Hydroxypropyl Cellulose Loaded with ZnO Nanoparticles for Enhancing the Mechanical Properties of Papyrus (*Cyperus papyrus* L.) Strips

Rushdya Rabee Ali Hassan,[a] Salwa Moustafa Amer Mahmoud,[a] Marina Atef Nessem,[a] Reham Tarek Abdel Aty,[a] Mariam George Ramzy,[a] Eldessoky S. Dessoky,[b] Ahmed Abdelkhalek,[c] and Mohamed Z. M. Salem [d,*]

Unfortunately, papyrus has not been sufficiently studied regarding improvement of the mechanical or optical properties, which degrade under the impact of aging factors over time. The aims of this research were studying the effects of hydroxypropylcellulose (HPC) loaded with 0.25% of ZnO nanoparticles (NP) at different concentrations (1% and 2%) on papyrus sheet properties before and after aging. Various analyses were used, such as visual assessment by a universal serial bus (USB) digital microscope, mechanical properties, Fourier-transform infrared (FTIR) analysis, color change, and pH measurement. A dramatic increase in mechanical properties was observed after treatment. Besides, FTIR illustrated increasing of CH_2 and OH stretching, which contribute to increasing the cellulose crystallinity index. There was no significant change in pH values after treatment or ageing. Slight changes of optical characteristics were observed for treated samples, after the artificial aging of the treated samples, the mechanical measurements showed that the values of tensile strength and elongation were close to the values of the standard sample, which may contribute to preventive protection of ZnO NP for treated samples from the artificial ageing.

Keywords: Papyrus; Consolidation; Hydroxypropyl cellulose; ZnO nanoparticles; FT-IR

*Contact information: a: Conservation Department, Faculty of Archaeology, Cairo University, Giza 12613, Egypt; b: Department of Biology, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia; c: Plant Protection and Biomolecular Diagnosis Department, ALCRI, City of Scientific Research and Technological Applications, New Borg El Arab City, Alexandria 21934, Egypt; d: Forestry and Wood Technology Department, Faculty of Agriculture (El-Shatby), Alexandria University, Alexandria 21545, Egypt;*Corresponding author: zidan_forest@yahoo.com*

INTRODUCTION

Since the time of ancient Egypt, papyrus (*Cyperus papyrus*, Cyperaceae) has been used in the creation of writing materials and the production of laminated layers, where the natural juices occurring in papyrus strips are sufficient to bond them into a sheet (Owen and Danzing 1993; Leach 2009).

Papyrus is composed of fibrous materials (Elnaggar *et al*. 2015), which are 97% cellulose, hemicellulose, and lignin and 3% proteinaceous materials (Menei 2015). The lignin content ranges from 12% to 34% (Katuščak *et al*. 2006). Papyrus is made using part of the papyrus stem: its outer shell is removed (Leach 2009; Taha *et al*. 2019), and the stem is formed to strips, which are moistened with water and placed on a board (Scora and Scora 1991; Taha *et al*. 2019). Then, another layer of strips is placed on top of them at right angles (Owen and Danzing 1993). They are squeezed together by wrapping them with a cylinder

and are then dried (Basile 1972). During manufacturing and handling of papyrus, the sheets can become contaminated with salt particles or dirt, which have negative effects when the consolidated materials are applied and especially affect the mechanical strength (Elnaggar *et al*. 2015).

Unfortunately, there are also several degrading factors affecting papyrus, such as high temperature, humidity, light, air pollution gases, manufacturing processes, and poor storage (Franceschi 2011), which cause decomposition by oxidation and acidification. The latter leads to the weakness and fragility of the papyrus (Ibáñez Domínguez 2019). Therefore, consolidation of the papyrus surface fibers is often necessary before further treatment is begun.

Several materials are used for cellulosic conservation as supports, such as starches, gums, cellulose ether, and proteins (Hamburg 1988). The preparation of durable and efficient materials for conserving cellulosic supports is of great importance, and new technologies have emerged for conservation processes, including nanotechnologies (Giorgi *et al*. 2002; Ali *et al*. 2018; Hassan and Mohamed 2018; Salem *et al*. 2019; Salim *et al*. 2020), which allow production of minute objects as small as a nanometer (Hahn 2011).

Zinc oxide (ZnO) nanoparticles (NPs) have been used for many purposes, such as wear proofing for rubber composites (Chen *et al*. 2017), strong UV absorption in cosmetics and sunscreen (Jiang *et al*. 2018), antimicrobial agents, and UV blocking and deodorant in the textile industry (Raguvaran *et al*. 2015). Zinc oxide NPs with cotton fabrics or paper sheets showed good antimicrobial properties (Sricharussin *et al*. 2011, Khojasteh Khosro *et al*. 2016; Khalaji *et al*. 2019). Zinc oxide NPs have a good self-cleaning function on surfaces when applied in the presence of UV light, where it prevents dust or dirt accumulation on the surface (El-Feky*et al*. 2014).

The authors found a general lack of studies of the use of ZnO as a consolidating agent. Most of the papers mentioned it as an antifungal and antibacterial agent. Consequently, this study used hydroxypropyl cellulose (HPC) as a loading material for ZnO NPs in the process of consolidation for the papyrus. The most important property of HPC is its solubility in water and polar solvents, and it is used to strengthen fragile and weak materials (Martin *et al*. 2011) and as an adhesive (Gill and Boersma 1997). It was subjected to acid hydrolysis and can be made alkaline to a pH of 6 to 8 with ammonium hydroxide, such that it can protect water-soluble colors (Hamburg 1988). This study evaluated the effects of HPC and HPC loaded with ZnO NPs on the mechanical and optical properties of the papyrus under accelerated aging.

EXPERIMENTAL

Transmission Electron Microscopy (TEM) Examination of ZnO NPs

The morphological analysis of the prepared ZnONPs (Sigma-Aldrich, Darmstadt, Germany) was performed *via* TEM using a JEM-1230 electron microscope (JEOL Ltd., Tokyo, Japan) operated at 60 kV. Before taking a TEM image, the sample was diluted at least 10 times by water. A drop of well-dispersed diluted sample was placed onto a copper grid (200 mesh and covered with a carbon membrane) and dried at ambient temperature (Abo Elgat *et al*. 2020).

Papyrus Samples and Accelerated Ageing

Papyrus plant was obtained from the village of Al-Qaramous, Abu-Kabir, Sharqia Governorate, Egypt. The papyrus specimens (Fig. 1) were prepared according to the method of strips stated by relevant studies of archaeological papyrus. The specimens were exposed to artificial aging at the National Institute of Standards (NIS), Giza, Egypt. The thermal aging was at 80 °C, and the relative humidity was 65% (ISO 5630-31996). Brushes were used in the application of consolidation materials. The specimen with the best results was subjected to a second period of accelerated aging (80 °C and 65% relative humidity. The time frame for the accelerated ageing (1st and 2nd time) was 5 days, which corresponds to 120 h and 50 years of the artificial aging (ISO 5630-3 1996). Aging was performed for all the original samples to reach a state similar to the archaeological samples, and then the treatment process was performed. All samples were evaluated using pH measurement - infrared spectroscopy - digital microscope examination, color change and mechanical properties. Based on all these multiple analyses, the best concentration was chosen, which was subjected to accelerating ageing for the second time, which makes the study integrated and smooth in a logical scientific way (Kolar *et al.* 2003; Kamel *et al.* 2004; Princi *et al.* 2005).

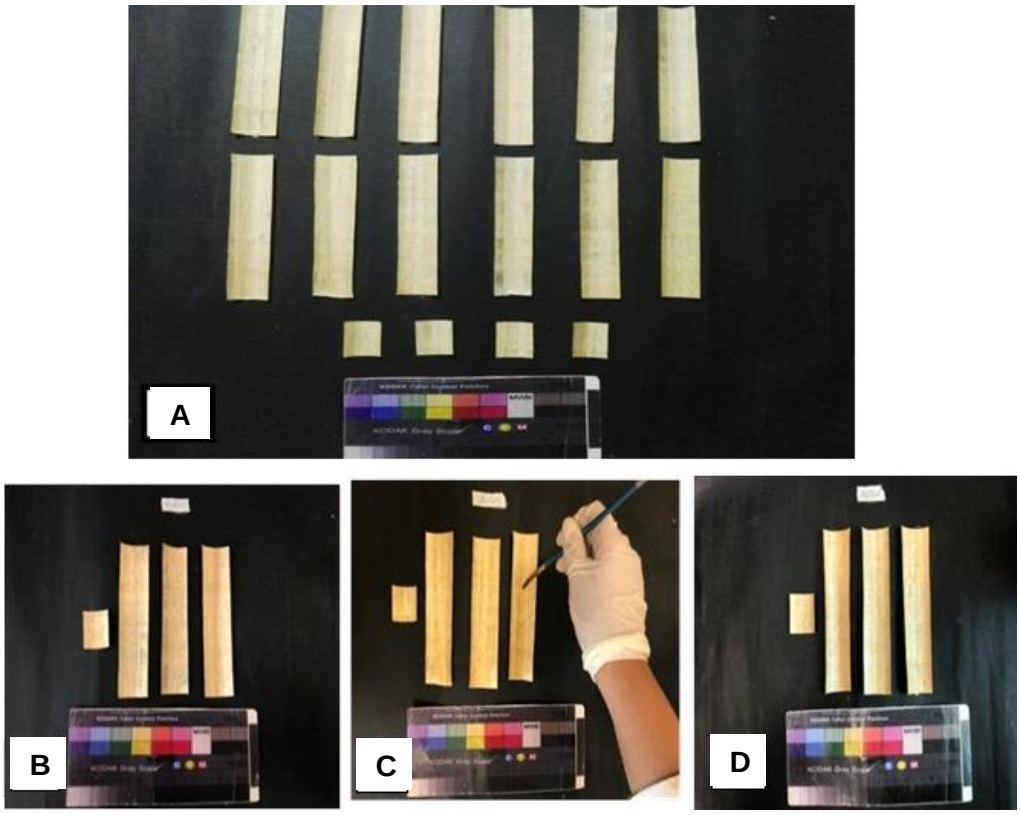

Fig. 1. (A) The treatment of papyrus samples with HPC; (B) treated samples with HPC loaded with ZnO NPs in different concentrations by the brushes; (C) during application; and (D) after application

HPC and ZnONPs

Hydroxypropyl cellulose (Klucel G, CTS Srl, Altavilla Vicentina, Italy) and ZnO NPs were chosen as consolidates. Concentrations of 1% and 2% of HPC in 95% ethyl alcohol were used. The steps of preparation as the following: i) 1% of HPC:100 mL of

ethyl alcohol were added inside a glass flask and 1 grams of hydroxypropyl cellulose (Klucel G) was measured and added to it. The mixture was stirred until complete dissolution ii) 2% of HPC: 100 mL of ethyl alcohol were added inside a glass flask and 2 grams of hydroxypropyl cellulose (Klucel G) was measured and added to it. The mixture was stirred until complete dissolution. The ZnO NP powder (Sigma-Aldrich, Darmstadt, Germany) was added to the 1% and 2% HPC solutions at a ratio of 0.25 wt% based on the weight of dry HPC after mixing, and the mixture was stirred again for 30 min. The solutions were homogenized using a high-shear homogenizer at 10,000 rpm (CAT high-speed homogenizer, Gmbh, Shanghai, China). The prepared consolidation solutions were applied to the papyrus samples by brushing (the aim of this paper is presenting a new consolidate for archeological papyrus. In the field of conservation of papyrus, the conservators use the brush in most the conservation treatment because papyrus is a very sensitive weak object. Therefore, immersion treatment is not recommended). Then, the samples were left to dry at room temperature. Samples were evaluated *via* several analyses.

Universal Serial Bus (USB) Digital Microscope

A USB digital microscope (200×) (model PZ01; Shenzhen Super Eyes Co., Ltd., Guangdong, China) was used for visual assessment of experimental samples.

Fourier-transform Infrared (FTIR) Analysis

Fourier-transform infrared analysis was used to monitor the chemical composition and changes that occurred in the papyrus due to treatment. The samples were analyzed with an FTIR spectrometer (Model6100, Jasco, Tokyo, Japan). The spectra were obtained in the transmission mode with a triglycine sulfate (TGS) detector using the KBr method and represent 2-mm/s co-added scans in the spectral region from 4000 cm^{-1} to 400 cm^{-1}, with a resolution of 4 cm^{-1} (Salim *et al*. 2020).

Color Change in the CIELAB System

The colors of the samples were measured with an Optimatch 3100 (Model No. CE 3100. Serial No. 31013780698, SDL, UK). All samples were measured in the visible region, *i.e*., a wavelength range from 400 nm to 700 nm, with an interval of 10 nm using a D65 light source and an observed angle of 10°. The colorimetric coordinates *L*, *a*, and *b* of the CIELA B color space were used to express color change. The CIELAB color space is organized in a cubic form. The *L* axis runs from top to bottom. The maximum for *L* is 100, which represents white. The minimum for *L* is zero, which represents black. The *a* and *b* axes have no specific numerical limits. Positive *a* is red, while negative *a* is green. Positive *b* is yellow, while negative *b* is blue (Sehlstedt-Persson 2005; Calienno *et al*. 2015; Hassan 2015a). The total color change of all treated papyrus was expressed as ΔE, according to the following Eq. 1,

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (1)$$

where $(\Delta L)^2$, $(\Delta a)^2$, and $(\Delta b)^2$ are the differences between the values of the color indices before and after treatment.

pH Measurement

pH values were measured by a cold extraction method according to ASTM D778-97 (2002) at room temperature using a pH meter. The samples were cut, with 50 g for one

sample, and were put in 40 mL of distilled water (pH = 7) for the measurement of the papyrus acidity (ISO 187 1990; Salim *et al*. 2020). The samples were soaked for 6 h.

Mechanical Properties Measurement

Before measurement, all papyrus samples (15 cm in length and 1.5 cm in width) were conditioned according to ISO 187 (1990), at a temperature of 23 °C and a relative humidity of 50% for 24 h (ISO 1924-3 2005). The mechanical properties of the samples were performed in compliance with ISO 187 (1990).

Using a testing machine (H5KT, SDL Atlas, Borås, Sweden) at the National Institute for Standards (NIS), at 25 °C and a cross-head speed of 50 mm/min. The mean values of tensile strength and elongation were calculated from 3 measurements with a precision in the ±10% range. The sample was cut in the machine direction. The brushes were used in applying the treatment.

RESULTS AND DISCUSSION

TEM of ZnO NPs

Electron microscopy is an excellent tool for characterizing features of NPs (Ao *et al*. 2006). The ZnO NPs were spherical, according to the TEM results shown in Fig. 2.

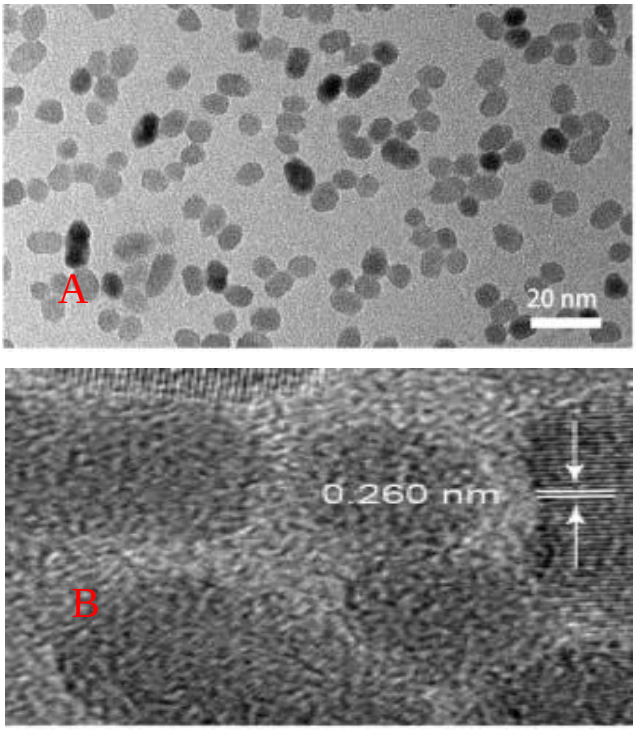

Fig. 2. Image of TEM examination of the prepared ZnO NPs (A), (B) confirmed that the size of partials is 0.26 nm.

It is clear from Fig. 2 that the synthesized ZnO NPs were single-crystal particles, with moderate agglomeration and a reasonably narrow particle size distribution. It was also noted that, at room temperature, they exhibited clear crystal faceting, suggesting substantial crystallinity. In addition, the particle sizes and the size distribution were much lower than

that already reported by mechanic-chemical reaction (Gedamu *et al*. 2014). Furthermore, particle size measurements from the TEM images were higher than those obtained from X-ray diffraction (Scherrer's formula), as the size reached 21 nm (Look 2001; Emamifar *et al*. 2010).

USB Digital Microscope

No visual change was detected by the naked eye, but the microscope examination showed black impurities (Fig. 3). These impurities may be a result of the papyrus manufacturing process (Scora and Scora 1991; Leach 2009). Figure 3 shows that the fibers became less transparent, compared to the untreated sample, which indicates increased thickness of the treated fibers from the absorption of HPC inside the cells of the cellulose fibers in the papyrus. The digital microscopy examination showed that the industrial aging processes did not affect the fibers, and the fibers were coherent. However, slight brightness was observed on the papyrus surface after ageing.

FTIR Analysis

The IR spectra of the reference sample showed the same basic structure as all the cellulosic samples (Calienno *et al*. 2015; Hassan *et al*. 2020; Salim *et al*. 2020). Results are listed in Table 1.

Table 1. Changes in Functional Groups of Treated Papyrus

Functional Group		Standard	HPC 1%	HPC 2%	HPC 1% mixed with 0.25% ZnO NPs	HPC 2% mixed with 0.25% ZnO NPs	HPC 2% mixed with 0.25% ZnO NPs after artificial aging
OH stretching	position	3310 cm^{-1}	3312 cm^{-1}	3312 cm^{-1}	3322 cm^{-1}	3322 cm^{-1}	3468 cm^{-1}
	Intensity	94.9	97.9	91.5	94.3	95.4	27.2
C-H stretching	position	2922 cm^{-1}	2919 cm^{-1}	2916 cm^{-1}	2916 cm^{-1}	2918 cm^{-1}	2874 cm^{-1}
	Intensity	95.9	98.1	91.5	94.9	96.5	46.3
C=O ester carbonyl	position	1616 cm^{-1}	1606 cm^{-1}	1609 cm^{-1}	1613 cm^{-1}	1613 cm^{-1}	1620 cm^{-1}
	Intensity	95.9	98.8	91.3	95.9	97.5	35.2
CH_2 banding	position	1321 cm^{-1}	1321 cm^{-1}	1321 cm^{-1}	1318 cm^{-1}	1318 cm^{-1}	1422 cm^{-1}
	Intensity	94.8	94.8	91.3	95.1	96.9	38.1
C-O-H banding	position	1159 cm^{-1}	1159 cm^{-1}	1154 cm^{-1}	1160 cm^{-1}	1156 cm^{-1}	1151
	Intensity	94.4	94.4	91	89.8	95.8	31.3
C-O stretching band	position	1029 cm^{-1}	1029 cm^{-1}	1026 cm^{-1}	1035 cm^{-1}	1055 cm^{-1}	900 cm^{-1}
	Intensity	90.9	90.9	86.9	89.2	90.4	61.9

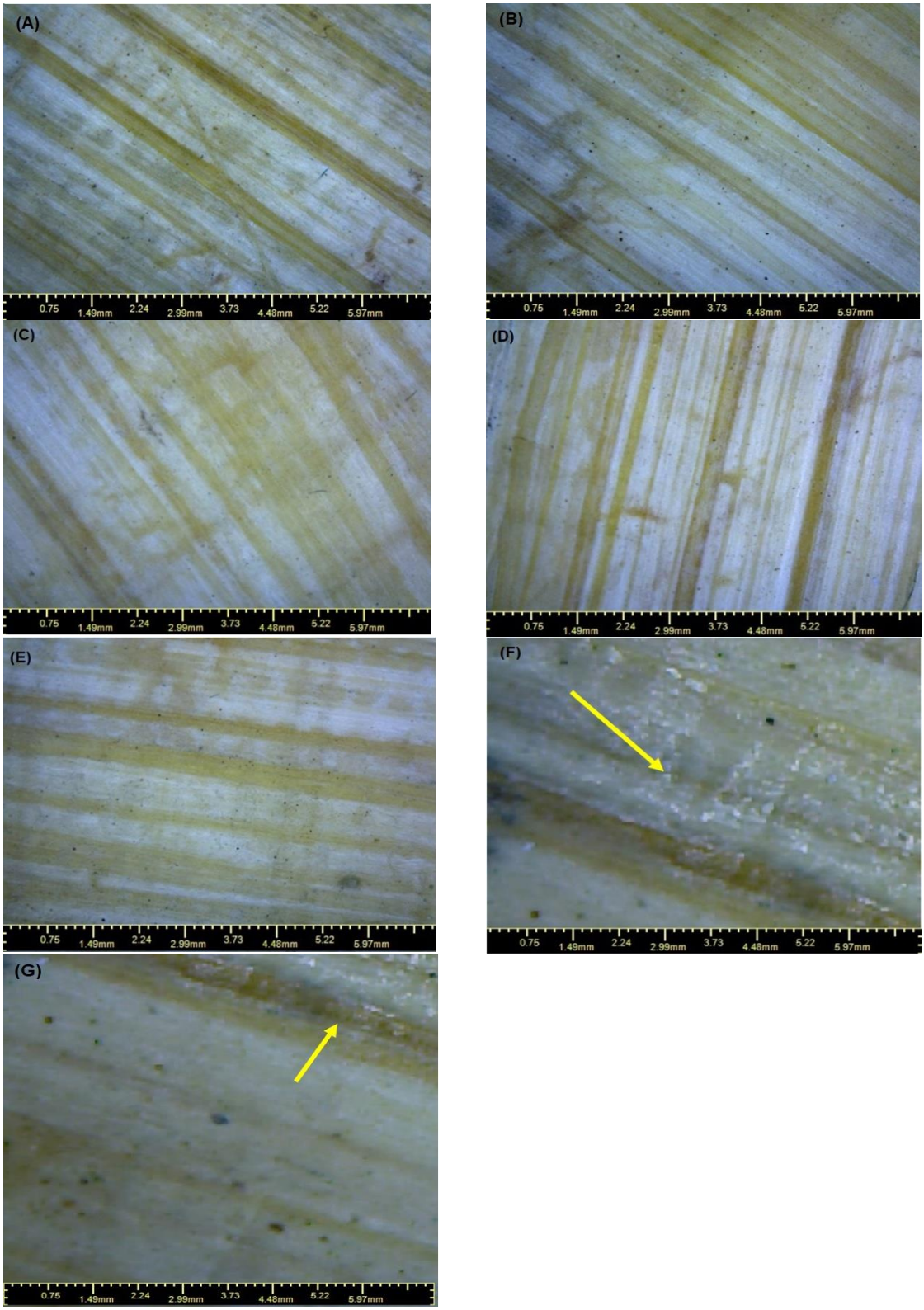

Fig. 3. USB digital microscope images of the four samples that were treated by different concentrations of HPC loaded with ZnO NPs, with images of HPC 2% + ZnO 0.25% showing shiny surfaces on the papyrus samples after the artificial aging: (A) standard; (B) HPC 1%, (C) HPC 2%, (D) HPC 1% + ZnO 0.25%, (E) HPC 2% + ZnO 0.25% before the artificial aging, and (F and G) HPC 2% + ZnO 0.25%after the artificial aging

There was a dramatic increase of intensities at 3498.8 (OH stretching), 1107, 1053, 1031, and 2894.7 cm^{-1}. Furthermore, there was a weak band at 460 cm^{-1} characteristic of a metal-oxygen (M-O) vibration band, possibly arising from $CaCO_3$, CaO, MgO, or silicates. The presence of $CaCO_3$ and other minerals is mentioned as maybe from papyrus sheet making or water. The manufacturing of experimental samples in the current study was carried out according to old recipes of methods for making papyrus such as the Bellini method, which described the technique of papyrus as the following: the ancient Egyptians used Nile water in the soaking the papyrus strips during making papyrus (Owen and Danzing 1993; Leach 2009; Menei 2015), so the presence of silica and calcium carbonate as impurities can be expected.

At 732 cm^{-1}, a weak, broad band was observed, which could be related to the overlapping of bands at 710 cm^{-1} and 750 cm^{-1}, which characterize cellulose (Iβ and Iα phases). Furthermore, this result indicated the presence of this mixture in the papyrus. The C–O and C–H vibrations of cellulose were presented in bands ranging from 900 cm^{-1} to 1300 cm^{-1} and 1300 cm^{-1} to 1500 cm^{-1}, respectively. The water absorbed in the cellulosic fibers from blank papyrus was associated with a band at 1640 cm^{-1} (Zotti *et al.* 2011; Kavkler *et al.* 2011). Hemicellulose was characterized at 1735 cm^{-1}. A broad band in the range of 3100 cm^{-1} to 3700 cm^{-1} centered at approximately 3367 cm^{-1}, which is characteristic of –OH functional groups (free and H-bonded) was also observed.

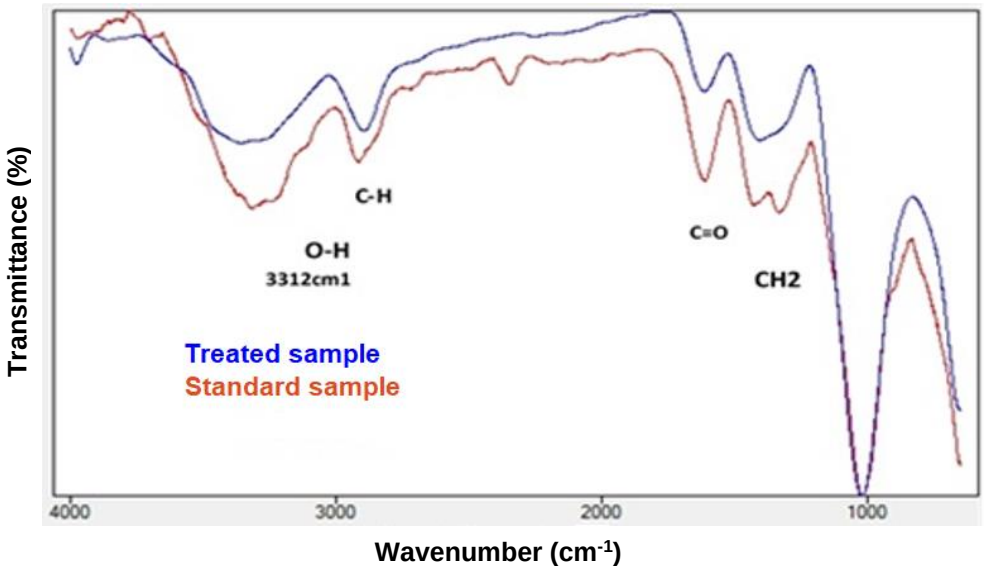

Fig. 4. Comparison between the stretching bands at 3312 $cm^{-1}$of a sample treated with 1% of HPC only and a standard sample

After aging, new bands at 900.6 cm^{-1}, 910.3 cm^{-1}, and 952.5 cm^{-1} appeared (in comparison to the untreated sample). This result may be due to C=O groups of ester formation or new C-OH groups resulting from opening of pyranose rings. In addition, more carbonyl groups were formed because of further oxidation of C-OH groups' cellulose molecules (Łojewska *et al*. 2005; Hassan 2015b), and there was a removal of associated CH stretching, as resulting from the oxidation of cellulose (Hassan 2021), where heat oxidized hydroxyl group cellulose molecules to carbonyl and carboxyl group. The FTIR spectra of the papyrus samples treated by 1% and 2% of HPC (Figs. 4 and 5) revealed a slightly increased intensity of OH stretching at 3312 cm^{-1} (Gill and Boersma 1997;

Afsharpour and Imani 2017; Hassan 2020), compared to a standard sample, and revealed some changes in C-H stretching, C=O ester carbonyl (Table 1), (CH_2), C-O-H, and C-O stretching bands (Fig. 6) (Calienno *et al*. 2015; Rushdy *et al*. 2017; Hadi and Kadhim 2019).

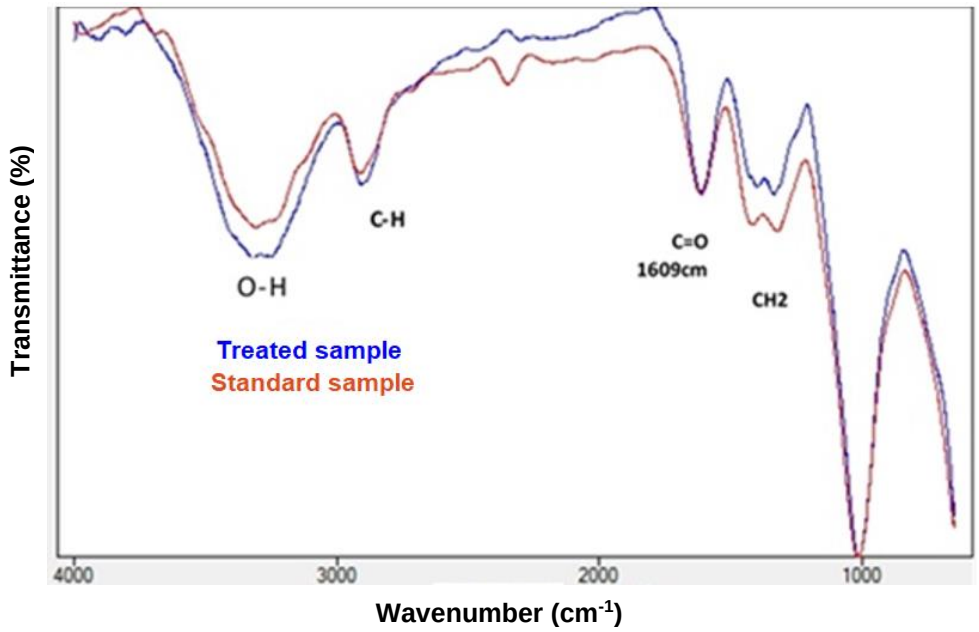

Fig. 5. Comparison between sample treated with 2% of HPC only and a standard sample. The band at 1609cm^{-1} decreased dramatically as compared to a standard sample.

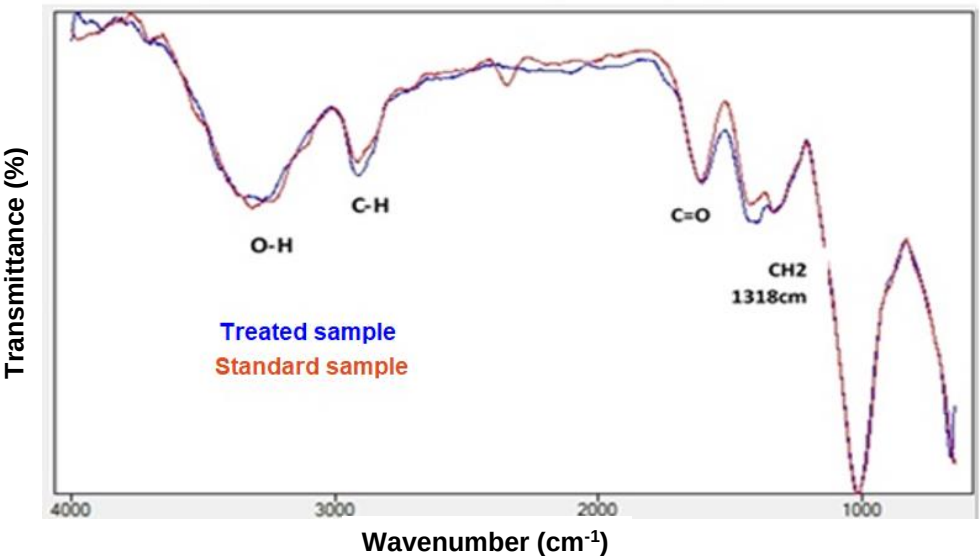

Fig. 6. Comparison between samples treated with 1% of HPC mixed with 0.25% of ZnO NPs.

The FTIR spectra of the papyrus samples (Fig. 7) treated with 2% of HPC mixed with 0.25% ZnO NPs revealed increased OH stretching. This result was attributed to the addition of ZnO NPs. The spectrum showed bands at 460 cm^{-1} and 560 cm^{-1}, corresponding to metal–oxygen (M–O) and metal–nitrogen (M–N) vibrational bands, respectively. Furthermore, the bands at 1486 cm^{-1} and 1630 cm^{-1} corresponded to N–H bending modes, and the band at 3416 cm^{-1} can be attributed to free NH stretching vibrations. The NH stretching confirms the presence of protein residues within the chemical composition of the papyrus, and this result is consistent with studies from a number of botanists, including Muthuri and Kinyamario (1989). They found 10.9% of crude protein in juvenile umbels and 3.9% in juvenile culms of papyrus while these percentages decreased to 4.2% and 1.9%, respectively, in dead tissue (Scora and Scora 1991).

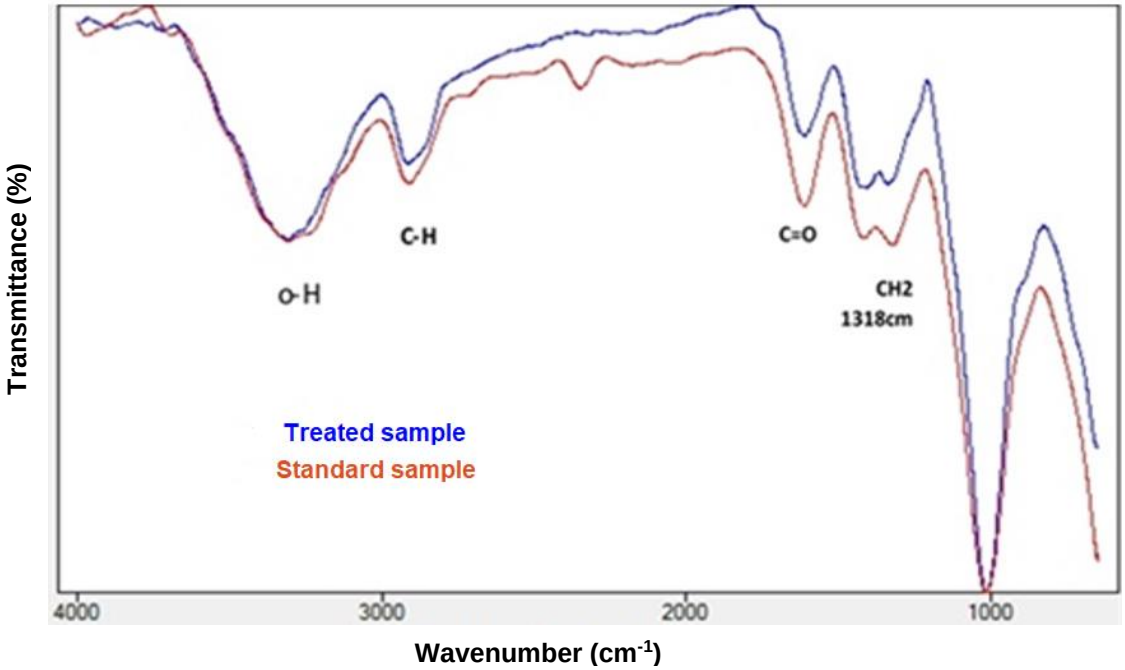

Fig. 7. Comparison between asample treated with 2% of HPC mixed with 0.25% of ZnO NPs. The band at 1318 cm^{-1} increased, referring to the crystallinity index of cellulose**.**

A slight change was observed in CH stretching, (CH) banding, C-O-H banding, and C=O ester carbonyl, which confirmed that adding ZnO NPs decreased the oxidation process to the papyrus samples, and that was observed in the (CH) group absorbance. There was an increase in peak intensity after treatment at 1318 cm^{-1} compared to a standard sample, which can help in increasing in the crystallinity index of cellulose (Hassan 2021). Furthermore, Fig. 7 shows a peak at 442 cm^{-1}, corresponding to the hexagonal ZnO symmetric bending vibration, and a peak at 878 cm^{-1} due to weak vibration of ZnO. The wide peaks present at 3434 cm^{-1} and 1117 cm^{-1} reflect the presence of OH and C-OH stretching vibrations, respectively. Smaller bond vibration peaks include 2925.48 cm^{-1}, which indicates C-H stretching vibrations. These results show that the solution of 2% of HPC mixed with 0.25% of ZnO NPs decreased oxidation in the cellulose under accelerated aging, which could be due to the percentage of ZnO NPs. Previous aging studies of cellulosic structure in the laboratory, in air (Kronkright 1990; Salim *et al.* 2020), showed an increase in absorbance in the FTIR spectrum in the region of 1600 cm^{-1} to 1700 cm^{-1}.

However, the changes were masked by sample-to-sample variation, due to the presence of OH stretching from free water in the papyrus at approximately 1700 cm^{-1}.

After aging, no major changes in the papyrus samples were observed in foraged, treated samples. For instance, there was a slight decrease in the relative intensity of OH stretching at 3310 cm^{-1}, which might indicate an increased rate of evaporation and increased molecular mobility. When cellulosic materials are exposed to elevated temperatures, changes can occur in their chemical structures that affect their performance. The extent of the changes depends on the temperature level and the length of time under exposure conditions. The changes in chemical structure may be manifested only as reduced strength and hygroscopic water. In contrast, very drastic chemical changes may result in reduced strength and substantial carbohydrate weight loss. Heat plays a major rule in paper degradation; heat has aging effect on papyrus and over long periods can do considerable damage to it. In general, exposure to high temperatures has a dramatic effect on the molecules of cellulose. Furthermore, there was a dramatic decrease in C=O ester carbonyl at 1613 cm^{-1}. In contrast, a small shift was detected in the expected OH stretching and C-H stretching due to aromatic and symmetric stretching at 3413.39 cm^{-1} and 2901.38 cm^{-1}. In addition, there were changes in intensities of C-H deformation in lignin and carbohydrates bands at 1159 cm^{-1}, 1330 cm^{-1}, and 1454 cm^{-1}, as shown in Fig. 8.

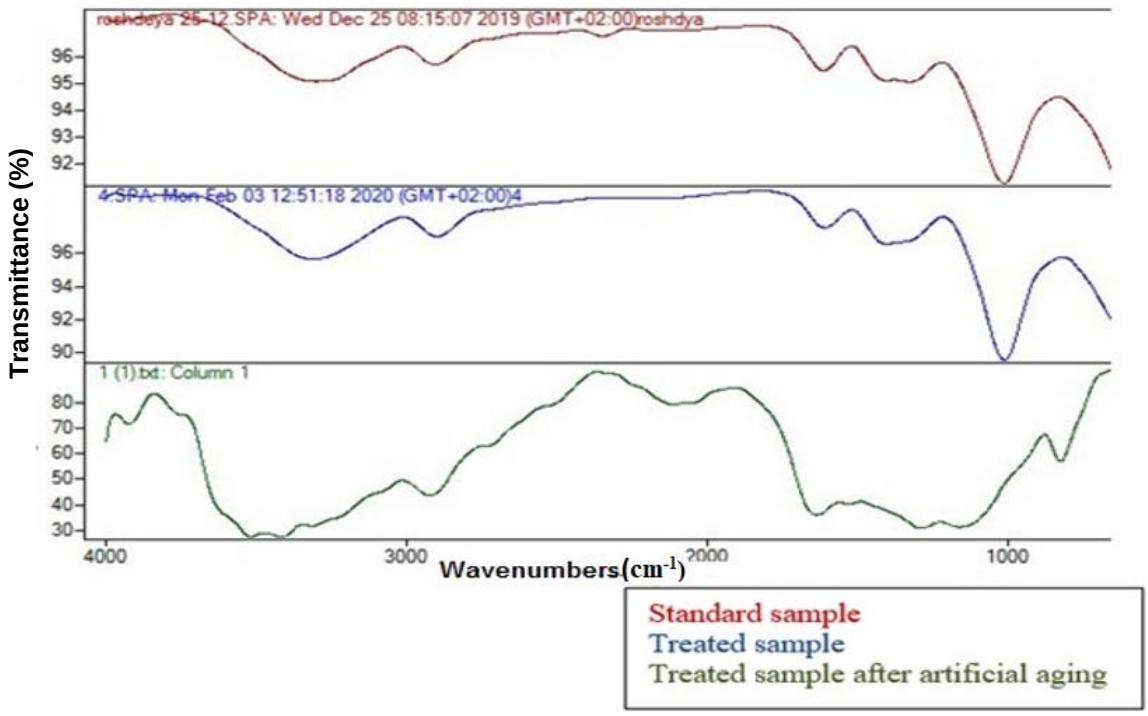

Fig. 8. Comparison of the standard sample and the treated samples of HPC 2% mixed with 0.25% ZnO NPs before and after the artifical aging

Color Change in the CIELAB System

Colorimetric testing was used to investigate the color changes induced by the treatment of the papyrus samples with the consolidation products and by the artificial accelerated aging tests. Based on the color parameters' measurements, the Δ*E* values were calculated. The Δ*E* scale in organic materials conservation is as follows in Table 2 (Darwish 2013):

Table 2. Relationship between Δ*E* and the Degree of Color Change

Δ*E*< 0.5	very small difference
Δ*E*< 2	small difference
Δ*E*< 3	fairly perceptible difference
Δ*E*< 6	perceptible difference
Δ*E*< 12	strong difference
Δ*E*> 12	different colors

The Δ*E* values for the samples treated with1% and 2% of HPC were 4.7 and 3.7, respectively. The values for samples treated with 1% and 2% of HPC loaded with ZnO NPs were 4.6 and 4.7, respectively (Table 2). The consolidation in the current study recorded acceptable Δ*E* values. Furthermore, the values of the aged samples treated with 2% of HPC and 2% of HPC loaded with ZnO NPs were 6.85 and 6.9, respectively, which confirmed the impact of the ZnO NPs in reducing the color change during artificial aging. Referring to Table 2, after artificial aging, the lightness (luminescence) index increased in treated samples compared to the state before the aging, which confirms more lightness of the papyrus. This result can essentially be attributed to the effect of NPs in decreasing the reactions related to the organic materials' decomposition and the breakage (split) of composite bounds. As shown in Table 3, the treated sample had an acceptable value of total color change index (Δ*E*), which represents greater resistance of 2% of HPC loaded with ZnO nanoparticles against the color change by effect of ageing.

Table 3. Δ*E* Measurements for Treated Samples with HPC only and HPC Loaded with 0.25% of ZnO NPs

Sample Type	*L*	*a*	*b*	Δ*E*
Standard	71.22	2.40	19.13	0.00^{c}
HPC 1%	72.44	4.71	25.69	$1.07^{c}\pm0.09$
HPC 2%	70.30	4.52	21.31	$3.29^{b}\pm1.28$
HPC 1% + ZnO 0.25%	72.77	5.11	23.03	$4.69^{b}\pm0.29$
HPC 2% + ZnO 0.25%	74.78	3.80	22.82	$4.76^{b}\pm2.49$
HPC 2% + ZnO 0.25% after the artificial aging	67.92	5.03	29.28	$6.87^{a}\pm0.81$
$LSD_{0.05}$				1.78

Means with the same letter are not significantly different according to $LSD_{0.05}$.

pH Measurement

Hydroxypropyl cellulose is a non-ionic water-soluble cellulose ether that contains no plasticizers; also it is reversibly soluble in water after drying (Hamed and Hassan 2019). Therefore, it was expected that the pH values would not change after treatment. The use of HPC individually or as a mixture with 0.25% ZnO NPs did not affect the pH of the papyrus samples that were treated with it (Fig. 9) (Gill and Boersma 1997).

As shown in in Fig. 9, there were no noticeable differences between the pH values of papyrus samples treated with HPC loaded with ZnO NPs before and after accelerated

aging. Therefore, HPC loaded with ZnO NPs reduced heat-degradation of the treated papyrus. Some studies stated that, for purposes of deacidification, solutions of zinc alkoxide and related carbonates are reacted with paper specimens that contain small amounts of water. The water reacts to form $Zn(OH)_2$, which serves as an alkaline agent that neutralizes acidity in the paper. The $Zn(OH)_2$ presumably is able to be converted into the carbonate form or maybe to the oxide form by subsequent reactions (Hubbe *et al*. 2018; Horst *et al*. 2020). Depended to these studies we can speculate that adding of ZnO NP might in fact play some role with respect to the deacidification results observed when treating papyrus with HPC loaded with ZnO NPs solutions.

During heat aging, cellulose depolymerization leaves carboxyl groups on the final chain, which would tend to accelerate and further paper decay by promoting acid hydrolysis. The decrease in surface pH suggests the creation of acidic end groups in lignin-free papers.

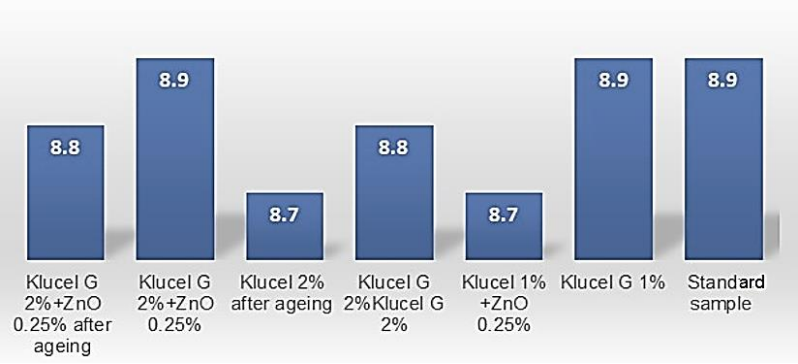

Fig. 9. The pH values of papyrus samples treated with HPC only and HPC loaded with ZnO NPs

Mechanical Properties

Conventional cellulosic fibers are held together by hydrogen bonds (Martin *et al*. 2011). These bonds affect the distance between the separate crosslink fibers. Water molecules play an integral role in the inter-fiber linkage. The free water causes paper weakness, which is manifested by the wet strength of cellulosic fibers. Table 4 shows that the mechanical strengths of the papyrus sheets were highly affected by the treatment of the papyrus sheets with HPC and HPC loaded with ZnO NPs. The strength force of the papyrus treated with 1% of HPC was 245 N/mm^2, while it decreased to 220.5 N/mm^2 in the samples treated with 1% of HPC loaded with ZnO NPs. It increased for treated samples with concentration of 2% especially that treated with HPC (2%) and ZnO NPs. Each of these polymeric materials must enable the inter-fiber bonding areas to remain chemically linked between cellulose fibers. Meanwhile, the samples with HPC (2%)+ZnO had more improvement in the strength of treated samples than the samples treated with HPC (1%), 2% HPC, and 1% HPC loaded with ZnO NPs. This result was attributed to ZnO ions not only increasing the fiber bonding (Gill and Boersma1997; Martin *et al.* 2011), and consequently increasing the hydrogen bonding between fibers, but also increasing the absorption of HPC within the fibers. From Table 4 it is clear that the relationship between the percent of the improvement in elongation and the percent of HPC is a direct relationship. The samples treated with HPC 2% became more elastic as the elongation of the sample was increased. Furthermore, the percent of the improvement in elongation increased after adding ZnO (NPs).

After aging, the values of mechanical properties for treated sample with HPC (2%) + ZnO decreased. The change in the mechanical properties can be correlated with the change in chemical groups with the aging procedures, where the cross linking was thermally degraded, but the tensile strength of the aged treated sample was slightly lower than the standard sample, which can attributed to ZnO NPs efficacy in decreasing the mechanical properties slightly after aging as compared with some previous studies (Hotle *et al*. 2008; Hamed and Hassan 2019), which indicated that the mechanical properties of cellulose lose above 40% of its value during thermal aging.

Table 4. Mechanical Properties (elongation ratio and tensile strength) Analysis after Artificial Aging

Treated Sample	Elongation ratio (%)	Tensile strength (N)
Standard	1.68±0.11	220.76^{c}±16.99
HPC 1%	1.60±0.52	245.30^{c}±34.96
HPC 1% + ZnO NPs	2.006±1.11	220.50^{c}±8.41
HPC 2%	2.01±0.18	320.13^{b}±29.11
HPC 2% + ZnO 0.25%	2.27±1.09	370.10^{a}±26.51
HPC 2% + ZnO 0.25% after aging	2.01±0.40	207.36^{c}±30.85
LSD 0.05	ns	46.41

ns: not significant. Means with the same letter are not significantly different according to $LSD_{0.05}$

The FTIR results supported the results of mechanical measurements. The intensity of CH_2 stretching band, which refers to the crystallinity index of cellulose (Gill and Boersma 1997), was increased with the use of 2% HPC loaded ZnO NPs, which explain the improvement in mechanical properties. This is because the nanostructures contain mineral particles, which improve the mechanical properties (El-Feky *et al*. 2014). After all, they reduce the effect of thermal damage on the cellulosic fibers and give them stability (Harandi *et al*. 2016; Ngo *et al*. 2018; Jia *et al*. 2019).

CONCLUSIONS

1. The treated sample with 2% HPC and 0.25% ZnO NPs had the highest value of mechanical properties, so it was the most effective concentration in the consolidation of paper samples. Therefore, this concentration was chosen for evaluation after artificial aging.
2. The results of FTIR analysis also illustrated an increase in CH_2 stretching band (refers to the index of crystallinity cellulose), where the peak intensity increased from 94.8 to 96.9 as compared with the standard sample.
3. Zinc oxide NPs that were loaded on the 2% HPC did not affect the pH values of the papyrus samples that were treated with it, and they caused a slight color change that ranged from 4.7 to 6.8. Digital microscopy showed black impurities, which might be from the manufacturing operations of papyrus, so it is preferable to use ZnO NPs with HPC instead of using HPC alone.
4. After the artificial aging of a sample that was treated with 2% of HPC and loaded with 0.25% of ZnO NPs, the pH value of the treated sample was 7.08. There were no noticeable differences between the pH values of the papyrus samples treated with HPC

loaded with ZnO NPs before and after accelerated aging.

5. The mechanical measurements showed great convergence between the aged treated sample and the standard sample in terms of tensile strength and elongation, which can be attributed to the role of ZnO NPs in protecting the papyrus structure from degradation during accelerated aging. Finally, the current research has opened promising horizons for the use of nanoparticles in the field of archaeological papyrus conservation, which opens the way for more future studies. Especially in the effect of nanoparticles on protection from light and moisture aging, as the current study focused on thermal aging only and on one type of nanoparticle, which requires further studies on other types of nanoparticles and different aging conditions.

ACKNOWLEDGMENTS

The authors extend their appreciation to Taif University for funding current work by Taif University Researchers Supporting Project number (TURSP-2020/85), Taif University, Taif, Saudi Arabia.

The authors want to thank Dr. Rasha from the National Institute for Standards (NIS) and give many thanks to Dr. Morad Fawzi, Dr. Eman Elbadri, Ahmed Elshabrawy, and Ola Younis for helping with this study from the Department of Conservation, Faculty of Archaeology, Cairo University, Giza, Egypt.

FUNDING

The current work was funded by Taif University Researchers Supporting Project number (TURSP-2020/85), Taif University, Taif, Saudi Arabia.

REFERENCES CITED

Abo Elgat, W. A. A., Taha, A. S., Böhm, M., Vejmelková, E., Mohamed, W. S., Fares, Y. G. D., and Salem, M. Z. M. (2020). "Evaluation of the mechanical, physical, and anti-fungal properties of flax laboratory papersheets with the nanoparticles treatment," *Materials* 13(2).DOI:10.3390/ma13020363

Afsharpour, M., and Imani, S. (2017). "Preventive protection of paper works by using nanocomposite coating of zinc oxide," *Journal of Cultural Heritage* 25, 142-148. DOI: 10.1016/j.culher.2016.12.007

Ali, M. F., Mansour, M. M. A., Badr, N. M., and Salem, M. Z. M. (2018). "A study of biodeterioration and chromatic alterations of painted and gilded mummy cartonnage at the Saqqara Museum Storeroom, Egypt," *Archaeometry* 60(4), 845-858. DOI: 10.1111/arcm.12340

Ao, W., Li, J., Yang, H., Zeng, X., and Ma, X. (2006). "Mechanochemical synthesis of zinc oxide nanocrystalline," *Powder Technology* 168(3), 148-151. DOI: 10.1016/j.powtec.2006.07.014

ASTM D778-97 (2002). "Standard test methods for hydrogen ion concentration (pH) of paper extracts (hot-extraction and cold-extraction procedures)," ASTM International,

West Conshohocken, PA, USA.

Basile, C. (1972). "A method of making papyrus and fixing and preserving it by means of a chemical treatment," *Studies in Conservation* 17(sup1), 901-905. DOI: 10.1179/sic.1972.17.s1.019i

Calienno, L., Pelosi, C., Picchio, R., Agresti, G., Santamaria, U., Balletti, F., and Monaco, A. L. (2015). "Light-induced color changes and chemical modification of treated and untreated chestnut wood surface," *Studies in Conservation* 60(2), 131-139. DOI: 10.1179/2047058413Y.0000000119

Chen, Y., Ding, H., and Sun, S. (2017). "Preparation and characterization of ZnO nanoparticles supported on amorphous SiO_2," *Nanomaterials* 7(8). DOI: 10.3390/nano7080217

Darwish, S. S. (2013). "Evaluation of the effectiveness of some consolidants used for the treatment of the XIXth century Egyptian cemetery wall painting," *International Journal of Conservation Science* 4(4), 413-422.

El-Feky, O. M., Hassan, E. A., Fadel, S. M., and Hassan, M. L. (2014). "Use of ZnO nanoparticles for protecting oil paintings on paper support against dirt, fungal attack, and UV aging," *Journal of Cultural Heritage* 15(2), 165-172. DOI: 10.1016/j.culher.2013.01.012

Elnaggar, A., Fitzsimons, P., Nevin, A., Watkins, K., and Strlič, M. (2015). "Viability of laser cleaning of papyrus: Conservation and scientific assessment," *Studies in Conservation* 60(sup1), S73-S81.DOI: 10.1179/0039363015Z.000000000211

Emamifar, A, Kadivar, M., Shahedi, M., and Soleimanian-Zad, S. (2010). "Evaluation of nanocomposite packaging containing Ag and ZnO on shelf life of fresh orange juice," *Innovative Food Science & Emerging Technologies* 11(4), 742-748. DOI: 10.1016/j.ifset.2010.06.003

Franceschi, E. (2011). "Thermoanalytical methods: A valuable tool for art and archaeology: A study of cellulose-based materials," *Journal of Thermal Analysis and Calorimetry* 104(2), 527-539. DOI: 10.1007/s10973-011-1343-x

Gedamu, D., Paulowicz, I., Kaps, S., Lupan, O., Wille, S., Haidarschin, G., Mishra, Y. K., and Adelung, R. (2014). "Rapid fabrication technique for interpenetrated ZnO nanotetrapod networks for fast UV sensors," *Advanced Materials* 26(10), 1541-1550. DOI: 10.1002/adma.201304363

Gill, K., and Boersma, F. (1997). "Solvent reactivation of hydroxypropyl cellulose (Klucel G®) in textile conservation: Recent developments," *The Conservator* 21(1), 12-20. DOI: 10.1080/01410096.1997.9995111

Giorgi, R., Dei, L., Ceccato, M., Schettino, C., and Baglioni, P. (2002). "Nanotechnologies for conservation of cultural heritage: Paper and canvas deacidification," *Langmuir* 18(21), 8198-8203. DOI: 10.1021/la025964d

Hadi, F. A., and Kadhim, R. G. (2019). "A study of the effect of nano zinc oxide on cure characteristics and mechanical properties of rubber composites," in: *The 1st International Scientific Conference on Pure Science*, Al Diwaniyah, Iraq.DOI:10.1088/1742-6596/1234/1/012043

Hahn, Y.-B. (2011). "Zinc oxide nanostructures and their applications," *Korean Journal of Chemical Engineering* 28(9). DOI: 10.1007/s11814-011-0213-3

Hamburg, D. A. (1988). "Paper conservation catalog," in: *Preprints of Papers Presented at the Sixteenth Annual Meeting of the AIC.* New Orleans, Louisiana, June 1-5, 1988, pp. 218-221.

Hamed, S. A. E. K. M., and Hassan, R. R. A. (2019). "Microscopic characterization of

acidic paper manuscripts," *Pigment and Resin Technology* 48(2), 119-128. DOI: 10.1108/PRT-05-2018-0048

Harandi, D., Ahmadi, H., and Achachluei, M. M. (2016). "Comparison of TiO_2 and ZnO nanoparticles for the improvement of consolidated wood with polyvinyl butyral against white rot," *International Biodeterioration& Biodegradation* 108, 142-148.DOI: 10.1016/j.ibiod.2015.12.017

Hassan, R. (2015a). "A 'Tafsiral khazen' manuscript (17th century AD). A technical study," *International Journal of Conservation Science* 6(3), 369-382.

Hassan, R. (2015b). "Behavior of archeological paper after cleaning by organic solvents under heat accelerated ageing," *Mediterranean Archaeology and Archaeometry* 15(3), 141-150. DOI:10.5281/zenodo.18365

Hassan, R. R. A. (2021). "Sodium dodecyl sulfate micro-emulsion as a smart cleaning agent for archeological manuscripts: Surface investigations," *European Physical Journal Plus* 136, 37. DOI: 10.1140/epjp/s13360-020-00973-w

Hassan, R. R. A. (2020). "Using polaroid zinc oxide nanocomposites in strengthening a historical printed paper: Application to 'Annales Agricoles' –1829 AD," *Pigment & Resin Technology* 49(5), 369-375. DOI: 10.1108/PRT-02-2020-0012

Hassan, R. R. A., Ali, M. F., Fahmy, A.-G. A., Ali, H. M., and Salem, M. Z. M. (2020). "Documentation and evaluation of an ancient paper manuscript with leather binding using spectrometric methods," *Journal of Chemistry*, Vol. 2020, article ID 6847910. DOI: 10.1155/2020/6847910

Hassan, R. R. A., and Mohamed, W. S. (2018). "The impact of methyl methacrylate hydroxyethyl methacrylate loaded with silver nanoparticles on mechanical properties of paper," *Applied Physics A* 124(8). DOI: 10.1007/s00339-018-1989-3

Horst, T. H., Smith, R. D., Potthast, A., and Hubbe, M. A. (2020). "Accelerated aging of deacidified and untreated book paper in 1967 compared with 52 years of natural aging," *Restaurator. International Journal for the Preservation of Library and Archival Material* 41(3), 131-152. DOI: 10.1515/res-2020-0006

Hotle, B. T., Considine, J. M., Wald, M. J., Rowlands, R. E., and Turner, K. T. (2008). "Effects of thermal aging on mechanical performance of paper," Proceedings: Progress in paper physics seminar, June 2-5, 2008, Helsinki University of Technology (TKK), Espoo, Finland. [Espoo, Finland]: Helsinki University of Technology, [2008]: pages 271-273.

Hubbe, M. A., Henniges, U., Potthast, A., Ahn, K., and Smith, R. D. (2018). "Nonaqueous solution deacidification treatments to prolong the storage life of acidic books: A review of mechanistic and process aspects," *BioResources* 13(3), 7096-7136.

Ibáñez Domínguez, M. C. (2019). "A proposal for the unified definition of damages to papyri," in: *Proceedings of the 28th Congress of Papyrology*, Barcelona, Spain, pp. 794-804.

ISO 187 (1990). "Paper, board and pulps – Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples," International Organization for Standardization, Geneva, Switzerland.

ISO 1924-3 (2005). "Paper and board – Determination of tensile properties– Part 3: Constant rate of elongation method (100 mm/min)," International Organization for Standardization, Geneva, Switzerland.

ISO 5630-3 (1996). "Paper and board – Accelerated ageing – Part 3: Moist heat treatment at 80 degrees C and 65 % relative humidity," International Organization for

Standardization, Geneva, Switzerland.

Jia, M., Zhang, X., Weng, J., Zhang, J., and Zhang, M. (2019). "Protective coating of paper works: ZnO/cellulose nanocrystal composites and analytical characterization," *Journal of Cultural Heritage* 38, 64-74. DOI: 10.1016/j.culher.2019.02.006

Jiang, J., Pi, J., and Cai, J. (2018). "The advancing of zinc oxide nanoparticles for biomedical applications," *Bioinorganic Chemistry and Applications* 2018. DOI: 10.1155/2018/1062562

Kamel, S., El-Sakhawy, M., and Nada, A. M. A. (2004). "Mechanical properties of the paper sheets treated with different polymers," *Thermochimica Acta* 421(1-2), 81-85. DOI: 10.1016/j.tca.2004.03.005

Katuščak, S., Polovka, M., Vrska, M., Tino, R., and Jablonsky, M. (2006). "The effect of paper degradation on uncertainty of determination of initial lignin content," *e-Preservation Science* 3, 69-72.

Kavkler, K., Gunde-Cimerman, N., Zalar, P., and Demšar, A. (2011). "FTIR spectroscopy of biodegraded historical textiles," *Polymer Degradation and Stability* 96(4), 574-580. DOI: 10.1016/j.polymdegradstab.2010.12.016

Khalaji, G., Maleki, M., and Memand, A. (2019). "An experimental investigation of ZnO nanoparticles effect on the acrylic coatings," *Oriental Journal of Chemistry* 35(1), 216-220. DOI: 10.13005/ojc/350125

Khojasteh Khosro, S., Ghofrani, M., and Ganjaee Sari, M. (2016). "The effect of adding zinc oxide nanoparticles on color change and adhesion strength of polyurethane coating on wood surface," *Iranian Journal of Wood and Paper Science Research* 30(4), 690-704.

Kronkright, D. P. (1990). "Deterioration of artifacts made from plant materials," in: *The Conservation of Artifacts Made from Plant Materials*, Princeton University Press, Princeton, NJ, USA.

Kolar, J., Strlič, M., Müller-Hess, D., Gruber, A., Troschke, K., Pentzien, S. and Kautek, W. (2003). "Laser cleaning of paper using Nd: YAG laser running at 532 nm," *Journal of Cultural Heritage* 4 (Supplement 1), 185-187. DOI: 10.1016/S1296-2074(02)01196-2

Leach, B. (2009). "Papyrus manufacture," in: *UCLA Encyclopedia of Egyptology*, W. Wendrich (ed.), Department of Near Eastern Languages and Cultures, University of California, Los Angeles, Los Angeles, CA, USA.

Łojewska, J., Lubańska, A., Łojewski, T., Miśkowiec, P., and Proniewicz, L. M. (2005). "Kinetic approach to degradation of paper. *In situ* FTIR transmission studies on hydrolysis and oxidation," *e-Preservation Science* 2, 1-12.

Look, D. C. (2001). "Recent advances in ZnO materials and devices," *Materials Science and Engineering: B* 80(1-3), 383-387. DOI: 10.1016/S0921-5107(00)00604-8

Martin, A., Rouchon, V., Aubry, T., Cauliez, N., Desroches, M., and Margez, M. (2011). "Local strengthening of mould-damaged manuscripts: A case study on logbooks of early French expeditions in Louisiana (1684-1722)," *Journal of Paper Conservation* 12(1), 21-29.

Menei, E. (2015). "Use of East Asian materials and techniques on papyrus: Inspiration and adaptation," in: *Adapt & Evolve 2015: East Asian Materials and Techniques in Western Conservation. Proceedings from the International Conference of the Icon Book & Paper Group*, London, UK, pp. 118-127.

Muthuri, F. M., and Kinyamario, J. I. (1989). "Nutritive value of papyrus (*Cyperus papyrus*, Cyperaceae), a tropical emergent macrophyte," *Economic Botany* 43(1), 23-

30.DOI: 10.1007/BF02859321

Ngo, T. M. P., Dang, T. M. Q., Tran, T. X., and Rachtanapun, P. (2018). "Effects of zinc oxide nanoparticles on the properties of pectin/alginate edible films," *International Journal of Polymer Science*2018. DOI: 10.1155/2018/5645797

Owen, A., and Danzing, R. (1993). "The history and treatment of the papyrus collection at the Brooklyn Museum," *The Book and Paper Group Annual* 12, 36-43.

Princi, E., Vicini, S., Pedemonte, E., Mulas, A., Franceschi, E., Luciano, G., and Trefiletti, V. (2005). "Thermal analysis and characterisation of cellulose grafted with acrylic monomers," *Thermochimica Acta* 425(1-2), 173-179.

Raguvaran, R., Manuja, A., and Manuja, B. K. (2015). "Zinc oxide nanoparticles: Opportunities and challenges in veterinary sciences," *Immunome Research* 11(2). DOI: 10.4172/1745-7580.1000095

Rushdy, A. M., Wahba, W. N., Abd-Aziz, M. S., Samahy, M. E., and Kamel, S. (2017). "A comparative study of consolidation materials for paper conservation," *International Journal of Conservation Science* 8(3), 441-452.

Salem, M. Z. M., Hamed, S. A. E.-K. M., and Mansour, M. M. A. (2019). "Assessment of efficacy and effectiveness of some extracted bio-chemicals as bio-fungicides on wood," *Drvna Industrija* 70(4), 337-350. DOI: 10.5552/drvind.2019.1837

Salim, E., Abdel-Hamied, M., Salim, S., Gamal, S., Mohamed, S., Galal, F. E.-Z., Tarek, F., Hassan, R. R. A., Ali, H. M., and Salem, M. Z. M. (2020). "Reduction of borax/ agar-based gel residues used to neutralize acidity of a historical manuscript with use of different paper barriers: Artificial ageing results," *BioResources* 15(3), 6576-6599. DOI: 10.15376/biores.15.3.6576-6599

Scora, P. E., and Scora, R. W. (1991). "Some observations on the nature of papyrus bonding," *Journal of Ethnobiology* 11(2), 193-202.

Sehlstedt-Persson, M. (2005). *Properties of Solid Wood: Responses to Drying and Heat Treatment*, Ph.D. Dissertation, Luleå University of Technology, Skellefteå, Sweden.

Sricharussin, W., Threepopnatkul, P., and Neamjan, N. (2011). "Effect of various shapes of zinc oxide nanoparticles on cotton fabric for UV-blocking and anti-bacterial properties," *Fibers and Polymers* 12(8), 1037-1041. DOI: 10.1007/s12221-011-1037-9

Taha, A. S., Salem, M. Z. M., Abo Elgat, W. A. A., Ali, H. M., Hatamleh, A. A., and Abdel-Salam, E. M. (2019). "Assessment of the impact of different treatments on technological and antifungal properties of papyrus (*Cyperus papyrus* L.) sheets," *Materials* 12(4).DOI: 10.3390/ma12040620.

Zotti, M., Ferroni, A. and Calvini, P. (2011). "Mycological and FTIR analysis of biotic foxing on paper substrates," *International Biodeterioration & Biodegradation* 65(4), 569-578. DOI: 10.1016/j.ibiod.2010.01.011

Article submitted: November 11, 2020; Peer review completed: January 2, 2021; Revised version received and accepted: February 14, 2021; Published: February 18, 2021.
DOI: 10.15376/biores.16.2.2607-2625