Colloids and Surfaces A: Physicochem. Eng. Aspects 513 (2017) 241–249

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Alcoholic nanolime dispersion obtained by the insolubilisation-precipitation method and its application for the deacidification of ancient paper

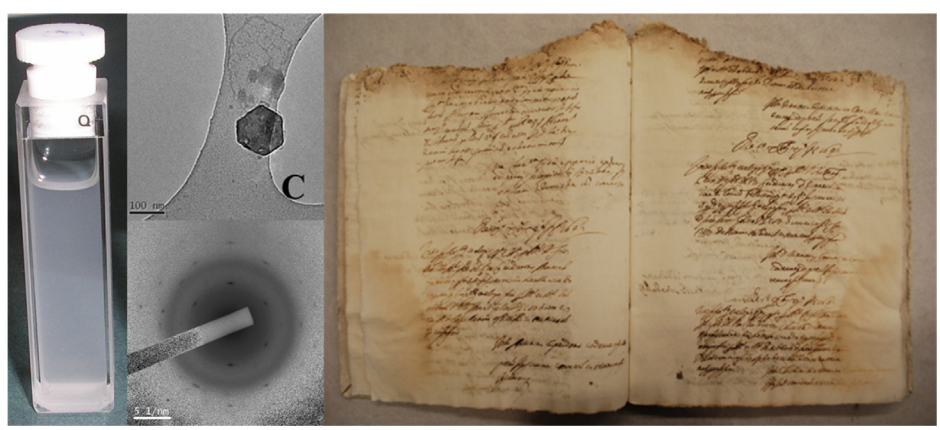
Stella Bastone[a], Delia F. Chillura Martino[a,b,*], Vincenzo Renda[a], Maria Luisa Saladino[a,b], Giovanna Poggi[c], Eugenio Caponetti[a,b]

[a] Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche – STEBICEF, Università degli Studi di Palermo, Parco d' Orleans II, Viale delle Scienze pad.17, Palermo I-90128, Italy
[b] Centro Grandi Apparecchiature-ATeN Center, Università degli Studi di Palermo, Via F. Marini 14, Palermo I-90128, Italy
[c] CSGI & Dipartimento di Chimica 'Ugo Schiff', Università di Firenze, Via della Lastruccia, 3-13, Sesto Fiorentino (FI), I-50019, Italy

HIGHLIGHTS

- A new method for the calcium hydroxide nanoparticles preparation is proposed.
- A correlation between synthesis conditions and stability of the dispersion and particle size and morphology is demonstrated.
- The efficiency of nanolime dispersion in deacidification of an ancient manuscript is tested.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 September 2016
Received in revised form 11 October 2016
Accepted 27 October 2016
Available online 28 October 2016

Keywords:
Nanolime
Insolubilisation-precipitation method
Paper deacidification

ABSTRACT

Nanolime dispersions for the deacidification of ancient paper constitute a valid alternative to the lime traditional ones. Their efficacy depends on particles size, polydispersity and agglomeration that can be controlled depending on the preparation method.

In this work, nanolime preparation by insolubilisation-precipitation method is reported. Nanoparticles dispersed in a water-isopropanol mixture were obtained without any manipulation of the dispersion. The stability of the dispersion together with particle size and morphology were found to be dependent on water to isopropanol molar ratio and on the synthesis temperature.

One of the dispersion was applied on a manuscript to assess its efficiency.

1. Introduction

In the last years, the use of $Ca(OH)_2$ nanoparticles in the field of cultural heritage has been extensively applied for its significant role proposed in the conservation treatments [1–4]. Many works have

* Corresponding author at: Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche—STEBICEF, Università degli Studi di Palermo, Parco d'Orleans II, Viale delle Scienze pad. 17, I–90128, Palermo, Italy.
E-mail address: delia.chilluramartino@unipa.it (D.F. Chillura Martino).

http://dx.doi.org/10.1016/j.colsurfa.2016.10.049
0927-7757/

been published about the application of $Ca(OH)_2$ nanoparticles to restoration of frescoes [5,6], wall paintings [7,8], stones [9,10] as well as to the deacidification of paper and canvas [11,12].

Nanolime is an excellent deacidifying agent for cellulosic materials. It ensures a good physicochemical compatibility with the support, and after its transformation into calcium carbonate, it works very well as an alkaline reservoir and does not originate any undesirable side products [13,14]. One of the most famous and lucky examples is the Vasa warship [15,16] that represents a unique case in the study of ancient waterlogged wood and a challenge for finding new methods for artifacts conservation. Several authors have investigated and reported about the efficacy of nanolime on the deacidification of paper and canvas [12,17–19]. Some of them successfully used nanolime for the deacidification of paper containing iron gall ink. In fact the solvents, usually short chain alcohols mixtures, are highly compatible with components of the inks so that no bleeding are expected [18–20]. It has been already demonstrated that nanolime improved mechanical properties of paper and protected iron gall inked areas from discoloration during artificial aging [19].

It is well known that the efficiency of the treatment depends on nanolime morphology and size distribution, therefore the interest on different methodologies of synthesis arises from the fine control that can be achieved on particles size as well as on their morphology by choosing properly a synthetic strategy. Thus, the efficient methodology of synthesis requires a good mixing of the starting materials and chemical homogeneity of products. Several methodologies of synthesis of $Ca(OH)_2$ nanoparticles have been developed such as solvothermal [16,21], in homogeneous phase [12], micelles assisted [22], microemulsion water/oil assisted [23] or sol-gel [4,24]. However, most of these methods are very sophisticated, time consuming and expensive and a series of manipulations are necessary thus introducing impurities.

The aim of this study is to prepare nanolime dispersions whose particles have low polydispersity, low size and low agglomeration. At the same time, by simplifying the reaction conditions, a scale up of the synthesis can easily be foreseen.

In order to reach this goal, the insolubilisation-precipitation method was used. To our knowledge, this method has not been proposed in literature for $Ca(OH)_2$ nanoparticles synthesis [25]. It involves the preparation of an aqueous solution of calcium hydroxide at the solubility limit, to which a certain amount of 2-propanol is added thus causing the nanolime formation. The final hydroxide concentration is determined by the amount of saturated aqueous calcium hydroxide solution at a given temperature [26].

The main advantage of this method is due to the use of calcium hydroxide that, by alcohol addition, precipitates thus forming the nanolime dispersion in one step. Due to the low polarity of the solvent, the resulting alcoholic dispersion can be used on paper safer with respect to the saturated aqueous solution of calcium hydroxide.

The kinetic stability of the obtained dispersion was investigated by means of UV–Vis Spectroscopy. The particle size, polydispersity, composition and crystal structure were investigated by means of Dynamic Light Scattering (DLS), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and Selected Area Electron Diffraction (SAED).

The nanolime dispersion having the best properties in terms of stability and particle size and polydispersity was used for the deacidification of an ancient manuscript of the *Archivio Storico Diocesano of Palermo*. This document belonged to the fund of the parish of *San Giovanni degli Eremiti (Palermo)*, later absorbed by the *Archivio Storico Diocesano of Palermo*, to which it still belongs. The archival document concerns the sentences dictated by the Grand Court of the Archbishop of Palermo in the years 1642 and 1643. It is divided into two parts. The first part is an index for easy reference: the list is in alphabetical order and it shows the names of those undergoing judgment, along with the page number. The second part of the book reports the actual judgments.

A preliminary diagnostic investigation on the document was performed before the treatment in order to get information on the pH of the paper, the nature of the ink and the conservation state of paper by using pHmetry, Raman and NMR Spectroscopy. The efficiency of the deacidification treatment was evaluated by the pH change.

2. Materials and methods

2.1. Sample preparation

2-propanol and calcium hydroxide were supplied by Merck, Darmstadt, Germany, and were used without any further purification. Water was purified by a Millipore Organex system ($R \geq 18\ M\Omega\ cm$) and de-carbonated by distillation on a substrate of potassium permanganate and sodium hydroxide (Sigma Aldrich).

The used experimental apparatus consists of a four necked flask connected to a six-bulb condenser, thermostated at 15 °C, to an optic-fibre thermometer, to a dropping funnel can and to a nitrogen tank to maintain the system under inert atmosphere. The flask is immersed in a bath of silicone oil at controlled temperature. The homogeneity of the dispersion is ensured by mechanical agitation via a magnetic stirrer.

Appropriate amounts of aqueous solutions of calcium hydroxide close to the solubility limit at 76 °C [26] were prepared by dissolving the appropriate quantity of the hydroxide in de-carbonated water. The solution concentration was 0.980 g/L.

In order to investigate the effect of temperature and of the amount of 2-propanol, the synthesis was carried out in the range 40–76 °C and of 20–90 vol.% of alcohol.

Dispersions A, B and C were prepared at 40, 60 and 76 °C and alcohol amount of 90 vol.%, by adding dropwise the alcohol to an aliquot of the calcium hydroxide aqueous solution. The latter temperature has been selected once known that the boiling temperature of the azeotrope water/2-propanol mixture, whose composition is 12 vol.% in water, is 80.4 °C [27].

Once established the best temperature to obtain a stable dispersion, in order to evaluate the effect of the alcohol amount on the kinetic stability of the suspensions and morphology of nanolime dispersions, two samples were prepared at 76 °C with different alcohol amount, 20 and 50 vol.% respectively, by adding dropwise the alcohol to aliquots of the calcium hydroxide aqueous solution. These two samples were called E and D.

The synthesis has been performed at atmospheric pressure and at controlled temperature as indicated above.

All prepared samples, whose composition is reported in Table 1, were analysed by turbidimetry and DLS. Samples E, D and C were investigated by TEM.

2.2. Sample characterization

The kinetic stability was evaluated via turbidimetric method [28] by computing the stability parameter $\xi = (A_t - A_\infty)/A_t$, as reported in the literature [12,29], where A_t is the absorbance value of the dispersion at a given time and A_∞ is the absorbance value at the end of the observations. UV–Vis spectra were recorded in the range 200–800 nm with resolution of 1.0 nm using a double beam Beckman DU-800 spectrophotometer. The absorbance values selected are those at 600 nm in correspondence of which the absorbance of species in suspension is negligible. ξ value ranges from 0 (complete sedimentation, unstable dispersion) to 1 (no settling of the particles, perfect kinetic stability of the dispersion).

Table 1
Composition of the samples, calcium hydroxide and alcohol concentration, and synthesis temperature. The error on the last digit is reported in parenthesis.

Sample	$[Ca(OH)_2]$[a] (mmol/L)	$[Ca(OH)_2]$[a] (g/L)	$C_{2\text{-propanol}}$ (vol.%)	Synthesis temperature (°C)
A	1.43 (1)	0.106 (1)	90.0 (1)	40 (1)
B	1.41 (1)	0.104 (1)	90.0 (1)	60 (1)
C	1.40 (1)	0.104 (1)	90.0 (1)	76 (1)
D	7.61 (1)	0.563 (1)	20.0 (1)	76 (1)
E	4.43 (1)	0.328 (1)	50.0 (1)	76 (1)

[a] Concentrations are referred to the total volume of hydro-alcoholic solution.

Dynamic light scattering (DLS) measurements were performed at 90° using a Brookhaven instrument equipped with a BI-9000AT digital autocorrelator, a He–Ne 632.8 nm laser source working at a power of 75 mW and a photomultiplier tube detector. Data were obtained in the form of electric field self-correlation function, $C(\tau)$, as function of the decay time, τ, using the software supplied by Brookhaven Inc.

Transmission Electron Microscopy (TEM) micrographs were acquired by using a JEM-2100 (Jeol, Japan) operating a 200 kV accelerating voltage, equipped with an energy dispersive X-ray spectrometer (EDS, Oxford, UK) suitable for element identification. A drop of each dispersion was deposited on a 300 mesh lacey-carbon grid and the solvent was let to evaporate completely before the analysis. The crystalline phase was identified by means of Selected Area Electron Diffraction (SAED) technique. SAED patterns were collected using a CCD camera (Gatan MSC KAF1000).

$^{13}C\ \{^1H\}$ CP MAS NMR spectra were obtained at room temperature with a Bruker Avance II 400 MHz (9.4 T) spectrometer operating at 100.63 MHz for the ^{13}C nucleus. 1800 scans were collected with spinning rate of 5 kHz, a contact time of 1.5 ms and a repetition delay of 2 s. The Hartmann-Hahn condition [30] was optimized on adamantane sample that was also used as the external reference. Samples were placed in 4 mm zirconia rotors and sealed with KEL-F caps using silica as a filler to avoid inhomogeneities inside the rotor. Paper sampling, necessary for NMR analysis, was carried out in such a way to minimally damage the artifact by taking a small stripe (c.a. 10 mg) of the upper edge of the sheet.

pH measurements were carried out with an HANNA Instruments pHmeter pH211 equipped with flat electrode HI1413 according to the TAPPI method [31].

Raman spectra were acquired through a Renishaw inVia Raman Microscope spectrometer equipped with a microprobe (50×) and a CCD detector with a Nd:YAG laser (532 nm). All measurements were performed at room temperature.

3. Results and discussion

3.1. Effect of temperature

The ξ values obtained by turbidimetric measurements for A, B and C dispersions versus time are reported in Fig. 1.

All dispersions showed a decrease in ξ as a function of time. In particular, the kinetic stability is higher for the sample C that was synthesised at higher temperature.

According to Giorgi et al. [12,32] the kinetic stability depends on the particle size and on the dielectric constant of the medium that affect the charge screening among particles. By considering the dielectric constant decrease with temperature [33], it is expected that nanoparticles dispersions prepared at lower temperature should result to be more stable, in opposition to the experimental finding. In order to rationalize the above observation, a DLS investigation was carried out. As an example, the correlation function $C(\tau)$ of C dispersion is reported in Fig. 2 (a).

The points represent experimental data acquired for 10 min, the solid line represents the best fit obtained by using the CONTIN method [34]. The computed function is in fair good agreement with the experimental data. The particle size distribution derived from the above method is reported in Fig. 2(b). The mean particles hydrodynamic diameter is 461 nm with a low degree of polydispersity.

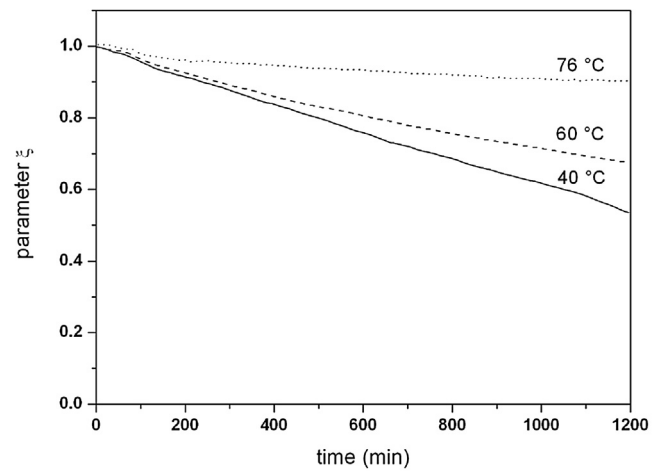


Fig. 1. – Parameter ξ vs. time for dispersions A, B and C obtained at 40, 60 and 76 °C, respectively.

Table 2
Hydrodynamic diameter (Dh), relative variance (Rel. Var.) of dispersion A, B, C, D and E.

Dispersion	Dh (nm)	Rel. Var.
A	1320	1.98
B	823	1.64
C	461	0.07
D	241	1.43
E	317	1.58

The hydrodynamic diameter (Dh) values and the relative variance (Rel. Var.) for the analysed samples are reported in Table 2.

Results clearly indicate that the lower stability observed at lower temperature must be ascribed to the formation of bigger and polydisperse particles. This is consistent with the higher solubility of $Ca(OH)_2$ at lower temperature [35]. On the basis of literature [36], the formation of nanoparticles in solution is the result of the nucleation and growth processes. The competition between the two processes can be rationalized on the basis of the La Mer model [37]. To obtain a monodisperse sample, the stage of nucleation must be as short as possible in such a way to allow a simultaneous formation of all nuclei and well separated from the stage of growth. Being the solubility of $Ca(OH)_2$ lower at higher temperature, it implies that in these conditions the nucleation stage is faster than that at lower temperatures and better separated from the growth process thus bringing to the formation of roughly monodisperse particles.

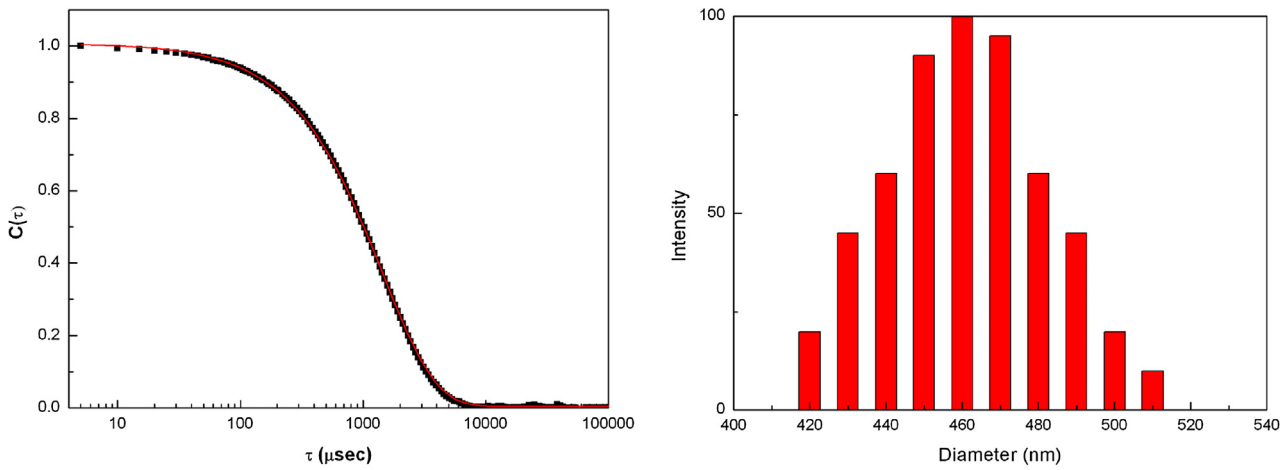


Fig. 2. (a) The correlation function C(τ) vs. τ of the C dispersion accumulated for 10 min (blue points: experimental points, red line: best fit). (b) the particle size distribution obtained by using the CONTIN method. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

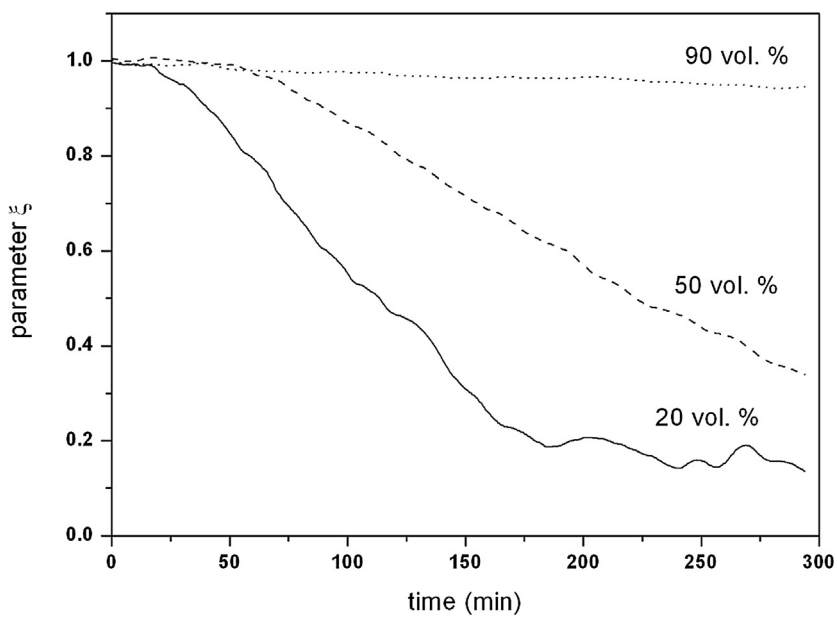


Fig. 3. Parameter ξ vs. time. Sample C: dotted line; sample D: dashed line; sample E: continuous line.

3.2. *Effect of alcohol amount*

Values of ξ as a function of the time for the C, D and E dispersions are reported in Fig. 3.

The kinetic stability increases on increasing the alcohol content. Even by accounting that the overall calcium hydroxide concentration is in the order D > E > C, the observed variation on the stability cannot be ascribed exclusively to the different nanoparticles amount in the dispersions. Therefore, the above observation can be rationalized on the same basis of the effect of temperature. In fact, on increasing the alcohol content the dielectric constant reduces [33] thus inducing a more stable dispersion. Moreover, the solubility of $Ca(OH)_2$ reduces [35] thus, on the basis of the above considerations, promoting the formation of smaller particles.

In order to investigate the effect of particles size on the kinetic stability [29], a DLS investigation was carried out on sample D and E. The hydrodynamic diameter (Dh) values and the relative variance (Rel. Var.) for the analysed samples are reported in Table 2. Results indicate that on increasing the alcohol amount (D < E < C) the hydrodynamic diameter increases but the particles synthesised at lower alcohol amount resulted polydisperse.

Therefore, the morphology of the particles was investigated by TEM. Micrographs at different magnifications of dispersions C, D and E are reported in Fig. 4.

The micrographs show that the nanoparticles in the dispersion C have a hexagonal shape with size of about 150 nm and are not aggregated. The identified hexagonal shape is typical of crystals of calcium hydroxide, as reported in literature [4,12,16,29,38] although some authors have reported the presence of nanolime needle-like [39] and cubic [4]. The size inferred from TEM micrographs is smaller than that evaluated by DLS for the same samples. As it is well known, DLS evaluates the diffusion of particles bearing their solvation shells.

The nanoparticles in the dispersion D have three shapes. Most of them are spherical, not aggregated and have size between 35 and 130 nm, some particles are hexagonal or rectangular with an average size of about 120 and 200 nm, respectively.

The nanoparticles in the dispersion E have an irregular spheroidal shape with a high degree of polydispersity and are

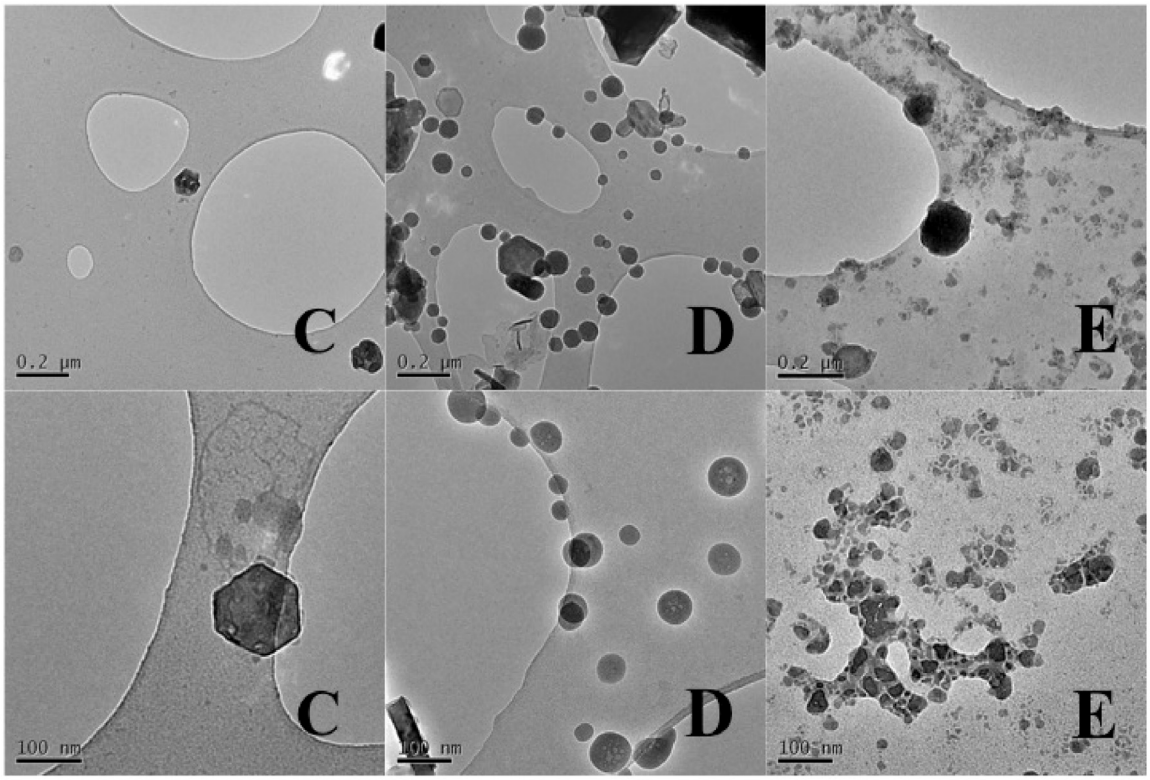


Fig. 4. TEM micrographs of C, D and E dispersions at different magnifications.

aggregated. The particles size ranges from 7 to 37 nm and the size of the agglomerates is bigger than 100 nm.

To our knowledge, the above is the first experimental evidence of spherical nanoparticles formation in solution. In fact, Liu et al. [40] have already synthetized spherical nanolime particles by hydrogen plasma-metal reaction method. The resulting porous nanoparticles had a mean size of 100 nm with a polynanocrystalline structure. The mean size of the nanoparticles here obtained is in line with those of the literature even if they are not porous. Anyway, the conversion of Ca-hydroxide in Ca-2propoxide cannot be excluded a priori. Navarro et al. [41] reported partial transformation of the hexagonal platelike portlandite crystals into pseudomorphs made up of amorphous Ca-alkoxide phase. This process could bring to irregular spheroidal nanoparticles.

In order to exclude the presence of contaminants and to determine the crystalline structure of nanoparticles, the composition and the structure were checked by EDS and by SAED, respectively.

The EDS spectra show peaks of calcium and oxygen from the analysed samples and copper and carbon from the grid used for TEM measurements. The latter element could derive also from some carbonation of the samples during the synthesis or the manipulation. The SAED patterns are superimposable for the three investigated samples. Thus indicating that, independently from the particle shape, the crystalline structure is *Portlandite* $Ca(OH)_2$. The presence of amorphous fringes could be explained by considering the conversion of some $Ca(OH)_2$ into $Ca(C_3H_7O)_2$, as reported in literature [41].

As an example, EDS spectrum and SAED pattern of dispersion E are reported in Fig. 5.

The above findings clearly demonstrate that the alcohol amount affects both the kinetic stability and the particles size and morphology. This could be ascribed to the decrease in solubility of $Ca(OH)_2$ on passing from the system at 20% vol. of alcohol to the one at 90% vol. The higher solubility favours a slower nucleation process not well separated from the growth, thus forming polydispersed particles that, as a consequence of electrostatic factors (higher dielectric constant), agglomerate and undergo a sedimentation process. On increasing of the alcohol amount, the solubility decreases thus favouring a faster nucleation, well separated from the growth process. The almost monodispersed particles are stably dispersed in the medium mainly as a consequence of electrostatic factors.

4. Application of the nanolime dispersion to the ancient document

In order to test the efficacy toward paper deacidification of dispersions prepared by using the insolubilisation-precipitation method, the dispersion C, which showed the best characteristic of stability, has been chosen for the deacidification treatment of a document belonging to the *Archivio Storico Diocesano of Palermo* (Italy) (Fig. 6).

The book was heavily damaged, in particular in the upper part. The top cut of the document has been completely lost, damaged by the water where it probably had remained immersed long enough to complete degradation and disintegration of the affected area. The sheets have, especially in the outer part of the page, large gore zones in which the water has dissolved part of the staining inks thus causing gaps in the text. Finally, there are holes due to the corrosive action of inks [42].

The document was completely restored during a thesis of Academy of Art of Palermo (Italy) [43]. Before the treatment, the characterization of the paper and the inks has been performed by $^{13}C\{^1H\}$ CP-MAS NMR and Raman spectroscopy, respectively.

$^{13}C\{^1H\}$ CP MAS NMR spectrum of the sample, collected following the procedure described in the experimental part, is reported in Fig. 7.

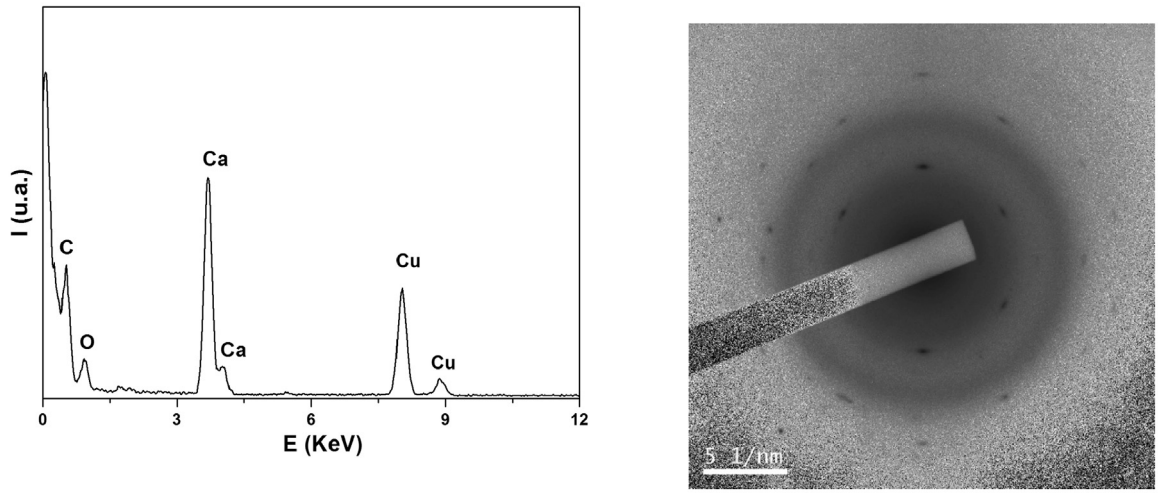


Fig. 5. EDS spectrum (left) and SAED pattern (right) of dispersion E.

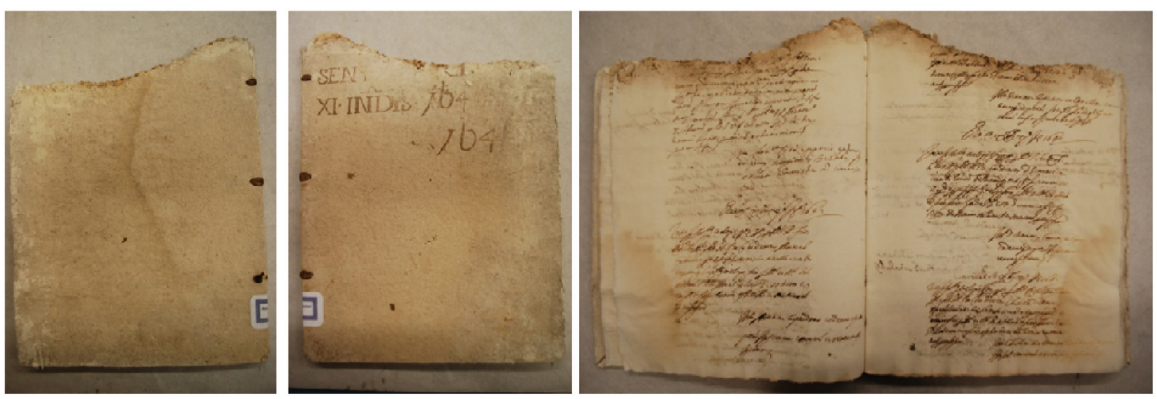


Fig. 6. Document belonging to Archivio Storico Diocesano of Palermo (Italy) used to test the efficacy toward paper deacification of dispersion prepared by insolubilisation-precipitation method.

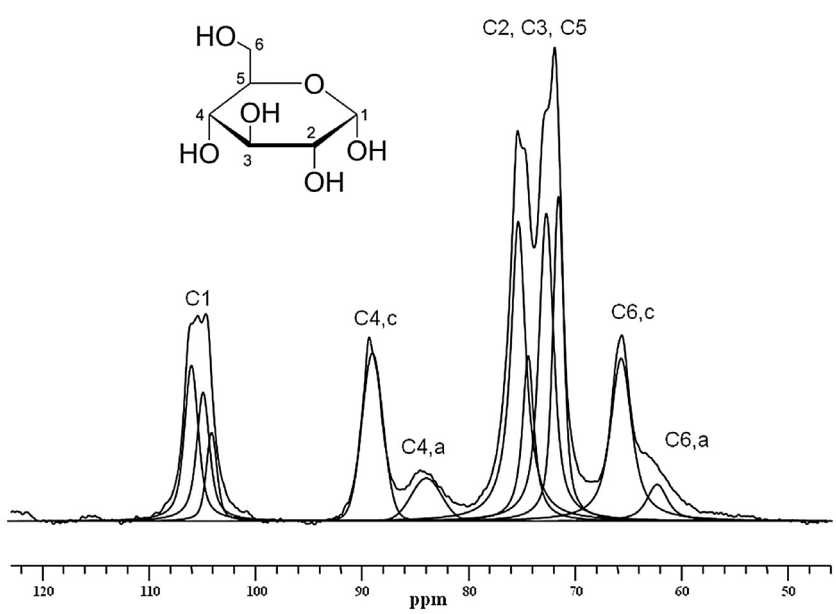


Fig. 7. $^{13}C\{^{1}H\}$ CP MAS NMR spectrum of paper.

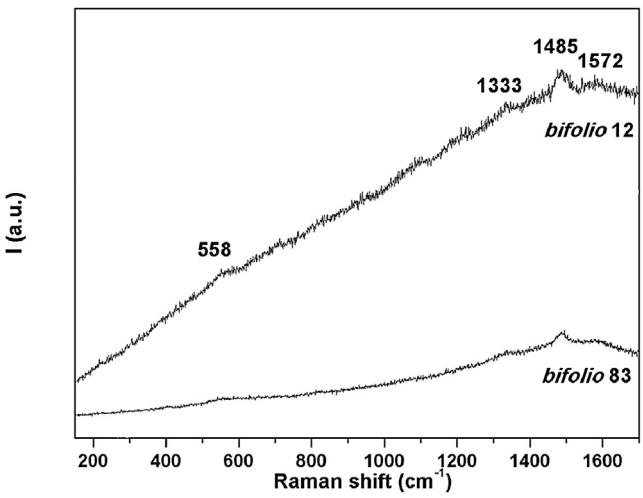


Fig. 8. Raman spectra of black ink of bifolios 12 and 83.

Only the characteristic signals of the cellulose are present in the $^{13}C\ \{^{1}H\}$ CP MAS NMR spectrum of the paper. This indicates that the paper is made from cloths [44]. All chemical shifts were assigned following the literature [44]. An intense signal, assigned to C1, is observed in the range between 110 and 100 ppm. This signal is the convolution of three contributions due to the Iα and Iβ forms of cellulose [45]. The signals at 88.7 and 83.8 ppm are due to the C4 of crystalline and amorphous cellulose, respectively. Peaks between 80 and 70 ppm are due to C2, C3 and C5 carbons. The signals at 67 and 63 ppm are due to C6 of crystalline and amorphous cellulose, respectively. It is well known in literature [45,46] that the conservation state of the paper is correlated to the crystallinity degree of the cellulose fibres. In fact, acid and bacterial degradation increase the crystallinity degree because the amorphous cellulose, more hydrophilic and thus sensitive to changes, is mostly hydrolysed with respect to the crystalline one. In order to deepen this aspect, the crystallinity degree was computed from the areas ratio of the signals at 88.77 and 84.4 ppm due to the C4 of amorphous and crystalline cellulose. Each area has been obtained by deconvolution of the signals by using the Levenberg—Marquardt algorithm, optimized with the Nelder—Mead method [44]. The obtained degree of crystallinity is 71%, indicative of a paper in advanced state of deterioration. In fact, for cotton linter as well as for paper in good state of conservation a value of c.a. 60% is reported [47,48].

In order to identify the nature of inks, Raman Spectroscopy has been applied. Spectra, acquired on several points of some bifolios, are similar. As an example, the Raman spectra of the inks of pages 12 and 83 are reported in Fig. 8.

The spectra are disturbed by the fluorescence background due probably to organic compounds such as glue of the paper. The identification of the bands has been performed by comparison with database [49,50]. The observed bands have been ascribed to Iron gall ink (peaks at 558 and 1485 cm^{-1}) and Carbon black (peaks at 1572 and 1333 cm^{-1}), indicating that the used ink is a mixture of both. The harmful effects of Iron gall ink were scientifically confirmed [42]. When used on paper, this ink causes loss of mechanical and optical properties due to the presence of organic acid that leads to acid hydrolysis of cellulose and to the presence of Iron (II) that catalyzes cellulose oxidation.

In order to evaluate the acidity of the paper, pH measurements were performed in different unwritten zones of every bifolio. The obtained values were in the range 7–8, thus indicating that the paper is slightly alkaline (see Table 3). These values are probably consequence of the action of a possible alkaline reserve due to the presence of calcium carbonate added during the manufacturing of paper. However, as expected, according to the nature of the identified inks, the pH values acquired on the inked part are lower by 1 unit than those acquired in the unwritten zones.

The procedure adopted by restorers on this document was the following: each bifolio has been preliminarily brushed to remove dust and dirt. This procedure was not considered sufficient to efficiently remove the dirt. Therefore each bifolio has been washed with deionized water.

The bifolios 14–23 washed with deionized water have been used as reference. pH measurements were carried out on each bifolio after 24 h, 30 days and one year from the above procedure. The pH values of bifolios 14–23 (only washed) are reported in Table 2.

The pH decreases over time after the washing treatment and indicates that the alkaline compounds are removed by the water. However, it reaches a constant value after 30 days and remains almost unchanged up to 1 year.

On the basis of the above result, even if the paper presented a low acidity, it has been decided to apply the deacidification procedure in order to restore the alkaline reserve lost during the washing preliminary to the restoration work. The deacidification has the purpose to reduce the acidity of the paper and therefore the consequent browning, also ensuring an alkaline buffer against further acids action.

Most of the pages of the document have been deacidificated by means of the traditional method, i.e. each bifolio has been washed in deionized water and then soaked for 1 h in an aqueous solution of calcium hydroxide (1 g/L).

In order to test the nanolime dispersion obtained by using the insolubilisation-precipitation method, the bifolios 26/35, 29/32 and 79/88 have been deacidificated by using the nanolime dispersion C, whose composition is reported in Table 1, following the same procedure: washing in deionized water followed by the soaking for 1 h in nanolime dispersion. The pH measurements have been performed after 24 h, 30 days and 1 year from the two treatments. The pH values, acquired on bifolios 39/46, 56/65 and 67/78 after the deacidification with the traditional method (calcium hydroxide concentration = 1 g/L) and on bifolios 26/35, 29/32 and 79/88 with the nanolime dispersion (calcium hydroxide concentration c.a. 0.1 g/L), are reported in Table 2.

The deacidifying effect is more marked in the bifolios treated with nanolime dispersion even if the amount of calcium hydroxide is 10 times lower than that of the traditional bath. The observed pH trend is similar to that observed for only washed paper but the measured values are still higher than those of untreated paper (only washed). The effect is more relevant on the inked areas. After 1 year the values are unvaried thus indicating that the treatment was effective in establishing an alkaline buffer against acidification.

This finding, on the basis of literature findings on similar systems, can be attributed to the nanoparticles entrapment within the cellulose fibres [51–54]. The obtained results clearly indicate that the nanolime dispersions obtained by the insolubilisation-precipitation method can be successfully used for the deacidification of paper.

5. Conclusions

The present work showed the insolubilisation-precipitation method as an innovative, economic and one-step route for the preparation of nanolime dispersion. The dispersion was obtained adding the 2-propanol in an aqueous solution of bulk $Ca(OH)_2$ under inert atmosphere. The synthesis was performed at different alcohol content (20, 50, 90 vol.%) and at different temperatures (40, 60 and 76 °C), in order to understand the role of alcohol amount or mixture composition and of temperature on the kinetic stability of the dispersions and on the morphology of the nanoparticles.

Table 3
pH values acquired on various bifolio before and after washing with deionized water and after the deacidification (24 h, 30 days and 1 year).

Page	Analysed zone	pH (before)	pH (after 24 h)	pH (after 30 days)	pH (after 1 year)
	Washing with deionised water				
14 (verso)	unwritten	8.6 ± 0.3	8.1 ± 0.3	7.4 ± 0.2	7.2 ± 0.2
23 (recto)	Inked	6.8 ± 0.3	6.5 ± 0.3	6.2 ± 0.2	6.1 ± 0.3
	Deacidification with the Traditional method				
56 (recto)	unwritten	7.1 ± 0.4	8.0 ± 0.3	6.8 ± 0.2	7.4 ± 0.3
78 (verso)	Inked	7.3 ± 0.3	7.7 ± 0.3	7.2 ± 0.3	6.9 ± 0.2
46 (verso)	Inked	6.4 ± 0.2	7.0 ± 0.3	7.2 ± 0.4	6.9 ± 0.2
	Deacidification with the nanolime dispersion				
88 (verso)	unwritten	8.2 ± 0.2	8.7 ± 0.3	8.0 ± 0.3	8.2 ± 0.3
35 (recto)	Inked	6.6 ± 0.2	8.4 ± 0.4	7.4 ± 0.2	7.4 ± 0.2
29 (recto)	Inked	6.2 ± 0.2	8.6 ± 0.2	6.8 ± 0.3	7.0 ± 0.3

The application of the nanolime dispersion having the better structural and mechanical properties to the deacidification of a document of the *Gran Corte Arcivescovile di Palermo* saved in the *Archivio Storico Diocesano of Palermo* (Italy) was followed by pH measures that indicate the efficiency of nanolime in stabilizing the pH values and restoring alkaline reserve.

Acknowledgments

This work is part of the project "Development and Application of Innovative Materials and processes for the diagnosis and restoration of Cultural Heritage—DELIAS"—PON03PE_00214_2 (Programma Operativo Nazionale Ricerca e Competitività 2007–2013).

Thanks are due to Mons. Giuseppe Randazzo and Dr. Giovanni Travagliato, Archivio Storico Diocesano di Palermo, to Arch. Gaetano Renna, Ufficio Beni Culturali Ecclesiastici dell'Arcidiocesi di Palermo, to Dr. Maria Romano, Soprintendenza Archivistica per la Sicilia of Ministero dei Beni e delle Attività Culturali e del Turismo (MIBACT) for their availability.

Thanks are due to Prof. Mauro Pellerito of Regione Siciliana and to Dr. Alba Adelfio of Ditta "Giordano s.r.l." for the availability to test the nanolime in their laboratory during the restoration work.

Thanks are due to Eng. Dr. Bartolomeo Megna of Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali of Università degli Studi di Palermo for the Raman spectra.

TEM-EDS-SAED and NMR experimental data were provided by Centro Grandi Apparecchiature of University of Palermo funded by P.O.R. Sicilia 2000–2006, Misura 3.15 Azione C Quota Regionale.

References

[1] P. Baglioni, D. Chelazzi, R. Giorgi, Nanotechnologies in the Conservation of Cultural Heritage: A Compendium of Materials and Techniques, Springer, 2014 (ISBN: 978-94-017-9302-5).
[2] P. Baglioni, D. Chelazzi, R. Giorgi, G. Poggi, Colloid and materials science for the conservation of cultural heritage: cleaning consolidation, and deacidification, Langmuir 29 (17) (2013) 5110–5122.
[3] R. Giorgi, M. Baglioni, D. Berti, P. Baglioni, New methodologies for the conservation of cultural heritage: micellar solutions, microemulsions, and hydroxide nanoparticles, Acc. Chem. Res. 43 (6) (2010) 695–704.
[4] C. Rodriguez-Navarro, E. Ruiz-Agudo, M. Ortega-Huertas, E. Hansen, Nanostructure and irreversible colloidal behavior of $Ca(OH)_2$: implications in cultural heritage conservation, Langmuir 21 (24) (2005) 10948–10957.
[5] I. Natali, M.L. Saladino, F. Andriulo, D.C. Martino, E. Caponetti, E. Carretti, L. Dei, Consolidation and protection by nanolime: recent advances for the conservation of the graffiti, Carceri dello Steri Palermo and of the 18th century lunettes, SS. Giuda e Simone Cloister, Corniola (Empoli), J. Cult. Heritage 15 (2) (2014) 151–158.
[6] Felice, B., Taglieri, G., Rigaglia, D., Arrizza, L., Romè, V., The byzantine fresco of Dormitio Virginis (12th century): diagnosis and conservation by means of innovative materials. Technart 2015 Conference: Non-destructive and microanalytical techniques in art and cultural heritage. Catania (Italy), April 27–30, 2015.
[7] L. Dei, B. Salvadori, Nanotechnology in cultural heritage conservation: nanometric slaked lime saves architectonic and artistic surfaces from decay, J. Cult. Heritage 7 (2) (2006) 110–115.
[8] P. D'Armada, E. Hirst, Nano-lime for consolidation of plaster and stone, J. Archit. Conserv. 18 (1) (2012) 63–80.
[9] V. Daniele, G. Taglieri, Nanolime suspensions applied on natural lithotypes: the influence of concentration and residual water content on carbonatation process and on treatment effectiveness, J. Cult. Heritage 11 (1) (2010) 102–106.
[10] S.A. Ruffolo, M.F. La Russa, P. Aloise, C.M. Belfiore, A. Macchia, A. Pezzino, G.M. Crisci, Efficacy of nanolime in restoration procedures of salt weathered limestone rock, Appl. Phys. A 114 (3) (2014) 753–758.
[11] R. Giorgi, et al., Nanoparticles of Mg $(OH)_2$: synthesis and application to paper conservation, Langmuir 21 (18) (2005) 8495–8501.
[12] R. Giorgi, L. Dei, M. Ceccato, et al., Nanotechnologies for conservation of cultural heritage: paper and canvas deacidification, Langmuir 18 (21) (2002) 8198–8203.
[13] J. Bogaard, P.M. Whitmore, Effects of dilute calcium washing treatments on paper, J. Am. Inst. Conserv. 40 (2) (2001) 105–123.
[14] A. Lienardy, P. Van Damme, Practical deacidification, Restaurator 11 (1) (1990) 1–21.
[15] R. Giorgi, D. Chelazzi, P. Baglioni, Nanoparticles of calcium hydroxide for wood conservation. The deacidification of the Vasa warship, Langmuir 21 (23) (2005) 10743–10748.
[16] G. Poggi, N. Toccafondi, D. Chelazzi, P. Canton, R. Giorgi, P. Baglioni, Calcium hydroxide nanoparticles from solvothermal reaction for the deacidification of degraded waterlogged wood, J. Colloid Interface Sci. 473 (2016) 1–8.
[17] G. Poggi, R. Giorgi, N. Toccafondi, et al., Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper, Langmuir 26 (24) (2010) 19081–19084.
[18] G. Poggi, P. Baglioni, R. Giorgi, Alkaline earth hydroxide nanoparticles for the inhibition of metal gall ink corrosion, Restaurator 32 (2011) 247–273.
[19] S. Sequeira, C. Casanova, E.J. Cabrita, Deacidification of paper using dispersions of $Ca(OH)_2$ nanoparticles in isopropanolo, J. Cult. Heritage 7 (2006) 264–272.
[20] E. Stefanis, C. Panayiotou, Deacidification of documents containing iron gall ink with dispersions of Ca $(OH)_2$ and Mg $(OH)_2$ nanoparticles, Restaurator 31 (1) (2010) 19–40.
[21] G. Poggi, et al., Calcium hydroxide nanoparticles for the conservation of cultural heritage: new formulations for the deacidification of cellulose-based artifacts, Appl. Phys. A 114 (3) (2014) 685–693.
[22] G. Taglieri, C. Mondelli, V. Daniele, E. Pusceddu, G. Scoccia, Synthesis, Textural and structural properties of calcium hydroxide nanoparticles in hydro-alcoholic suspension, Adv. Mater. Phys. Chem. 4 (2014) 50–59.
[23] A. Nanni, L. Dei, $Ca(OH)_2$ nanoparticles from W/O microemulsions, Langmuir 19 (2003) 933–938.
[24] O. Darčanova, B. Aldona, K. Aivaras, Sol–gel synthesis of calcium nanomaterial for paper conservation, Chemija 26 (1) (2015) 25–31.
[25] D. Chelazzi, G. Poggi, Y. Jaidar, N. Toccafondi, R. Giorgi, P. Baglioni, Hydroxide nanoparticles for cultural heritage: consolidation and protection of wall paintings and carbonate materials, J. Colloid Interface Sci. 392 (2013) 42–49.
[26] Mellor J. W. A comprehensive treatise on inorganic and theoretical chemistry vol. III 1972, 677.
[27] R.B. Lebo, Properties of mixtures of isopropyl alcohol and water, J. Am. Chem. Soc. 43 (1921) 1005–1011.
[28] G. Gabrielli, F. Cantale, G.G. Guarini, Adsorption of amphiphilic mixtures and stabilization of suspensions of hydrophobic solids in water, Coll. Surf. A 119 (2) (1996) 163–174.
[29] M. Ambrosi, L. Dei, R. Giorgi, C. Neto, P. Baglioni, Colloidal particles of $Ca(OH)_2$: properties and applications to restoration of frescoes, Langmuir 17 (2001) 4251–4255.
[30] S.R. Hartmann, E.L. Hahn, Nuclear double resonance in the rotating frame, Phys. Rev. 128 (5) (1962) 2042.
[31] T. Ray Charles, Flat electrode measurement of pH in printing papers, Tappi 55 (3) (1972) 393–395.
[32] E. Fratini, M.G. Page, R. Giorgi, H. Cölfen, P. Baglioni, B. Demé, T. Zemb, Competitive surface adsorption of solvent molecules and compactness of agglomeration in calcium hydroxide nanoparticles, Langmuir 23 (5) (2007) 2330–2338.
[33] G. Akerlof, Dielectric constants of some organic solvent-water mixtures at various temperatures, J. Am. Chem. Soc. 54 (11) (1932) 4125–4139.
[34] B.J. Berne, R. Pecora, Dynamic Light Scattering, Wiley, New York, 1976, pp. 41155–41159 (ISBN: 0–486-41155-9).

[35] S. Ali, A.S. Ali, Determination of thermodynamic parameters from the dissolution of calcium hydroxide in mixed solvent systems by pH-metric method, J. Phys. Chem. Biophys. 3 (2013) 116.
[36] M. Bonini, P. Baglioni, D. Chelazzi, Nanoscience for the conservation of works of art, Nanosci. Nanotechnol. 28 (2013) 315.
[37] V.K. LaMer, R.H. Dinegar, Theory, production and mechanism of formation of monodispersed hydrosols, J. Am. Chem. Soc. 72 (11) (1950) 4847–4854.
[38] V. Daniele, G. Taglieri, R. Quaresima, The nanolimes in cultural heritage conservation: characterisation and analysis of the carbonatation process, J. Cult. Heritage 9 (2008) 294–301.
[39] D. Valeria, G. Taglieri, Synthesis of $Ca(OH)_2$ nanoparticles with the addition of Triton X-100. Protective treatments on natural stones: preliminary results, J. Cult. Heritage 13 (1) (2012) 40–46.
[40] T. Liu, Y. Zhu, X. Zhang, T. Zhang, T. Zhang, X. Li, Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method, Mater. Lett. 64 (23) (2010) 2575–2577.
[41] C. Rodriguez-Navarro, I. Vettori, E. Ruiz-Agudo, Kinetics and mechanism of calcium hydroxide conversion into calcium alkoxides: implications in heritage conservation using nanolimes, Langmuir 32 (2016) 5183–5194.
[42] J. Kolar, M. Strlic, M. Budnar, J. Malesic, V.S. Selih, J. Simcic, Stabilisation of corrosive iron gall inks, Acta Chim. Slovenica 50 (4) (2003) 763–770.
[43] Trainito M. Deacidificazione della carta. Confronto di due metodologie d'intervento, Bachelor thesis on paper conservation. Accademia di Belle Arti di Palermo, 2012.
[44] N. Proietti, D. Capitani, E. Pedemonte, B. Blümich, A.L. Segre, Monitoring degradation in paper: non-invasive analysis by unilateral NMR Part II, J. Magn. Reson. 170 (1) (2004) 113–120.
[45] M. Paci, C. Federici, D. Capitani, N. Perenze, A.L. Segre, NMR study of paper, Carbohydr. Polym. 26 (4) (1995) 289–297.
[46] D. Attanasio, D. Capitani, C. Federici, M. Paci, A.L. Segre, Electron paramagnetic resonance and ^{1}H and ^{13}C NMR study of paper, ACS Symp. Ser. 598 (1995) 333.
[47] A. Spinella, D. Capitani, S. Bastone, E. Caponetti, Solid State NMR to Characterize Paper and Parchment Samples from a 16th Century Book, Conservation Science for the Cultural Heritage, 208–217, Ed., Springer, Thessaloniki, Greece, 2012.
[48] Rajai H. Atalla, David L. Vanderhart, Native cellulose: a composite of two distinct crystalline forms, Science 223 (4633) (1984) 283–285.
[49] J.A. Nelder, R. Mead, A simplex method for function minimization, Comput. J. 7 (4) (1965) 308–313.
[50] http://www.chem.ucl.ac.uk/resources/raman/index.html.
[51] D. Li, Q. He, Y. Cui, K. Wang, X. Zhang, J. Li, Thermosensitive copolymer networks modify gold nanoparticles for nanocomposite entrapment, Chem.-A: Eur. J. 13 (8) (2007) 2224–2229.
[52] Y. Cui, C. Tao, Y. Tian, Q. He, J. Li, Synthesis of PNIPAM-co-MBAA copolymer nanotubes with composite control, Langmuir 22 (19) (2006) 8205–8208.
[53] D. Li, Q. He, J. Li, Smart core/shell nanocomposites: intelligent polymers modified gold nanoparticles, Adv. Colloid Interface Sci. 149 (1) (2009) 28–38.
[54] D. Li, Q. He, Y. Cui, J. Li, Fabrication of pH-responsive nanocomposites of gold nanoparticles/poly (4-vinylpyridine), Chem. Mater. 19 (3) (2007) 412–417.