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NANO MAGNESIUM HYDROXIDE VIS CALCIUM PROPIONATE IN PAPER DEACIDIFICATION: A COMPARATIVE STUDY

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Abstract:

Historical papers such as documents, manuscripts, and early printed book pages, exposed to different conditions during storage (such as humidity and air pollution) may lead to degradation and embrittlement, due to depolymerization of cellulose fibres caused by acidity. As a result, one of the most important conservation measures is paper deacidification to protect historical papers from damage. For this purpose, two deacidification agent were used, calcium propionate in aqueous media, and Nano Magnesium Hydroxide in nonaqueous media. A comparative study of the efficiency of these eco- friendly deacidification methods has been conducted on two types of papers (natural acidity book paper and Whatman paper no.1) with elaborate findings. To assess the efficacy of the two deacidification agents on paper stability, Scientific analyses have been carried out including scanning electron Microscope, pH measurements, atomic absorption spectroscopy, colourimetry, Mechanical proprieties (tensile strength, double folds), FTIR and XRD. Both methods exhibit highly efficient in acid neutralization with a positive impact on the chemical and physical properties of the tested paper after accelerated aging. The examined treated samples confirmed how these methods suppressed the degradation of cellulose compared with the control samples enhances paper durability by introducing, moderate alkalinity (pH = 6.8-7.5 for acidic paper; 8.4-8.9 Whatman paper) and sufficient alkaline reserve. There is also a slight color variation (E = 2.06 MH treated samples); Medium color variation (E*= 4.48 CP treated samples). Thermal aging indicates that the paper treated with these methods has enhanced stability. The findings indicate that $Mg(OH)_2$ nano particles exhibits a better impact on the mechanical and chemical properties of treated paper than Calcium propionate.*

1. Introduction

Paper documents stored in archives and libraries become so fragile over time. One of the most dominant mechanisms that causes the shortening of paper documents life is acid hydrolysis, which attacks the paper fibers and breaks down the cellulose chains [1]. Papers produced in the middle of the 19th century from wood materials were created under conditions that ranged from almost neutral to slightly alkaline, which leads to rapid deterioration of the paper if it is exposed to improper storage conditions [2]. Several factors contribute to the acidic-catalysed degradation of paper, including acidic components added to the cellulose fibers during papermaking, such as the use of natural alum in sizing or residual of bleaching materials. Other external factors, such as extremes of temperature, relative humidity, light exposure [3,4]; and atmospheric gaseous pollutants, especially these of sulfur dioxide, play a very important role in the damage of paper [5]. As a result, the paper's primary components, cellulose, lignin, and hemicellulose, oxidize and form acidic degradation products that break down through the fibers, causing a substantial decrease in paper strength. There are two main chemical degradation pathways of paper: acid-catalyzed hydrolysis and oxidation [6]. It is reported that dissociation of the cellulose polymeric structure, as well as lignin, is commonly caused by acidic hydrolysis of the glucopyranose rings and oxidation [7]. The hydrolysis of a cellulose macromolecule engages in the breaking of the β(1→4) bonds between specific D-glucose units [8]. Hydrolysis results in cellulose degradation when polysaccharides are degraded to form oligosaccharides and monosaccharides. The shortening of the cellulose chain is expressed in the form of a decrease in the degree of its polymerization (DP) [9]. Above all, the glycosidic bonds of cellulose can only ensure its stability in a slightly alkaline or neutral environment, while increasing the hydronium concentration in an acidic medium can accelerate the hydrolysis

process that breaks the glycosidic bond [10]. On the other hand, hydrolysis and oxidation processes catalyze each other [11]. The formation of carbonyl groups because of oxidation weakens the glycosidic bonds, thus making them more susceptible to hydrolysis [12,13]. Hydrolysis of the glycosidic bonds results in the creation of new end-groups (reducing), which are sensible to oxidation. Furthermore, water, being the byproduct of cellulose oxidation, may be a substrate for hydrolysis, which empowers the transportation of protons, radicals, and oxygen in dynamic shapes within the paper structure [14]. Oxidation, therefore, contributes to the creation of carboxyl groups, thus promoting acid hydrolysis [15]. These processes can be hindered by a deacidification treatment, which is the most effective preference for preserving our paper and book cultural relics [16]. Deacidification is a chemical procedure that includes neutralizing acids and creates an alkaline buffer in the treated paper to prevent future acidity [17]. Several deacidification methods and products have been created and used [14]. The effectiveness of these methods must be assessed according to several criteria [18]. The ability to neutralize the acidic content of paper and deposit an alkaline buffer encounter further acidity; no visible alteration of paper substrate; improve or at least Maintain the mechanical properties of the paper [19]. Since The aqueous solution of calcium hydroxide is one of the most common and broadly used methods for paper deacidification in Egypt and due to concerns regarding the aqueous and non-aqueous solubility of alkaline earth hydroxide, recent studies have focused on the use of other alternatives to avoid the disadvantages of calcium hydroxide. The authors had presented in previous research two alternatives that avoided the disadvantages of calcium hydroxide method [20]; based on the same principle, two echo-friendly methods of de-acidification have been selected for a comparative study and evaluated in situ to provide several options that can be used according to the paper condition. The two methods are the aqueous solution of calcium propionate and the non-aqueous dispersion of magnesium hydroxide nanoparticles ($Mg(OH)_2$). Calcium propionate was presented in 1990 as a deacidification method, which is characterized by its high solubility and non-toxicity as it is permitted for use in the food industry. Several studies reported an increase of pH values and sufficient alkaline reserve after treatment with CP [21,22]. A new novel method using supercritical carbon dioxide (CO_2) containing calcium propionate was investigated; it exhibits a sufficient deacidification effect in addition to enhancing the mechanical properties of paper [23]. On other hand number of tests carried out on strains cultured in suitable media reported that saturated solutions (3.5 g/l) of calcium propionate in alcohol inhibit the fungal growing [24]. Nano Technology has great importance in the field of paper preservation; number of studies proposed new methods based on the use of nanoparticles in deacidification of paper such as suspension of nanoparticles dispersions of $Ca(OH)_2$ in alcohols [25]; and magnesium hydroxide NP, which reported [26,27] effective deacidification agents, including their use of items inscribed with iron gall ink. When evaluating the application of magnesium compounds, we must mention research revealing its stabilizing capabilities in relation to cellulose subjected to oxidizing treatment, notably in terms of the potential to reduce free radical concentrations [28-31]. Sequeira et al. [32] synthesized magnesium hydroxide $Mg(OH)_2$ nanoparticles and assessed their use in paper conservation. Stefanis and Panayiotou [33] deacidified paper with micro and nano particulate dispersions of $Ca(OH)_2$ or $Mg(OH)_2$ and reported evidence of cellulose breakdown when unaged papers were treated with micro particles; these adverse effects were attributed to excessively high pH. However, certain investigations have shown a limited homogeneity in the distribution of the alkaline reserve [34]. On the contrary, the nanoparticles once transported to the paper are immediately ready for de-acidification or buffering. Avoid exposing the paper to high alkaline levels during the conversion to carbonates [35]; it has recently been established that magnesium carbonate slows the oxidative degradation of cellulose fibers induced by light exposure [36]. The aim of this research is to study the effects of two worldwide common deacidification methods on the chemical and physical properties of paper to be applied in Egyptian archives and libraries based on confirmed assessment findings under Egyptian environmental conditions, taking into consideration choosing two methods available on the Egyptian market at a reasonable price. The following deacidification treatments were investigated: calcium propionate with microsized particles and magnesium hydroxide $Mg(OH)_2$ nanopowder. $Mg(OH)_2$ was characterized using X-ray diffraction and transmission electron microscopy (TEM) [37]; The two methods indicated have been successfully applied to several types of paper samples, including Whatman filter paper and several pages remaining from naturally acidic book paper from the nineteenth century. Changes promoted in paper as a result of these treatments were measured and registered according to the consideration of the following criteria: changes in the surface of the paper through SEM-EDX inspection, changes in the chemical structure of the cellulose through Fourier transform infrared spectroscopy (FTIR), crystallinity index by X-ray diffraction, changes in color through Spectro colorimetric measurements, changes in pH of the paper, alkaline reserve by atomic absorption, and changes in the mechanical properties of paper. Measurements were carried out before and after the treatments. Test results gave an indication of the benefits and potential problems of each treatment.

2. Materials and Methods

2.1. *Materials*

2.1.1. Chemicals

All chemicals were reagent grade and used as purchased with no additional purification. Nano Magnesium Hydroxide, $Mg(OH)_2$ NP nano (CAS No. 1309-42-8, powder <100nm particle size (laser PSA); 99.8% trace metals basis; mp:350˚C (lit.); surface area 94.8 m^2/g; Molecular weight 58.32 g/mol (Sigma -Aldrich). Calcium propionate, $C_6H_{10}CaO_4$ (CAS No. 4075-81-4, 95%, Molecular weight 186.22g/mol; Sigma-Aldrich). Isopropyl alcohol (2 Propanol), $(CH_3)_2CHOH$ Molecular weight 60.10. Deionized Water ($R \geq 18$ MΩ cm).

2.1.2. Preparation procedure

2.1.2.1. *$Mg(OH)_2$ nanoparticles dispersion*

To prepare 0.5 wt/wt% non-aqueous dispersion of nano-$Mg(OH)_2$, approximately 5 g of $Mg(OH)_2$ nanopowder were

dispersed in 1 liter of 2 propanol (pH = 6.3), and both ultrasonication and vigorous stirring were continuously applied during the preparation as well as during dispersion for 30 minutes [38, 25]. A pH value of 9.2 was obtained in the prepared solution.

2.1.2.2. *Calcium propionate solution*

To prepare a 5% aqueous solution of calcium propionate, approximately 5 g/100 ml were dissolved in deionized water (pH = 6.9) with continuous stirring until the milky white solution became clear. A solution of pH value 8.9 was obtained [21,32].

2.1.3. Paper samples

2.1.3.1. *Whatman® paper*

Whatman® paper—Ashless Quantitative—100 Circles/Box—24 cm—Cat No. 1442-240 42—Whatman International Ltd., Maid Stone, Made in England. Supplied by Al Gomhoria Company, Egypt. pH= 6.8-7.

2.1.3.2. Acidic *Book Paper*

Acidic Book paper printed in 1896; paper grammage 60 g/m^2, 75% groundwood pulp and 25% chemical pulp, pH = 4-4.5. Several pages remaining of an acidic book (found neglected with a hawker on a sidewalk) were chosen to conduct experimental study to provide an assessment of the treatment that is comparable with that of the original paper at libraries and archives.

2.1.4. Paper sample preparation

Samples were cut into sizes of 18 × 1.5, 12 × 1.5, and 2.5 cm in diameter. This was carried out according to ISO 7213. The samples conditioned at 50% RH and 23°C [37]. The samples were immersed in nano-$Mg(OH)_2$ dispersion or $C_6H_{10}CaO_4$ solution for 30 minutes and vacuum dried. Subsequently, all the samples were conditioned at laboratory temperature of 23 °C and 50% RH for 48 hours.

2.1.5. Accelerated degradation.

Samples were thermally aged by keeping them for 2 weeks in a drying oven at 105 ± 2 °C in accordance with TAPPI test T 453ts-63, as every three days of accelerated aging equivalent 25 years of natural aging.

2.2. *Methods*

2.2.1. Characterization of $Mg(OH)_2$ NP

The phase composition and crystallinity of the magnesium hydroxide particles were analyzed by X-ray diffraction (XRD) using an X-ray diffractometer Brucker DS advanced equipped with a Cu Kα (λ = 1.54Å) source. About 1 mg of the dried $Mg(OH)_2$ particles were deposited as powder onto a plexiglass sample container, and the XRD patterns were recorded at a scan rate of 2°/min under nitrogen. The morphology and size of the particles were studied by a transmission electron microscope, TEM (JEOL, JEM-2100, Tokyo, Japan) apparatus operating at 80 KV. The suspension of $Mg(OH)_2$ was sonicated for 10 minutes by Ultrasonic Crop., New Jersey, USA; then a few drops were loaded on a carbon-coated grid and left to dry. Then the grid loaded with the sample was examined by HR-TEM.

2.2.2. Analysis of paper samples

To compare the effects of the two deacidification methods on the characteristics of the treated paper samples, several investigations and analyses were conducted. pH measurements were collected by HI 2211 benchtop pH meters (Hanna instruments) according to the TAPPI standard using the procedure of cold-water extraction; a 1 gm sample of paper was extracted in 70 mL of distilled water (pH = 7). Alkaline buffer: to determine the concentration of magnesium or calcium existing as an alkaline buffer in the treated paper samples, an atomic absorption spectroscopy method was performed using a Unicam AAS Model spectrophotometer in flam mode, burning by acetylene air following TAPPI test methods T266–T623 om-94. Scanning Electron Microscope (SEM/EDX), the changes in the surface morphology of the treated paper sample were observed using SEM and compared with the control sample. The SEM instrument, FEI Quanta 3D 200i, was operated under the following conditions: low vacuum for acceleration voltage 20 KV and large field detector with working distance from 16.4 to 19 mm. Also, an analysis of the magnesium and calcium amounts within the paper fibers was performed using the energy dispersive X-ray (EDX) unit. The color characteristics of the paper samples provide us with important information about the color change of treated paper samples. It has been found that the most proper colorimetry system for paper deacidification assessment is CIE Lab. This color system determines color using 3 color coordinates, which are L (lightness), a (red-green axis), and b (yellow-blue axis). The processes of chromatic characteristics change after deacidification before and after aging were investigated according to ASTM D 1925 using (Optimatch 3100 SDL) spectrophotometer. For the bookpaper samples, the color changes were measured and expressed as ΔL, Δa, and Δb. The total color changes (ΔE). As for the Whatman paper, the whiteness and yellowness index were detected and expressed as ΔW, ΔY, and the total color change (ΔE). The result was interpreted according to Drzewinska [39,40]. Tensile strength (TS) was obtained by (Tinius Olsen, Tensile Tester), according to standard EN ISO 13934-1; 1999 Maximum Force & Elongation-Strip method. A set of 10 paper strips (120 × 20 mm size), previously aged at 25 °C and 50% R.H. for 24 h, was investigated. The estimated error is about 5%. The results obtained from papers treated with the $Mg(OH)_2$ nanoparticles were compared with paper samples treated with calcium propionate solution. number of double folds was collected using shopper folding tester according to ASTM D 2176. FTIR analysis, the chemical structural change in the surface of the treated paper samples was estimated using FTIR (model Shimazu IR prestige 21) using the KBr technique. The FTIR light source was used in the middle infrared range; the spectrum collection was obtained using 32 scans, from 4000 to 400 cm^{-1}, and compared to the control samples. The spectra were baseline corrected and normalized using maximum-minimum normalization to the highest peak of cellulose at 1030 cm^{-1}. Crystallinity index, using x-ray diffraction analysis, data were obtained using an X-ray diffractometer (Brucker DS Advanced). The instrument is equipped with a copper anode, producing Cu K X-rays using an accelerating voltage of 45 kV with a tube current of 30 mA. The goniometer scanned a 2Θ range between 10° and 58° with a scan rate of 0.026°/18.8 sec. Paper samples were fixed using holders into a flat sample stage. Diffractometer system: EMPYREAN; measurement wavelength K-Alpha1 [Å]: 1.54060-K-Alpha2 [Å]: 1.54443. The crystallinity indexes were calculated using Eva software.

3. Results

3.1. *Nano particles characterization*

From XRD investigations, fig. (1-a), performed on the dry powder obtained of MH(NP)s the pattern perfectly matched the hexagonal brucite structure (ICSD #98-007-9031), with no secondary phases. As denoting the formation of pure crystalline $Mg(OH)_2$ compound, average <D> values of (21±1) nm were obtained. From TEM and AFM characterizations, the MH(NP)s appeared as hexagonal Lamellas, with side dimensions mostly less than 100 nm, fig. (2-a). Each lamella seems to consist of a thick superimposition of NPs, fig. (2-b), of few nanometers in length. The observations by AFM show that the lamellas were characterized by a thic-kness ranging between 20 and 5nm**.**

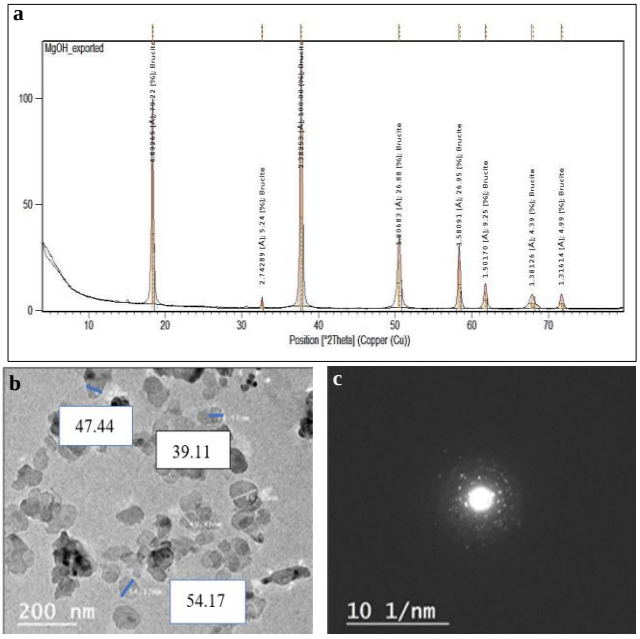


Figure (1) **a.** XRD pattern of $Mg(OH)_2$ nanoparticles, the pattern matches the hexagonal brucite structure, **b.** TEM photomicrographs of (MH) Nps magnification 200nm show NPs size, **c.** AFM image of MH nanoparticles.

3.2. *pH values*

Three readings were collected for each sample, showing that Deacidification treatments (MH(NP)s, CP) resulted in an obvious increase in the pH values of paper samples after treatments up to (3-4 pH units), tab. (1). The results of the deacidification treatment of CP show an increase in pH after aging for book paper samples; but this increase was very slight and not very significant. It may be due to a minor change in some conditions during the test such as room temperature.

Table (1) pH values of paper samples (RW), (RB) before aging (BA) and After aging (AA).

S.	Whatman (RW)				Book Paper (RB)			
	BA	***SD***	***AA***	***SD***	***BA***	***SD***	AA	SD
UN	6.68	0.2	6.02	0.14	4.02	0.12	3.8	0.06
MH	8.50	0.47	8.20	0.51	7.60	0.40	7.40	0.41
CP	7.93	0.38	7.54	0.20	7.20	0.30	7.30	0.35

3.3. *Amounts of magnesium or calcium deposited*

After the treatment, a considerable amount of Mg^{2+} and Ca^{2+} were detected, tab. (2). The average amount of content exceeded alkaline reserve requirements (3.6 mg) [41], with amounts deposited differing significantly from method to method. For immersion in an aqueous solution of CP, a deposited from 8.6 to 10.9 mg Ca^{+2}/ g paper was detected. While immersion in non-aqueous dispersion of MH(NPs) ranged from 3.9 to 5.0 mg Mg^{+2}/g paper.

Table (2) results of atomic absorption spectroscopy shows Mg^{+2} and Ca^{+2} by milligrams / g of paper samples (RW), (RB) before (BA) and After (AA) aging

Sample	**Mg^{++} concentration mg/g paper**			
	(RW) BA	***(RW) AA***	***(RB) BA***	***(RB) AA***
UT	0.02	0.04	0.8	0.6
MH	4.8	5.0	4.2	3.9
Sample	**Ca^{++} concentration mg/g paper**			
	(RW) BA	***(RW) AA***	***(RB) BA***	***(RB) AA***
UT	0.01	0.00	0.13	0.15
CP	10.9	10.5	9.2	8.6

3.4. *Penetration of deacidification solutions*

Investigation using SEM for Whatman paper samples, fig. (2-a: f), and Acidic Book paper samples, fig. (2-g: l), showed a homogeneous distribution of Mg^{+2} and Ca^{+2} particles over the entire surface area of the treated samples for both methods with no accumulation of alkaline substances or morphological change of cellulose fibers.

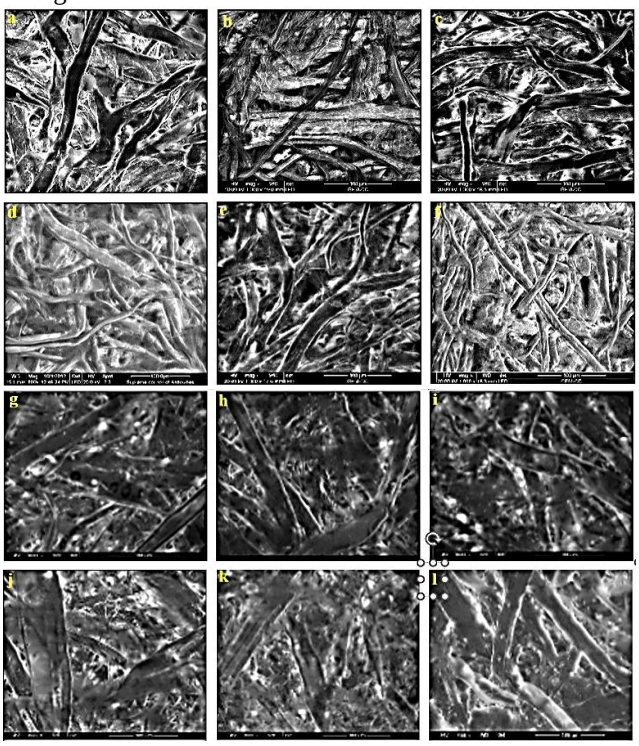


Figure (2) SEM photomicrograph 800× for Whatman paper samples; **a.** Untreated paper sample, **b.** Untreated paper sample after aging, **c.** CP treatment, **d.** CP treatment after aging, **e.** MH(NPs) treatment, **f.** MH(NPs) treatment after aging, for acidic book paper samples; **g.** untreated paper samples, **h.** untreated paper samples after aging, **i.** CP treatment, **j.** CP treatment after aging, **k.** MH(NPs) treatment, **l.** MH(NPs) treatment after aging

By analyzing the treated samples using EDX to measure the percentage of calcium and magnesium ions in both Watman paper and Acidic book paper. the untreated Whatman paper

sample (RW), fig. (3-a: c), revealed no peak in the SEM/ EDX spectrum for magnesium or Calcium and a weak peak for them in untreated Book paper samples (RB); they are likely present as impurities or additives during the paper-making process, fig. (3-d: f). However, after deacidification treatments, a strong peak of Mg^{+2} and Ca^{+2} was obtained from magnesium hydroxide NPs and Calcium propionate was detected by EDX.

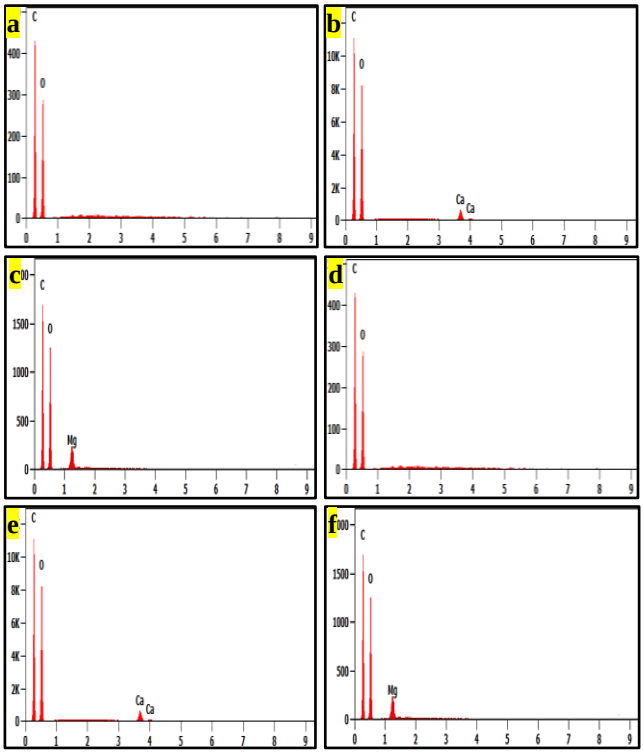


Figure (3) EDX spectra of Whatman paper, **a.** untreated control shows no Mg^{+2} or Ca^{+2} peaks, **b.** CP treatment show Ca^{+2} peak, **c.** (C) MH(NPs) treatment show Mg^{+2} peak, **d.** untreated control shows no Mg^{+2} or Ca^{+2} peaks, **e.** CP treatment show Ca^{+2} strong peak, **f.** (C) MH(NPs) treatment show Mg^{+2} strong peak.

3.5. *Colorimetric results*

Color changes of the treated and untreated book papers are displayed in tab$_s$. (3-a & b). The three parameters represent **L*** lightness, **a*** the red-green coordinate, and **b*** the yellow-blue coordinate. The total colour difference between treated and untreated before thermal aging for the CP method was a medium difference (**ΔE*= 2.54**), while for the MH (NPs) method it was a very small difference (**ΔE*= 1.33**). After aging, there was a statistically significant variation in **L***, **a***, and **b*** reported total colour change (**ΔE* > 3.5**) for untreated control and CP treated paper. This variation is high in **L*** and **b*** coordinates, which is interpreted to darkening and yellowing of paper [22]. However, the MH(NPs)-treated papers changed color slightly (**ΔE* ≤ 2**). The lightness of both untreated and treated paper samples decreased, and yellowing increased in treated paper in contrast to untreated control, which showed a decrease in yellowness and an increase in blue during thermal accelerated aging, the measuring of yellowness and whiteness indexes for Whatman paper untreated and treated samples is illustrated. In all samples, whiteness declined, and yellowness increased after accelerating aging.

Table (3-a) colorimetric coordinates of the treated and untreated Book papers after thermal accelerated degradation test, **(3-b)** Whiteness and Yellowness indexes of the treated and untreated Whatman Paper samples before and after thermal accelerated degradation test

S.	Before aging				After aging			
	*L**	*a**	*b**	*ΔE**	*L**	*a**	*b**	*ΔE**
UN control	75.88	5.90	19.96		71.13	6.61	18.97	4.90
CP	75.01	4.67	17.92	2.54	71.41	6.00	20.17	4.48
MH	76.41	5.30	18.90	1.33	73.84	5.96	19.70	2.06

S.	Whiteness				Yellowness			
	Before	*After*	*Difference*	*Reduction (%)*	*Before*	*After*	*Difference*	*Increase (%)*
UN control	76.62	69.14	-7.48	-9.76	1.49	4.35	+2.86	+191.9
CP	77.86	71.67	-6.19	-7.95	1.06	3.05	+1.99	+187.7
MH	77.80	73.93	-3.87	-4.97	0.57	1.18	+0.61	+107.0

3.6. *Mechanical properties tests*

Before thermal degradation, papers treated with MH and CP exhibited decreased tensile strength (TS), elongation (E), and double folds (DF). After 2 weeks of accelerated thermal aging, untreated papers showed a remarkable decrease in TS, while the treated papers (MH) and (CP) showed good stability. Table (4) summarizes the double-fold results of both treated and untreated samples before and after aging. It is obvious that the deacidification treatment of both methods caused an initial slight decrease in DF.

Table (4) mechanical properties result from untreated and treated paper samples. Each value is an average of ten replicates ± SD

Sample	Whatman Paper Samples						Book Paper Samples					
	Tensile Strength		*Elongation at Break*		*Double folds*		*Tensile Strength*		*Elongation at Break*		*Double folds*	
	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After
RW(UN)	46.5±2.3	42.7±3.1	2.0±0.13	1.07±0.1	79	38	21.8±0.9	14.3±1.2	0.35±0.05	0.21±0.2	5	2
CP	44.6±1.7	47.9±2.8	1.5±0.29	1.35±0.2	78	46	14.2±0.5	17.4±0.2	0.29±0.02	0.27±0.1	3	3
MH (NPs)	43.3±1.5	50.4±1.4	1.9±0.15	1.71±0.1	63	58	19.9±0.6	21.9±0.6	0.32±0.15	0.34±0.1	3	4

3.7. Identification of chemical changes

Investigation of the deacidified paper samples has been performed by FTIR. Although paper FT-IR spectra are convoluted, several absorption frequencies indicate the deacidification process and the formation of alkaline magnesium and calcium derivative particles. Untreated Whatman paper samples show the standard cellulose infrared spectrum. with bands at 3400 cm^{-1} (ν OH); 2900 cm^{-1} (ν CH_2); 1635 (adsorbed water); 1427 cm^{-1} (δ C-H); 1314 cm^{-1} (δ C-H); 1218 cm^{-1} (δ C-OH); 1162 cm^{-1} (ν C-C); 1108 cm^{-1} (ν C-O-C); 1060 cm^{-1} (ν C-OH, 2nd alcohol); 1028 cm^{-1} (ν C-OH, 1st alcohol); 998- 982 cm^{-1} (ρ-CH-); and 897 cm^{-1} (ν C-O-C), fig. (4) [34] revealed that thermally aged UN RW samples did not differ notably from unaged UN samples. The FTIR spectrum of unaged and aged untreated samples of acidic book paper revealed a band in 1720 to 1740 cm^{-1}, which was assigned to the carbonyl/ carboxylate groups, referring to the occurrence of oxidation or a degradation process due to paper acidity. The presence of the C=C stretching of the aromatic ring at around 1508

cm^{-1} indicates the presence of the lignin, which explains the embrittlement and yellowing of paper. After deacidification using MH(NPs) dispersion, a pronounced peak at 3700 cm^{-1} was detected. Changes such as a decrease in the broadening of the carboxyl group (COOH) at 3400-3100 cm^{-1} were observed. As well as changes at 1600 cm^{-1}, which have been assigned to water and hydrogen-bonded structures. Also, a significant decrease in the intensity of the carbonyl/carboxylate groups has been detected in the 1720 to 1740 cm^{-1} and 1630 to 1650 cm^{-1} wavenumber regions. Similar results were obtained concerning the acidic Book paper treated with an aqueous solution of CP. A notable decrease in the intensity of the carbonyl and carboxyl groups has been reported.

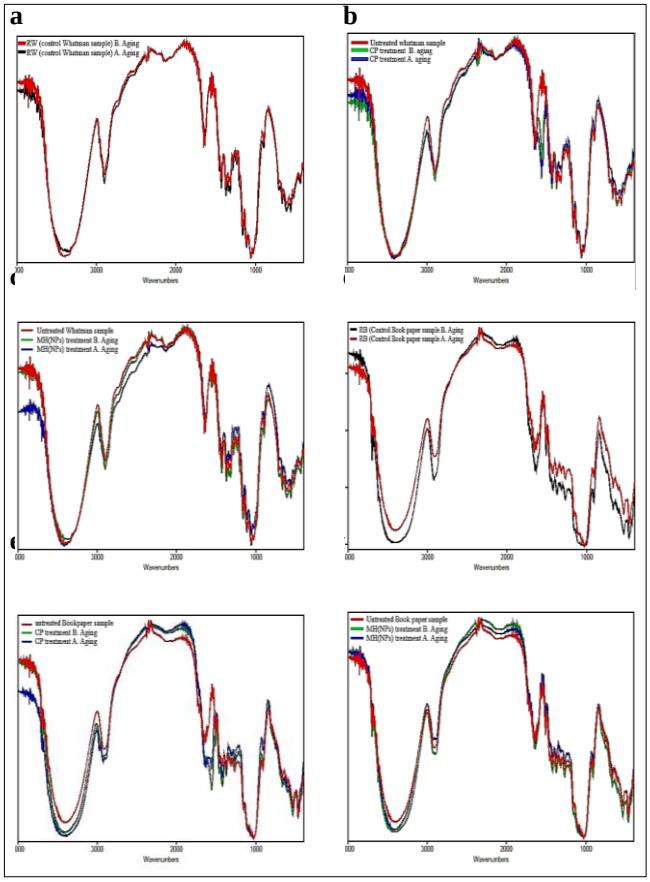


Figure (4) IR spectra of *Whatman paper samples*; **a.** (***black***) untreated control sample before & (***red***) after artificial aging, **b.** (***red***) untreated sample, (***green***) CP treated sample before aging & (***blue***) after aging, **c.** (red) untreated sample, (***green***) MH(NPs) treated sample before aging & (***blue***) after aging, **d.** IR spectra of *Acidic book paper samples* (***black***) untreated control sample before aging & (***red***) after aging, **e.** (***red***) treated sample before aging, (***green***) CP treated sample before aging & (***blue***) after aging, **f.** (***red***) untreated sample, (***green***) MH(NPs) treated sample before aging & (***blue***) after aging.

3.8. Crystallinity changes

The crystallinity index of cellulose was measured by X-ray diffraction using EVA X-ray diffraction analysis software, Version 8. A comparison between the cellulose crystallinity of the untreated Whatman paper samples and the treated samples before and after thermal aging indicated a slight decrease in untreated aged samples, tab. (5) fig. (5). However, no significant change is reported for the book paper-treated sample with either CP solution or MH dispersion except for a very slight increase in crystallinity indexes for the treated samples, tab. (5) fig. (6).

Table (5) crystallinity index (%) of paper samples (RW), (RB) before aging (BA) and After aging (AA)

Samples	Whatman (RW)		Book Paper (RB)	
	BA	***AA***	***BA***	***AA***
UN	79.06	77.30	34.4	35.3
MH	79.90	78.80	37.5	34.3
CP	79.75	78.60	36.3	35.2

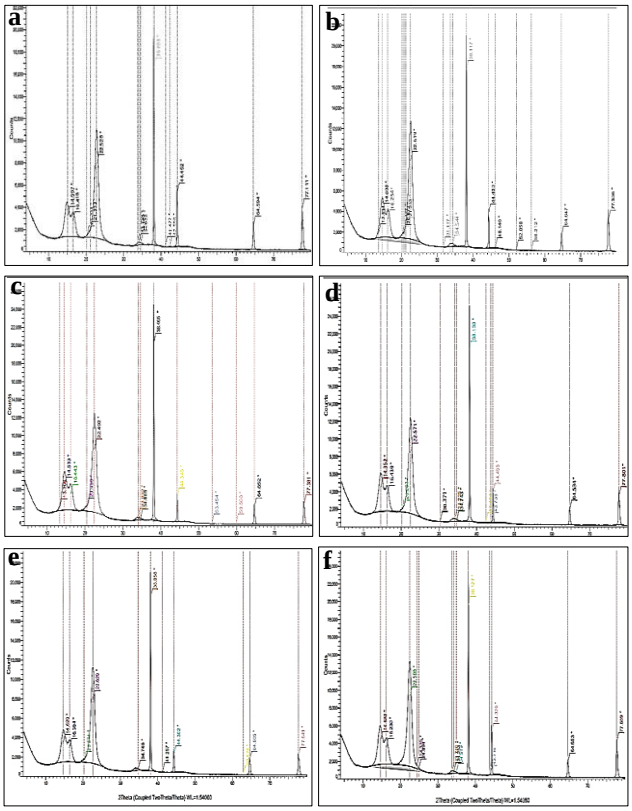
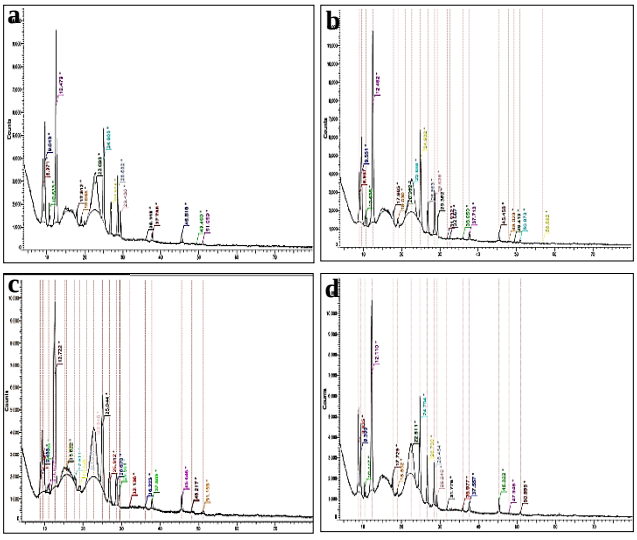


Figure (5) XRD patterns for (RW) samples; **a.** UN sample before aging, **b.** after aging, **c.** CP treated sample before aging, **d.** after aging, **e.** MH(NPs) treated sample before aging, **f.** after aging



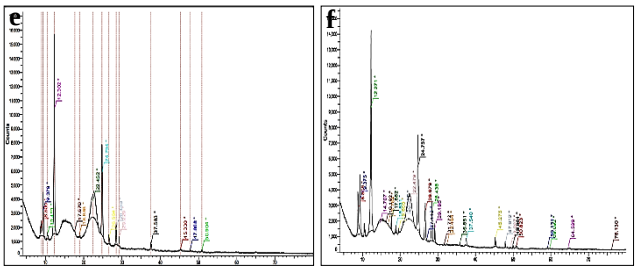


Figure (6) XRD patterns for (RB) samples; **a.** UN sample before aging, **b.** after aging, **c.** CP treated sample before aging, **d.** after aging, **e.** MH(NPs) treated sample before aging, **f.** after aging

4. Discussion

An earlier analysis had shown that after deacidification with the two methods, the non-aqueous MH(NPs) treatment caused higher pH values than the aqueous CP method. Since the alkaline buffer would be consumed over time, the pH should be above neutral after treatment but not too high to avoid alkaline depolymerization. The resulting pH values obtained following the MH treatment varied between 7.4 and 8.5, whereas the pH values obtained following the aqueous CP treatment ranged between 7.2 and 7.9, tab. (1), depending on the initial pH of paper samples. The optimum amount of Mg^{2+} or Ca^{2+} according to the TAPPI test is 3.6 mg/1 g paper [41]. The untreated control of book paper recorded minor magnesium and calcium contents before treatment; nonetheless, it should be emphasized that this paper was fragile and damaged and had a low pH value, which indicates that Mg^{2+} and Ca^{2+} contents were most probably not in the form of alkaline reserves, and it was less than the amount that was required as a buffer. However, the quantity of Mg^{+2} or Ca^{+2} relies on the pH of the paper; if the tested paper is acidic, then a part of the alkaline reserve will be consumed during the treatment and continually after treatment while the paper drying in the air. So, the amount of Mg^{+2} or Ca^{+2} reported stable values at neutral Whatman paper samples (RW) on the contrary of the acidic book paper sample (RB). Although investigation by SEM showed a homogeneous distribution of Mg^{+2} and Ca^{+2} particles inside paper, the CP aqueous treatment showed a chalky white precipitate in contrast of the non-aqueous treatment with (MH), probably due to the small size of the nanoparticles. The analysis using SEM/EDX has proven that the deacidification treatment with both methods deposited a sufficient alkaline buffer in paper, since a strong peak of Mg^{+2} and Ca^{+2} was detected, and although weak peaks for both elements were detected in untreated book paper samples, it was most likely not in the form of the alkaline reserve. Color change measurements show significant alterations in samples treated with CP, which are probably caused by oxidation reactions since oxidation is the dominant degradation pathway in alkaline paper. Oxidized functional groups in cellulose may act as chromophores, causing paper yellowing. While the darkening of paper is possibly associated with polymer degradation. The colorimetric measurements indicate that the MH NPs-treated papers were protected from acid hydrolysis and oxidation. This could be attributed to the protective action of Mg^{2+} during thermal degradation [42], as proven by the results presented in tab. (4) The lower change of whiteness and yellowness values is reported in MH-treated paper samples in comparison to the untreated and CP-treated samples, probably due to the inhibition effect of $Mg(OH)_2$NPs integrated into the cellulose structure. As a result of the above, the paper treated with $Mg(OH)_2$ showed the best behavior after accelerated thermal degradation in color changes. The mechanical properties of deacidified paper samples show a dramatically decrease, which is possibly attributed to exposure of paper samples to the highly alkaline deacidification condition and sizing removal. On the other hand, after the accelerated aging, the untreated paper samples showed remarkable decreases in TS, which may have been caused by acid hydrolysis and oxidation. However, the treated papers (MH) and (CP) showed good stability, which was attributed to the existence of alkaline particles within the cellulose fibers. The alkaline particles efficiently restrain cellulose deterioration, which is the major component of paper. As for double folds, test paper samples treated with Cp and MH methods show after aging higher values than the untreated samples, which indicates that MH and CP considerably inhibited double fold loss with aging. This protective effect is remarkable in samples treated with MH. Mechanical tests highlight that a sample treated with an MH nano dispersion provides better results than a CP solution. On the other hand, untreated samples reported a dramatic decrease in mechanical resistance after thermal aging. Investigation of the chemical changes by FTIR revealed that thermally aged, untreated Whatman paper samples did not differ notably from unaged control samples. Although artificial aging induces molecular disintegration in paper samples, as seen by pH decrease, yellowing, and loss of mechanical qualities, the infrared spectroscopy results fail to indicate this deterioration. The degradation of cellulose is predicted to cause molecular changes such as polymeric scission, which could be observed in the C-O-C fingerprint, and the production of carbonyl and carboxyl groups at absorption bands in the 1700/1600 cm^{-1}. Nevertheless, detecting carbonyl bands in cellulose infrared spectra is difficult, if not impossible, because they are located in the same spectral area as the wide band of absorbed and bound water [43]. Furthermore, the number of functional groups formed as a result of polymer breakdown was most likely insufficient to be detected in the infrared spectrum. In the current study, the only chemical alterations found by FTIR are linked to CP degradation, as stated below. The infrared spectrum of samples treated with CP solution shows that the aqueous treatment reduced the intensity of the absorbance band 3419 cm^{-1}, which refers to the hydrogen bond H-OH, indicates cellulose hydrolysis. The occurrence of new bands at (1560 cm^{-1}, 1546 cm^{-1}). After thermal aging, these bands lose intensity or disappear, fig. (4-c), indicating the degradation of CP under the aging conditions. At the same time, the increase and broadening of the band centered at 1428 cm^{-1} with a shoulder near 1404 cm^{-1} is noted. These two bands may be assigned to calcium carbonate $CaCO_3$ [44], implying CP dissociation and carbonate production from free calcium ions. Whereas a peak at 3700 cm-^{1}, was detected in the deacidified samples assigned to OH groups correlated to metal ions probably (Mg^{+2}) [45]. The FTIR findings illustrate that deacidification treatment using CP solution achieved minimal

deacidification of Book paper samples, reducing the intensity of the peak at 1720 cm^{-1}. However, the deacidification treatment using MH(NPs) dispersion eliminated it, providing a satisfactory result. On the other hand, the results of XRD show slight differences in the crystalline and amorphous regions before and after deacidification. A change in the XRD pattern of the treated paper samples is observed, probably due to the existence of the alkaline metal ions used for deacidification. Comparing the data collected by XRD of treated and untreated paper samples, the results show a slight increase in the crystallinity index of cellulose, indicating that a positive change has occurred in the chemical and mechanical properties of the cellulose molecule and confirming the FTIR results.

5. Conclusions

This study focused on a comparison of the working characteristics and deacidification efficacy of $Mg(OH)_2$ NPs, and calcium propionate as eco-friendly deacidification methods used in individual immersion applications. The application of $Mg(OH)_2$ nano dispersions in 2-propanol for paper deacidification was effective and protected the cellulose against hydrolytic degradation and depolymerization. Nanoparticles penetrate within the cellulose fibers of the paper and neutralize the inherent acidity. After the treatment, the pH increased to 8.5 and an AR of 4% was obtained, which effectively inhibits acid-catalyzed degradation of paper. Deacidified paper appears to be more resistant to artificial aging; tensile strength of $Mg(OH)_2$ NPs treated papers exhibits good stability during thermally accelerated degradation compared to the aged, untreated samples. Furthermore, magnesium hydroxide nanoparticles cause an imperceptible increase in ISO brightness and yellowing of paper. Deacidification stabilizes the changes of cellulose chromophores, preserving paper from yellowing during thermal aging tests. The rates of the degradation processes are significantly reduced, supporting the theory that natural aging could be minimized by deacidification. In comparison to the commonly used deacidification method calcium propionate (CP); $Mg(OH)_2$ nanoparticles demonstrate better effectiveness in the deacidification treatment. Although some disadvantages shown by the CP method are basically related to the chemical change of the cellulose structure observed by FTIR, and medium color variation ($\Delta E^* < 4.5$) after accelerated aging, CP proved a good deacidification properties of paper. The loss of mechanical properties on aged paper was also prevented in CP treated samples. Finally, we remark that both deacidification methods were applied in this work, are very applicable, easy to use and do not require any special safety procedure, it means the methods are eco-friendly.

Abbreviations

- ***CP:*** *Deacidification by aqueous solution of calcium propionate.*
- ***MH:*** *Deacidification by non-aqueous dispersion of Magnesium hydroxide Nano Particles.*
- ***UN:*** *Untreated control sample*
- ***RW:*** *Whatman paper*
- ***RB:*** *Acidic book paper*

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