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A COMPARATIVE STUDY TO EVALUATE CONVENTIONAL AND NONCONVENTIONAL CLEANING TREATMENTS OF CELLULOSIC PAPER SUPPORTS

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ABSTRACT

Aqueous cleaning of ancient paper samples is a common treatment for the removal of degradation products, external contaminants and salts, which can cause degradation of cellulose by hydrolysis or oxidation processes. The present study examined the influence of selected cleaning treatments on chemical properties of some historical paper samples and studying the efficiency of cleaning methods in removing of degradation products. It also investigated the effects of five different cleaning treatments, namely immersion in deionized water, akapad paper sponge, hydro gellan gum, Cellulose nano Crystal gel and cleaning with wolbers solvent gels on ancient cellulosic paper supports. In particular, the effect of the cleaning treatments on different properties of cellulosic paper supports, namely colorimetric properties (CIE L*a*b* coordinates), crystallinity index (X-Ray diffraction), Fourier transform infrared spectroscopy(FTIR), scanning electron microscopy (SEM) and pH (cold-extraction method), were investigated. The study concluded that all cleaning treatments affected the colorimetric properties of the selected paper samples.

KEYWORDS: Cellulosic paper supports, akapad paper, deionized water, cleaning, gellan gum, solvent gels, Cellulose Nano Gel

1. INTRODUCTION

Conservation treatment is performed in order to preserve or restore artifacts. Therefore, only trained conservators who have experience in the appropriate material (such as paper, books art of works on paper, textiles, furniture, photographs, archeological objects, ethnographic objects and natural history specimens) should perform conservation treatments on ancient artifacts.

The preservation of cultural heritage to future generations is one of the main duties of humanity. Unfortunately natural, archaeological, historical and artistic materials are constantly subject to the action of many detrimental actions due to environmental pollutants, wrong handling practices, natural disasters, accidental damage, or simply to neglect. Thus, in order to ensure the durability of the whole human cultural heritage, any further decay shall be minimized (DeI, 2013).

Conservation treatments must ensure the most appropriate treatments for their continued preservation and use for objects, archives, and specimens and take into consideration an object's condition, history, significance, and use, treatments to be performed by skilled, experienced conservators and properly documented.

The preservation and conservation of paper documents are a necessary operation which applied in order to prolong the life time of artifacts by reducing chemical and physical deterioration in order to prevent and reverse further decay. There are several aqueous and non aqueous conservation treatments for paper artifacts, e.g. cleaning, consolidation, deacidification, neutralization, and aqueous methods for the ink fixatives. The effectiveness of these processes has been mainly studied by analysing changes in paper properties.

For example, wet cleaning of ancient papers is one of the most critical steps during a conservation treatment. It is used to improve the optical qualities of a graphic work and to remove dust and by-products resulting from cellulose degradation. Nevertheless, washing treatment usually involves a substantial impact on the original morphological structure of paper and can sometimes be dangerous for water sensitive inks and pigments. The use of rigid hydrogel of Gellan gum as an alternative paper cleaning treatment is developed. It was reported that the application of a rigid hydrogel minimizes damages caused by water. Therefore, it is much more respectful for the original integrity of ancient paper (Mazzuca et al. 2014).

The aqueous, non-aqueous and mechanical surface cleaning of cellulosic paper supports are long held techniques in the conservation treatments of paper manuscripts. In the twentieth century, paper conservation practice often involved the washing of degraded or discoloured paper artefacts. After bathing, paper artefacts were often perceived to be whiter, stronger, and healthier (Vitale, 1992).

Washing and deacidification processes are intended to convert the paper from an acidic to an alkaline condition by removing soluble discoloration at the same time. Therefore, it is necessary to begin by listing sources of the paper's acidity so that these could be properly counteracted and the deacidification treatments could have the required long-term benefit. Hence, knowledge of cellulose chemistry and paper making technology is essential when investigating paper conservation procedures (Hey, 2014).

aqueous treatments of cellulosic supports currently outweigh the risks. Among their potential benefits: (1) aqueous surface cleaning is a quick and effective means to remove dirt and discoloration; (2) immersion in deionized water is often a reliable method for removing manuscripts from degraded and damaged mounts; and (3) the washing of cellulosic manuscripts reduces the presence of degradation products in the paper support and may decrease the yellow/brown discoloration (Fench et al., 2011).

Solvent Cleaning used in removed types of spots or stains such as stains penetrate in to paper fibres and cannot be easily removed .The basis of stain removal with solvent its solubility in the selected chemical, their efficacy will depend on the nature of the stains and nature of the paper. (Rabee, 2015).

Akapad sponge has been designed for the cleaning of sensitive surfaces. It is used to carry out the convenient and safe dry cleaning of surface soiling on dry, non-staining nor chalking walls, ceilings, pictures, frescos, mural paintings, wallpaper, paper, textiles, coats of paint etc. The composition of the akapad white sponge has been especially formulated to provide excellent results in cleaning the works of art on paper (PH neutral). It leaves no residue and it is safe for use on sensitive surfaces. The wishab paper sponge consists of a blue grip and an attached cleaning sponge. The sponge works by absorbing dirt particles, then crumbling of to avoid polishing the treated surface (Scbotte et al., 2012).

Recently, gellan gum hydrogels have been proposed as effective tools to remove contaminant from paper supports due to the controlled water release and adhesive properties of gellan gum. Several polymers have been used by conservators for the formulation of gels and viscous polymeric dispersions either with organic solvents or water-based cleaning systems. The captive of a given cleaning (e.g. water, organic solvent, enzymes

solutions, chelating agents, etc.) is fluid (Bonelli et al., 2016).

The use of hydrogels as a new tool in the conservation of cultural heritage or cleaning and diagenostic is important because it does not require liquid treatments that could induce damage on artworks, while electrochemical biosensors are not only easy to prepare, but they can also be selective for a specific compound. Therefore, they are suitable for monitoring the cleaning process. In the field of restoration of paper artworks, more efforts have to be done in order to know how to perform the best way for an effective restoration. Rigid Gellan gel, made up of Gellan gum and calcium acetate, was proposed as a paper cleaning treatment (Micheli et al., 2014).

The present research aimed to evaluate the effect of the various cleaning treatments chemical and mechanical stability of cellulosic paper supports, the benefits of immersion in deionized water cleaning, akapad paper sponge and hydro gel gum cleaning the paper supports were treated by aqueous and non aqueous surface cleaning. Colour, as well as mechanical properties measurements were applied after this surface cleaning procedure.

2. MATERIALS AND METHODS

2.1. Materials

Archaeological unsized cellulosic paper support (cotton pulp paper) was selected for the study.

- Akapad Paper Sponge soft, White, Size: 90 x 67 x 42 mm (length, width, height) pH-Wert: Neutral. Purchased from Kremer pigments247 west 29th Street New York, NY1001.
- Deionized water and water from which dissolved ions have been removed by passing the water through cationic and anionic ion exchange resin, prepared in the chemistry lab at NCSU.
- Hydrogel gellan gum prepared in the lab, Gellan gum (Gelzan CM Geletric) and calcium acetate was delivered from Sigma (Sigma–Aldrich,Mo, St. Louis, USA.) To prepare the hydrogel an aqueous solution of Gelzanpowder 20 g (conc. 1-4%) and calcium acetate (0.40 g/ L) was put for a minute in the microwave at 600 W until complete hydration. (According to Casoli et al. 2013)
- Cellulose Nano Crystal gel. Cellulose Nanocrystal (CNC) purchased from The University of Maine a public research university in Orono, Maine, United States (process Development Center) 1-3 wt% of Cellulose Nanocrystals (CNC) (Freeze dried solid, Grade CNC 0.85 wt% sulfur on dry CNC Sodium form).
- Wolbers solvent gels (acetone gel, 2-propanol gel) Purchased from Kremer pigments247 west 29th Street New York, NY100.

2.1. *Cleaning procedures*

The paper supports were divided into five samples depending on the type of cleaning procedure. While the first sample was cleaned by immersion in de ionized water, the second sample was cleaned with akapad paper sponge, the third sample was cleaned by hydro gellan gum, the forth sample was cleaned with Cellulose Nano Gel and the last sample was cleaned with Wolbers solvent gel.

2.2. *Accelerated aging of paper after cleaning*

In order to evaluate the long-term of cleaning treatments, the selected paper samples were exposed to heat accelerated-aging procedures. The samples were exposed to 105 ± 2°C in a laboratory oven for 28 days. The samples were analyzed for surface pH, CIE L*a*b*, tensile strength (TS). Previous to and immediately after the tests, samples were equilibrated at 23°C and 50% RH for 24 hours. (Wang et al, 2013)

2.3. *Scanning electron microscope (SEM)*

Scanning electron Microscopic examinations of the samples was carried out using an Electron Microscope Survey Nanoscience instrument FEI Company MVE00001162, FP 3950/00 at NCSU. All the samples examined were prepared according to the standard procedures. The samples were coated with gold using EMITECH K450X sputter coater to avoid charging. The SEM has a scan area of 50 mm x 50 mm as standard. Optionally, the motorized scan area can be upgraded to 100 mm x 100 mm. The examination of samples was performed at the SEM Laboratory, Department of Polymer and Color Science, the University of North Carolina.

2.4. *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR spectroscopy was used to study the functional groups present in paper and the changes that have occurred due to 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, in the frequency range of 4000 - 500 cm^{-1}, in reflectance mode.

2.5. CIELab color variations measured with Color iMatch Spectrophotometer

The colorimetric coordinates L*, a*, and b*of the CIE L*a*b* color space were used to express color change.

The colour change resulted from cleaning was registered by measuring the L*a*b* parameters which define the colour in CIE L*a*b* colour space. The total changes of the L*a* b* value was described as the colour change (ΔE), which is calculated according to the given formula (Jeżewskaetal, 2016):

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)\ 2]^{1/2}$$

In which: ΔL*, Δa*, Δb* stand for – in our studies – changes of the values resulted from the deacidification. Measuring the color difference was performed on the Color iMatch spectrophotometer manufactured by X-rite Michigan USA. This instrument enables the direct read out of the ΔE value.

2.6. Evaluation of pH values before and after cleaning treatments

Determinations of pH were performed with an Oakton pH/mv/c Meter737850 manufactured by Eutech instruments, thermo fisher scientific Measurement of pH was performed on samples according to. The paper is mixed with water, and after letting it stand for 1 hour in the cold, the pH is determined in the unfiltered mixture, using a glass electrode (Launer, 1939).

2.7. Determination of paper crystallinity with X-ray Diffraction

This technique was employed to study the crystallinity degree of cellulose for the treated samples compared to the control samples.

The cellulose crystallinity for the measured samples control sample and the treated samples with consolidants were calculated according to the following equation:

$$Cr.I\% = \frac{I(002) + I\ 18º * 100}{I\ (002)}$$

Where I (002) and I 18^o are the maximum scattering intensities of the diffraction from the (002) plane at 2θ = 2.26° and the diffraction intensity of the background scatter measured at 2θ = 18°, respectively, and the latter value being attributed to the non-crystalline cellulose form (Zidan et al., 2016).

$$Crystallinity\ (\%) = \frac{Area\ under\ crystalline\ peaks\ * 100}{Total\ area\ under\ all\ peaks}$$

XRD of the treated and untreated paper samples before and after cleaning treatments was carried out on a Philips XLF diffractometer, ATPS XRD 1000 with OMNI instruments, Luc customized Auto mount with cupper tube.

2.7. Physical Testing (Tensile strength and elongation for paper samples after Cleaning treatments)

Mechanical behaviour of the samples (tensile strength, elongation % and breaking factor) were studied using the MTS Q-Test/5 Universal Testing Machine, according to ASTM_D828-Modified-250-load.msm.

The samples were cut in the machine direction to strips of 2 cm × 10 cm. All measurements were made before and after treatment and compared to that of the control sample. The procedure was carried out in aging ovens at the physical testing lab at college of textile North Carolina State University.

3. RESULTS AN DISCUSSION

3.1. Scanning Electron Microscopic analysis

SEM of the samples was carried out using an Electron Microscope Survey Nanoscience instrument FEI Company MVE00001162, FP 3950/00 at NCSU. All the samples examined were prepared according to the standard procedures. The samples were coated with gold using EMITECH K450X sputter coater to avoid charging. The SEM has a scan area of 50 mm x 50 mm as standard. Optionally, the motorized scan area can be upgraded to 100 mm x 100 mm.

The scanning electron microscope (SEM) produces detailed images at a higher magnification than a light microscope. In our study we used the SEM to study the surface of paper support, and the effects of different cleaning treatments. SEM is particularly useful for looking for subtle signs of deterioration in paper, such as the initial stages of defibrillation of plant fibers; the morphology of fracture surface.

SEM examination of paper support revealed the source of cellulose fiber which has been identified as cotton pulp paper. The SEM examination also showed a high degradation degree with the cellulose fibers broken (Fig. 1). SEM observation also revealed mechanical damage.

SEM photos of examined paper samples before cleaning treatments are illustrated in Fig.1. These photos show that the paper support is extremely degraded. Comparing all the obtain SEM photos it can be noticed that CNC gel and hydro gellan gum were most effective treatments in removing of degradation products, soils and dust.

SEM examination also revealed a superficial coating on the treated paper samples hydro gellan gum (Fig. 4).

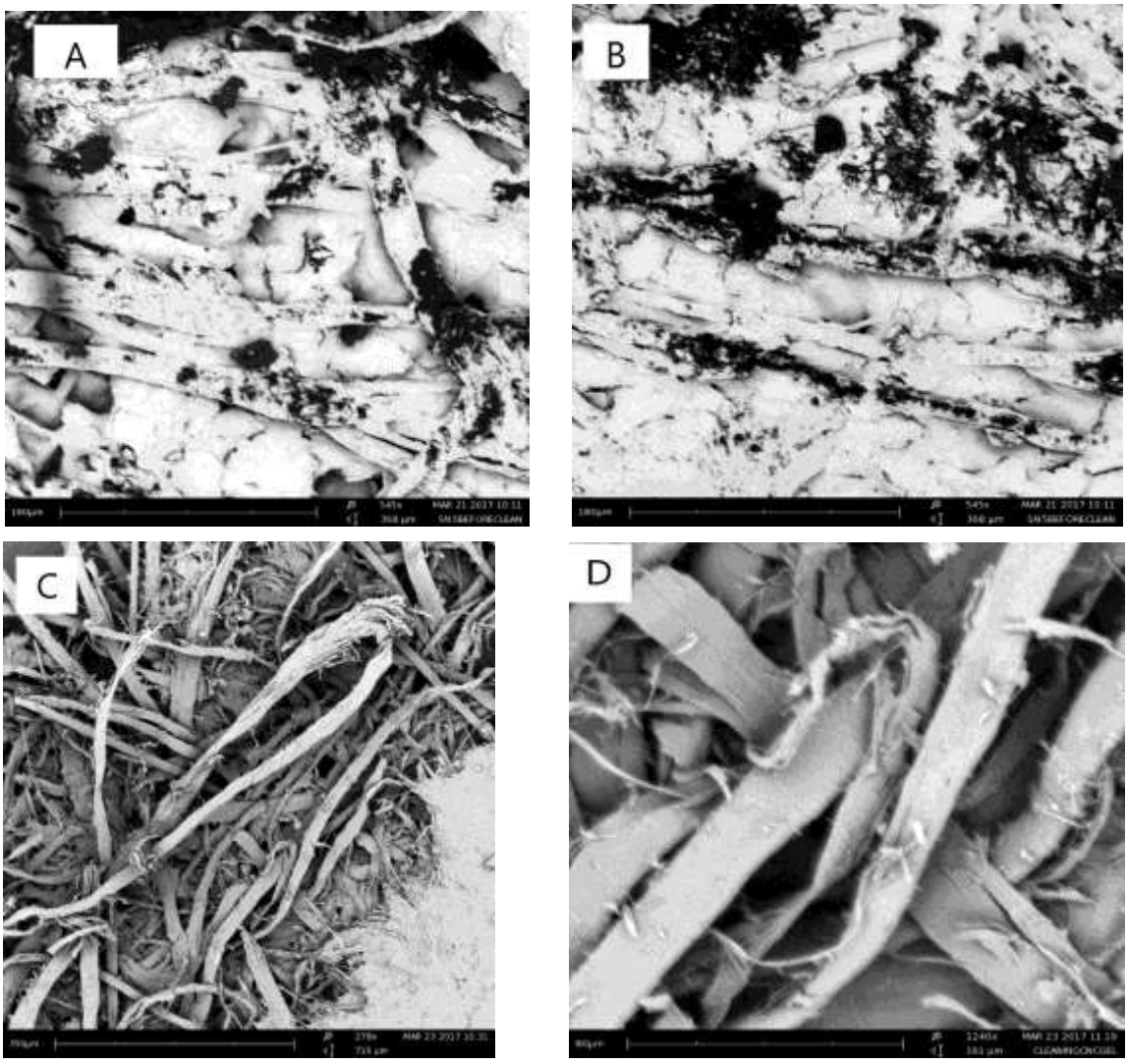

Figure 1. SEM micrographs of historical sample before and after cleaning methods.; Photo A and B show critical damage of paper support while C,D show SEM image of cotton fibres used to make the paper support.

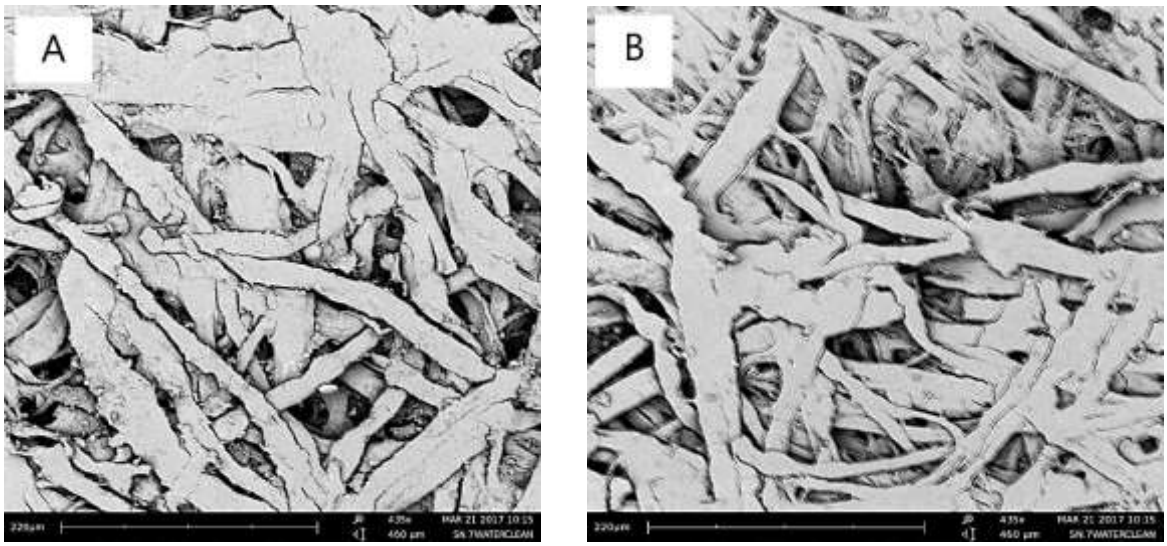

Figure 2. SEM micrographs of paper sample after cleaning with deionized water; photo A show the paper surface after cleaning treatment while B show the paper Surface after aging. (wet cleaning)

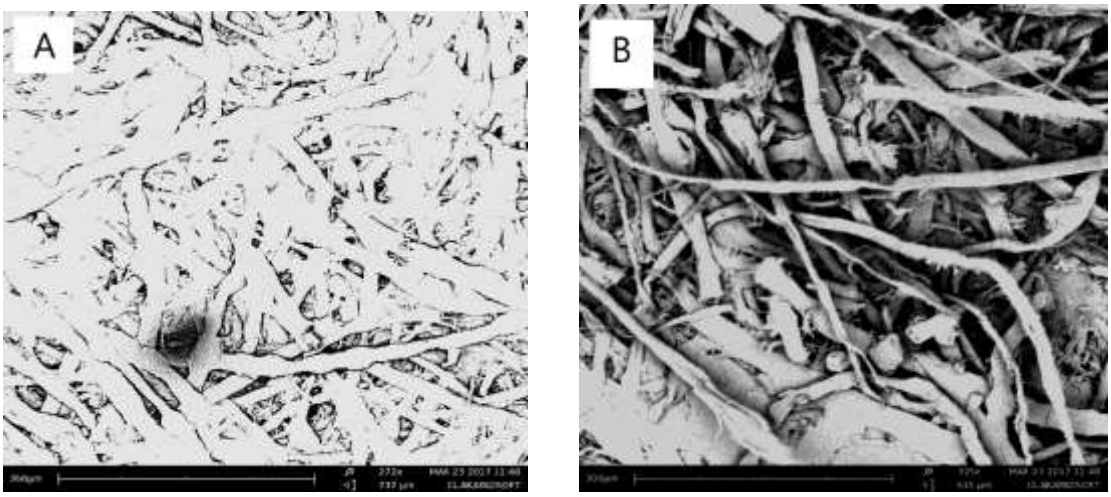

Figure 3. SEM micrographs of paper sample ;Photo A shows the paper surface after cleaning with akapad soft sponge the sponge works by absorbing dirt particles, then crumbling of to avoid polishing the treated surface while B shows the cellulose fibre after ageing . (Mechanical cleaning)

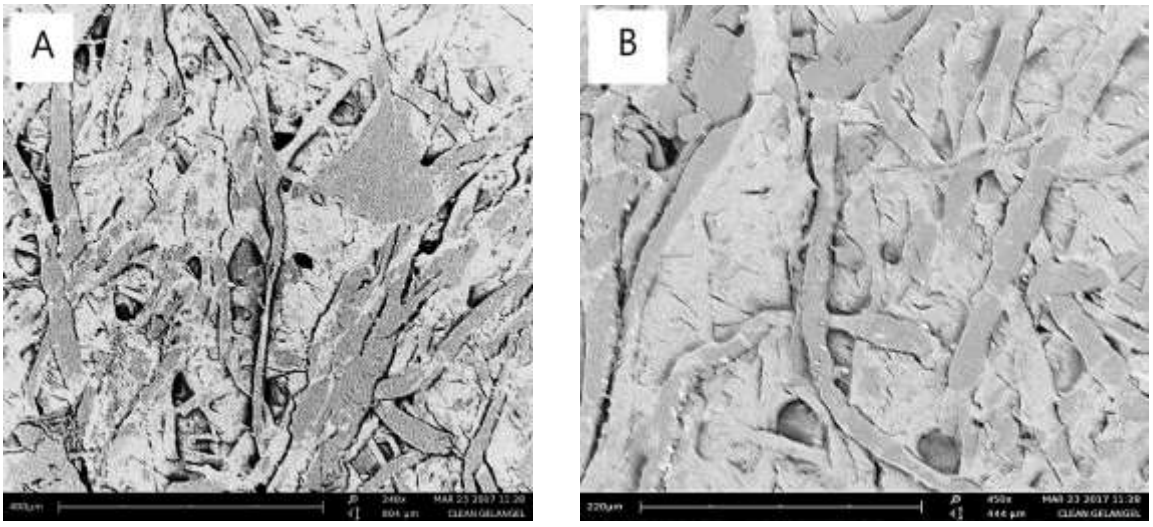

Figure 4. SEM micrographs of paper sample; Photo A shows the paper support after cleaning with hydro gellan gel prepared in the lab. B shows the paper support after aging.

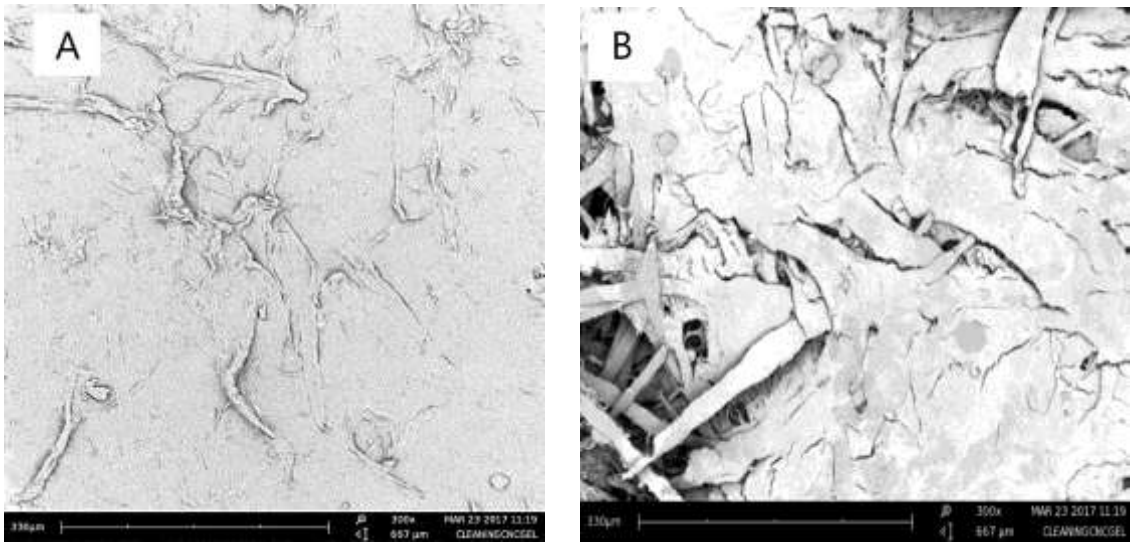

Figure 5. SEM micrographs of paper sample; Photo A shows the paper support after cleaning with Cellulose Nano Crystal gel prepared in the lab, this method was performed in order to clean and consolidate paper while B shows the surface after accelerated thermal ageing.

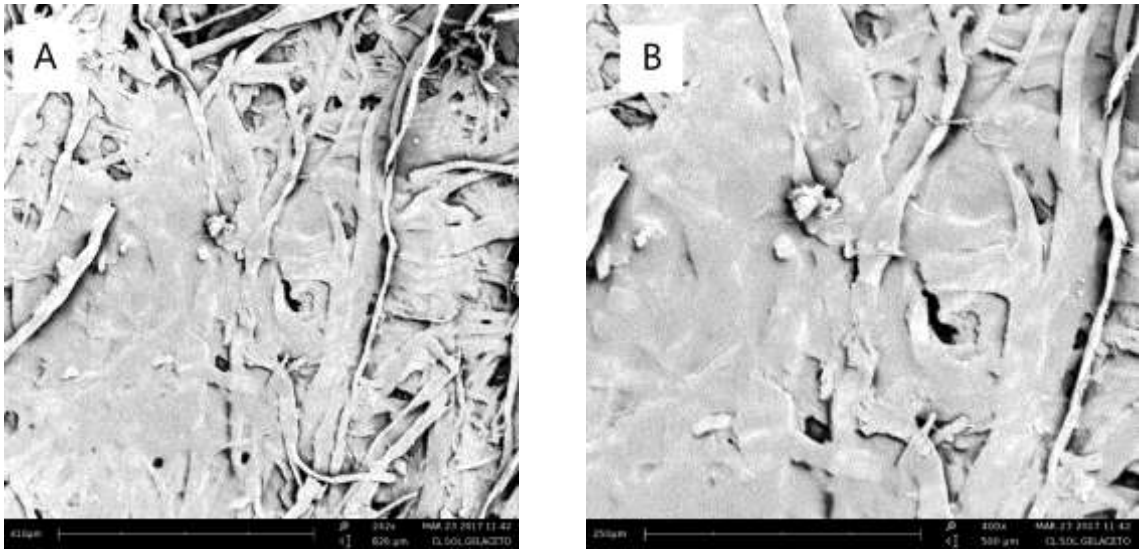

Figure 6. SEM micrographs of paper sample; Photo A shows the paper support after cleaning with Wolbers solvent gel acetone while B shows the surface after accelerated thermal ageing.

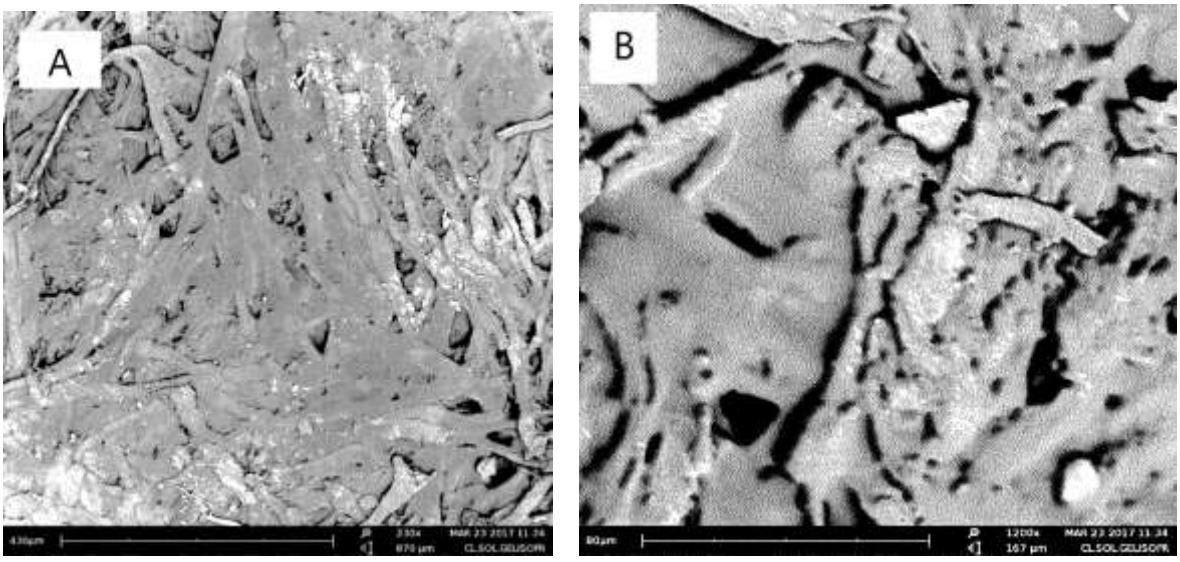

Figure 7. SEM micrographs of paper sample Photo A shows the paper support after cleaning with Wolbers Solvent gel isopropanol while B shows the surface after accelerated thermal ageing.

3.2. *Fourier Transform Infrared Spectroscopy (FTIR)*

Fourier-transform infrared (FTIR) spectroscopy is an important analytical tool used in the examination of historical materials. The technique produces a spectrum that provides intrinsic details about bonding features between atoms or characteristic functional groups in a molecule. It also provides information regarding chemical changes due to chemical treatment or aging, based on appearance of a new band, band shift, or intensity change of individual bands. One of the important advantages of using this technique is the ability to perform non-destructive analysis on historical objects.

Since the FTIR is very useful for examining the variation of hydrogen-bonds due to various defects. The structure of cellulose has a remarkable and complex influence on the course of chemical reactions of the polymer (cellulosic materials). Generally, the structure of cellulose consists of three structural levels: namely (i) the molecular level of the single macromolecule; (ii) the supramolecular level of packing and mutual ordering of the macromolecules; (iii) the morphological level concerning the architecture of already rather complex structural entities, as well as the corresponding pore system. (Fan et al, 2012)

The (FTIR) spectroscopy is very important tool for detecting the functional groups. The paper samples were identified by the interpretation of the absorption spectra from IR spectrometric analysis. It was noticed from the FTIR chart in Fig. 8 that the broad peak at 3320cm^{-1} is due to OH stretching vibration it is assigned to the hydroxyl groups in cellulose, and

the band at 2900 cm^{-1} is related to CH_2 stretching vibration of CH3 group and it is assigned to the hydrocarbon group in cellulose, hemicellulose and lignin. The band at 1642 cm^{-1} is assigned to stretching vibration of -C=O and it is due to cellulose oxidation and formation of carbonyl and carboxyl groups. (Rabee 2015)

The paper support has been slightly hydrolyzed, showing an in-crease in the OH stretching band region at around 3320cm^{-1}, the presence of the C-O stretching band, and the presence of the H_2O band at 1642 cm^{-1} (figure 8, 9). The spectrum of the treated sample with akapad sponge peak at around 1650cm^{-1} which indicates the presence of carbonyl groups (C=O) which are due to cellulose oxidation. The increase in the OH stretching band is due to the hydrolysis of the cellulose and formation of hydroxyl groups. In addition, the very broad OH stretching band indicates more hydrogen bonding.

The FTIR absorption band at 1426 cm^{-1}, assigned to the CH_2 band, which is known as the "crystallinity band", decreaces in its intensity; this reflects reduction in the degree of crystallinity of cellulose. (Ferrer and Sistach, 2007).

A comparison of results for treated samples with different cleaning procedures shows spectra with relevant differences depending on the internal acidity of paper support. These differences are most evident the efficiency of cleaning methods in removing of degradation products; therefore, the most acidic samples are those which show the most important changes in the carbonyl band depending on the cleaning procedure.

After cleaning treatment, dried samples were analyzed to assess treatment efficiency. FTIR analysis shows that hydro gellan gel applications do not leave residues on paper material. The hydrogel displays a very characteristic IR spectrum, whose peaks are not present in every spectrum of the treated samples, as shown in Fig. 11. The spectra obtained before and after treatment, are indeed comparable, also suggesting that no detectable chemical degradation of cellulose takes place as a result of the hydrogel treatment. SEM images (Fig. 2, 4) confirm these results as both samples after immersion in deionized water and hydrogel treatment, seem cleaner and no swelling are present.

The spectrum of the treated sample with deionized water has no changes are observed in the functional groups characteristic of cellulose, an increase in the OH group at around 3332cm^{-1} is observed and this indicates the hydrolysis process, an increase is also noticed in the C=O absorption band at 1648 cm^{-1} indicating the oxidation process of cellulose molecule. A decrease is also noticed at the band of –CH stretching (2917-2900) due to the reduction of the hydrocarbon group in cellulose, hemicellulose and lignin. Peak at around 1650 cm^{-1} which indicates the presence of carbonyl groups (C=O) which are due to cellulose oxidation. The increase in the OH stretching band is due to the hydrolysis of the cellulose and formation of hydroxyl groups. In addition, the very broad OH stretching band indicates more hydrogen bonding (Fig. 10).

Similar case was observed in the treated sample with cellulose nano crystal gel (Fig. 12). FTIR spectrum no changes are observed in the functional groups characteristic of cellulose, a slight increase in the OH group at around 3331cm^{-1} is observed, an increase is also noticed in the C=O absorption band at 1649 cm^{-1} indicates to the oxidation process of cellulose molecule. A decrease also noticed at the band of –CH stretching at around 2917-2899. (Batterham and Rai, 2008)

FTIR spectrum of paper treated with wolbers solvent gels reveals the presence of the carbonyl groups at around 1650 cm^{-1} indicating the occurrence of slight oxidation. The presence of the C=C stretching of the aromatic ring at around 1506 cm^{-1} indicates the presence of lignin which explains the embrittlement and yellowing of paper support. A slight increase of carbonyl vibrations at around 1644 cm^{-1} and carboxyl vibrations at around 3466 cm^{-1} Oxidation of the cellulose molecule. Changes are also observed in the functional groups characteristic of cellulose, a slight increase in the OH group at around 3333cm^{-1} this indicates the hydrolysis process (Fig. 13, 14)

Table 1: shows the function groups for the historical paper sample.

Wave number cm^{-1}	Functional group
3320 cm^{-1}	**-OH Stretching**
2917 cm^{-1}	**-CH Stretching**
1642 cm^{-1}	**-C=O Stretching**
1426 - 1315 cm^{-1}	**-C=C Stretching**
1103- 1128 cm^{-1}	**C-O Stretching**
556-435 cm^{-1}	**-C=C-H**

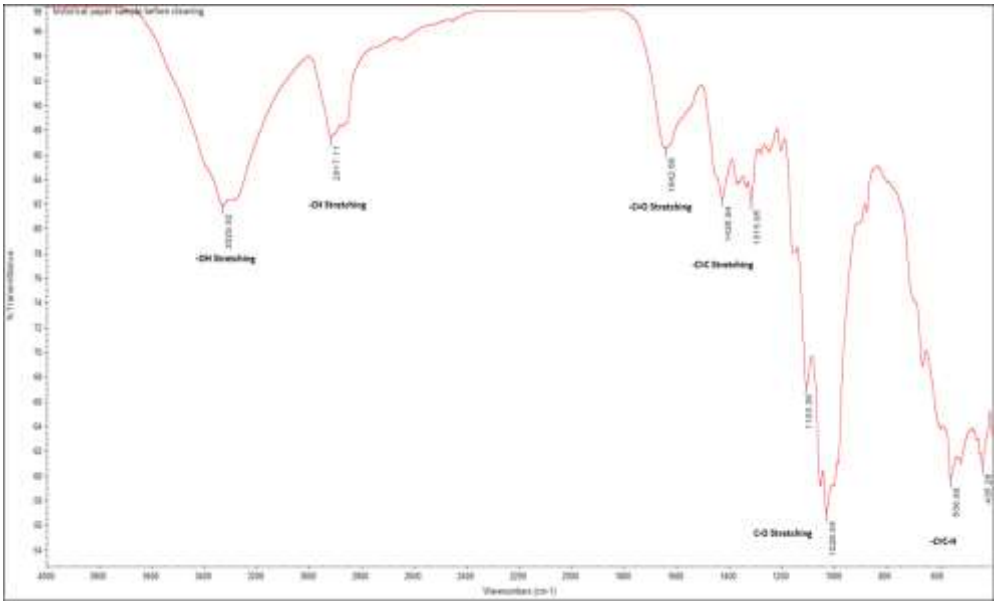

Figure 8. FTIR spectrum of historical paper sample before cleaning The broad peak at 3320cm^{-1} is due to OH stretching vibration it is assigned to the hydroxyl groups in cellulose, and the band at 2900 cm^{-1} is related to CH_2 stretching vibration of CH_3 group and it is assigned to the hydrocarbon group in cellulose, hemicellulose and lignin. The band at 1642 cm^{-1} is assigned to stretching vibration of -C=O and it is due to cellulose oxidation and formation of carbonyl and carboxyl groups.

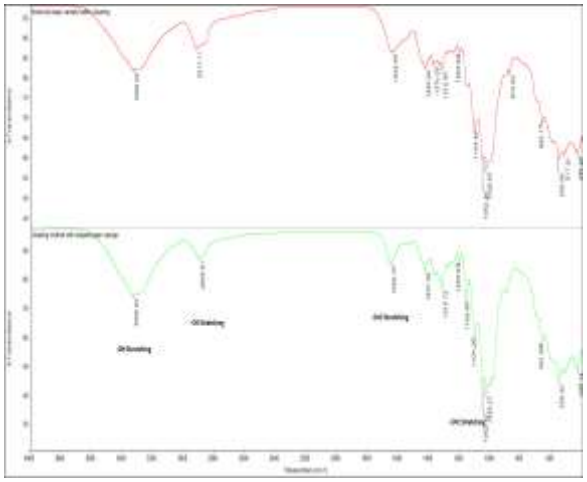

Figure 9. FTIR spectrum of historical paper sample before cleaning compared to the cleaned sample with Akapad paper soft sponge.

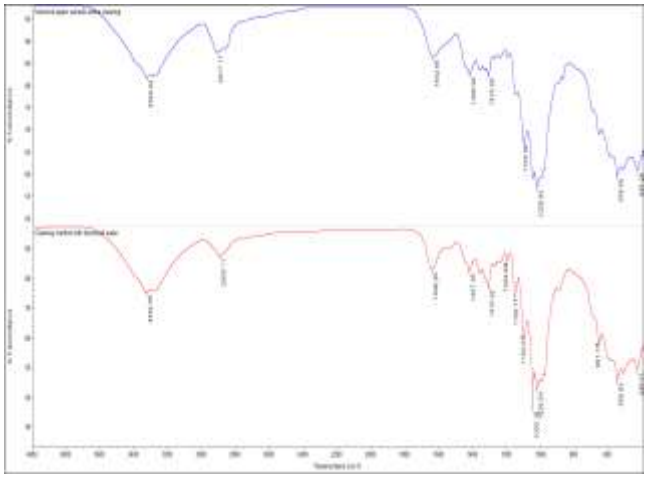

Figure10. FTIR spectrum of historical paper sample compared to the cleaned sample with deionized water.

There is no changes are observed in the functional groups characteristic of cellulose, an increase in the OH group at around 3332cm^{-1} is observed and this indicates the hydrolysis process, an increase is also noticed in the C=O absorption band at 1650 cm^{-1} which indicates the oxidation process of cellulose molecule. A decrease is also noticed at the band of –CH stretching (2917-2899) due to the reduction of the hydrocarbon group in cellulose, hemicellulose and lignin.

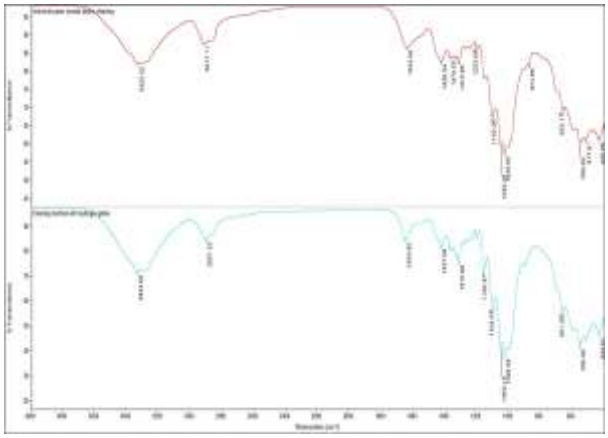

Figure 11. FTIR spectrum of historical paper sample before cleaning compared to cleaned sample with hydro gellan gel.

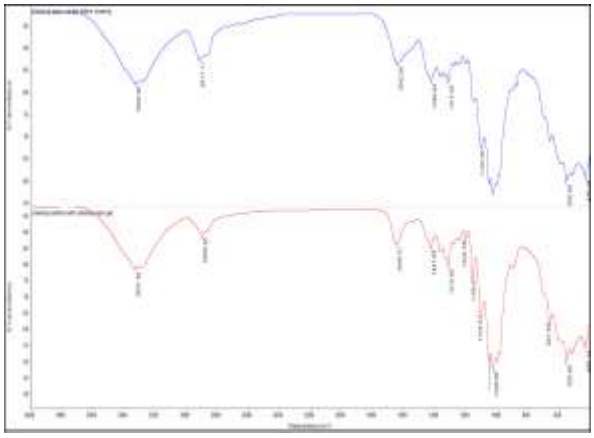

Figure 12 . FTIR spectrum of historical paper sample before cleaning compared to cleaned sample with cellulose nanocrystal gel

There is no changes are observed in the functional groups characteristic of cellulose, a slight increase in the OH group at around 3331cm^{-1} is observed and this indicates to hydrolysis process, an increase is also noticed in the C=O absorption band at 1649 cm^{-1} indicates to the oxidation process of cellulose molecule. A decrease also noticed at the band of –CH stretching at (2917-2899) it is assigned to reduce the hydrocarbon group in cellulose, hemicellulose and lignin.

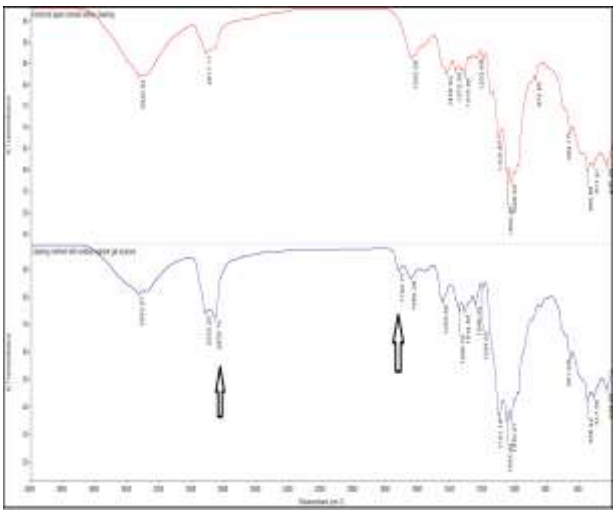

Figure 13. FTIR spectrum of historical paper sample before cleaning compared the cleaned sample with acetone Wolbers solvent gel.

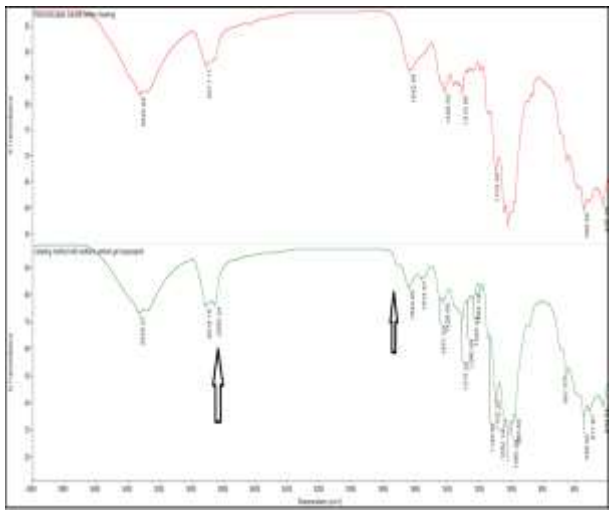

Figure14. FTIR spectrum of historical paper sample before cleaning compared the cleaned sample with isopropanol Wolbers solvent gel

Changes are observed in the functional groups characteristic of cellulose, a slight increase in the OH group at around 3333cm^{-1} is observed and this indicates the hydrolysis process, an increase is also noticed in the C=O absorption band at 1650cm^{-1} indicates to the oxidation process of cellulose molecule. An increase also noticed at the band of –CH stretching (2917-2920cm^{-1}) due to the hydrocarbon group in cellulose, hemicellulose and lignin.

3.3. CIELab color variations measured with Color iMatch Spectrophotometer

Colorimetric measurements were carried out on untreated, treated samples to assess chromatic variations. Chromatic values are expressed in the CIE L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue).

CIELab b* values Test results are provided in Table 2. Lower (more negative) CIELab b* values and higher positive values indicate that more blueing, or whitening effect .The data showed that the total color change ΔE for the sample treated with wolbers solvent gel were lower than the treated with akapad sponge . It was observed also that ΔE value in sam-

ples treated with cellulose nano crystal gel higher as compared to the control sample, with all values still in the acceptable range.

Slight color changes were measured in the aqueous treatment (immersion in deionized water) these changes are primarily due to the removal of dirt. A layer of dirt behaves much like a neutral-density filter; each wavelength in the visible spectrum receives a slight boost in reflectance when it is removed. The slight increases in all three of the CIE L*a*b* parameters, L* lightness, a* redness and b*yellowness, should be interpreted as an increase resulting from a slight increase in reflectance for all wavelengths. One can't observe an increase in yellowness and redness while ignoring the increase in lightness. The increases in both spectral reflectance and CIE L*a*b* are favourable. The CIE L*a*b* data for some of the historical paper samples (summarized in Table 3) immersion in deionized water treatment increased lightness, and decreased yellowness and redness for the paper support. (Messier & Vitale, 1994)

Table 2. Presents all colorimetric results for the historical paper support measured before cleaning treatments, and after cleaning treatments. Note the relatively large gains for the L* value for paper support after cleaning with cellulose nano gel.

Samples	L	a	b	ΔE	ΔL*	Δa*	Δb*	ΔE*
Control sample before cleaning	73.06	7.23	26.55	0	0	0	0	0
akapad Paper Sponge soft	81.73	2.99	17.32	6.89	10.51	-4.24	-9.22	11.82
Immersion in deionized water	78.90	4.48	20.67	4.20	5.83	-2.75	-5.88	8.37
Hydrogel gellan gum	83.57	3.90	19.23	5.51	8.67	-3.33	-7.32	14.61
cellulose nano crystal gel	84.10	2.79	15.99	7.50	11.04	-4.44	-10.56	15.91
Wolbers solvent acetone gel	77.42	5.53	24.16	2.45	4.35	-1.70	-2.38	5.24
Wolbers solvent 2-propanol gel	77.45	5.54	24.07	2.47	4.39	-1.69	-2.48	5.31

3.4. Measurement of pH values before and after cleaning treatments:-

pH measurements (Table 3) give information on the amount of acidity present in the paper and so to the preservation state of the historical samples. pH value detected in the paper sample is probably due to the presence of lignin. The increase of pH values obtained after cleaning procedures indicates that acidic components, involved in degradation processes are removed; anyhow it should be noted that the pH values are acidity is lightly higher after Gellan hydro gel cleaning procedure. These results indicate that hydro gel treatment is an efficient cleaning method and does not cause change in the morphology of paper (Fig. 14). It can be observed that there is an increase in the pH values of the treated samples with both Cellulose Nano Crystal gel and hydro gellan gel compared to the control sample before cleaning. The samples treated with akapad paper sponge showing no change in the pH values.

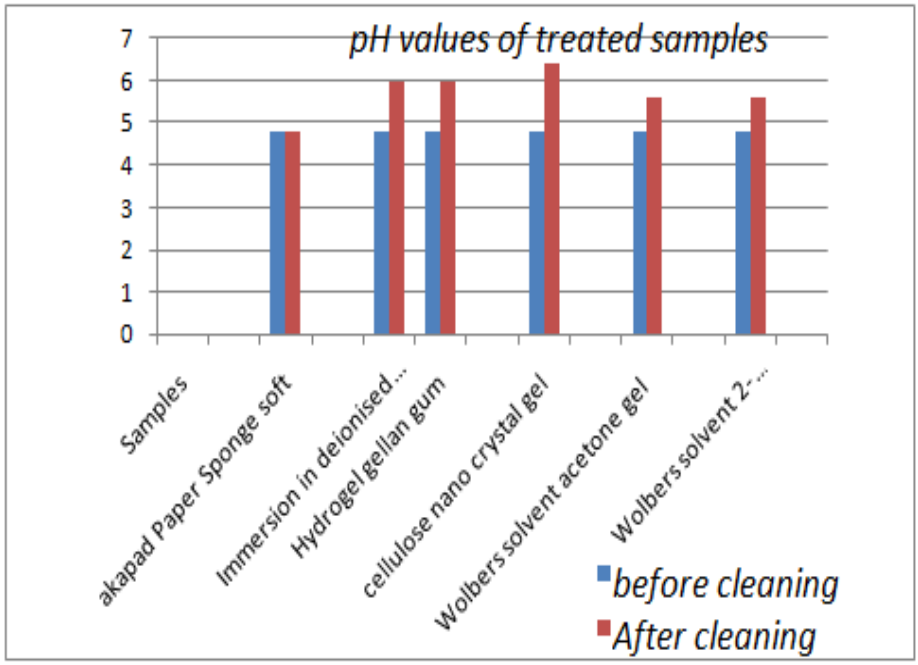

Figure 14. pH values of untreated & treated paper samples.

Table 3 shows pH values before and after cleaning procedures

Samples	pH values before cleaning	pH values after cleaning
Akapad Paper Sponge soft	4.8	4.8
Immersion in deionised water	4.8	6
Hydrogel gellan gum	4.8	6
Cellulose nano crystal gel	4.8	6.4
Wolbers solvent acetone gel	4.8	5.6
Wolbers solvent 2-propanol gel	4.8	5.6

3.5. *X-ray Diffraction Analysis (XRD)*

X-ray diffraction was also used to measure crystallinity index of cellulose according to Segal equation. Where: (Cr) expresses the crystallinity of cellulose (I002) express the maximum intensity of the crystallinity peak at (2θ = 22-24°) and (Iam) represents the intensity of diffraction of the non-crystalline cellulose at (2θ = 18°) Comparison between the cellulose crystallinity of the historical paper sample and the sample after cleaning with selected cleaning procedures indicated a decrease in the crystalline index of the treated samples.

The results of XRD show that there are noticeable differences in the crystalline & amorphous areas in the paper before and after cleaning treatments (see Fig. 15, 16, 17, 18, 19 and 20). They illustrate that the paper samples were affected by the selected cleaning procedures. Also, the results show that there was a change in the XRD pattern of the untreated and treated paper samples after cleaning treatments. Crystalline regions of the treated paper samples were slightly decreased. By comparing the results of x ray diffractograms of treated samples (with deionized water, akapad sponge, and wolbers solvent gels) and untreated sample, the data shows that a large decrease in the crystallinity index of cellulose, indicating that a significant change has occurred in the chemical and mechanical properties of cellulose molecule.

Cellulose Nano Crystal treatment showing a slight increase in the crystallinity index in the cellulose crystallinity compared to the control sample, which means that a moderate change has occurred in the chemical and mechanical properties of cellulose molecule (Fig. 20).

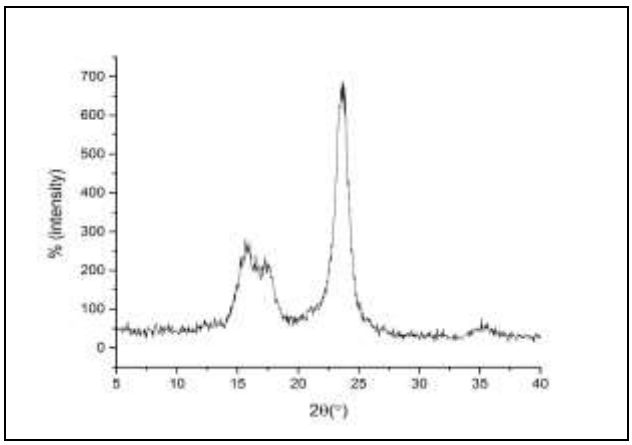

Figure 15. XRD pattern for the control sample before cleaning Crystallinity index=61

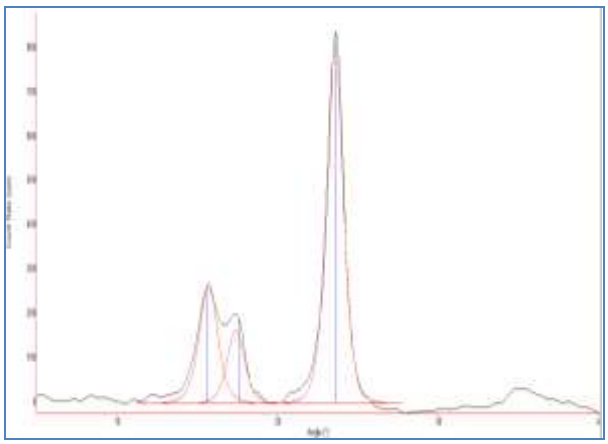

Figure 16. X-ray diffraction pattern of historical paper sample explaining how the crystallinity peaks of cellulose are measured

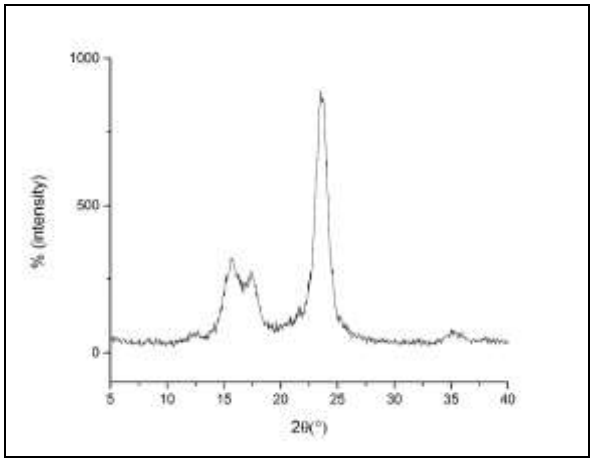

Figure 17. XRD pattern for the cleaning method with deionized water crystallinity index=11 showing a large decrease in the crystallinity index of cellulose indicating that a significant change has occurred in the chemical and mechanical properties of cellulose molecule.

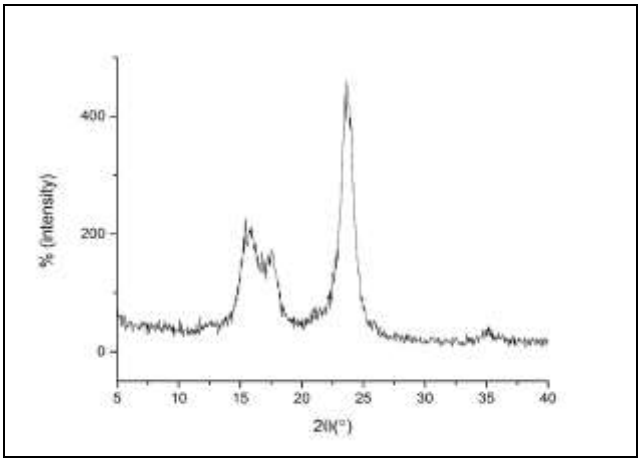

Figure 18. XRD pattern for the cleaning method with akapad paper sponge Crystallinity index=11.16 showing a large decrease in the crystallinity index of cellulose, indicating that a significant change has occurred in the chemical and mechanical Properties of cellulose molecule.

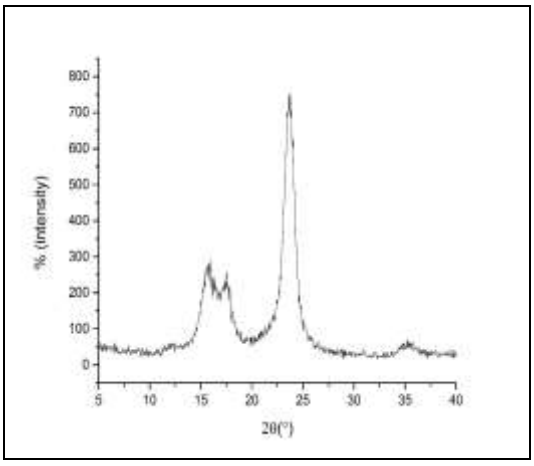

Figure 19. XRD pattern for the cleaning method with hydro Gellan gum crystallinity index=58.3 showing a slight decrease in the crystallinity index of cellulose indicating that only a less change has occur the chemical and mechanical properties of cellulose molecule.

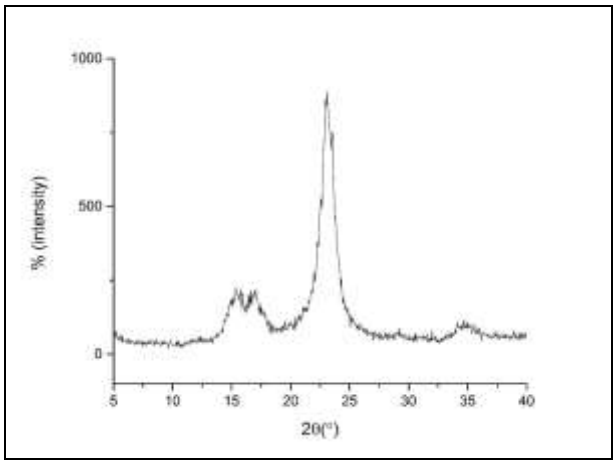

Figure 20. XRD pattern for the cleaning method with Cellulose Nano Crystal gel crystallinity index=17.00 showing a large decrease in the crystallinity index of cellulose, indicating that a significant change has occurred in the chemical and mechanical properties of cellulose molecule at the crystalline regions.

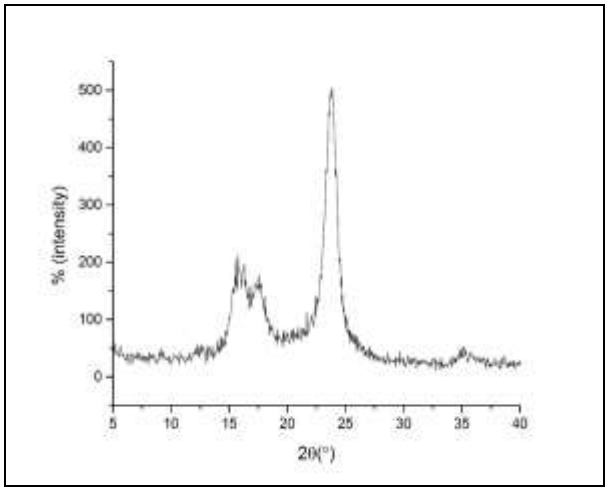

Figure 21. XRD pattern for the cleaning method with Wolbers solvent acetone gel crystallinity index=61.4 showing a slight increase in the crystallinity index in the cellulose crystallinity compared to the control sample which means that a moderate change has occurred in the chemical and mechanical properties of cellulose molecule

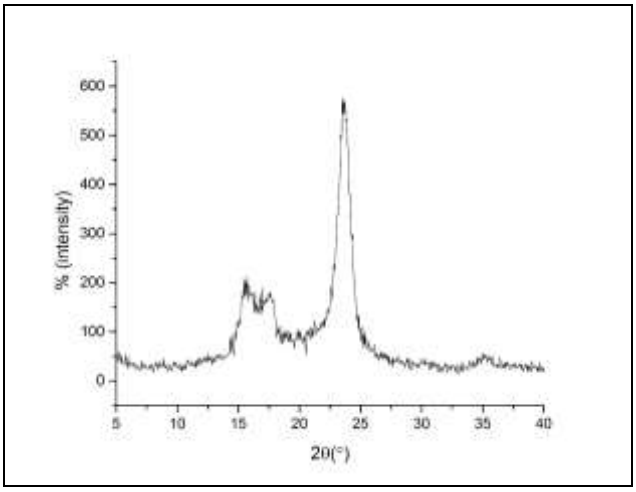

Figure 22. XRD pattern for the cleaning method with Wolbers solvent 2-propanol gel crystallinity index=18.5 showing a large decrease in the crystallinity index of cellulose, indicating that a significant change has occurred in the chemical and mechanical properties of cellulose molecule at the crystalline regions

3.6. *Mechanical behaviour of the samples (tensile strength, elongation % and breaking factor)*

The values of tensile strength and elongation (%) are shown in Table 4. The results reported are the average of five measurements with standard deviation. The Values of tensile strength reflect the detailed structure of the paper and the properties of its individual fibers, i.e., the dimension and strength of fibres, their arrangements, and inter fibre bonding Values of tensile strength reflect the detailed structure of the paper and the properties of its individual fibers, i.e., the dimension and strength of fibers, their arrangements, and inter fiber bonding (Caulfield& Gunderson, 2008). The percent loss in tensile strength of treated paper samples with akapad paper and wolbers solvent gels revealed a high sensitivity of tensile strength to the effects of cleaning procedures. (Rabee, 2015). Treated papers with acetone and isopropanol solvent gel caused a noticeable decrease of tensile strength while in the case of wet cleaning procedure (deionizied water treatment) treated samples exhibited a statistically significant decrease in tensile strength From these results, it can also be concluded that preconditioning can satisfactorily bring the moisture content of the treated paper to levels that do not affect tensile strength.Which is capable of swelling the carbohydrate components of celluloses and may accelerate further degradation, and can also dissolve and extract the starch and decayed hemicelluloses (Zervo, 2013).

Treated sample with CNC Gel gave the highest increase in tensile strength and elongation compared to the other samples, while treated sample with deionized water gave the lowest values for tensile strength and elongation. The results for Hydro gellan gum indicate average values.

Table 4. All Physical Testing results; Tensile strength and elongation for paper samples after cleaning treatments - According to ASTM_D828-Modified-250-load.msm.

Samples	Elongation @ pkLd mm	Tensile Strn @ pk %	Breaking Factor N/mm
Control sample	2.6	3.42	1.36
Akapad Paper Sponge soft	1.7	2.24	0.83
Immersion in deionized water	2.4	2.19	0.89
Hydrogel gellan gum	2.5	3.30	0.85
Cellulose nano crystal gel	4.1	5.37	1.07
Wolbers solvent acetone gel	2.2	2.91	0.60
Wolbers solvent 2-propanol gel	2.1	2.79	1.77

4. CONCLUSION

Conventional and nonconventional cleaning treatments of cellulosic manuscripts were evaluated using different experimental techniques including the mechanical properties, pH measurements, FTIR spectroscopy, measurement of color change and XRD after thermal accelerated aging. The study concludes that:

CNC gel & hydro gellan gum appeared to be more effective in removing of surface soils and dust. Additionally, an improvement was noticed in the mechanical properties of paper samples. Thus, it can be used safely in the conservation treatments of cellulosic supports, but water treatment should be used in the case of uncoloured paper to avoid bleeding of dyes or pigments. Although the data obtained from both mechanical properties and pH were completely compatible, it is useful to evaluate the chemical composition of treated samples using FTIR. It appeared that the all treatments were relatively safe to use on cellulosic paper samples.

Color changes occurred in treated samples, and these generally increased with post-treatment ageing time. The color changes, which were documented by colori Match, may be due to: 1) a loss of brightness resulting from the action of the akapad paper, and 2) deposition of akapad powder on the surface and within the fibres of the paper. The papers cleaned with the akapad Paper Sponge soft lost their brightness.

On comparing the effective method in cleaning and removal of ageing products (soils &dust) the most effective methods followed in order: Cellulose Nano Crystal Gel> Hydrogel gellan gum > akapad Paper Sponge soft > Immersion in deionised water> Wolbers solvent 2-propanol gel> Wolbers solvent acetone gel.

Washing treatments usually involves significant effects on the original morphological structure of paper and can sometimes be dangerous for water sensitive inks and pigments. The use of hydro gel of Gellan gum & CNC gel as an alternative paper cleaning treatment is developed. The application of hydrogels in conservation treatments minimizes damages caused by the use of water.

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REFERENCES

Adam W. (2015) Washing, spraying and brushing. A comparison of paper deacidification by magnesium hydroxide nanoparticles. *Restaurator: International Journal for the Preservation of Library and Archival Materials*, Vol .36, N.1, 3-23.

Angel M. et al. (2014) First experiments for the use of microblasting technique with powdered cellulose as a new tool for dry cleaning artworks on paper. *Journal of Cultural Heritage*, Vol. 15, No. 4, 365–372.

Antonella, C., Paolo, C., Clelia, I., Roberto, G., Stefano, P. and Nicola, S. (2013) Evaluation of the effect of cleaning on the morphological properties of ancient paper surface. *Springer Link*, Vol. 20, No. 4, 2027–2043.

Ardelean, E., Bobu, E., Niculesu, G. and Groza, C. (2011) Effect of different consolidation additives on ageing behaviour of archived document paper. *Cellulose Chem.Technol.*, Vol. 45, No. 1-2, 97-103.

Bansa, H. (1998) Aqueous deacidification – with calcium or with magnesium?". *Restaurator*, Vol. 19, PP.1–40.

Batterham, I., Rai, R. (2008) A Comparison of Artificial Ageing with 27 Years of Natural Aging. *AICCM Book, Paper and Photographic Materials Symposium*.

Bogaard, J. and Paual, W. (2001) Effect of dilute calcium washing treatments on paper. *The American Institute for Conservation of Historic & Artistic Works*, 105-123.

Calvini, P., Grosso, V., Hey, M., Rossi, L. and Santucci, L. (1988) Deacidification of paper-A more fundamental approach. *The Paper Conservator*,35-39.

Cannoletta, D., Lionetto, F., Del Sole, R., Vasapollo, Maffezzoli, A. (2012) Monitoring Wood Degradation during Weathering by Cellulose Crystallinity. *Materials*, Vol. 5.

Caulfield, D.F. and Gunderson, D.E. (1988) Paper testing and strength characteristics. *Proceedings of the Paper Preservation Symposium, Paper Preservation*, 31–40.

Giorgi, R., Dei, L., Schettino, C. and Baglioni, P. (2002) A new method for paper deacidification based on calcium hydroxide dispersed in nonaqueous media. *Works of art on paper: books, documents and photographs: techniques and conservation: contributions to the Baltimore Congress*, 69-73

Darwish, S., El Hadidi, N., & Mansour, M. (2013). The Effect of Fungal Decay on Ficus sycomorus wood. *International Journal for Conservation Science*, 271-282

Fenech , A., Schiro ,J., Farrugia ,C., and Baluci, C.(2011)A Comparative Study of the Effects of Cleaning Treatments on Two Historic Papers: A Preliminary Study" in Varella, E.A. and Caponetti E. In: Proceedings of the 2nd *Chemistry and Conservation Science Residential Summer School* (Societa Chimica Italiana & ECTN).

Ferrer, N., Sistach, C. (2007) FTIR Technique Used to Study Acidic Paper Manuscripts Dating from the Thirteenth to the Sixteenth Century from the Archive of the Crown of Aragón, *The Book and Paper Group Annual*, Vol. 26, 21-25.

Herbert F. (1939) Determination of the pH value of papers. *Journal of Research of the National Bureau of Standards*, Vol. 22, 553-564.

Heyun, W., Gang, L., Jinping, Z. and Dongqing, Z. (2013) Multifunctional nanocomposites for paper conservation. *The International Institute for Conservation of Historic and Artistic Works, Studies in Conservation*, Vol. 58, No. 1, 23-29.

Kolar J. et al. (2003) Laser cleaning of paper using Nd: YAG laser running at 532 nm. *Journal of Cultural Heritage*, Vol. 4, 185–187.

Kwiatowska, A., Wojech, R. and Wojciak, A. (2014) Paper deacidification with the use of magnesium oxide nanoparticles. *Annals of Warsaw University of Life Sciences – SGGW, Forestry and Wood Technology*, No. 85, 144-148.

Li-Ming, Z., Lu-E, S., Zhi-Liang, Z., Jian-Min, C., Dong-Dong, S., Jie, Y. and Zhen-Xing, T. (2011) Preparation and application of chitosan nanoparticles and nanofibrers. *Brazilian Journal of Chemical Engineering*, Vol. 28, No. 03, 353 – 362.

Maryam, A., Saleh, I. and Shahrzad, A. (2011) Zno nanocomposites: Control of environmental effects for preservation of old manuscripts. *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, Vol:5, No.4, 298-300.

Maryam, A., Fereshteh, T. and Hamid, M. (2011) New cellulosic titanium dioxide nanocomposite as a protective coating for preserving paper art works. *Journal of Cultural Heritage*, Vol. 12, Np. 4, PP.380-383.

Mazzuca, C., Micheli, L. and Carbone, M. (2014) Gellan hydrogel as a powerful tool in paper cleaning process: A detailed study. *Journal of Colloid and Interface Science*, Vol. 416, 205–211.

Moropoulou, A. and Zervos, S. (2003) The immediate impact of aqueous treatments on the strength properties of paper. *Restaurator. International Journal for the Preservation of Library and Archival Material*, Vol. 24, No. 3, 160–177.

Nicole, B., David, C., Michele, B., Rodorico, G. and Piero, B. (2016) Confined aqueous media for the cleaning of cultural heritage: Innovative gels and amphiphile-based nanofluids. *Nanoscience and Cultural Heritage*, 283-311.

Paolo, C. (2012) *Rigid gels and enzyme cleaning*. The Centre for the Study of Materials for Restoration, Via Lombardia Saonara, Italy, 180-183.

Peter, D.V. (1989) Basic paper treatments for printed book materials. *Proceedings of the Guild of Book Worker' 9th Anniversary Seminar on the Standards of Excellence*, Portland, Oregon.

Piero, B., David, C., Rodorico, G. and Giovonna, P. (2015) *Cultural heritage conservation: Paper and Wood Nanoparticles, Encyclopaedia of Surface and Colloid Science*, Third Edition DOI: 10.1081/E-ESCS3-120047373, 1597-1612.

Piero, B., Luigi, D., Emiliano, C. and Rodorico, G. (2009) Gels for the conservation of cultural heritage. *American Chemical Society*, 8373–8374.

Poggi, G., Giorgi, R., Toccafondi, N., Katzur, V. and Baglioni, P. (2010) Hydroxide nanoparticles for deacidification and concomitant inhibition of iron-gall ink corrosion of paper, *Langmuir*, 21;26 .

Rabee, R. (2015) Behavior of archaeological paper after cleaning by organic solvents under heat accelerated ageing, *Mediterranean Archaeology and Archaeometry*, Vol. 15, No. 3, 141-150.

Rodorico, G., Luigi, D., Massimo, C., Claudius, S. and Piero, B. (2002) Nanotechnologies for conservation of cultural heritage: Paper and canvas deacidification. *American Chemical Society*, 8198-8203.

Rodorico, G., Claudio, B., Luigi, D., Chiara, G., Barry, N. and Piero, B. (2005) Nanoparticles of Mg(OH)2: Synthesis and application to paper conservation. *Langmuir*, Vol. 21, 8495-8501.

Sequeiraa, S., Casanovab, C. and Cabrita, E. J. (2006) Deacidification of paper using dispersions of Ca(OH)2 nanoparticles in isopropanol: Study of efficiency. *Journal of Cultural Heritage*, Vol. 7, 264–272.

Tella, B., Delia, F., Chillura, M., Vincenzo, R., Maria, L. S., Giovanna, P. and Eugenio, C. (2016) Alcoholic nanolime dispersion obtained by the insolubilisation-precipitation method and its application for the deacidification of ancient paper. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 513, 241-249.

Ulla, K., Istvan, K., llkka, H. and Tuomo, R. (2012) Control *of aqueous paper treatments with ion chromatography*. EVTEK Institute of Art and Design, Vantaa, Finland.

Viera, J., Eva, B., Zuzana, M. and Bohuslava, H. (2015) Influence of deacidification on Arylmethane dyes on paper. *Restaur*, Vol. 36, No. 3, 211–228.

Zervos, S. (2013) Revising established tenets in paper conservation. *Procedia - Social and Behavioral Sciences*, Vol. 73, 35 – 42.

Zidan, Y.,El Hadidi ,N.,Mohamed ,M.,(2016)Examination and analysis of a wooden face at the museum storage at the faculty of archaeology, Cairo University. *Mediterranean Archaeology and Archaeometry,* Vol. 16, No 2, 1-11.

Zou, X., Gurnagul, N., Uesaka, T. and Bouchard, J. (1994) Accelerated aging of papers of pure cellulose: mechanism of cellulose degradation and paper embrittlement. *Polymer Degradation and Stabilit*y, 393–402.