Synthesis of calcium hydroxide for heritage conservation

N. T. Ali, R. Kh. Abraham, H. F. Saad, N. K. Jabr, S. S. Hindal, Dh. R. Hussain, and A. M. Sekp

Materials Research Department, Ministry of science and technology, Baghdad, Iraq

E-mail: nagam2105@gmail.

Abstract. This research aims to employ nanotechnology and spectroscopy in the field of heritage conservation. In this research nanomaterial (calcium hydroxide) used in conservation of manuscripts, paintings and relics because of their impact on reducing the pH of paper which is the basic reason for cellulosic fiber break. The study done in stages, where calcium hydroxide had prepared by chemical method and analysis it by using atomic force microscopes (AFM), scanning electron microscope (SEM), x-ray diffraction (XRD), infrared spectroscopy (FTIR) as a first stage. In the second phase, initialize and the preparation of samples and study the properties of synthetic and hardness and microscopic study of the state of fiber cellulosic. Third phase includes spraying the mixture of nanoparticles with the solvent (ethanol or brobanol) and then left to dry and studying their properties again, where the study proved the effectiveness of nano scale mixture to reduce the pH to a long-term period. This new style in dealing with manuscripts is clean and inexpensive.

Keywords: Culture Heritage, Conservation, nanoparticles, Ca (OH)₂

1. Introduction

Nanotechnology is a new technological revolution that touches all aspects of human society and can be applied successfully for the preservation of cultural heritage. In the last 20 years many research has focused on developing appropriate materials to enhance and protect materials as well as many structures and materials have been used with varying degrees of success, but as a result of most of these methods is to increase some of the possibilities in the applications of nanotechnology in the field of preservation of historical cultural heritage[1][9].

Manuscripts are a scientific wealth in various fields of knowledge, which libraries are eager to acquire for a long time. They are keen not only on loss but on damage and destruction, which necessitated studying how to preserve this scientific wealth. The use of nanotechnology in the field of cultural heritage in general is not born of the moment we live in. Nanoparticles were used in the manufacture of works of art nearly four centuries ago, when examining one of the Roman works using X-ray, it contain nanomaterials in the manufacture and installation[2][6].

The use of nanotechnology in the field of protection of cultural and civilization heritage began in 2001 because nanomaterials possess various characteristics (chemical, physical, mechanical and magnetic), where their use does not cause damage to treated materials, as there is no change in paper material, unlike chemicals, to change the properties Paper (yellow spots, swelling). Nanomaterials are used in dry cleaning and de-acidification of leaves[3].

Nanotechnology open the way to restore art and manuscripts works, a new methodology can be created to delay its death and lengthen its life for future generations as it relates to the commemoration of part of human history[4].

Acidity over the years has affected the breakdown of cellulose fibers within the paper, which turns yellow, leading to weakness. The dissolved nanomaterials are sprayed into an alkaline alcohol or even submerged, where it react with the carbon dioxide in the atmosphere to form calcium carbonate that forms (crushed chalk) and is an acid equivalent [5][10].

Ca(OH)₂ + CO₂ → CaCO₃ + H₂O ……….(1)
2. Experimental part
Nanomaterial is prepared in the chemical way. Calcium chloride (Merck 99.9%) was mixed with distilled water and heated to 90 °C, Then sodium hydroxide base (Riedel-fill) is added in the form of gradual drops with 1M concentration in a preparation time (105) minutes and several washings. The produced nanoparticles were examined by XRD, SEM, AFM, FTIR. as following reaction:

\[ \text{CaCl}_2 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + \text{NaCl}_2 \]

After calcium hydroxide preparation, paper samples are prepared in different dimensions depending on measuring type.

3. Materials and Methods
This can be done in three stages:
3.1. Formation of samples and study their structural properties where the surface, hardness, acidity and the status of cellulose fiber was checked by using a microscope.
3.2. Preparation of nanomaterial in the chemical way and procedure laboratory tests (XRD, SEM, AFM, FTIR) and others. Where XRD (Shimadzu XRD-6000, Cu target, Volt.40 kv, curr.30 mA). SEM of model (ZEISS) operated in SE2 mode. The voltage (10.00 kV) and the current were optimized for high resolution image. AFM scanning probe microscope (SPM) depend on scanning tunnelling microscope (STM) technician with high resolution power (0.1-1.0 nm) and high magnification power under atmospherically pressure without vacuum. (Shimadzu FTIR spectrophotometer) was used scanning from 4000 - 400 cm\(^{-1}\) All spectra are a result at normal incidence. infrared spectrum in a short time (~1s).
3.3. Spraying of dissolved nanomaterial by spray gun on paper samples and re-measurement of the first stage after treatment.

4. Results
In reviewing the results of this research, nanomaterial were prepared and the results of the preparation and analysis of the characteristics of the paper forms were integrated before and after treatment for the purpose of a clear comparison by the reader.

4.1. Nanomaterial characteristic
X-ray diffraction showed the standard crystalline trends of calcium hydroxide at the top of the peak [100], as well as some calcium carbonate phases according to standard JCPPS card No. 004-0733 (Fig. 1). The particle size was measured at 80.5 nm, calculated using the Scharr equation.

![Figure (1) XRD analysis of calcium hydroxide](image-url)
To study the surface topography, shape and particle size of the calcium hydroxide particles, an atomic force microscope (AFM) and a scanning electron microscope (SEM) are used for this purpose. AFM Images of the calcium hydroxide nanomaterial in (2 D) showed a homogeneous distribution with surface roughness (1.02) nanometres and a ripple rate (0.274) nanometres as shown in Fig.(2).

Figure (2) two dimensions (2D) AFM analysis of calcium hydroxide

A (3D) AFM image shows the emergence of nanotubes growth in different dimensions (fig.3) that accordance with the SEM results.

Figure (3) three dimensions (3D) AFM analysis of calcium hydroxide
For quantitative information on sample morphology, surface height distributions plan is analyzed, showing that the average diameter was 88 nm, Figure (4).

![Figure (4) Distribution plot of different heights surveyed for calcium hydroxide](image)

Figure (4) Distribution plot of different heights surveyed for calcium hydroxide

A nanotubes in of different dimensions were observed from SEM images of calcium hydroxide with grain size (86 nm). Figure(5) shows the microscopic images of the various magnification of the nanocrystalline calcium hydroxide in various dimensions.

![Figure (5) SEM image in different magnification for calcium hydroxide nanoparticles](image)

Figure (5) SEM image in different magnification for calcium hydroxide nanoparticles
The results of the FTIR analysis also showed the emergence of the main vibration patterns of carbonates, calcium hydroxide and their main peaks (2352, 1408, 1091, 872) cm⁻¹ as shown in Fig. (6).

![FTIR Spectrum for calcium hydroxide](image)

Figure (6) (FTIR) Spectrum for calcium hydroxide recorded for the range (400-4000) cm⁻¹

4.2. Paper samples tests before and after treatment

In this stage, the paper samples are prepared in different dimensions. Mechanical, optical, pH and other spectral measurements are used to determine the degree of variation in all different measurements and their effect on the strength of the cellulose fiber and the increase in pH. Paper samples are examined in the following steps:

4.2.1. Formation of models with dimension (1 * 14 cm) for tensile strength measurement, and (6.3 * 8 cm) for the strength test of rupture.

4.2.2. In this test, the tensile strength and tear strength for paper are measured using (D882 Tensile Prop.) before and after processing. The tensile and tear strength of paper samples of different ages are measured as in Table (1).

| age (Year) | a(50) | b(100) | c(120) | d(150) | e(300) |
|------------|-------|--------|--------|--------|--------|
| Thickness (mm) | 0.091 | 0.070 | 0.70 | 0.060 | 0.070 |
| tensile strength (MP) | 13.3 | 12.0 | 25.3 | 9.89 | 2.78 |
| horizontal tear strength (Mn) | 117.7 | 39.22 | 62.76 | 54.9 | - |
| vertical tear strength (Mn) | 94.1 | 39.22 | 54.9 | 47.07 | - |
4.2.3. This phase included the re-assaying of the tensile strength for all paper samples after treatment. Calcium hydroxide (Ca (OH)\textsubscript{2}) (0.05 gm) was dissolved in (60 ml) propanol, the samples were sprayed for 2-3 minutes (table 2).

Table (2) tensile strength of different paper samples after treatment using propanol mixture

| (age) Year | a(50) | b(100) | c(120) | d(150) | e(300) |
|-----------|-------|--------|--------|--------|--------|
| thickness (mm) | 0.091 | 0.070 | 0.70 | 0.060 | 0.070 |
| tensile strength (MP) | 21.3 | 15.4 | 25.3 | 11.1 | 2.84 |

4.2.4. The solvent type was changed here, a( 0.051 gm) of calcium hydroxide (Ca (OH)\textsubscript{2}) dissolved in (80 ml) of ethanol. The samples were sprayed for 2-3 minutes (table 3).

Table (3) Mechanical measurements of paper after processing using ethanol mixture.

| age( Year) | a(50) | b(100) | c(120) | d(150) | e(300) |
|-----------|-------|--------|--------|--------|--------|
| thickness (mm) | 0.091 | 0.070 | 0.70 | 0.060 | 0.070 |
| tensile strength (MP) | 22.0 | 16.92 | 27.4 | 11.2 | 3.1 |
| horizontal tear strength (Mn) | 203.9 | 47 | 109.8 | 94.1 | - |
| vertical tear strength (Mn) | 141.2 | 47 | 62 | 62.7 | - |

4.3. Dynamic light scattering (DLS): That use( Brookharan Instrument DLS Grapher,) to observe the distribution of the nanoscale size in unit size. Note that the material has an accumulation or a nanocompatibility that varies according to the method of mixing:

4.3.1. Two sample were selected for a different preparation time as shown in table(4).

Table (4) DLS measurement of volume distribution in different preparation time

| DLS distribution of unit volume (nm) % | preparation time (min.) |
|--------------------------------------|-------------------------|
| 280                                  | 60                      |
| 1990                                 | 105                     |

4.3.2 The second sample was selected (105) minutes and soluble in propanol and ethanol. The results of the DLS were as follows Table (5).
Table (5) DLS measurement of volume distribution for different solvents

| Solvent   | DLS distribution of unit volume (nm) % |
|-----------|---------------------------------------|
| ethanol   | 1350                                   |
| propanol  | 772                                    |

4.4. Microscopy images:

The light microscopy of magnification (28 times), measured before and after treatment with calcium hydroxide (Ca (OH)₂). The images showed that the cellulose fibers were broken and distorted in most samples prior to treatment. The gaps and cracks were left in the paper material for the sample. After treatment, the filling of these gaps and the distortions in cellulose fibers were observed as shown in Figure (7).

Figure (7) light microscope images with a magnification (28) times for different ages paper samples (a, b, c, d, e)
4.5. pH paper measure tests
In this test, the paper acidity scale (pH 5.4-7) is adopted. The results are recorded before and after treatment for different paper forms of different ages, as shown in figure (8).

![Figure (8) pH scale with paper sample(E)](image)

In Table (6), a pH values for all paper samples before and after treatment shows the ability of these nanoparticles to reduce acidity of paper while enhancing the pH value of the surface.

Table (6) Calculate the pH value of all samples before and after treatment

| sample | Age | pH (before) | pH (after) |
|--------|-----|-------------|------------|
| a      | 50  | 4           | 4.9        |
| b      | 100 | 5.6         | 5.7        |
| c      | 120 | 5.9         | 6          |
| d      | 150 | 5           | 6.2        |
| e      | 300 | 6           | 6.4        |

5. Conclusions
1-Nanoparticle calcium hydroxide has been successfully prepared using a chemical method with a grain size of less than 100 nanometres in the form of nanotubes.
2-Mechanical tests of paper showed a good improvement of tensile strength and the strength of the two-way tearing for ethanol and propanol mixture.
3-from the results of the light microscope can be observed to support the fiber cellulose paper because of the conglomerate of nanoparticles in the mixture of alcohol and this is consistent with the results of dynamic light scattering.
4-Enhancing sample surface pH after processing with nanomixture.
5.All materials that used in this research are simple and inexpensive.

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