

THE EFFECTIVENESS OF AQUEOUS AND NONAQUEOUS MAGNESIUM HYDROXIDE NANOPOWDER ON THE COLOR STABILITY OF DYED COTTON PAPER PULP

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Abstract

De-acidification treatments are a key process for conserving and restoring highly significant materials. Authors utilize numerous methods to carry out paper de-acidification. The paper studies the effect of aqueous and nonaqueous deacidification treatment on the colorfastness rates of dyed paper samples. The authors investigated the physical, chemical, and optical properties of treated and untreated paper samples. They used X-ray diffraction to estimate the Crystallinity degree, Fourier-transform infrared spectroscopy to identify the change in the functional group of paper and dye molecule, and spectrophotometry to evaluate the variations in the total color difference (ΔE^) of the dyed paper samples. pH measurements were also detected.*

Keywords: Deacidification; Magnesium hydroxide nanopowder; Dyed paper; Color measurements

Introduction

De-acidification is the major chemical stabilization method for paper artifacts. It is the most significant conservation intervention with regard to the long-term preservation of paper. Barrow recognized the negative effect of acidity on the longevity of the paper [1]. In order to prolong paper life, many methods of the neutralization of acids within the paper and to create an alkaline buffer have been developed. De-acidification treatments are either aqueous or nonaqueous. Nonaqueous processes should be used when the paper is sensitive to water or contain water-soluble inks and dyes. The most important nonaqueous methods are Wei'to and Bookeeper [2].

De-acidification treatments are a major process for conserving and restoring highly significant material. Therefore, researchers adopt many strategies for paper de-acidification. For example, they use nanotechnologies applications to create kinetically stable dispersions of nano- and micron-sized calcium hydroxide particles in alcohol media. Although having the finest de-acidification properties, calcium hydroxide has never been utilized as a dispersion in nonaqueous media. When calcium hydroxide particles are deposited onto paper cellulose fibers, they de-acidify the fibers and react with carbon dioxide from the air to form calcium carbonate into these fibers. Accordingly, long-term control of paper pH is allowed with outstanding de-acidification properties. The de-acidification of the 14th, 17th, 19th, and 20th centuries' acid yellowed paper samples taken from rag and wood pulp (20th century) has been achieved with admirable outcomes. Furthermore, nano-particles and microparticle dispersions can be applied

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to the paper based on traditional measures. This newly developed method has many features, such as being environmentally clean and cheap. It also has industrial applications [3]. Aqueous treatments have disadvantages, e.g. the swelling of cellulose fibers and the leaching of inks. Aqueous de-acidification lies in the actual condition of the object's ink, color, or anything else that could be alkaline sensitive. Aqueous alkaline solutions have been used for many decades to de-acidify cellulose-based artifacts, but their use involves severe effects. Water results in the swelling of the hydrophilic cellulose fibers and may solve several compounds and materials associated with the artifact, such as inks on paper documents. Moreover, alkaline solutions cause the depolymerization of oxidized cellulose [4]. Aqueous de-acidification is effective, simple, and without any health issues for users and conservators. However, it has two critical disadvantages: It cannot be applied to artifacts that contain water-sensitive inks and dyes and does not fit mass treatments. Such disadvantages were treated with developing de-acidification strategies based on organic solvents. Organic solvents are employed because they result in a more rapid wet paper than water. Moreover, their swelling or distortion effect on paper is lower, and they are easier to dry from paper than water. In this work, methods that do not necessitate sophisticated equipment and are appropriate for workshop applications are introduced [5]. Aqueous treatments with calcium hydroxide, such as alkaline solutions have been utilized continuously since the earliest paper restoration practice, but they have drawbacks on paper due to the exposure of paper to strongly basic conditions [6].

The effects of five widely utilized aqueous conservation treatments (washing in distilled water, washing in deionized water, bleaching, de-acidifying, and bleaching followed by de-acidifying) on the mechanical and physical properties of two non-aged papers, machine-made paper, and handmade paper were defined. Using a factorial experimental design, tensile strength, ultimate tensile stress, modulus of elasticity, tensile energy absorption, stretch at the break, and maximum strain of two non-aged papers were identified. The machine-made paper was stronger and extended less in the machine-direction than the cross-direction. The handmade paper was thought to have comparable extension and strength properties in both directions. Yet, this was not always the case. Based on the paper type, the explored aqueous conservation treatments had different effects on the measured physical and mechanical properties [7].

Aqueous solutions of calcium or magnesium bicarbonate and calcium hydroxide are widely utilized. Due to the high mobility of hydroxide ions, neutralizing cellulose-based material by aqueous alkaline treatments is very effective. Furthermore, aqueous treatments help enhance the samples' visual aspect because of the direct washing of hydro-soluble dirt and sizing the compounds that are often involved in the browning of paper [8]. A resizing bath is required after aqueous treatments. However, aqueous treatments have serious effects. The excess of free hydroxide ions interacts with cellulose that may be depolymerized and degraded in highly alkaline aqueous environments. Moreover, the aqueous medium and the alkaline environment may remove the original material (inks, sizing), and, in some cases, cause ink discoloration due to the decomposition of the ink complex [9].

The use of nonaqueous methods overcomes the disadvantages of the aqueous method. The available commercial nonaqueous treatments are all based on solutions or dispersions of oxides and carbonates precursors, i.e for paper preservation, magnesium and calcium hydroxide nanoparticles in propanol lead to safe and stable de-acidification treatment and leave a mild alkaline carbonate buffer reserve against reoccurring acidity on the treated paper. Alkaline earth metal hydroxide nanoparticles dispersed in alcohol are an efficient de-acidification method for paper and proved to be promising tools for the de-acidification of archeological wood [10].

This paper presents the effectiveness of aqueous and nonaqueous magnesium hydroxide nanopowder at two concentrations on the color stability of dyed cotton pulp paper. Four de-acidification procedures were used to determine the concentration levels of the de-acidification solution and the ideal method could be applied in the case of dyed substrates. Dyed specimens were qualitatively evaluated for color stability. Fourier-transform infrared spectroscopy was used for detecting the changes in the paper's functional group. Additionally, the spectrophotometer was used to detect the colorimetric measurements.

Experimental

Materials

All chemical reagents used in the experimental study were of analytical grade and directly used without further treatment. $Mg(OH)_2$ nanopowder purchased from Sigma-Aldrich (100nm particle size, 99.8% trace metals basis). MgO Nanoparticles (99.8% trace metal basis, Aldrich). Model quantitative filter Whatman ashless, grade 41 paper diam. 55.

Methods

The experimental procedures were as follows: 1) Paper samples were dyed with selected natural dyes; 2) acidified in HCl solution until they reached the reaction of $pH = 1 - 4$. Samples were dried between two sheets of blotting paper. Then, they were left at room temperature for 10 days until drying out; 3) Samples were de-acidified with aqueous magnesium hydroxide and with the use of a dispersion of sol-gel magnesium oxide in 2-isopropanol alcohol. Aqueous and nonaqueous de-acidification treatment was achieved using four methods (spray, brushing, immersion, and gelifying); 4) The color change of dyed samples was evaluated after deacidification procedures and measurements of color strength (K/S) in the tested specimens. Washing: samples were placed on Petri dishes, immersed in 100mL of aqueous dispersion solution, whereas the nonaqueous solution of magnesium oxide nanopowder was de-acidified for 30 minutes.

Spraying: Samples were sprayed until complete surface wetting. This action was carried out on both sides of the paper. The total application time of samples in multiple spraying was about 4 weeks.

Brushing: Using a soft brush, both sides of the samples were brushed with magnesium hydroxide dispersion in water and the magnesium dioxide in 2-iso propanol alcohol until complete wetting of the samples. When performing multiple brushing, samples were left for 7 days to dry (undercover, on Petri dishes) after each application. The total period of application was up to 4 weeks.

Gelifying: Hydrogel was prepared according to *A. Casoli et al.* [11]. The weight percentage of gellan gum (Gelzan CM Geletic) and calcium acetate was purchased from Sigma (Sigma-Aldrich, Mo, St. Louis, USA) to prepare the hydrogel of an aqueous solution of Gelzan powder 20g (conc.1-4%), and calcium acetate (0.40g/L) was put for a minute in the microwave until complete hydration. Deacidifying reagent 1.0% $Mg(OH)_2$ nanoparticles was added during stirring the gelzan 40mL of gellan hydrogel was applied to the recto of paper samples and was covered with a Mylar sheet (pkg/50) obtained from Sigma-Aldrich. After de-acidification treatment, paper samples were put between Whatman paper sheets and pressed slightly with a sheet of Mylar to have a smooth surface. Treated samples were then subjected to analysis after 10 days since the process of deacidification was completed and the formation of magnesium carbonate into paper samples as a buffer [12].

Accelerated degradation tests followed ISO 5630-1. The samples were exposed to $105 \pm 2^\circ C$ in a laboratory oven for 28 days. They were analyzed for surface pH, CIE $L^*a^*b^*$, and tensile strength. Before and after testing, the samples were equilibrated at $23^\circ C$ and 50% RH for 24 hours [10].

The evaluation of acidified and deacidified paper samples was controlled by measuring pH determined by cold water extraction based on Tappi T 509 om-02. pH was using an Oakton pH/mv/c Meter737850 manufactured by Eutech instruments, thermo fisher scientific accurate to 0.01; 10 days after application of $Mg(OH)_2$ dispersion.

Characterization of dyed historical paper samples

Scanning Electron Microscopy (SEM)

SEM of treated and untreated fibers was performed using an Electron Microscope Survey Nanoscience instrument FEI Company MVE00001162, FP 3950/00 at NCSU. All samples were prepared following the standard measures. They were coated with gold using EMITECH K450X sputter coater to avoid charging. SEM has a scan area of 50×50 mm as standard, but the motorized scan area can be upgraded to 100×100 mm. The examination of the samples was performed at the SEM Laboratory, Department of Polymer and Color Science, the University of North Carolina.

Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR was employed to investigate the functional groups of the paper and the changes made by the treatments compared to the control paper sample. FTIR spectra of paper samples were measured on a thermo scientific FTIR Nicolet IS10 GE Crystal 64 scans, 4 resolution, 4000 - 500cm⁻¹ frequency range, in a reflectance mode.

Evaluation of pH values before and after de-acidification treatments

With the aim of identifying the acidity of the treated and untreated paper samples, the authors did a pH test following the TAPPI Standard Test Method T509 om-11 (TAPPI 2011) and using hydrogen ion concentration (pH) of the paper extracts (cold extraction method). In this test, they compared the pH of the untreated samples with the ones treated with the selected dyes before and after de-acidification treatments. The TAPPI method includes soaking equivalent amounts of the sample with de-ionized water for an hour. A small piece (2.5 × 2.5 cm) of each paper was prepared and cut into 0.5cm squares using a scalpel. After that, it was placed in a beaker with 12mL deionized water to cover it entirely. The solution was stirred and covered with a watch glass for at least an hour. Then, Whatman Cellulose Filter Paper was used to filter the mixture. After preparation, a pH meter (Oakton Thermo Fisher) was used to measure the pH of the solution at 25°C.

Colorimetric measurements

As far as the colorimetric evolution is concerned, the change in colour was calculated in the case of every coordinate (L*, a* and b*), as compared with its initial value, on the same sample and in the same point. The chromatic deviation (ΔE^*) was determined with the aid of equation [13-22]: in which:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

ΔL^* represents the change in light intensity in the respective point, at different time intervals, as compared to the initial value:

$$\Delta L^* = L^*_f - L^*_i;$$

Δa^* represents the chromatic modification of the coordinates of axis a* (colours blue and green), from the same point, at different time intervals, as compared to its initial value:

$$\Delta a^* = a^*_f - a^*_i;$$

Δb^* represents the chromatic modification of the coordinates of axis b* (colours blue and yellow), while respecting the same method of calculation:

$$\Delta b^* = b^*_f - b^*_i$$

Results and discussion

The dyed paper samples illustrated lower lightness (ΔL^*) after artificial aging. They were remarkably darker. Color changes of the papers treated with saffron showed higher redness (Δa^*) and yellowness (Δb^*). Papers dyed with cochineal dye showed a fairly large color change due to darkening, lower yellowness, and higher redness. Dyed paper with turmeric dye resulted in a smaller color change than those with cochineal dye due to darkening and lower yellowness and redness (Table 1). Because of the accelerated aging of the dyed paper samples, the color change arose mostly in saffron dye tannic acid post-treatment ($\Delta E^* = 8.07$). The color darkened notably (decrease of L* coordinate up to 71) and the values of axis a* and b* declined. In turmeric dye, a significant total color difference ($\Delta E^* = 2.63$) was also measured. The dyes had pH less than 4 before accelerated aging. In cochineal dye tannic acid post treatment ($\Delta E^* = 5.55$), the color darkened notably (decrease of L* coordinate up to 47), and the values of axis a* and b* declined.

SEM photographs show to a certain extent the process of precipitation of the above-mentioned larger particles of magnesium hydroxide on the paper surface. Although a considerable amount of the hydroxide dispersion is precipitated in the form of agglomerates on the paper surface [23], there was no visible change with the untreated paper samples. Slight precipitation was visible at a magnification of 340× on the papers treated with aqueous magnesium hydroxide nanopowder and nonaqueous magnesium hydroxide. SEM micrographs of the paper sample after nonaqueous de-acidification treatment indicated a clear dryness on the

fiber surface. There is no apparent improvement in the histological structure of the paper and the fibers appear uncoordinated.

Table 1. Changes of lightness L* and chromatic coordinates a* and b* for dyed paper samples induced by de-acidification (Magnesium hydroxide nanopowder aqueous treatment) and accelerated aging

S. No	Color component values	L*	a*	b*	k/s	ΔE*
Saffron dye de-acidified samples						
1	Standarad dyed sample Lemon juice post treatment	92.27	1.59	25.64	0.253	0
2	Lemon juice post treatment wash treatment	92.32	-1.06	23.27	0.221	2.79
3	Lemon juice post treatment spray treatment 0.5%	91.96	1.57	26.26	0.259	1.36
4	Lemon juice post treatment spray treatment 1%	91.57	-1.02	24.45	0.269	2.55
5	Lemon juice post treatment brushing treatment	91.61	-0.39	27.36	0.30	2.11
6	Lemon juice post treatment gelifying treatment	90.78	0.60	24.68	0.256	1.14
7	Standarad dyed sample tannic acid post-treatment	64.05	6.43	28.14	6.674	0
8	Tannic acid post treatment wash treatment	45.62	1.36	11.88	6.127	11.55
9	Tannic acid post treatment spray treatment 0.5%	55.76	3.64	14.96	2.831	7.61
10	Tannic acid post treatment spray treatment 1%	48.18	4.54	17.46	6.318	8.49
11	Tannic acid post-treatment brushing treatment	48.00	4.14	15.86	6.018	9.10
12	Tannic acid post treatment gelifying treatment	53.64	5.14	20.29	6.108	5.86
13	Standarad dyed sample chitosan post treatment	88.59	7.25	50.43	0.497	0
14	Chitosan treated paper wash treatment	92.97	-0.51	17.84	0.133	13.41
15	Chitosan treated paper spray treatment 0.5%	90.52	-0.74	29.75	0.390	9.45
16	Chitosan treated paper spray treatment 1%	91.46	1.81	27.04	0.338	10.44
17	Chitosan treated paper brushing treatment	90.20	-0.58	26.38	0.255	11.32
18	Chitosan treated paper gelifying treatment	89.57	-1.05	33.29	0.523	8.54

The width of fiber increased significantly, and the internal walls of fibers were completely filled with aqueous de-acidification treatment, which may lead to the high mechanical properties of paper. SEM observations revealed improvement in the paper morphology and the structure of fibers as a result of reducing the impurities (Fig. 1).

Acidified dyed paper samples were tested. The findings of the non-treated samples and those of the aqueous traditional treatment with a saturated aqueous Mg(OH)₂ solution were compared and showed higher neutralization reaction kinetics than the nonaqueous one. After treatment, the treated samples maintained closer coloration to the original, while the aqueous treatment that has a notable effect on the color strength (K/S) of dyed samples. Artificial aging tests showed an overall increase in the aging stability of deacidified dyed samples. The Mg(OH)₂ nanoparticles in isopropanol treatment can be an alternative for dyed papers which have poor stability for the aqueous treatments. The aqueous treatment with magnesium hydroxide Mg(OH)₂ nanopowder tends to de-acidify paper more effectively than the same reagent with a polar solvent. The increase of the pH of paper samples after de-acidification with Mg(OH)₂ nanoparticles relates to the better penetration of the reagent into the structure of paper support. The results of comparing the values of the L*, a*, b* coordinates of dyed paper samples and their changes due to de-acidification carried out by magnesium hydroxide and accelerated aging are presented. The de-acidification process influenced the color coordinates of dyed paper samples with selected dyes only minimally (ΔE* = 2.6). Regarding the paper sample de-acidified with the gelifying technique, the values of the color differences varied to a certain extent. The most compelling color difference resulting from de-acidification was noticed for the cochineal dye (ΔE* = 26). It was the highest in b* coordinate. On the contrary, in the case of saffron dye (ΔE* = 2.7), de-acidification resulted in a relatively small change.

Comparing the (ΔE*) values of examined dyed samples treated with aqueous de-acidification illustrated that the treated samples using the gelifying technique showed the lowest (ΔE*) and the highest resistance. Wash treatment showed the highest (ΔE*) values as shown in table 1. Based on the results given in (Tables 2-6), the samples treated with nonaqueous treatment showed less color change compared with the aqueous treatment. Wash treatment showed great color change for the dyed samples with saffron dye. The dyed samples with tannic acid showed the highest (ΔE*) values after de-acidification treatment.

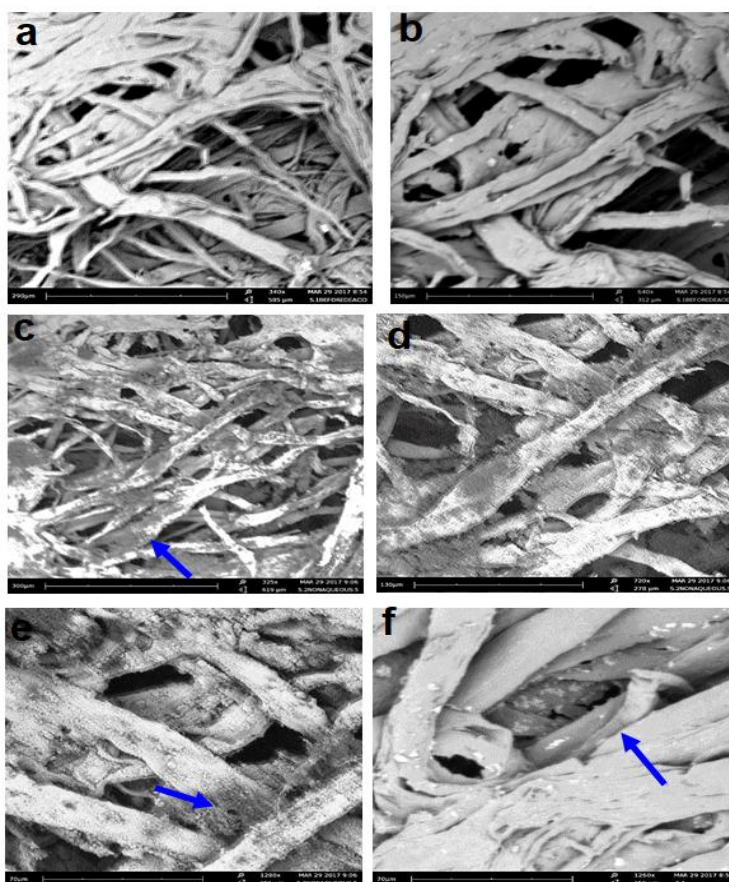


Fig. 1. SEM micrographs (A&B) represent paper samples before de-acidification treatments. Where signs of weakness appear on fibrous bundles of paper. Also, Wide gaps have been observed between the fibers. (C&D) show dryness on the fiber surface. There is no apparent improvement in the histological structure of the paper and the fibers appear uncoordinated. While (E&F) represents paper sample after aqueous de-acidification treatment; we notice a significant increase in the width of fiber as well as the internal walls of fibers completely filled with aqueous de-acidification treatment, which may lead to the high mechanical properties of paper.

The total color difference of the dye layer demonstrated the changes in the structure of dyes resulting from accelerated aging. The degree of change varies depending on the dye. In other words, some dyes are more prone to change by de-acidification than others. The impact of de-acidification on the color stability differed for the investigated dyes. The decrease in the value of color difference in de-acidified samples was detected in both Anthraquinone dyes and flavonoid (cochineal and saffron). On the contrary, higher values of ΔE^* were detected in saffron dye and turmeric dyes, which originally had the lowest pH on paper before and after accelerated aging. Moreover, the increase of pH due to de-acidification of these samples was most dramatic (2–4 units). In sum, the high pH relates to the de-acidification procedures which have a significant effect on the color stability of the dyed paper samples. The results of color change of the treated samples with aqueous magnesium nanopowder and nonaqueous magnesium oxide nanoparticles (washing, spraying, brushing, and gelifying), the low effect of de-acidification treatments followed the order: Spray treatment 0.5% > gelifying treatment > brushing > spray 1% > wash treatment. De-acidification caused considerable changes connected with the increase of intensity mostly in the region assigned to the C-O stretching band, suggesting the effectiveness of this method.

THE EFFECTIVENESS OF AQUEOUS AND NONAQUEOUS MAGNESIUM HYDROXIDE NANPOWDER

Table 2. Changes of lightness L* and chromatic coordinates a* and b* for Saffron dye deacidified samples induced by the de-acidification treatment (Magnesium hydroxide nanopowder nonaqueous treatment) and accelerated aging

S. No	Color components values	L*	a*	b*	k/s	ΔE*
1	Standarad dyed sample Lemon juice post treatment	91.60	2.97	32.99	0.401	0
2	Lemon juice post treatment wash treatment	93.53	-0.70	18.75	0.140	7.34
3	Lemon juice post treatment spray treatment 0.5%	91.78	0.48	24.58	0.239	4.39
4	Lemon juice post treatment spray treatment 1%	93.16	-0.99	25.29	0.232	4.89
5	Lemon juice post treatment brushing treatment	91.90	-0.56	26.77	0.282	4.10
6	Lemon juice post treatment gelifying treatment	92.69	1.46	24.71	0.229	4.05
7	Standarad dyed sample tannic acid post-treatment	75.38	12.51	46.72	4.595	0
8	Tannic acid post treatment wash treatment	44.97	-0.02	8.92	5.295	19.85
9	Tannic acid post treatment spray treatment 0.5%	51.29	4.71	19.42	5.856	14.46
10	Tannic acid post-treatment spray treatment 1%	49.06	5.96	14.35	5.533	16.46
11	Tannic acid post treatment brushing treatment	46.03	4.19	16.22	5.582	14.86
12	Tannic acid post treatment gelifying treatment	51.64	4.18	18.00	5.714	14.35
13	Standarad dyed sample chitosan post treatment	89.45	6.16	47.42	0.935	0
14	Chitosan treated paper wash treatment	92.76	-1.41	27.10	0.280	9.57
15	Chitosan treated paper spray treatment 0.5%	90.90	-1.08	29.33	0.379	8.64
16	Chitosan treated paper spray treatment 1%	92.30	-1.43	29.52	0.337	8.80
17	Chitosan treated paper brushing treatment	91.17	-0.62	29.33	0.357	8.44
18	Chitosan treated paper gelifying treatment	90.42	-1.06	33.26	0.488	7.45

Table 3. Changes of lightness L* and chromatic coordinates a* and b* for turmeric dye de-acidified paper samples induced by the de-acidification (Magnesium hydroxide nanopowder aqueous treatment) and accelerated aging

S. No	Color components values	L*	a*	b*	k/s	ΔE*
1	Standarad dyed sample Lemon juice post treatment	92.54	-3.91	52.20	1.05	0
2	Lemon juice post treatment wash treatment	65.17	7.76	34.60	0.422	13.94
3	Lemon juice post treatment spray treatment 0.5%	90.81	-2.17	48.47	0.960	1.84
4	Lemon juice post treatment spray treatment 1%	92.17	-2.61	42.01	0.645	3.93
5	Lemon juice post treatment brushing treatment	68.67	6.41	44.70	0.499	10.92
6	Lemon juice post treatment gelifying treatment	91.95	-3.23	52.84	0.703	0.54
7	Standarad dyed sample tannic acid post-treatment	78.22	4.36	47.73	3.340	0
8	Tannic acid post treatment wash treatment	66.81	6.27	36.52	5.358	6.50
9	Tannic acid post treatment spray treatment 0.5%	68.74	5.43	43.19	4.379	4.08
10	Tannic acid post treatment spray treatment 1%	68.53	6.48	44.74	4.802	4.14
11	Tannic acid post-treatment brushing treatment	68.86	8.20	46.49	4.587	4.49
12	Tannic acid post treatment gelifying treatment	70.44	4.78	41.54	3.530	3.58
13	Standarad dyed sample chitosan post treatment	89.98	-0.65	38.56	0.631	0
14	Chitosan treated paper wash treatment	87.37	1.91	20.06	0.363	8.47
15	Chitosan treated paper spray treatment 0.5%	86.47	0.98	29.52	0.561	4.34
16	Chitosan treated paper spray treatment 1%	87.16	-0.01	27.66	0.437	4.91
17	Chitosan treated paper brushing treatment	85.98	2.68	22.67	0.499	7.66
18	Chitosan treated paper gelifying treatment	87.52	-1.15	42.37	0.924	1.91

Table 4. Changes of lightness L* and chromatic coordinates a* and b* for Turmeric dye deacidified samples induced by the de-acidification treatment (Magnesium hydroxide nanoparticles nonaqueous treatment) and accelerated aging

S. No	Color components values	L*	a*	b*	k/s	ΔE*
1	Standarad dyed sample Lemon juice post treatment	93.48	- 4.34	63.00	1.529	0
2	Lemon juice post treatment wash treatment	91.29	-2.06	41.27	0.661	7.73
3	Lemon juice post treatment spray treatment 0.5%	93.27	-4.18	52.49	0.973	3.71
4	Lemon juice post treatment spray treatment 1%	92.09	-2.40	42.83	0.681	7.15
5	Lemon juice post treatment brushing treatment	91.71	-3.57	48.02	0.888	6.12
6	Lemon juice post treatment gelifying treatment	93.35	-4.21	48.50	0.824	5.12
7	Standarad dyed sample tannic acid post-treatment	80.40	2.09	54.48	2.961	0
8	Tannic acid post treatment wash treatment	70.50	5.70	41.66	3.730	7.06
9	Tannic acid post treatment spray treatment 0.5%	70.06	5.56	44.04	4.326	6.51
10	Tannic acid post-treatment spray treatment 1%	69.73	6.16	43.89	4.462	6.80
11	Tannic acid post treatment brushing treatment	70.55	6.25	44.97	4.459	6.38
12	Tannic acid post treatment gelifying treatment	77.21	2.50	41.85	2.264	5.13
13	Standarad dyed sample chitosan post treatment	88.62	2.39	50.76	1.193	0
14	Chitosan treated paper wash treatment	88.45	1.26	19.77	0.335	12.00
15	Chitosan treated paper spray treatment 0.5%	87.74	0.58	29.46	0.523	8.30
16	Chitosan treated paper spray treatment 1%	86.21	2.63	27.67	0.608	9.03
17	Chitosan treated paper brushing treatment	87.65	2.32	21.18	0.421	11.51
18	Chitosan treated paper gelifying treatment	88.22	-2.29	41.83	0.836	4.69

Table 5. Changes of lightness L* and chromatic coordinates a* and b* for cochineal dye deacidified samples induced by the de-acidification (Magnesium hydroxide nanopowder aqueous treatment) and accelerated aging

S. No	Color components values	L*	a*	b*	k/s	ΔE*
1	Standarad dyed sample Lemon juice post treatment	59.78	47.20	27.70	3.881	0
2	Lemon juice post treatment wash treatment	51.55	40.14	18.50	4.835	6.28
3	Lemon juice post treatment spray treatment 0.5%	58.02	42.67	26.34	4.135	2.04
4	Lemon juice post treatment spray treatment 1%	56.55	41.84	23.87	4.176	2.84
5	Lemon juice post treatment brushing treatment	49.77	45.03	26.77	7.075	4.29
6	Lemon juice post treatment gelifying treatment	54.12	45.55	28.61	5.791	2.66
7	Standarad dyed sample tannic acid post-treatment	63.16	24.50	21.15	4.989	0
8	Tannic acid post treatment wash treatment	48.48	12.53	17.92	2.889	26.96
9	Tannic acid post treatment spray treatment 0.5%	58.25	16.97	13.79	6.197	8.76
10	Tannic acid post-treatment spray treatment 1%	49.01	16.49	14.08	5.579	7.72
11	Tannic acid post treatment brushing treatment	47.21	16.51	11.12	4.220	9.38
12	Tannic acid post treatment gelifying treatment	51.63	24.46	-4.87	6.372	6.94
13	Standarad dyed sample chitosan post treatment	70.40	28.15	15.43	1.051	0
14	Chitosan treated paper wash treatment	49.24	19.50	-6.57	1.574	20.95
15	Chitosan treated paper spray treatment 0.5%	57.43	20.01	-3.68	2.618	17.08
16	Chitosan treated paper spray treatment 1%	51.12	19.73	-6.12	2.333	20.24
17	Chitosan treated paper brushing treatment	58.20	16.97	-4.65	1.578	18.04
18	Chitosan treated paper gelifying treatment	48.24	21.68	8.46	5.652	10.16

Table 6. Changes of lightness L* and chromatic coordinates a* and b* for cochineal dye deacidified samples induced by the de-acidification treatment (Magnesium hydroxide nanoparticles nonaqueous treatment) and accelerated aging

S. No	Color components values	L*	a*	b*	k/s	ΔE*
1	Standarad dyed sample Lemon juice post treatment	60.12	47.26	27.72	3.841	0
2	Lemon juice post treatment wash treatment	52.31	45.46	27.28	6.136	3.36
3	Lemon juice post treatment spray treatment 0.5%	59.42	42.61	26.45	5.313	1.99
4	Lemon juice post treatment spray treatment 1%	54.49	44.66	26.79	5.326	2.59
5	Lemon juice post treatment brushing treatment	56.27	46.07	29.87	3.786	2.37
6	Lemon juice post treatment gelifying treatment	58.81	43.01	25.50	3.832	1.88
7	Standarad dyed sample tannic acid post treatment	58.65	24.59	14.33	3.881	0
8	Tannic acid post treatment wash treatment	60.62	12.56	17.81	3.670	10.79
9	Tannic acid post treatment spray treatment 0.5%	50.01	16.47	12.32	5.263	6.06
10	Tannic acid post treatment spray treatment 1%	50.12	17.33	14.91	6.162	6.44
11	Tannic acid post treatment brushing treatment	49.81	16.24	11.29	5.339	6.08
12	Tannic acid post treatment gelifying treatment	48.97	23.31	9.09	5.556	5.99
13	Standarad dyed sample chitosan post treatment	46.25	19.51	-6.33	3.209	0
14	Chitosan treated paper wash treatment	59.34	16.94	-5.15	1.374	6.50
15	Chitosan treated paper spray treatment 0.5%	52.61	17.83	-5.82	2.102	3.22
16	Chitosan treated paper spray treatment 1%	56.97	18.12	-4.65	1.704	5.34
17	Chitosan treated paper brushing treatment	49.80	26.42	-3.98	2.922	5.15
18	Chitosan treated paper gelifying treatment	52.38	19.56	-6.59	2.136	2.94

Cellulose has been widely studied by FTIR, and many of the absorption maxima can be assigned to certain bond vibrations [24, 25]. The hydroxyl group is probably one of the most informative characteristics of all of the infrared group frequencies. It does not exist in isolation. The high association results from extensive hydrogen bonding with other hydroxyl groups. Natural polysaccharides, e.g. cellulose and hemicelluloses contained in the paper with their extensive hydrogen-bonding network significantly interact and bind additional water. Figures 2 and 3 show that a corresponding broad absorption maximum at about 3300cm^{-1} due to OH groups with intramolecular hydrogen bonding can be noticed. A notable change of this absorption maximum during accelerated aging in both acidified and de-acidified paper samples. By comparing the FTIR spectrum of the deacidified paper sample and the control sample, the data revealed that the blue spectrum representing the control sample (B) gave rise to the carboxyl group (COOH) at $3100 - 3400\text{cm}^{-1}$ and carbonyl group (C=O) at around $1620-1650\text{cm}^{-1}$, which indicates the occurrence of oxidation or a degradation process due to paper acidity. We observed in the aqueous treatment with magnesium hydroxide nanopowder spectrum, represented in red color, a decrease in the broadening of the carboxyl group and a decrease in the intensity of the carbonyl group (Fig. 2).

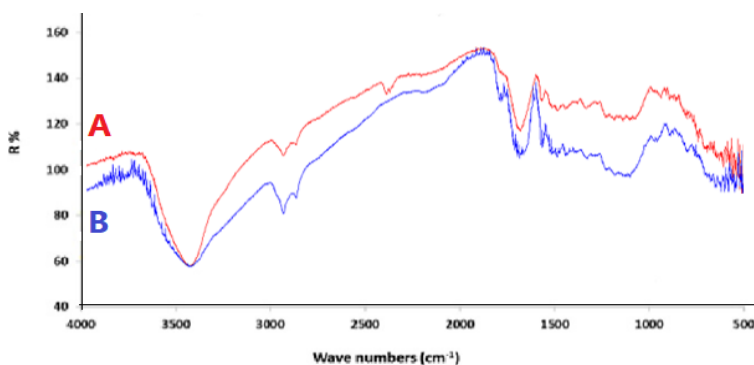


Fig. 2. FTIR spectra of the sample treated with magnesium hydroxide; A graph the spectrum of (aqueous treatment) and B the control sample

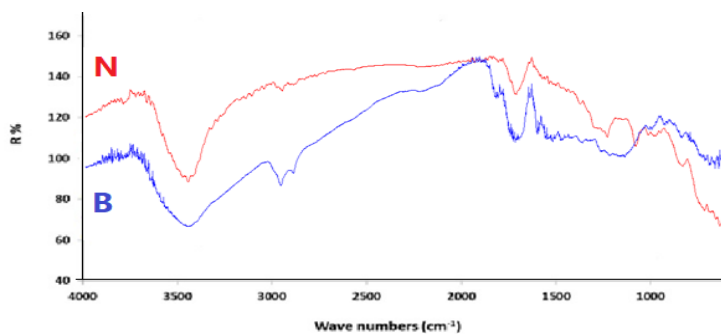


Fig. 3. FTIR spectra of the sample treated with magnesium hydroxide; N graph refers to the spectrum of the nonaqueous treatment, while B spectrum refers to the control sample

Similar results appeared concerning the nonaqueous treatment with magnesium hydroxide solution spectrum (Fig. 3). These results indicate minor deacidification of acidified paper samples. Good results appeared concerning the sample treated with the aqueous magnesium hydroxide nanopowder. The spectrum shows that the carboxyl group, a product of degradation, has disappeared and the OH band which is characteristic of cellulose has been recovered. There is also a notable decrease in the intensity of the carbonyl group indicating another product of degradation.

A comparison of results for the treated samples with different techniques representing different pH values, the FTIR spectra shows relevant differences according to the primary pH of the paper. The differences are most obvious when the solutions used have high alkaline pH or different concentrations, e.g. Magnesium hydroxide, and react with oxidized cellulose. The initial oxidation degree of the paper support relates to acidity. Thus, the most acidic samples are the ones with the most considerable changes in the carbonyl band based on the pH of the aqueous solution.

Treated samples with the immersion technique in aqueous Magnesium hydroxide demonstrated the most significant decline in the carbonyl band with the simultaneous formation of carboxylates. When they were soaked in magnesium hydroxide, a decrease of the carbonyl group resulted. Less acidic samples ($\text{pH} > 5.5$) illustrated minor decreases of the carbonyl band when soaked in magnesium hydroxide. The spectra of the samples whose pH was around 6.5 showed no differences when utilizing diverse deacidifying solutions [26]. The different behavior of deacidified agents indicated that numerous factors should be considered: The initial pH of the sample (together with the oxidation of cellulose), the pH of the aqueous solution (the pH of magnesium hydroxide between 10.5 and 12), and the technique used. The hydrolysis of oxidized cellulose resulted when utilizing alkaline solutions with highly alkaline pH at room temperature because the cellulose chain was broken at the β -glycoside bond. Mg^{2+} ions could

stabilize oxidized cellulose by aiding the complex between glucopyranoside units and the coordination of Mg^{2+} . This structure stabilizes the glycosidic bond and prevents later depolymerization [27].

Table 7. pH values of acidified paper samples dyed with selected dyes before and after de-acidification treatments (washing, spraying, brushing, and gelifying)

Sample No	pH value before deacidification	Washing	Spraying	Brushing	Gelifying
Saffron dye					
Standard sample	6.0	6.0	6.0	6.0	6.0
Dyed sample without mordant	4.0	8.2	7.2	7.4	9.7
Acidified lemon juice post treatment	3.0	7.8	7.3	7.0	9.0
Acidified tannic acid post treatment	3.0	8.0	6.8	7.2	8.9
Acidified chitosan treated paper	4.0	8.3	7.0	8.0	9.5
Turmeric dye					
Dyed sample without mordant	4.5	8.8	7.8	7.4	9.6
Acidified Lemon juice post treatment	2.0	8.0	7.0	6.8	8.5
Acidified tannic acid post treatment	3.0	7.8	7.0	7.0	9.3
Acidified chitosan treated paper	3.0	7.8	6.9	7.0	9.0
Cochineal dye					
Dyed sample without mordant	4.5	8.8	7.5	7.6	8.8
Acidified lemon juice post treatment	2.0	8.0	6.8	7.0	9.3
Acidified tannic acid post treatment	1.0	8.0	6.7	6.8	8.0
Acidified chitosan treated paper	2.0	8.4	6.8	6.7	9.5

The de-acidified papers had a pH greater than 6. The highest pH values were achieved in the samples treated with aqueous magnesium hydroxide nanopowder (Table 7). The treated samples by spray and brushing technique did not acquire a high alkaline pH after de-acidification treatment. De-acidification of the paper support had a relevant impact on changes of pH that shifted from 2 to neutral region (pH = 6.8) in the case of dyed paper samples in accordance with other de-acidification procedures. In the treated samples with the gelifying technique, the pH values shifted to the alkaline region (pH = 9.7) measured after 28 days of accelerated aging, the pH value in the neutral region (6.6–7.8). The abundance of the alkaline reserve considerably affected the protection of cellulosic fibers against acid hydrolysis. The pH data of all samples were in a mild alkaline medium. The lowest pH was obtained for paper samples treated with a nonaqueous magnesium hydroxide treatment with a value of 8.5. Samples treated with aqueous magnesium hydroxide also provided a very close pH reading of 8.8. Changes in pH may result in alterations in the colorimetric parameters of the applied dyes [28–31].

Conclusions

The present study stresses that color change values considerably relate to pH, and that nearly all plant-dyed paper samples were acidic. The relationship between pH and the long-term stability of paper samples demonstrates the results of the correlation between the acidity of papers and the lack of mechanical strength. Comprehending the mechanisms affecting the long-term stability of paper objects is vital for identifying papers that might be prone to rapid deterioration. Accordingly, adequate conservation treatments can be developed to increase the stability of papers. High pH paper specimens are associated with (low color change) that favors the stability of papers. Low pH paper specimens illustrated negative signs in conservation terms, such as a greater color change. pH may be a key factor affecting the long-term stability of the dyed paper samples. It is advisable to use magnesium hydroxide prepared through nanotechnology in the deacidification of paper. However, it must be applied following a technique known as gelification to improve the optical and mechanical properties of paper while efficiently deacidifying the acidity without causing damage to the treated artifacts. This technique was applied for the first time in the manuscript conservation field, by which magnesium hydroxide nanopowder was added to gellan gum and calcium acetate. This mixture was then placed in the microwave to obtain a gel-like substance. The gel would then be applied on the acidified paper with a Mylar sheet covering the treated surface until the acidity is neutralized. This technique reduces the damaging effects of aqueous treatments.

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