D) the magnetic nano particles inside the magnetic nano gel mixed with ME Xylene power magnification X-160_{PPL}.

4. RESULTS AND DISCUSSION

The cleaning of artworks is a complex and challenging task due to the multiple materials used to construct an art piece (Blee, 2008).The using of nano gel in cleaning and removing undesired layers away of the surfaces proved successful but with lifting a little residues (as shown in Fig. 8).

Figure 8 (left) The area of spot of wax with the circled area showing the area to be treated under day light and (right) area cleaned by removing the wax Spot under day light).

The new nano gel proved it's succeed in removing wax and glue spots which were popular on mural paintings in churches and Monasteries such as the monastery of Saint Jeremiah in Saqqara, the draw backs of using nano gel in cleaning are as follows notes:

a) The nano gel left residues on the treated surface which can attract the dust and turned in to a hard black spots.

b) The surfaces were sticky after treatment

c) The treated area was conducive to the growth of Fungi and Bacteria, which in turn would cause the surface to darken in color (Baglioni, 2012). In an effort to avoid all of the abovementioned draw backs the magnetic nano particles were added through the synthesis of the nano gel which turned The color of nano gel from white in black color The magnetic nano particles gave the nano gel magnetic property which aided in it's removal from the treated surfaces by use of an external magnet which didn't touch the treated surface directly (as shown in Fig. 9).

Figure 9 (left) The area of spot of wax in square area showing the area to be cleaned and (right) area cleaned by removing the wax spot using with magnetic nano gel using an external magnet.

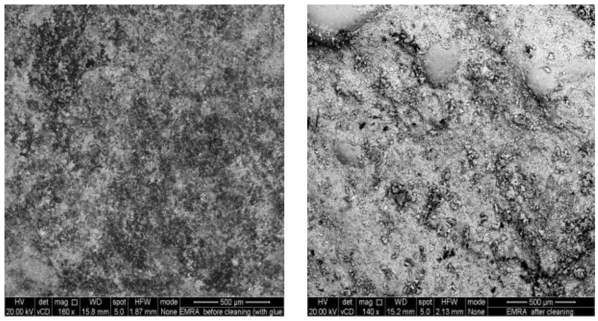

Figure 10 Scanning electron microscope shows the area of spot of wax before treatment with force 100X and (right) area cleaned by removing the wax spot using with magnetic nano gel using external magnet with force 100X.

4.1 The new advantages of using magnetic nano gel

The advantages are:

1. An area can be cleaned without touching the treated surface.
2. The residues of nano gel is limited (as shown in Fig. 10).
3. Manipulation of magnetic nano gel is possible with an external magnet
4. Magnetic nano gel can also be cut and shaped for easily application, allowing much control and flexibility during the cleaning process (Baglioni, 2013).
5. Magnetic nano gel can be easily moved with Tweezers or cut with a knife, so that the size is always appropriate for the area that needs to be cleaned (Bonini, 2007)
6. The availability of mixture with organic materials and microemulsion to increase the activity of removing undesired layers out of the surfaces.

4.2 The mixture with microemulsions

In order to load the nano gel with the microemulsion, The nano gel was immersed into a closed flask containing the microemulsion for Three days on the magnetic stirrer RPM 500 without additional temperature. A variety of additives (different solvents, microemulsions, detergents etc.) can loaded into the nanogel in this way (Blee, 2008). The nano gel mixed with Toluene microemulsion and the magnetic nanogel mixed with Xylene microemulsion. Once the microemulsion has been taken up, it migrates to the surface of the nano gel, that which can then be directly reacted with magnetic nano particles, so that it can be applied to artwork. It is in direct contact to the painted surface. The heterogeneity and pores of the Polyacrylamide allow the microemulsion to move through the gelled network At the Surface, the microemulsion droplets solubilize the material to be removed. The nano gel with microemulsion Toluene became more active in removing the undesired layers from the models of an Egyptian Coptic fresco but lifting residues is more difficult as the nanogel became too soft. The magnetic nano gel was removed using a Permanent external magnet. Since nano magnetic particles have enhanced magnetic properties (Blee, 2008) the magnetic nanoparticles within the nanogel can be manipulated at a distance. This provides a distinct advantage in conservation, as it promotes a step in the treatment where the artifact does not need to be touched (as shown in Fig. 11).

Figure 11 (Left) The area of spot of wax with the circled area showing the area to be cleaned and (Right) area cleaned by removing the wax spot using with magnetic nano gel with external magnet.

On other hand the magntic nano gel after mixture with microemulsion Xylene it is became too soft and greasy so it left a very little amount of magnetic nano particles that can be noticed through portable optical microscope (as shown in Fig. 12).

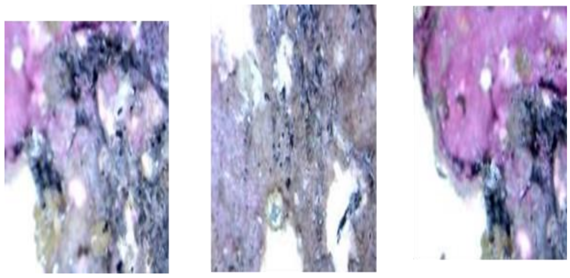

Figure 12 The resides of magnetic nano particles as the magnetic nao gel became soft so it lefts so little magnetic nano particles on the treated area which seen only by Optical microscope.

5. CONCLUSION

In this study, Nano gel was synthesized in a new way for cleaning art works the former problem of leaving residues on the treated surfaces can be prevented by adding the magnetic nano particles through synthesis with 3-octadecyl -1-vinyl imidazolium bromide ($C_{18}VIBr$) and N,N′-Methylenebis acrylamide. The nano gel earned an important property, It is earned a magnetic property as the magnetic nano gel can be removed from the treated surfaces using an external magnet, The mixture of nano gel and microemulsions can improve their role in removing undesired layers from the surfaces but in the case of nanogel with microemulsion Toluene and xylene proved their success. However, a small amount of magnetic nano particle residue was observed through a portable optical microscope only in the case of magnetic nano gel with microemulsion Xylen.

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