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Evaluating The Use of Sodium Alginate Polymer for Eco-friendly Consolidation and De-acidification of Ancient Printed Papers

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Abstract

This study handles the efficiency of sodium alginate polymer and sodium alginate nanocomposites for consolidating degraded papers dating back to 200 years. The paper samples were from wood derivatives. The characterization of untreated and treated papers was performed using SEM, ATR-FTIR analysis, XRD analysis for crystallinity estimation, pH measurements, and color change analysis. The study proved the positive effect of sodium alginate polymer for consolidating fragile papers. However, treated papers with SA polymer increased the pH towards an alkaline value, indicating that SA polymer was efficient in paper de-acidification; as the untreated sample recorded (p H 5.8), and the recorded measures for treated samples were 8.2, 8.4, 7.9, and 8.5. The surface morphology of SA alginate treated paper showed a strengthened structure because of the SA molecule self-aggregation, as the paper structure became more coherent and integrated. There is no color change could be detected by the human eye. Furthermore, the sample treated with SA/ ZnO gave (Δ E 0.87), but it was considered a slight difference, confirming that the zinc oxide had remarkable role in reducing the yellowness of the paper sample so it was recommended for consolidation treatments to enhance the performance of historical papers towards harmful effects of thermal aging.

Kyewords*:Sodium alginate; Crystallinity; ATR-FTIR; TEM; Acidity; Consolidation*

1. Introduction

Paper can deteriorate much, resulting in the irremediable degradation of important documents and artworks. The humidity of the atmosphere plays a crucial role in such deterioration [1,2]. Therefore, researchers endeavor to apply many restoration and preservation processes to extend the life of paper documents. They minimize physical and chemical deterioration to hinder and reverse more damage. They also take measures to renovate the document, artifact, or physical structure entirely. In archives and libraries, documentary cultural heritage and manuscripts suffer from loss because of natural aging because they are weak and fragile and require consolidation after receiving preliminary treatment, such as cleaning, washing, and deacidification treatments, to increase their lifespan and maintain safe handling [3, 4]. The consolidation strategy of the degraded paper is based on enforcing the mechanical properties and resistance to deterioration. It is also applied to replace the lost sizing agent, enhance its characteristic and reduce sticky dust on the document surface Zinc oxide (ZnO) nanoparticles (NPs) have been used for many purposes, such as wear proofing for rubber composites, strong UV absorption in cosmetics and sunscreen, antimicrobial agents, and UV blocking and deodorant in the textile industry, Zinc oxide NPs with cotton fabrics or paper sheets showed good antimicrobial properties. 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 [5].

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Consolidation is important for restoring manuscripts and primarily aims to highlight old papers' resistance. Currently, various cellulose derivatives are utilized to consolidate such papers. Klucel G, hydroxyl propyl cellulose, and Funori are frequently used [6,7]. Researchers are interested in providing urgent and efficient solutions to issues relevant to conserving and restoring documentary heritage [8, 9]. Paper conservation and restoration denotes a set of operations to extend the life of papers. Furthermore, it causes no change in the luster, opacity degree, morphology, or loss of transparency of papers. Consolidating materials are a sub-group of adhesive materials that compensate for the loss of the binding media and always infiltrate the surface [10, 11, 12]. An adequate adhesive bond results from the ideal mixture for proper surface treatments, as well as the application methods of the adhesive [13].

Sodium alginate (NaAlg) is a linear polysaccharide extracted from brown seaweed. SA seems an economic biopolymer comprising β-D mannuronic acid and α-L guluronic acid associated with glycosidic bonds of 1 → 4 [1–3]. It is relatively cheap, water-soluble, and biodegradable [14,15]. It can be used independently or with other polymers in many industries, including tissue engineering, pharmaceuticals, and food. The first use of alginate from seaweed was in 1940. Previous studies reported the extraction of alginate from brown algae. It was utilized as the gelling means in food and textile fields [16, 17, 18].

There are several uses of alginate in different industries, including textiles, food, cosmetics, wastewater treatments, and paper industry due to its excellent biocompatibility and biodegradability.

Alginates are soluble in cold water without need to heating and cooling cycle to form gel. They are particularly biodegradable, biocompatible, bioactive anionic polysaccharide, and they have low toxicity and low cost. They are widely used in the food and textile industries as thickeners, and stabilizers [19].Therefore, the authors suggested that it may be useful for consolidating aged paper by using two different concentrations.

The research aimed to evaluate the efficiency of sodium alginate polymer (SA) and sodium alginate/ ZnO for the consolidation of historical papers. Characterization of the paper samples were performed using ATR-FTIR spectroscopy, XRD analysis, scanning electron microscopy (SEM), as well as p H and chromatic measurements.

2. Materials and methods

2.1. Materials

Sodium alginate (SA) polymer solutions with two different concentrations, 1 and 3%, were prepared by dissolving 1 and 3 gm of SA polymer as a solute separately in 100 ml deionized water. Each solution was introduced to 400 watt ultrasonic sonifier for 15 min.

Sodium alginate nanocomposite (SA/ ZnO) was prepared by the addition of the ZnO nanopowder 0.5 gm to 100 ml of to the sodium alginate solution, where the amount of zinc oxide was 0.5% from the prepared sodium alginate which was dissolved using an ultrasonic stirrer.

2.2. Sampling

Degraded historical paper samples were selected for the consolidation treatments with chosen consolidating material. The samples dating back to 200 years were purchased from Al-Sayda Aisha, Cairo, Egypt.

2.3. Application of consolidation treatment

The consolidation materials previously prepared SA polymer with two concentrations (1% &3%) and SA/ZnO have been applied to paper samples using the topical application technique using a soft brush.
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2.4. Laboratory aging

The aging test was carried out at 90 °C and dry environment by a laboratory dryer (Memmert HCP246) ("DRY" procedure). Comparable samples were aged following ASTM standards.

3. Characterization methods

3.1 Transmission Electron Microscope

Zinc oxide nanoparticles ZnO NPs were examined by a JEOL (JEM- 1400 TEM, Japan) the images of ZnO NPs were captured under operating conditions of 100 Kv.

3.2 Scanning electron microscopy

Studying the morphology of paper samples before and post consolidation treatment was performed using a variable pressure SEM (FEL Quanta 3D 200i Edx / Thermo fisher pathfinder in the Grand Egyptian Museum.

3.3 Spectrophotometer for colorimetric measurements

The color change of paper samples post-consolidation treatment was detected by measuring the total color difference Δ E, using Optimatch 3160 (SDL Company) in Egyptian NIS (National Institute

of Standards), Cairo. Measuring those samples was made in the visible region with the wavelength of 400- 700nm, the 10nm- interval by the D65 light source, as well as the observed angle of 10°. Δ E was expressed by CIE L*, CIE a*, and CIE b* colorimetric coordinates.

3.4 FTIR analysis

FTIR helped evaluate the films' chemical composition and examine the possible interactions between SA and cellulose molecules. FTIR spectra were recorded with a Jasco spectrophotometer (Model6100, Tokyo, Japan) in the Attenuated Total Reflectance mode (ATR). Each spectrum represented 50 scans in average and gathered at 4 cm–1 resolution from 4000 to 600 cm^{-1}.

3.5 XRD analysis

XRD analysis used a diffractometer of X-ray PW 1480 model, Netherlands having a tube of Cu-Ka X-ray and running at 35KV -20MA. The wavelength was 1.541874A. While the angle of the beginning was 10, the angle of the end was 60 at the X-Ray Laboratory, NIS, Egypt. XRD was used to define the crystalline structure of cellulose and determine the efficacy of the consolidation materials on cellulose Crystallinity.

3.6 pH measurements

p H was measured following the Tappi 509 om-02 standard method (the cold extraction method). p H values were calculated at about 6 h, to allow ions to migrate into the solution. p H was measured before and after treatment using ADWA kft., Szeged-HUNGARY, made in Europe, Romania.

4. Results and Discussion

4.1 Transmission electron microscopy

TEM image shows the roughly spherical shape of ZnO NPs with weak agglomeration as illustrated in Fig.1, which appears with average particle size ranging from 22 to 54 nm. **SEM observations**

SEM analysis of microstructure morphology revealed accurate data about the fiber's internal damage due to the effect of aging on the paper and distinguished erosion in the internal paper fibers [20]. Micrographs of the untreated aged paper (Fig.2) showed the gaps between fibers; the fibers are completely incoherent and detached. The treated samples SA/ZnO showed fibrils coherence due to the deposition of nano zinc in the gaps between fibers. Additionally, it could be noted that the aggregate structures of sodium alginate/ ZnO and the good distribution into the paper structure. The surface morphology of SA treated paper (Fig.3, 4) showed a strong structure because of SA molecule self-aggregation, as the paper structure became more coherent and integrated [21, 22].

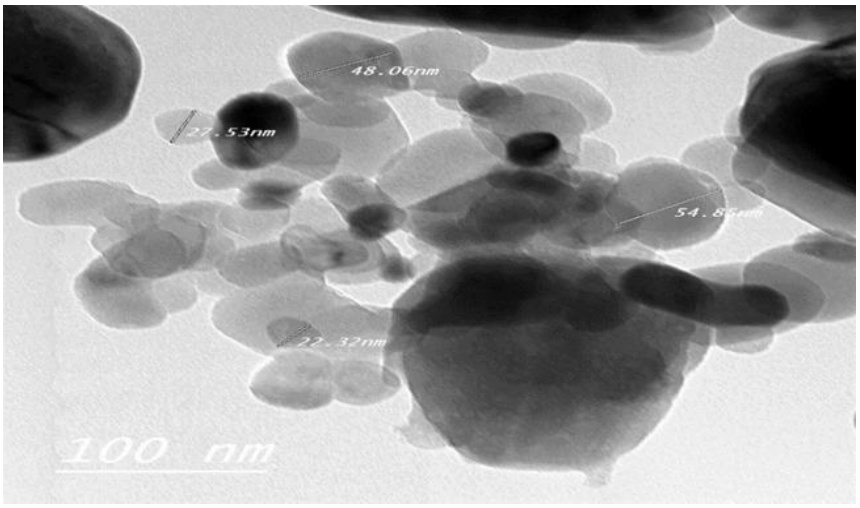

Fig. 1: TEM image illustrates the particle size of ZnO nanoparticles.

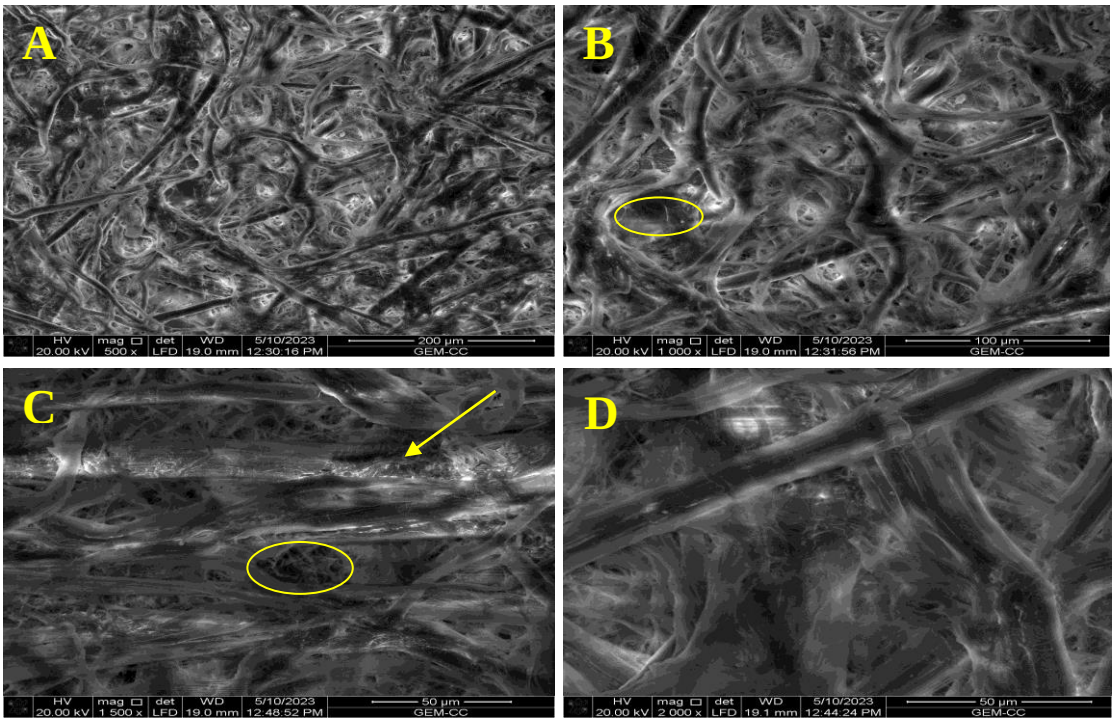

Fig.2: SEM micrograph of the paper morphology of the untreated sample; A and B show the gaps between fibers, and C and D show the erosion and incoherence between fibers.

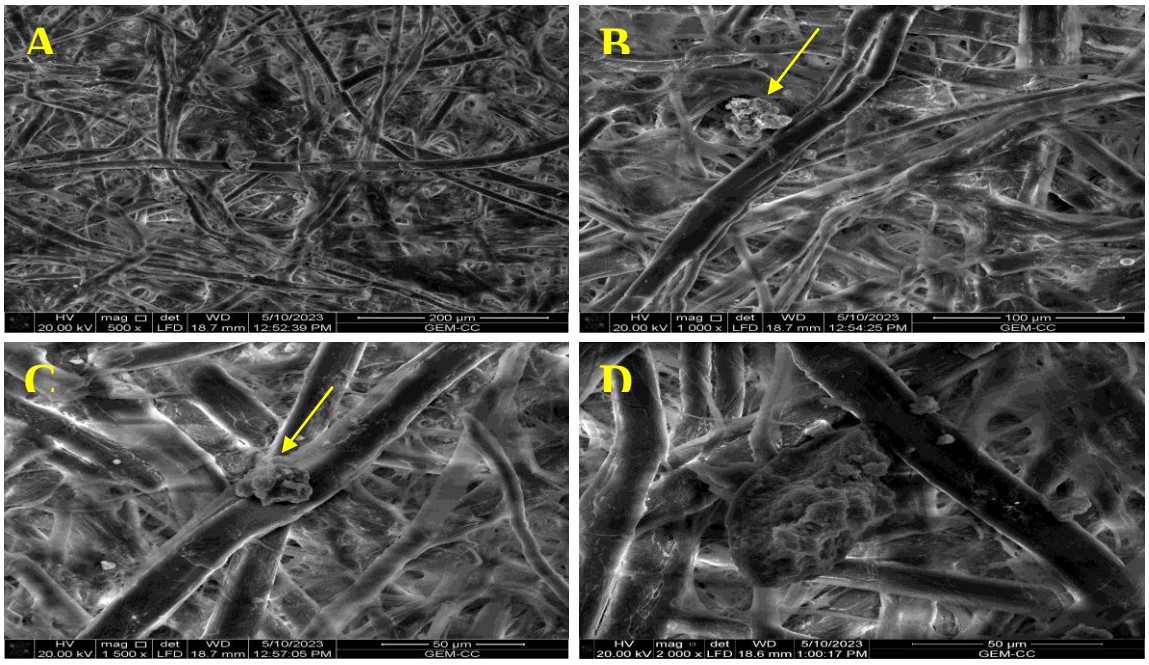

Fig.3: SEM micrograph of the paper morphology of treated sample with sodium alginate polymer; A and B show a thin layer of alginate polymer inside the walls of fibers, and C and D show that the treatment increased the fiber width.

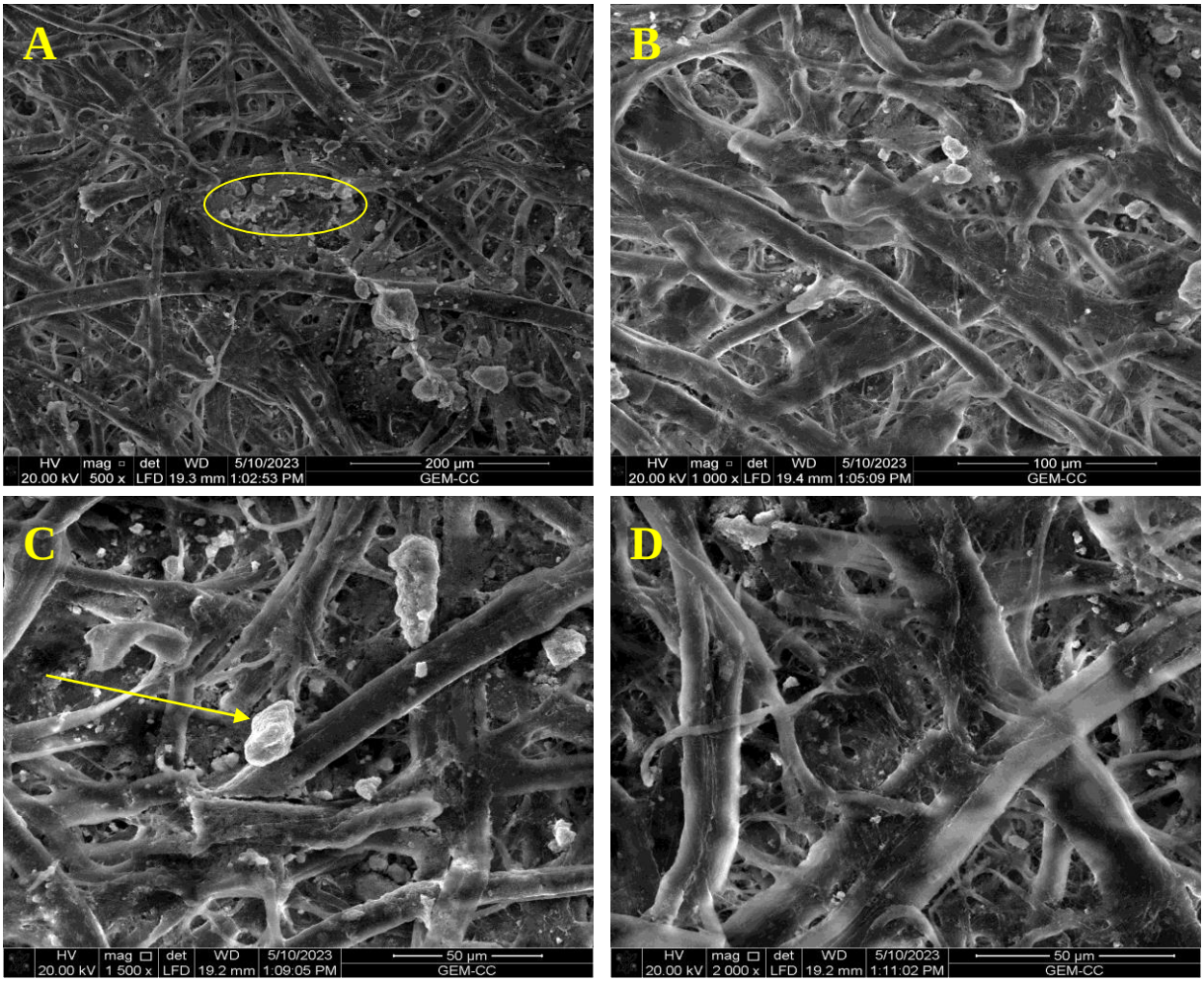

Fig.4: SEM micrograph of the paper morphology of treated sample with SA/ZnO; A and B show a thin layer of alginate polymer into the paper structure, C and D show the agglomerates of ZnONPs and the microfibrils became more integrated due to the good penetration of sodium alginate polymer.

4.3 Colorimetric measurements

From the results of color parameters (Table.1), it was found that by comparing ΔE values for untreated and treated paper samples, a minor color change was detected, and all values were in an acceptable range. The ΔE values < 5, which means no color change could be detected by the human eye; the results showed that the paper sample treated with sodium alginate polymer /nanocomposites became lighter than the treated with sodium alginate polymer. The treated sample with SA recorded (ΔE= 0.67) indicated a slight change. Furthermore, the sample treated with SA/ ZnO gave (Δ E 0.87), but it was considered a slight difference, confirming that the zinc oxide had remarkable role in reducing the yellowness of the paper sample [22,23]. According to the results (Table 1), after thermal aging, the treated sample with SA/ZnO became lighter than the untreated sample. Moreover, all aged treated samples had no significant chromatic alteration, indicating the durability of treated papers with sodium alginate polymer when exposed to thermal aging.

Table.1: Color parameters for untreated and treated aged paper

Samples	CIEL*coordinates	CIE a*coordinates	CIE b*coordinates	ΔE
	Color parameters			
Blank	83.76	1.84	13.75	-----
Treated with 1% SA	84.36	1.65	13.52	0.67
Aged treated with 1% SA	84.12	1.86	14.17	1.46
Treated with SA/ZnO 0.5%	84.30	1.60	13.24	0.87
Aged treated with SA /ZnO	86.01	1.78	13.60	2.24
Treated with 3%SA	84.00	1.79	13.58	0.63
Aged treated with 3%SA	83.26	1.17	9.02	3.65
Treated with 3% SA/ZnO	85.60	1.62	13.36	1.89
Aged treated with SA/ZnO	82.18	0.71	14.13	2.01

4.4 ATR- FTIR analysis

The FTIR spectra of aged untreated paper (Fig.5) illustrated that carbonyl group C=O appeared at 1620- 1638 cm^{-1}, indicating the oxidation of cellulose due to natural aging [24,25]. The spectra of the ATR-FTIR of the treated sample with SA illustrated a wide absorption band ranging from 3600 to 3000 cm^{-1} because the OH group had stretching vibration band and the -CH vibration bands scored at 2930 – 2845 cm^{-1}. The bands noted at 1590 and 1400 cm^{-1} resulted from the symmetric and asymmetric stretching vibrations of the COO– groups and were associated with the ionic binding (Table. 2) [26,27]. The results of the SA/ treated paper revealed that consolidation treatment caused a slight change were detected for the cellulose water content. SA cross-linking was detected in the reduced intensity and slightly decreased wavenumber of the carbonyl peak. The 1080 cm^{-1} band was attributable to cross-linking bond into the cellulose structure. C–C peak at 1027 cm^{-1} showed more intensity and stronger stretching O-H bending vibration to guluronic acid from sodium [28, 29, and 30]. Furthermore, the stretching vibration bands noted at 945 cm^{-1}, 887 $cm^{-1,}$ and 816 cm^{-1} corresponded to the guluronic and mannuronic acids [31]. The carboxyl groups' minor shifts indicated the ionic binding between cellulose and SA chains (Fig.6). SA chains' functional groups tended to make a complex structure with cellulose molecules because of the carboxylate groups [32, 33]. The most noticeable change was observed in the aged treated samples. The wavenumber of OH (strong hydrogen bonded vibration) decreased from 3339 cm^{-1} to 3331 cm^{-1}, showing hydrolysis due to the breakdown of hydrogen bonding[34,35]. On the other hand, in the C-H stretching band at around 2918 cm^{-1}, the slight change means that the consolidation treatment did not cause any changes in the cellulose molecule's water content [36].

Table.2: FTIR data of the aged and treated paper

Functional Group	Blank	SA(B)	SA(A)	SA/ZnO(B)	SA/ZnO(A)
				Wavenumber cm^{-1}	
OH stretching	3339	3331	3329	3337	3334
C-H stretching	2924	2917	2917	2917	2920
C=O	1638	1620	1630	1627	1624
C=C	1520	1517	1502	1514	1537
CH2 bending	1426	1423	1418	1420	1418
CH bending	1314	1314	1316	1314	1318
C-O- C pyranose ring vibration	1026	1028	1028	1025	1026

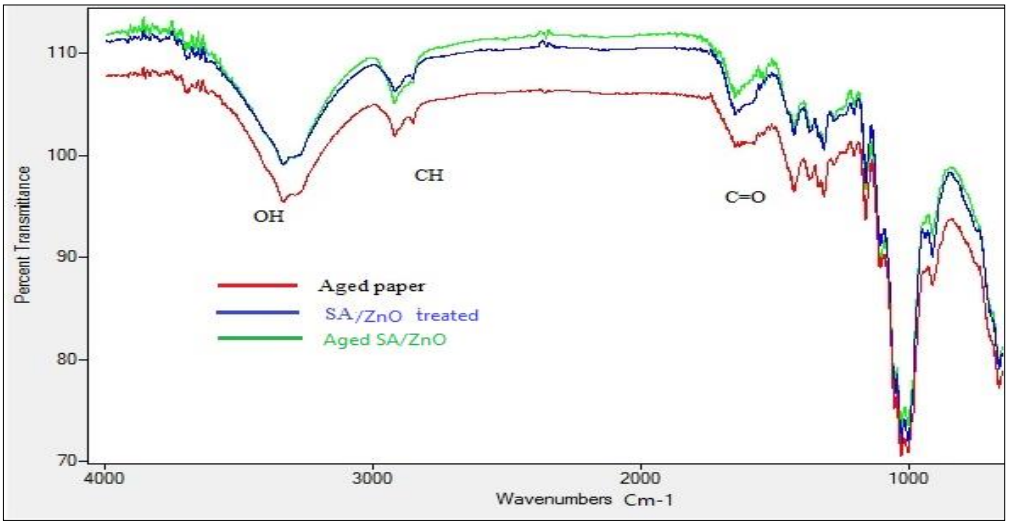

Fig.5: FTIR bands for treated and aged paper samples using SA/ZnO NPs

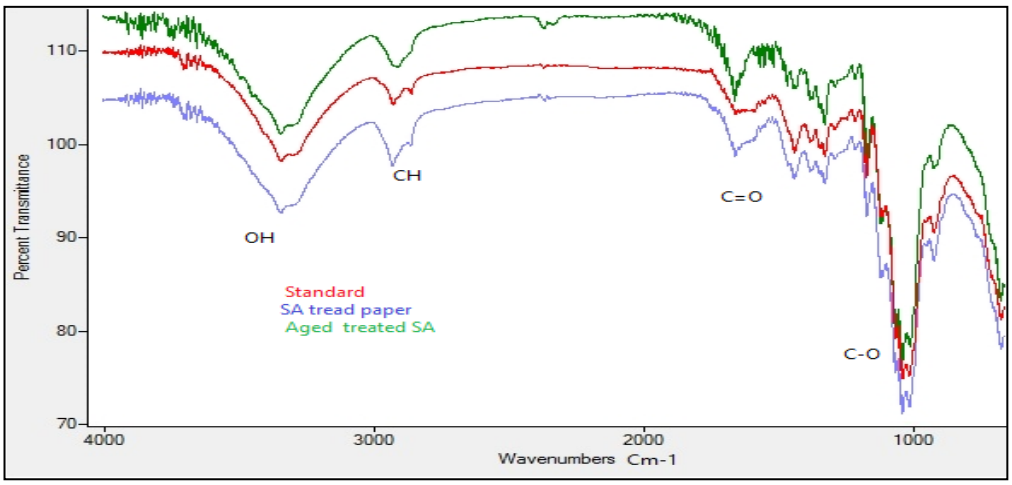

Fig.6: FTIR bands of treated and aged paper samples using SA polymer

4.5 XRD analysis

The crystalline structure of cellulose constituent of paper support was identified by XRD. The samples showed observable differences in crystallinity. The crystalline reflections from the historical and treated samples were characterized. The XRD curve of the aged sample displayed broad peaks at 2θ =15 and the diffraction peaks intensity in the region between 18 and 21θ[37]. Compared to the diffraction patterns of treated samples, treated samples with SA showed a slight increase in peak intensity and broadening, indicating that the consolidation with SA increased the crystallinity. Noticeable changes occurred in the untreated samples due to exposure to natural aging under variable conditions. As a result, the fibril structure became more fragile, indicating an increase in the amorphous regions compared with the ratio of crystalline structure. The XRD spectra (Fig.7,8) showed a decrease in the crystallinity of untreated samples compared to treated samples with SA/ZnO. Sodium alginate polymer is a polymer with abundant free OH and COOH groups that has the tendency to create a complex structure with cellulose molecules due to the carboxylate groups, reconstruction of hydrogen bonds in the cellulose chains' crystalline region, resulting in the increasing of the crystallinity [38,39,40]. This finding agreed with the results obtained from the FTIR analysis, i.e., the ratio of the band intensity detected at 2900 cm^{-1} and 1370 cm^{-1}.

Table.3: XRD data of aged and treated paper

Samples	I_{am}	I_{101}	I_{002}	Percentage of Cr%
Aged paper sample	451	345	984	53.6%
SA treated paper	359	199	921	61%
SA/ZnO treated paper	495	280	994	68.3%

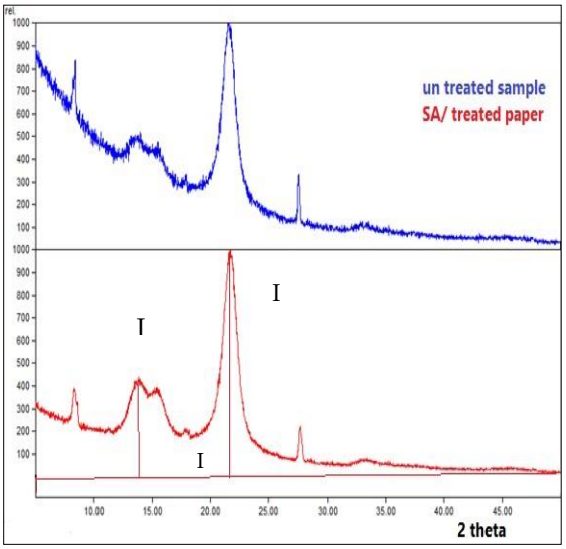

Fig.7: XRD bands of the historical samples before and post consolidation with SA polymer.

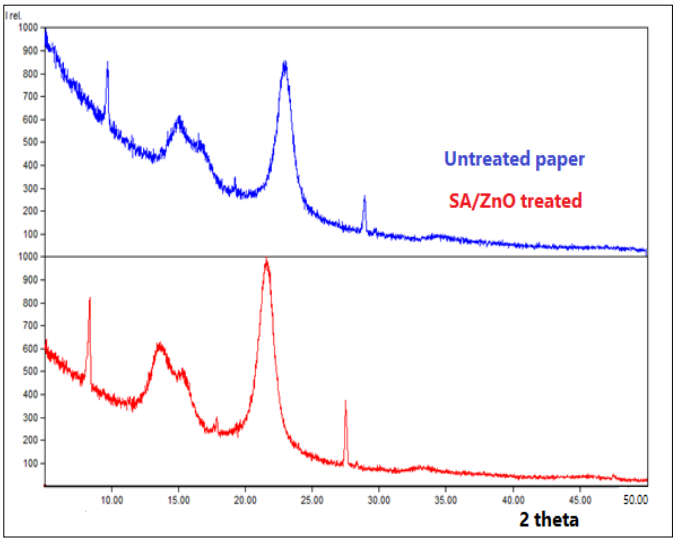

Fig.8: XRD spectra of historical samples before and post consolidation with SA/ZnO NPs.

Table 4: Results of the pre- and post- treatment pH of paper samples

Samples	pH value
Blank	5.8 ± 0.2
Treated with 1% SA	8.2± 0.2
Aged treated with 1% SA	8.0± 0.2
Treated with SA/ZnO 0.5%	8.4± 0.2
Aged treated with SA /ZnO	6.4± 0.2
Treated with 3%SA	7.9± 0.2
Aged treated with 3%SA	6.8± 0.2
Treated with 3% SA/ ZnO	8.5± 0.2
Aged treated with SA/ ZnO	7.3± 0.2

5. Conclusion

In this study, Sodium alginate polymer (SA) and Sodium alginate loaded with Zinc oxide nanoparticles (SA/ZnO) was used for paper consolidation. Analytical techniques including (Scanning Electron Microscope (SEM), Colorimetric measurements, ATR FTIR analysis, XRD analysis, and p H measurements) were used to evaluate the efficiency of sodium alginate polymer and SA/ ZnO NPs for consolidation and acidity reduction of aged papers under accelerated thermal aging. The determination of cellulose crystallinity was done using ATR-FTIR and XRD analysis, the results illustrated that (SA) polymer potentially affected ancient papers. The XRD pattern of aged untreated paper revealed a crystallinity degree of 53%. The crystallinity degree increased to 61% and 68% after the consolidation treatment with SA polymer. The results also revealed that the functional groups of SA chains tended to make a complex structure with cellulose molecules because of the carboxylate groups and the interactions between paper fibers, denoting the efficiency of various SA concentrations. Furthermore, color change data showed a negligible color difference, and all values were in an acceptable range, where the ΔE values < 5, which means no color change and imperceptible by the human eye. SA/ZnO formed a thin film on the surface of the paper as a protective layer for the treated fibers. The study concluded that SA polymer represents a positive effect on the pH of aged papers, and enhanced the aged paper characteristics due to its good penetration within the paper structure in addition to its good performance under thermal aging. Therefore, using sodium alginate nanocomposites reduces the acidity of the paper so it could be used to induce deacidification reduction and fibre reinforcement in a single procedure.

6. Conflicts of interest

The authors declare that there are no conflicts of interest

7. Acknowledgments

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