Calcium hydroxide nanoparticles for deacidification of canvas oil paintings

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Abstract

Oil paintings consist of several layers, cellulose is the main components of all types supports of oil painting either it was canvas, paper or wood. The deacidification of canvas oil painting was studied. Cellulose is oxidized by air and hydrolyzed by water vapor. The oxidation process creates acid groups that lower the pH of the canvas which cause the loss of canvas oil paintings mechanical properties. Nanoparticles of Ca(OH)2 can be dispersed in different solvents (e.g. short chain alcohols) and applied on canvas, to balance acidity and long-term protection. The characterization of nanoparticles was carried out by transmission electron microscopy (TEM), regular shape of particles can be seen. Scanning electron microscope (SEM) show stable fiber of cellulose. Canvas samples were artificially aged after deacidification using calcium hydroxide nanoparticles dispersed in short chain alcohols. Cellulose pyrolysis temperature and samples’ pH were evaluated after and before the artificially aging, the applied deacidification treatments raised samples pH to slightly basic values, these values remained constant upon artificial aging.

Keywords: canvas, cellulose, Calcium hydroxide, Nanoparticles, acidification, deacidification

1_Introduction

Canvas as a support for oil paintings was used in ancient Egyptian civilization and introduced in Italy by the end of the 15th century (Bruyn et al. 1986).
Linen used in ancient oil painting supports, the main component of it was the Cellulose (Cataldi et al 2015). Cellulose, a natural polymer consists of several hundred to over ten thousand D-glucose units linked each other by a β-(1,4)-glycosidic bond, which can be presented as linear chains. The degree of polymerization (DP) of native cellulose varies between 7,000 and 15,000 (Baglioni et al 2016). A great number of hydrogen bonds formed between hydroxyl groups either of the same chain (intramolecular bonds) or of different chains (intermolecular bonds), which cause the structure of cellulose (Medronho et al 2012). The main cause of cellulose degradation is both of hydrolysis and oxidation that affected by pH degree, temperature, moisture content and degree of crystallinity and happened for β-(1,4)-glycosidic bonds of cellulose linear chains, which results in the depolymerization of cellulose then the loss of mechanical properties of canvas oil paintings (Calvini 2005; Banait & Jencks 1991; Lundgaard et al 2004). Glucuronic, glucaric, uronic and aldaric acids that promote hydrolysis can found as a result for cellulose oxidation in the so-called spiraling effect (Shanani and Harrison 2002). In the case of canvas, EU-PROPAIN project have shown that levels of trapped organic acids within a frame of easel paintings exceed recommended levels of 1,000 μg/m³ and could cause long-term damage (Grøntoft 2010). Several methods have been proposed and applied in the past decades to counter cellulose degradation and work out a methodology for conservation and restoration of the effects of acidity (Baty et al 2010). Aqueous solutions of bicarbonate (PH = 8.5) or hydroxides such as Ca (OH) 2 (PH = 10.5) were used to treat acidity in paper either by immersion or spraying (Barrow & Sproull 1959), but aqueous treatments lead to swelling of cellulose fibers (Hackney & Ernst 1994). Wei T’O (magnesium methoxy methylcarbonate in a volatile solvent) non-aqueous method used for deacidification treatment (Burgess et al 1992). Academic and technical backgrounds was provided by nanoscience and nanotechnology to formulate innovative systems for conservation and restoration science (Baglioni & Giorgi 2006; Baglioni et al 2009; Blee & Matisons 2008). Numerous methods and applications of nanoscience have been introduced in the conservation of cultural heritage, especially the calcium hydroxide nanoparticles for wall painting consolidation and paper, canvas and wood deacidification (Ambrosi et al 2001; Daniele et al 2008; Rodriguez-Navarro & Ruiz-Agudo 2018; Hansen et al 2003; Giorgi et al 2002; Giorgi et al 2005; Giorgi & Chelazzi & Baglioni 2005; Poggi et all 2011). Carbonates and hydroxides such as calcium and magnesium, are selected for the deacidification of cellulose-based artworks (Baglioni et al 2013; Chelazzi et al 2013).
due to their high reactivity in nanoparticles size they provide a stable neutral environment by rapidly turning into carbonates (Poggi et al 2013). Crystalline calcium carbonate is produced only a few days after treatment with the calcium hydroxide nanoparticles, due to the reaction of hydroxide with carbon dioxide from the air. (Giorgi et al 2010)

In this paper, the effects of the deacidification for canvas with calcium hydroxide nanoparticles dispersed in alcohols obtained and investigated. Low polar solvents (such as short chain alcohols usually used for dispersing nanoparticles). Nanoparticles were characterized by transmission electron microscopy (TEM), scanning electron microscope (SEM). The deacidification efficacy was assessed by pH, TGA upon an aging at high temperature and relative humidity (RH).

2_ Materials and Methods:

2.1. Materials

For nanoparticles syntheses, n-propanol (99%), calcium chloride and sodium hydroxide were used. Linen used as canvas samples, Sulfuric acid (96 %) was used for the acidification of canvas samples. pure water (having a resistivity of 18 MΩ cm) was Used while measuring pH. (Daniele et al 2008).

2.2. Synthesis of Ca(OH)2 Nanoparticles and characterization

The method started from two aqueous solution of calcium chloride (0.3 M) and sodium hydroxide (0.6 M), a surfactant agent (Triton X-100) was added and then the solutions were mixed together maintained at the temperature of about 90˚C, the alkaline solution of NaOH was added “drop by drop” to the CaCl2. (Taglieri 2013; Daniele et al 2008) several deionised water washings were performed to remove the NaCl produced and the surfactant too, we carried out a partially substitution of the initial dispersing medium (water) with 2-propanol (Taglieri 2014; Rodriguez-Navarro& Ruiz-Agudo 2018).

Transmission electron microscopy (TEM) was carried out using high-resolution transmission electron microscopy, HR-TEM (JEM-2100 transmission electron microscope, JEOL, Tokyo, Japan), the dried particles morphology of the samples under study, canvas samples were investigated using a FEI Quanta 200 scanning electron microscope SEM (FEI Company, Eindhoven, The Netherlands) at an acceleration voltage of 20 Kv, after treatment using Ca(OH)2 Nanoparticles.
2.3. Preparation of canvas sample

Linen canvas samples were prepared about 5 pieces each one (about $3 \times 3$ cm) and (Weight $0.256$ g) kept at 25 °C and 50 %RH for 2 days.

2.3.1. pH measurement

Canvas (Blank sample) placed in 20mL of ultrapure water (having a resistivity $8 \text{M} \Omega \text{cm}$ & pH = 7.4) in Closed vial, the vial were kept under stirring for 1 h, before measuring the pH of the extraction using a digital pH meter (Hanna Microprocessor-based Bench pH/mV/°C Meters, PH210) (Poggi et al 2013).

2.3.2. Canvas acidification

Canvas samples were immersed in H2SO4 aqueous solution (pH = 2) for 40 min. The canvas samples were left to dry for 1 day in ambient conditions. Samples' pH were recorded before and after the acidification treatment.

2.3.3. Canvas deacidification

After acidification canvas sample was treated with 10ml of nanoparticle dispersions 8g / L. The treatments were applied using a micropipette, directly dropping on to the samples to wet them as possible, The treated samples were then left to drying and carbonation procedure in the air at 50 % RH (controlled) for 10 days. Then PH were recorded and compared with canvas sample which have acidification treatment.

2.3.4. Thermal Behavior

The thermal behavior of all canvas samples was studied using an (SDT Q600 TA Instrument) sample were placed inside an aluminum pan and analyzed. From the thermal curves, the temperature defined as the maximum of the weight loss derivative, was recorded (Soares 1995 ; Franceschi 2001 ; Sandu et al 2003 ).

2.3.5. Evaluation the treatment of ca(HO)2 nano particles by hydrothermal aging

Blank Samples were treated with (6ml) of nanoparticle dispersions 8g / L. Strong hydrothermal conditions for aging the sample artificially, the samples were placed in a sealed vessel.
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which was put in an oven set at 80 °C. Inside the sealed vessel, the humidity was kept at 75 % using a sodium chloride saturated aqueous solution. Before the aging samples were kept for 1 week at 25 °C and 50 %RH. (Poggi et al 2013). Sample pH and Tmax were monitored before and after the aging.

2.3.6. FTIR analysis

The FTIR spectrometer is used to study textile fibers and the extent of cellulose fiber degradation and also to evaluate treatments (Garside & Wyeth 2003). The measurement was performed on the ORIGIN JASCO infrared spectroscopy in the wave range 400: 4000 cm$^{-1}$. Measurements were made for the blank sample, the sample treated with sulfuric acid, and the sample treated with nano-calcium hydroxide for the deacidification.

3. Results and discussion

TEM image of calcium hydroxide nanoparticles is shown in Figure.1, where the regular shape of particles can be seen, the diameter of the nanoparticles ranged from 5–8 nm.

Fig.1   TEM image of Ca(OH)$_2$ nanoparticles dispersed in n-propanol
**SEM image** in Figure 2 reported some calcium hydroxide particles bound to the cellulose fibers after deacidification by Ca(OH)$_2$ nanoparticles dispersed in n-propanol.

![SEM image of deacidified canvas](image1.png)

Fig. 2 SEM image of deacidified canvas, particles bound to the cellulose fibers which appear stable bar=100µm

**SEM images** in Figures 3 show calcium hydroxide particles bound to the cellulose fibers after aging.

![SEM images of deacidified canvas after aging](image2.png)

(a) ![SEM image of deacidified canvas after aging for 150 hrs](image3.png)
(b) ![SEM image of deacidified canvas after aging for 300 hrs](image4.png)

Fig. 3 SEM images of deacidified canvas after aging for 150 hrs (a) and 300 hrs (b). bar=100µm.
The recorded pH of artificially acidified canvas samples was (pH=3.7). The applied deacidification treatments raised samples pH to slightly basic values (pH = 8). After 10 days at 50 % RH, samples show pH =7

Table 1. pH of canvass samples blank , after acidification and after deacidification.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank sample before acidification</td>
<td>7.4</td>
</tr>
<tr>
<td>Sample after acidification</td>
<td>3.7</td>
</tr>
<tr>
<td>Sample after deacidification</td>
<td>7</td>
</tr>
</tbody>
</table>

The recorded pH of artificially aging for 150 hrs canvas sample was (PH =7) and still recording (PH =7) after aging for 300 hrs, almost reestablished the PH of the original canvas cellulose

Table 2. pH of canvass samples after ca(HO)2 nano particles treatment and after aging.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample after treatment</td>
<td>8</td>
</tr>
<tr>
<td>Sample after aging 150 hrs</td>
<td>7</td>
</tr>
<tr>
<td>Sample after aging 300 hrs</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3. Maximum weight loss temperature (T\textsubscript{max}) from TGA curves of canvass samples before and after acidification ,deacidification and after aging.
<table>
<thead>
<tr>
<th>Sample name</th>
<th>$T_{\text{max}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank sample before acidification</td>
<td>373</td>
</tr>
<tr>
<td>Sample after acidification</td>
<td>360</td>
</tr>
<tr>
<td>Sample after deacidification</td>
<td>363</td>
</tr>
<tr>
<td>Sample after aging for 150 hrs</td>
<td>374</td>
</tr>
<tr>
<td>Sample after aging for 300 hrs</td>
<td>370</td>
</tr>
</tbody>
</table>

First derivative of TGA curves in Figures 5 show that the acidifying treatment decreased the $T_m$ value of cellulose in the canvas samples from 373 to 360°C. The benefits arising from the deacidification treatments to be 363 °C, in terms of resistance to thermal degradation.

After aging for 150 hrs $T_m$ value was 373°C and after aging for 300 hrs $T_m$ value was 370 °C almost reestablished the thermal behavior of the original canvas cellulose.
Figure 5. First derivative of thermogravimetric analysis curves of canvas samples. (a) blank canvas, (b) canvas sample after acidification, (c) canvas sample after deacidification, (d) canvas sample after aging for 150 hrs, (e) canvas sample after aging for 300 hrs.

Characteristic infrared bands of Blank Linen sample (Łojewski et al 2010) is shown in Table 4. Figure 6. The strong band centered at 3442 cm⁻¹ of linen, indicates the presence of hydroxyl groups and is assigned to the stretching ν(OH) vibrations.
These bands are indicative of inter and intermolecular hydrogen bonds. The band at 2900 cm$^{-1}$ is assigned to stretching vibrations of methyl and ethyl groups $\nu$(CH3) and $\nu$(CH2) (cellulose compounds). The broad band at 1640 cm$^{-1}$ is assigned to vibrations of $\nu$(C=C) (lignin compounds), $\delta$(OH), and $\nu$(CO) bonds (derived from carbonyl, or aldehydic, or carboxyl groups). The bands at 1426 and 1381 cm$^{-1}$ are assigned to bending vibrations of methyl and ethyl groups $\nu$(CH3) and $\nu$(CH2) (cellulose compounds). The band at 1054 cm$^{-1}$ is assigned to C–O bridge stretching and C–O–C pyranose ring skeletal vibration ($\beta$-glycoside linkages, cellulose compounds). The band at 612 cm$^{-1}$ is assigned to C-OH out-of-plane bending.

**Table 4.** The functional groups in Linen sample

<table>
<thead>
<tr>
<th>Wave-number (cm$^{-1}$)</th>
<th>Functional group bands</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3442</td>
<td>$\nu$(OH) stretching</td>
<td>Cellulose</td>
</tr>
<tr>
<td>2921</td>
<td>C-H2 and CH3 stretching</td>
<td>(cellulose compounds)</td>
</tr>
<tr>
<td>1640</td>
<td>$\nu$(C=C) vibrations of $\nu$(C=C)</td>
<td>lignin compounds</td>
</tr>
<tr>
<td></td>
<td>Absorbed O-H and conjugated C = O</td>
<td>derived from carbonyl, or aldehydic, or carboxyl groups</td>
</tr>
<tr>
<td>1426 and 1381</td>
<td>$\nu$(CH3) and $\nu$(CH2)</td>
<td>(cellulose compounds)</td>
</tr>
<tr>
<td>1054</td>
<td>C–O bridge stretching C–O–C</td>
<td>($\beta$-glycoside linkages, cellulose compounds)</td>
</tr>
<tr>
<td>612</td>
<td>COH out-of-plane bending</td>
<td>Cellulose</td>
</tr>
</tbody>
</table>
Figures 7&8 Show characteristic infrared bands of the sample treated with sulfuric acid, and the sample treated with nano-calcium hydroxide for the deacidification.

Figure 6. Infrared bands of Blank sample in the wave range 400: 4000 cm\(^{-1}\)
Figure 7. Infrared bands of the sample treated with sulfuric acid in the wave range 400: 4000 cm\(^{-1}\)

Figure 8. Infrared bands of the sample treated with nano-calcium hydroxide for the deacidification in the wave range 400: 4000 cm\(^{-1}\)
Spectrum of the sample treated with sulfuric acid have a change occurred, various carbonyl groups have formed in the next oxidation step or aldehydes ending as carboxyls at stretching between 1160-1057 cm$^{-1}$. Spectrum of the sample treated with nano-calcium hydroxide for the deacidification is similar to the characteristic of blank sample. That means the perfect effect of using calcium nano hydroxide without side effects in the deacidification of canvas.

4. Conclusions

Calcium hydroxide nanoparticles, were used for the deacidification of cellulose-based material such as canvas oil painting. Calcium hydroxide nanoparticles showed high stability and dispersibility even at high concentrations in n-propanol, and did not require any further treatment before the application. A higher surface area grants higher reactivity to acids and carbon dioxide. The latter transforms the excess of hydroxides in carbonates, which are milder deacidifying agents that remain as a buffer against reoccurring acidity. The prepared nanostructures were highly crystalline with average diameter of about 8 nm. The deacidification efficacy of dispersion was evaluated on acidified canvas model samples, artificially aged at high temperature and RH. After the deacidification, the pH of samples was almost neutral and remained constant upon the aging, creating a safe environment in which cellulose depolymerization is inhibited. TGA measurements showed resistance of treated cellulose to thermal degradation. Infrared bands of the Linen treated with nano-calcium hydroxide for the deacidification show that it can return acidification Linen to the original similar to natural linen.

In conclusion, these new formulations expand the palette of available tools for the conservation of canvas oil paintings, these treatments aim to impart an alkaline reserve which will act to buffer the cellulose against the further development of acidity.

References


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