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Evaluation The Condition of Historical Manuscript" Al-MUTAWIL by Al-Qazwini " from the 14th Century AD is kept in Egypt's (Al – Azhar library): A Case Study

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ABSTRACT
The goal of this study is to determine the state of a manuscript by the name of "Al-Mutawil by Al-Qazwini," a rare manuscript from the 8th century A.H./14th century A.D. Various analytical techniques are used to examine the paper and the bookbinding leather to determine the manuscript's condition due to natural aging. To discuss the manuscript's process of deterioration, visual evaluation and surface morphology research utilizing SEM-EDAX, FTIR, and X.R.D analysis are used. Model reference leather samples and ancient leather artifacts were examined to determine the types of animal skin. The morphological analysis revealed that goat skin was used in making leather for bookbinding, and cotton was used to produce paper. The study provides an example of the scientific procedures used to examine a deteriorated paper manuscript. The archaeological documentation, SEM-EDAX, FTIR spectroscopy, and X-ray diffraction were used to identify the paper components and various deterioration aspects of the manuscript. The use of these results may enable the possibility of developing a plan for restoring and conserving manuscripts within libraries.

INTRODUCTION:

Apart from paper, additional materials used in libraries include board, cloth, leather, ink, glue, and other organic materials prone to natural decay. All of these materials are food for some living things. Birds, rats, and insects can all damage collections (Pinniger, 2004). Manuscripts, books, and paintings made of paper are all susceptible to different types of damage. Even though the paper starts out strong and white, over time, due to physical, chemical, and biological factors, its properties change, causing it to deteriorate and become damaged (Sahoo and Mohanty, 2003). Depending on the ultimate application, paper is produced as both an uncoated and a coated substrate. Therefore, a thin layer of polymeric binder and mineral pigment is frequently applied to the surface fibers to enhance the mechanical qualities of coated papers. Kaolin, talc, and calcium carbonate (both natural ground and precipitated) are common minerals used for coating and filling. Filler minerals are frequently manufactured as flocculated slurries or with minimal amounts of dispersant (Hubbe et al., 2008; Isogai et al., 2003). In the middle of the 11th century, Islamic Spain became the first European region to make paper. Western

Europe had embraced the use of paper by the second part of the 14th-century. Prior to 1850, hemp, flax, and cotton fibers were used to make paper from cellulose and water. The paper of the past is very different from the paper of today. While modern paper can be produced from short fibers, hemicellulose and lignin and may contain non-fibrous components such as different coloring agents, fillers, and coatings, the antique paper was entirely made from rags, i.e., from linear long cellulose fibers, with only the addition of a sizing compound. Initially, this sizing compound was made from animal glue. In the 19th century, rosin and alum were used as substitutes and, more recently, other synthetic compounds have been used. (Berrie, 1997; Kolbe, 2004). The main cause of the deterioration of paper-based products is the use of cellulose, which is subject to a variety of attacks, including chemical assault from acidic hydrolysis, oxidative agents, light, air pollution, and biological attack from the presence of bacteria and fungi (Prasad and Kumar, 1995). Poor handling, inadequate storage, incorrect exhibition techniques, and wear and tear are the most frequent types of damage noted. For bookbinding, the damage is caused by repeated usage, chemical changes in the components of the leather products, and exposure to contaminating gases for the leathers used in bookbinding. An old book exposed to light and air revealed a significant amount of sulphuric acid from the contaminating atmosphere (Zervos, 2007). Both internal (endogenous) and exterior (exogenous) factors can contribute to deterioration. When a paper's constituent parts are reasonably pure, as in the first scenario, it has good durability and a sizable life expectancy. The majority of papers created up until the 19th century are in this situation. Sadly, the quality declined once wood pulp became popular in the 19th century. The paper created from wood pulp was thoroughly purified, depending on the mechanical or chemical technique used. Compared to earlier papers, the paper pulp that was then scaled with rosin in an acidic medium age was significantly slower (Shamsian et al., 2006; Blanchette et al., 1994). It is more common to analyze these things using non-destructive equipment, particularly optical spectroscopic or imaging techniques. The XRF technique is nearly always used to analyze artworks, and this type of study is supplemented with other atomic techniques (XRD) or other molecular techniques (FTIR). Due to the lack of clear chemical distinctions between the various ink types and potential interferences from the paper substrate in the analysis, identifying inks is more challenging. SEM has been shown to provide a wealth of information regarding not only the morphological alterations of old archaeological papers but also the elemental content of the various layers that were utilized in the past to cover and embellish manuscripts (Rifai and El Hadidi, 2010). For instance, a recent study found that old spring paper is more prone to damage than samples of paper from various paper species, which can be explained by the fact that the walls of the pulp in spring paper are thinner and weaker than those in fall paper. When working with historical artifacts, approaches involving neither sample preparation nor sampling are chosen due to the close correlation between the materials' durability and paper (Blanchette, 2003; Helman-WaŻNy and Van Schaik, 2013). Therefore, this research aimed to identify the materials used in the examined manuscripts, apply the most efficient analytical techniques to determine paper degradation and explain the degradation mechanisms.

MATERIALS AND METHODS:

Description and conditions:

Al-Azhar Library in Cairo, Egypt, has a manuscript titled "Al-Mutawil by Al-Qazwini" that dates from the eighth century (AH) to the fourteenth century AD. The public number is 84638, and the unique number is 2916. Its length is 26 $cm^{2,}$ and its

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width is 18 cm^2; the number of manuscript pages 197; the font type is Persian, and the condition of the manuscript is severely damaged. It suffers from many different types of damage such as disintegration, erosion, and biological damage, and all the paper sheets are separated. Red and black ink was used to write the titles and texts, respectively. Some visual deterioration is evident, including yellowing and staining from improper storage, ink smears from water effects or high relative humidity, and broken, divided folds from careless handling. Due to aging, they have lost their adherence and leave discolored patches underneath. (Fig.1).

Fig.1. Showing the historical paper (a), the deteriorated paper pages of the manuscript (b), and documentation of the deterioration aspects of paper and leather (c, d).

Investigation methodologies:

The old paper was characterized and identified using a variety of analytical techniques. By combining the methods, we utilized, the majority of which are non-destructive and suited for identifying anionic groups, crystalline phases, structure, and elemental composition, we were able to sufficiently characterize the used documents and technique.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDAX):

The scanning electron microscope was used for the morphological study: The surface morphology was examined using a scan electron scope, which is 100/50000 times powerful, Mag:240000, Resolution (ev) 122.8, (FEL Company), Model: QUANTA FEG 250/20,00 KV, Low volume 60 pascal, and located at the National Research Centre in Cairo. At 20–30 KV, the gold coating was applied. The surface morphology of the treated and untreated samples was examined to reveal any alterations or damage to the fibres. The microstructure of the samples was investigated using an EDXS-equipped scanning electron microscope (SEM) in accordance with Arai's methodology. (Arai, 2000; Bennis et al., 2010).

Isolation and identification of fungal strains:

The surface of the "Al-Mutawil by Al-Qazwini" manuscript was wiped under aseptic conditions by a sterile wet cotton swab. The surface of the potato dextrose agar (PDA)

medium, which was poured into plates, was wiped under aseptic conditions by the cotton swabs. The Petri dishes were then incubated for 5-7 days at 25 – 30°C. During the incubation period, any emerging fungus was isolated onto PDA slides. Fungi were purified by using the single spore technique (Manandhar et al., 1995). The obtained isolates were identified using the microscopic and cultured characteristics according to (Nelson et al., 1982) and (Barnett and Hunter 1986) .

Fourier Transform Spectral analysis (FTIR):

Infrared spectroscopy is an easy method for determining the chemical structural alterations and crystallinity of cellulose samples that occur in paper fibres over time. An FTIR spectrometer (Model 6100, Jasco, Tokyo, Japan) was used to measure the materials. The spectra were collected in transmission mode using a triglycine sulphate (TGS) detector using the KBr technique at a rate of 2 mm/sec, co-added scans in the spectral region between 4000 cm^{-1} and 400 cm^{-1}, and a resolution of 4 cm^{-1} (Baty et al., 2010).

X-Ray Diffraction Analysis (X.R.D):

Compact X-ray Diffract Metre System PW 1840 - Analytical Equipment - Philips-Eindhoven - the Netherlands (Cu K radiation with Ni-filter) is used for the X-ray diffraction analyses. The following equation was used to compute the cellulose crystallinity:

$$\textbf{Cr. I. \%} = \frac{\textbf{1(002)- 180}^{o}\textbf{)}}{\textbf{I (002)}} \times \textbf{100}$$

Where I (002) and I 18^{o} are, respectively, the maximum scattering intensities of the diffraction from the (002) plane recorded at $2\theta = 2.26°$ and the background scatter measured at $2\theta = 18°$, with the latter value being attributed to the non-crystalline cellulose form.

Measurement of the pH:

The most crucial element, the pH, was thought to influence how stable papers were in natural environments. The TAPPI method was used to conduct cold extraction measurements (Kočar et al., 2004; ISO6588-1, 2021; Launer, 1939). The paper was mechanically removed from the surface (grain) as near to the affected area as possible by loose fibres. The paper samples were divided up into tiny fragments.

RESULTS AND DISCUSSION:

SEM examination of the reference leather samples and archaeological leather objects:

The morphology of the historical surface leather (Fig. 2 a,b) and the model reference leather samples (Fig. 2 c,d) were investigated by SEM. The observation Regarding the shape of the exterior of the model reference leather samples revealed the smooth and compact structure of leather, the uniform distributions of the pores, and the fine follicles on the grain layer were easily observed (Fig. 2 c,d). In contrast, the archaeological leather revealed coarse and un homogenous surfaces (Fig. 2 a,b). Moreover, the morphology of the archaeological leather samples showed severe and total degradation of the grain layer (Fig. 2 a,b), which could be related to the growth of microorganisms.

Lipolytic species of fungi are able to attack the leather and utilize the presence of fats in leather as a source of C (Choudhary et al., 2004). When fungi attack the protein of the skin, stain spots and a decrease in tensile strength were found, and subsequently,

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hydrolysis of the leather occurs (Larsen et al., 2002; Von Endt and Jessup, 1986). Free amino acids can be utilized by fungi after collagen degradation by bacteria or chemically or physically (Florian, 1994).

According to a report, the top grain layer of every animal skin has a similar structure and is primarily made up of collagen fiber bundles, while the middle layer (corium) and the flesh layer are made of fibrils (Haines, 2006). Goatskin has a soft surface and glossy grain pattern with a mixture of widely spaced fine and coarse hair follicles arranged in groups and wave-like rows (Elnaggar et al., 2017).

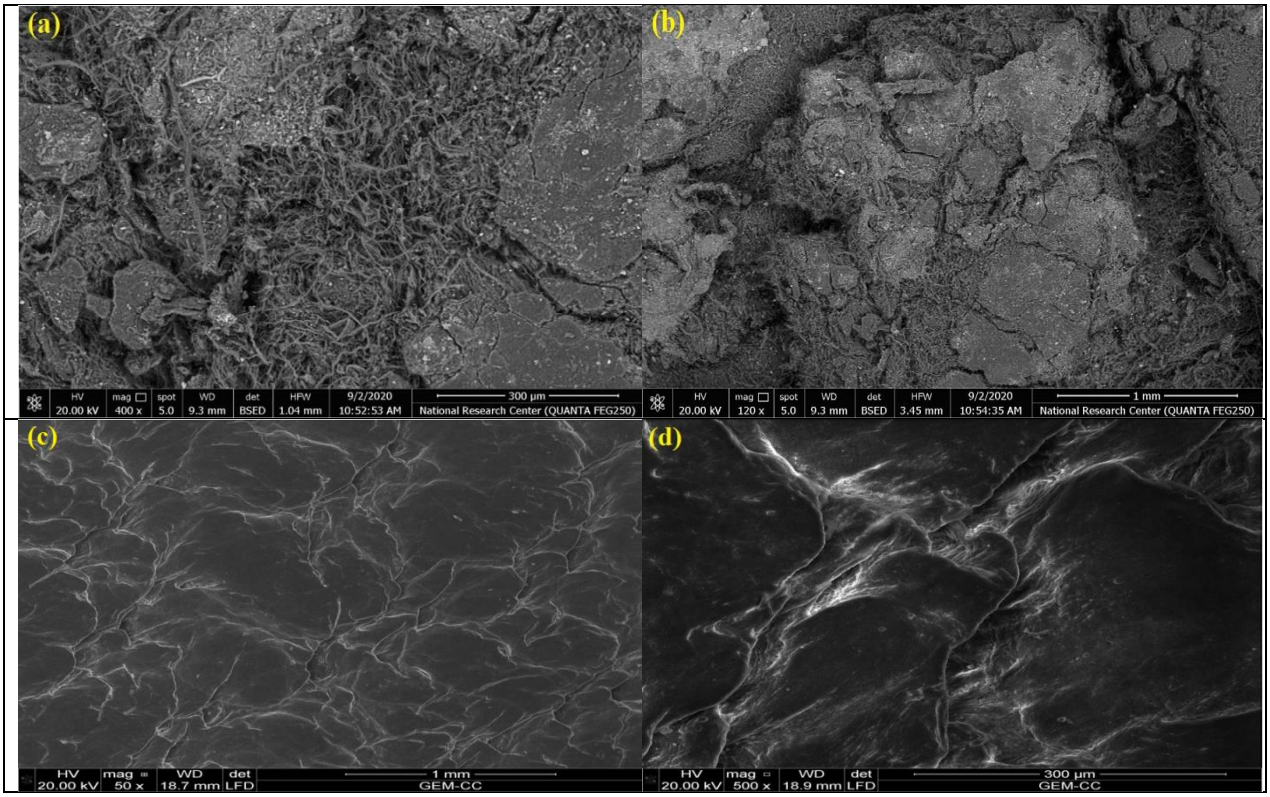

Fig. 2. SEM images of the archaeological leather (a, b) and the model reference leather or the mimic goat leather (c, d).

SEM-EDAX examination of the deteriorated historical paper manuscript:

SEM is particularly useful for looking for subtle signs of deterioration in the paper, such as the initial stages of defibrillation of plant fibres and the morphology of the fracture surface. SEM examination of paper samples (Figure 3a1a, 2) revealed the source of cellulose fibre, which has been identified as cotton fibres; the images showed the morphology of historical paper specimens with a non-homogenous structure, and gaps and filler materials can be seen between the fibres. It is noticeable due to the smooth surface of the cotton fibres.

Table.1. Shows the elemental composition of the historical paper from two points, where the atomic % of the highest elements C (41.87, 39.89%) and O (49.42, 48.34%), followed by other elements Al (3.74%), Si (0.51, 4.93%), S (2.18%), K (0.4, 0.27%), Ca (3.67, 0.17%) and Fe (1.24%). The SEM-EDAX demonstrated that it displays typical signs of biodegradation. Additionally, the cotton fibres' preservation status and an analysis of their elemental makeup in C, K, Si, Ca, Fe, Cl, Mg, Na, S, and Al may be seen in the structure of the paper manuscripts. The creation of spots was significantly influenced by the presence of iron and aluminum. SEM-EDAX gives information about

the small particles and impurities or additives that settled in the paper, which were identified as calcium from calcium carbonate. It is clear from the spectrum that deteriorated paper contains different percentages of silica, aluminum, magnesium, and iron impurities (Fig. 3b2).

An SEM Review of the 'Paper A' sample was performed on previously researched antique cotton rag paper (Fig.2) and demonstrated how the self-oxidation reactions cause the paper's fibres, which are a part of its makeup, to weaken and become dry. The manuscript had been poorly stored, which had accelerated its deterioration. We discuss the general hardness, fungi-induced patches, insect-caused holes, and the missing pieces of ancient paper. In the manuscript paper, the following signs of deterioration were observed: localized missing pieces, localized corners damaged with numerous folds and creases, and stains originating from various sources (fungi and dust) (Fig.4,5). The elemental analysis of the old paper with the EDXS unit was done to identify the paper's components (Table 1 – 5) where using carbon ink, which is often manufactured from lampblack or soot, and a binding agent like gum Arabic, was used to create the black ink. The binding substance maintains the suspension and adhesion of the carbon particles on the paper. Even after exposure to sunshine or after being bleached, the carbon particles do not deteriorate over time. One advantage of carbon ink is that it doesn't harm paper; because the ink is chemically stable, over time it does not jeopardize the paper's durability. Even with these advantages, carbon ink is not the best for durability and preservation ease. In humid conditions, carbon ink has a propensity to smear and can be wiped off a surface. Ensuring a document produced in carbon ink is preserved in a dry environment is the best way to preserve it (Hassan, 2015). Examination indicated carbon was the primary component of the ink used to write on these old pages. Analysis of the old sample paper revealed that it includes a significant amount of Si, Ca, C, and Al, as well as traces of Cl, K, and Mg. The antique paper manuscripts have high silicon and aluminum content. K, Ca, and Si concentrations were also found to be the highest identified as trace elements (Abdel-Ghani et al., 2012; Goldstein et al., 2003). Because of the abundance of Al and Si, the paper industry is likely to employ kaolinite ($Al_2Si_2O_5(OH)_4$) as a filler. Additionally, the high amount of Ca shows that $CaCO_3$ was used as a filler in the paper industry. The old paper has certain fillers, like calcite that has been collected from calcite crystals. There are also signs of erosion in the paper fibres, brittleness, and noticeable damage to the mineral crystals of the fillers. CaCO3 was commonly employed as filler in the old paper; therefore, conservators utilized it to deacidify old paper that had been harmed by exposure to the outside world (Garside et al., 2014). The paper also displays several fungal species, such as mycelium and spores. Acids and enzymes produced by microbes as a result of their metabolic activities can potentially cause degradation (Sahab et al., 2003). Due to their significant enzymatic activity, fungi can have a significant impact on how quickly old paper degrades.

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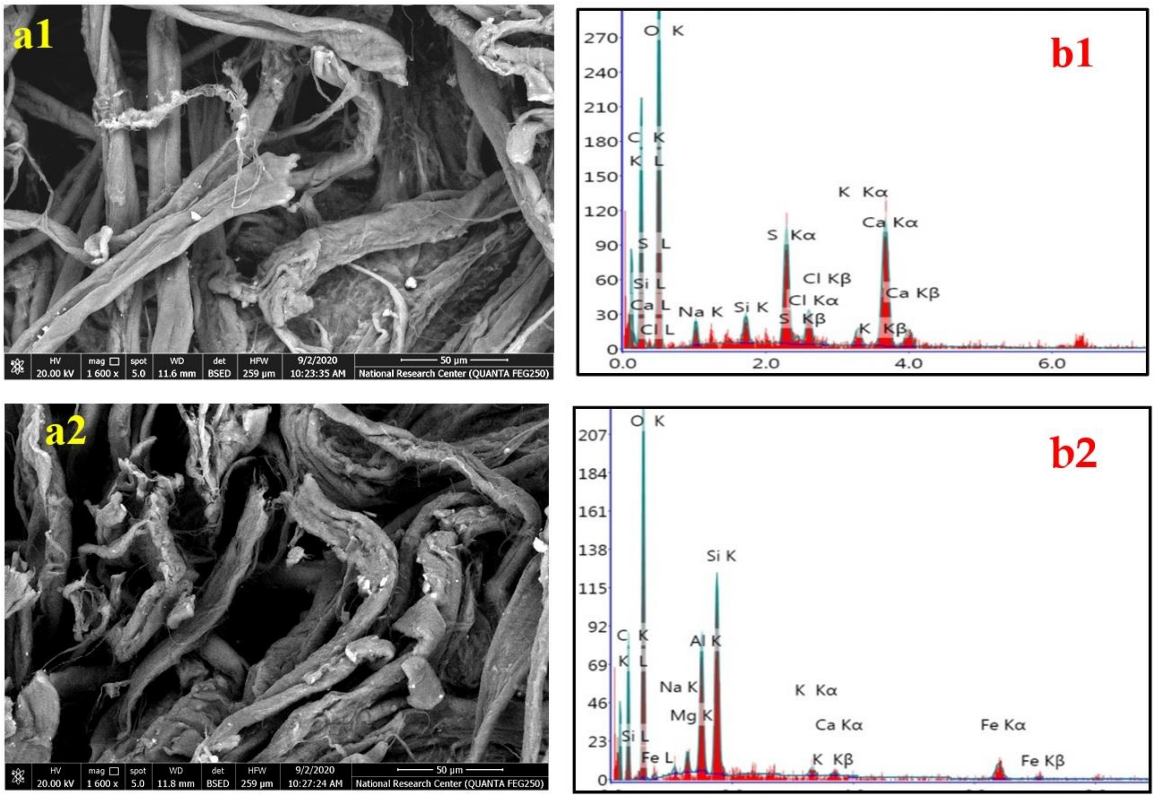

Fig. 3. SEM images of the historical paper sample (a1,a2) and EDAX spectrum of the same area (b1,b2).

Table 1. Elemental composition of the historical paper samples from two points

Element	Point 1 (a1b1)		Point 2 (a2b2)	
	Weight %	Atomic %	Weight %	Atomic %
C	31.54	41.87	29.72	39.89
O	49.59	49.42	47.97	48.34
Na	1.79	1.24	0.93	0.65
Mg	-	-	1.15	0.76
Al	-	-	6.26	3.74
Si	0.9	0.51	8.59	4.93
S	4.39	2.18	-	-
Cl	1.57	0.7	-	-
K	0.99	0.4	0.64	0.27
Ca	9.23	3.67	0.43	0.17
Fe	-	-	4.31	1.24

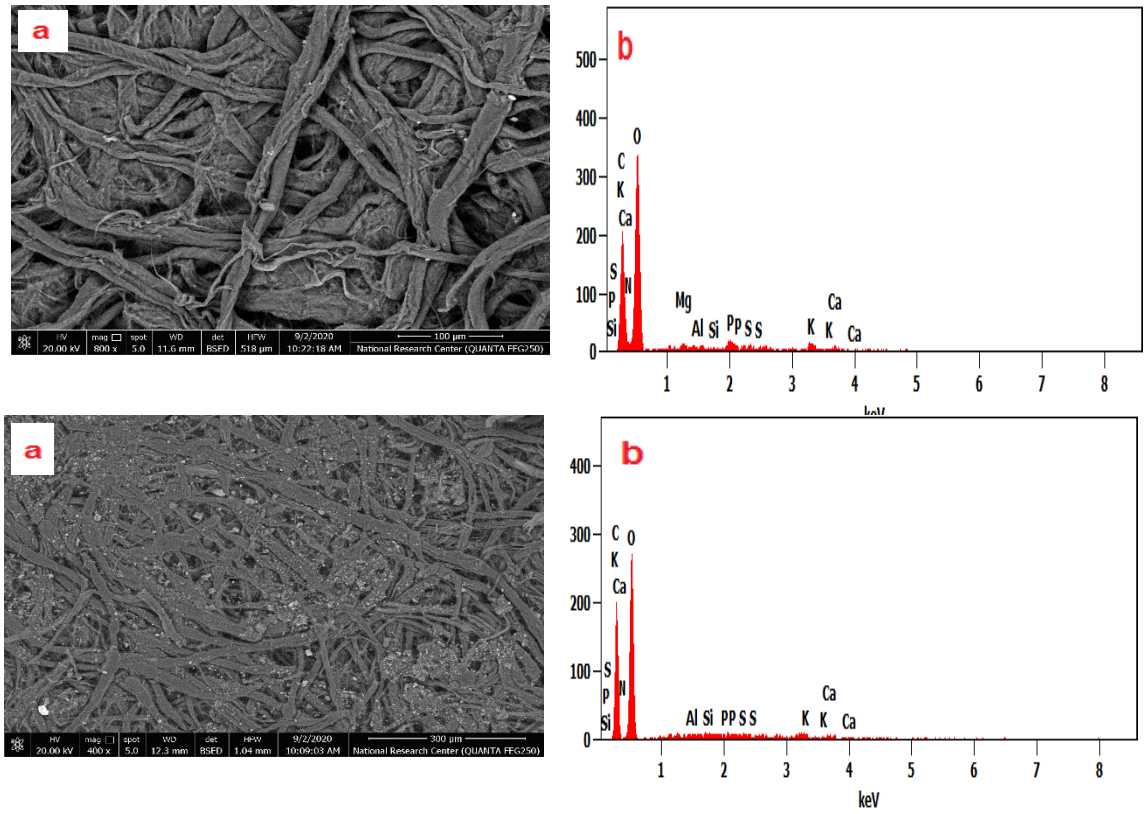

Fig.4. Investigation of the fibers of old paper from cotton by SEM showed damage caused by deterioration factors.

Table.2 shows the main compound element of old paper manuscript

	Intensity	Net Counts	Weight %	Atom %
C K	5.09	1526	22.41	28.23
N K	0.19	56	3.27	3.54
O K	9.34	2803	70.23	66.40
Mg K	0.16	48	0.45	0.28
Al K	0.04	11	0.08	0.04
Si K	0.07	20	0.13	0.07
Si L (D)	0.00	0	---	---
P K	0.53	159	0.96	0.47
P L (D)	0.00	0	---	---
S K	0.19	56	0.33	0.16
S L (D)	0.00	1	---	---
K K	0.61	182	1.50	0.58
K L (D)	0.00	0	---	---
Ca K	0.24	71	0.64	0.24
Ca L (D)	0.00	0	---	---
			100.00	100.00

Table.3 shows the main compound element of old paper manuscript

	Intensity	Net Counts	Weight %	Atom %
C K	4.47	1340	25.54	31.44
N K	0.13	38	3.28	3.46
O K	6.42	1925	69.78	64.50
Al K	0.05	15	0.16	0.09
Si K	0.07	22	0.20	0.11
Si L (D)	0.00	0	---	---
P K (D)	0.00	0	---	---
P L (D)	0.00	0	---	---
S K	0.08	25	0.21	0.10
S L (D)	0.01	2	---	---
K K	0.06	19	0.22	0.09
K L (D)	0.00	0	---	---
Ca K	0.16	48	0.62	0.23
Ca L (D)	0.00	0	---	---
			100.00	100.00

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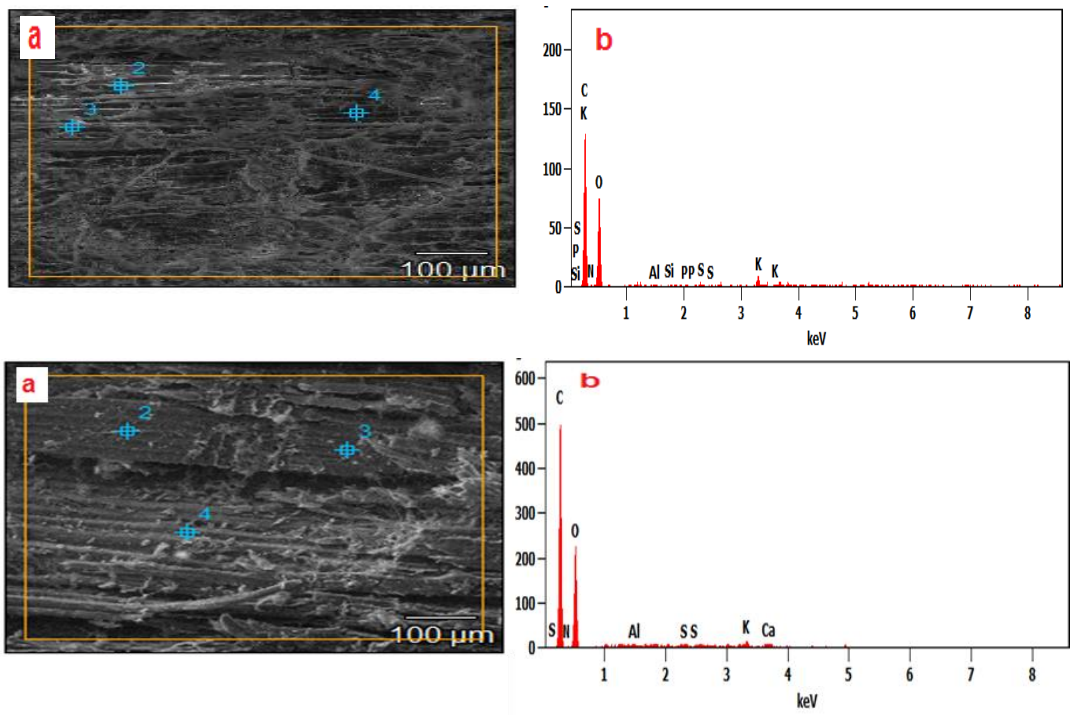

Fig.5. Investigation of the fibres of old paper from cotton by SEM showed damage caused by deterioration.

Table.4 shows the main compound element of the old paper manuscript.

	Intensity	Net Counts	Weight %	Atom %
C K	2.35	706	30.53	36.76
N K	0.16	49	12.37	12.77
O K	1.36	407	54.77	49.52
Al K	0.04	11	0.28	0.15
Si K	0.00	1	0.03	0.02
Si L (D)	0.00	0	---	---
P K	0.01	2	0.03	0.02
P L (D)	0.00	0	---	---
S K	0.06	18	0.36	0.16
S L (D)	0.01	3	---	---
K K	0.19	58	1.64	0.61
K L (D)	0.00	0	---	---
			100.00	100.00

Table.5 shows the main compound element of the old paper manuscript.

	Intensity	Net Counts	Weight %	Atom %
C K	8.23	2468	32.40	38.77
N K	0.52	156	12.87	13.21
O K	3.94	1183	52.51	47.17
Al K	0.05	15	0.11	0.06
S K	0.19	58	0.36	0.16
S L	0.13	40	---	---
K K	0.40	119	1.05	0.39
K L	0.00	0	---	---
Ca K	0.24	71	0.69	0.25
Ca L	0.00	0	---	---
			100.00	100.00

SEM-EDAX examination of the deteriorated archaeological leather of the manuscript:

SEM images (Fig. 6, a1, a2) showed the grain layer of archaeological leather, which suffers from dryness, brittleness, and cracks due to deterioration factors. It is clear from the shape of the grain layer that goatskin was used in the manufacture of the leather used in bookbinding.

Table 6 and Fig. 6 (b1, b2) present the elemental composition of the archaeological leather from two points, where the atomic (%) of the abundant elements C (60.82, 59.06%) and O (36.66, 34.55%), followed by other elements Si (0.47, 0.73%), S (1.15, 1.14%), Cl (3.19%), and Ca (0.89, 1.33%). It was also possible to highlight the structure of the archaeological leather of the manuscript along with their state of preservation and an assessment of the elemental makeup of C, K, Si, Ca, Cl, Mg, Na, and S.

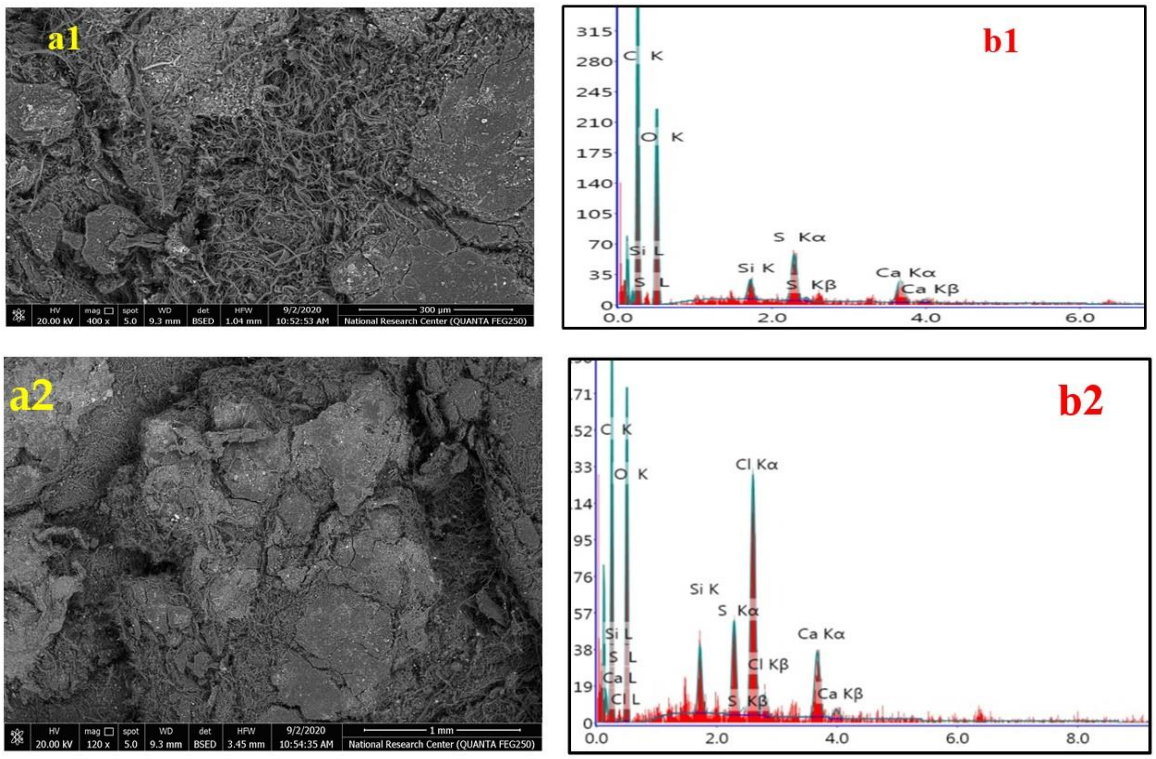

Fig. 6. Examination under the SEM image of the leather sample (a1,a2) and EDAX spectrum of the same area (b1,b2).

Table 6. Elemental composition of the archaeological leather samples from two points

Element	Point 1 (a1b1)		Point 2 (a2b2)	
	Weight %	Atomic %	Weight %	Atomic %
C	52.07	60.82	47.75	59.06
O	41.8	36.66	37.21	34.55
Si	0.95	0.47	1.38	0.73
S	2.64	1.15	2.46	1.14
Cl	-	-	7.61	3.19
Ca	2.54	0.89	3.59	1.33

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Fungi isolated and identified:

Microbial swabs were taken from old paper manuscripts in the Azhar Library in Cairo, Egypt. A sample was isolated on prepared potato dextrose agar (PDA) media. On the same media, the fungus was isolated and purified. By comparing the fungal isolates to closely related strains accessed from the Gen Bank *(Aspergillus terreus Ate456, Aspergillus niger Ani245, and Fusarium culmorum Fcu761, which were deposited in GenBank under accession numbers MH355953, MH355954, and MH355955,* respectively), the isolates were identified using a molecular approach (Taha et al., 2019).

FTIR analysis:

As shown in Figs. 7, 8, 9, and 10, infrared spectroscopy has been successfully utilized to analyze samples of leather and paper from archaeological sites. The typical cellulose-related absorption bands (O-H stretching band, C-H stretching vibration band, C=O stretching band, and C-O stretching band) found in the FTIR spectra of historical and contemporary paper samples are displayed in Table 7. The historical paper sample (Figs. 7, 10) exhibits a rather strong band at 1420 cm^{-1} that denotes the presence of calcium carbonate, which was found when they were analyzed using SEM-EDX. By contrasting the functional groups of the typical sample with the archaeological paper samples, the results of the FTIR study (Table 7) supported this; when hydrolysis occurred, it was noted that the wavenumber of the O-H stretching band rose from 3402 cm^{-1} to 3434 cm^{-1}. Indicating the oxidation of the cellulose molecule, the C=O increased from 1657 cm^{-1} to 1669 cm^{-1} (Fig. 8). Furthermore, a sharp decline in the C-H stretching band from 2935 cm^{-1} to 2986 cm^{-1} suggests a reduction in crystallinity. The carbonyl group C=O experienced a striking decline from 1657 cm^{-1} to 1653 cm^{-1} and 1651 cm^{-1}, which is indicative of damaged paper (Fig. 8); however, the C=C area in the historical paper samples remained stable at 1431–1433 cm^{-1} when compared to the control sample (Fig. 9). Results for current and historical samples show a decrease in C-O stretching in the region (1000-1300 cm^{-1}), indicating that the historical samples' water content was impacted, which may have been caused by the oxidation process. The findings also suggest that a small amount of hydrolysis, which increased the OH stretching bands, was responsible for destroying the cellulose papers. While the band at 3331 cm^{-1} is recognizable as the stretching vibration of the OH groups in the sample, the reference spectra of cellulose fibres have very comparable absorption bands in the wavenumber range of 3600-2900 cm^{-1} (the stretching vibration of OH and CH bonds in polysaccharides) (Fig. 10). Old paper's infrared absorption spectra revealed distinctive absorption bands attributed to the C-O, O-H, and C=O stretching bands. The vibrations of the OH and C-O absorption bands indicate the degree of cellulose oxidation. More damaged sheets exhibit a more significant rise in C-O intensity. The FTIR spectra of leather samples (Figs. 8, 10), the model reference leather, and the archaeological leather sample revealed the presence of collagen typical bands at 2926 cm^{-1} and 2852 cm^{-1}. Collagen in leather structure can be assessed by investigating the amide I and amide II spectral bands. These corresponding two bands are found in regions between 1500-1800cm^{-1}; the position and shape of these bands are easily affected due to the secondary structure of collagen and its interaction with environmental factors. The main absorption bands of collagen were detected and attributed to amide I, appearing at 3300 $cm^{-1,}$ related to the vibrations of N-H bonds; the amide II region appeared at 1500-1600 cm^{-1}.

The amide I appeared at 1600 $cm^{-1,}$ arising from the C=O stretching vibrations coupled with C-N stretching and N-H bending, while the amide II at 1530 cm^{-1} was attributed to NH bending. The results proved that the main collagen bands of historical leather decreased compared to the vegetable-tanned leather (control). By comparing with the spectra presented in Fig. 12, the spectral bands assigned to vegetable tannins were detected at around 3300 cm^{-1}, 1600 cm^{-1}, 1508 cm^{-1} (assigned to C=C aromatic ring), and 1180 cm^{-1} (assigned to C-OH). Calcium carbonate ($CaCO_3$) is commonly detected in historical leather samples (Fig. 9,10), resulting from the alteration of lime (calcium hydroxide) used during manufacturing. The stretching vibrations of CO_3 appeared in the spectral region at around 1416-1400 cm^{-1}, along with a sharp spectral band at around 875 cm^{-1}. These results agreed with other studies when dealing with the identification of goat leather from ancient objects or other skins (Srinivasan et al., 2010; Ali Hassan, 2019; Sionkowska et al., 2004; Marušić et al., 2022; Vyskočilová et al., 2022; Mansour et al., 2017; Vichi et al., 2018; Sebestyén et al., 2022; Li et al., 2003).

Table .7 FTIR readings from the samples used to study archaeology.

				Fig.8 (A1,2)	**Fig.8 (A3,4)**	**Fig.10**
Functional groups	Compound Type	Frequency range (cm^{-1})	Appearance	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})	Wavenumber (cm^{-1})
C-H	Alkanes	2850 - 3000	medium, stretch	2935	2986	2938
$C-H_2$	alkenes	1290 - 1430	Broadband	1423	1426	1381
O-H	Alcohols, Phenols	3160 - 3640	stretch, broadband	3402	3434	3468
$C-O_3$	Carbonates	1350 - 1450	broadband	1420	1420	1400
	ethers (aromatic), alcohols, esters, carboxylic acids	1000 - 1300	strong, stretch	1098	1086	1052
C=O	amides, esters	1500 - 1700	strong, stretch	1657	1662	1669
C=C	Aromatics-alkenes	1400 - 1500	stretch (in–ring)	1431	1428	1422
C-N	amines (alkyl)	1025 - 1200	strong, stretch	-	-	1180
N-H	Primary amines-amides	3400-3500	strong	-	-	3300
	amines	1500 - 1640	medium, band	-	-	1530

The FTIR equipment was used to ascertain the chemical characteristics of the paper. The data in Fig. 6 reveal that chemical changes in the paper may occur as a result of big organic molecules breaking down into smaller compounds (which have other chemical functional groups) and other chemical groups dissipating. The following bands were obtained when considering the different functional groups in uninfected samples (control) against the infected sample (Łojewski et al., 2010; Kolar and Strlic, 2006). Change in the shape of (C-H) asymmetric bending linkage movement at wave

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number area (1450-1422 cm^{-1}) and Change in the shape of (C=C) bending linkage movement at wave number area (1636-1508 cm^{-1}).

Noticeable absorption bands associated with the C-O, O-H, and C=O stretching bands were visible in the infrared absorption spectra of infected old paper. Carbonyl groups were discovered in the foxing region as a result of cellulose being catalytically oxidized in the presence of iron and copper compounds, where the carbon atoms were occupying different places within the cellulose ring C1, C2.....C6, gradually oxidizing into distinct carbonyl groups. An extra carbonyl band indicates that cellulose oxidation is accelerated (Boukir et al., 2019). We can distinguish the cellulose crystalline and amorphous by comparing the O-H stretching represented by the amorphous located at 1333.53 cm^{-1} and the stretching band of CH_2 expressing the cellulose crystalline located at 1314.25 cm^{-1}. All samples marked by intensity increasing for 1315.21 cm^{-1} region) (Castro et al., 2011).

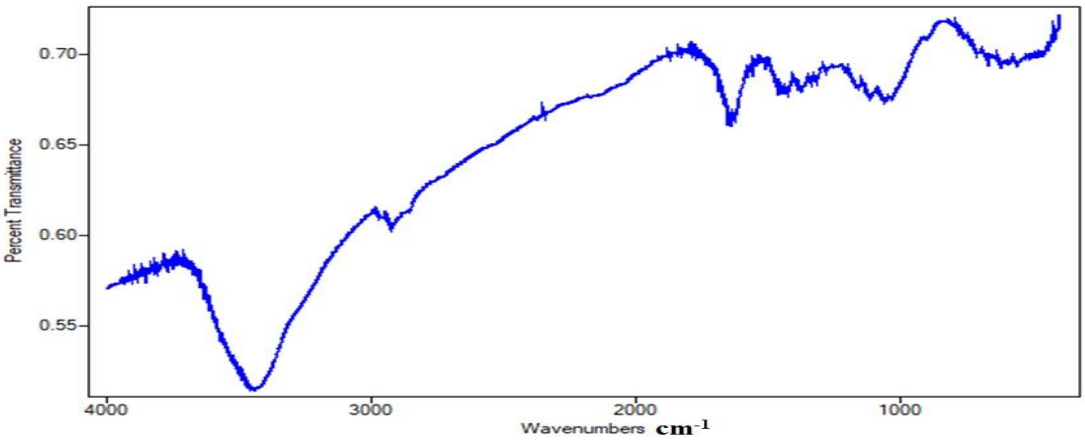

Fig. 7. FTIR spectrum of cotton paper pulp sample (standard)

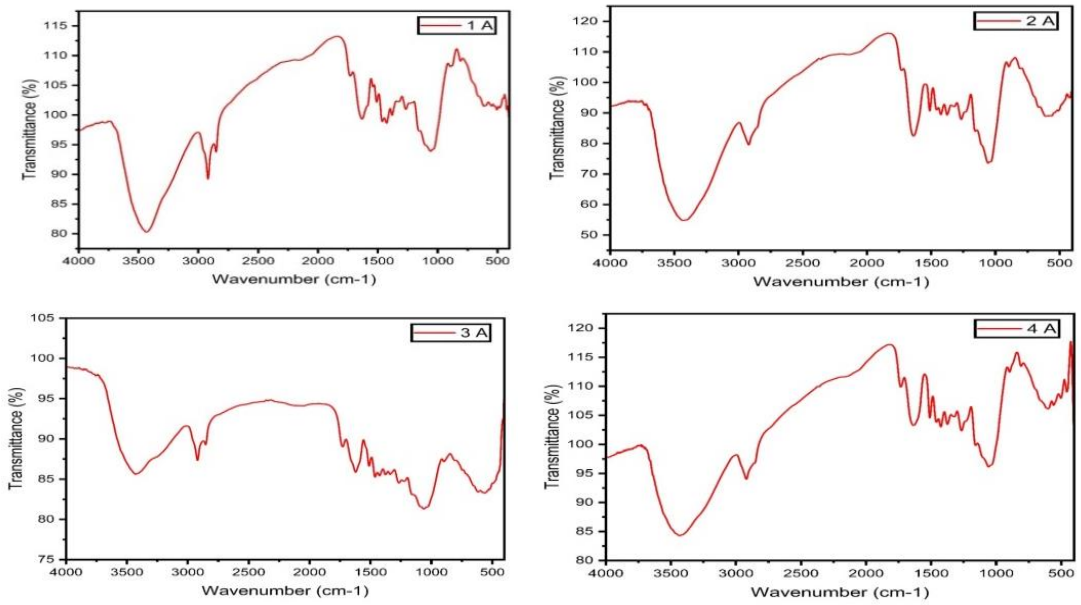

Fig. 8. FTIR spectrum of a piece of old paper

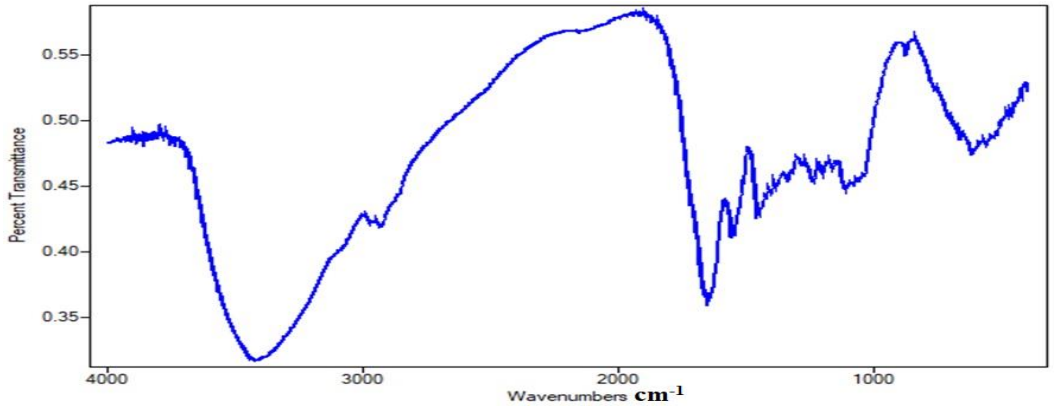

Fig. 9. FTIR spectrum of leather used in bookbinding sample.

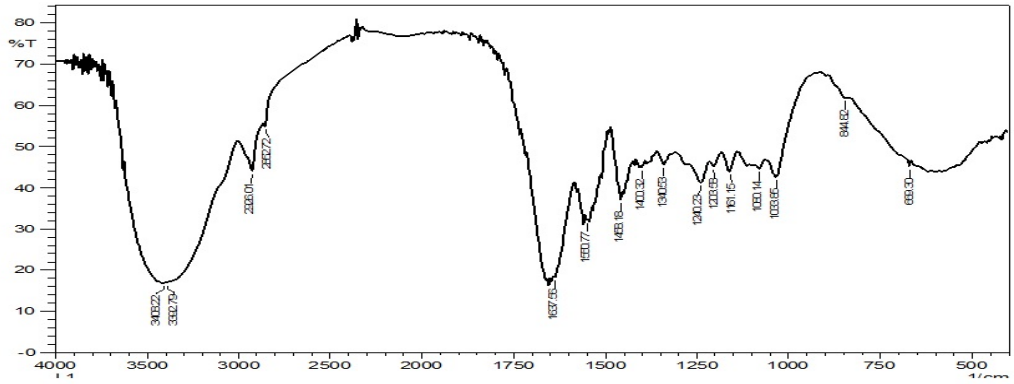

Fig. 10. FTIR spectrum of the leather control sample (standard)

Measurement of pH:

Acidity is an essential factor in the breakdown of old paper; the paper had a pH of 4.5. Possible causes include acids generated inside the old paper or taken in from the environment, but neutralization occurred before they could break down the cellulose chains. It was claimed that cellulose-chain fibres deteriorate in an acidic environment when combined with moisture. As long as the acid source remains and is still present in the paper, cellulose strands are continually broken down into smaller fragments during this acid hydrolysis cycle. The alkaline buildup in the paper could result from inadequate elimination of alkaline processing residues or air pollutants like ammonia. Ammonia is a byproduct of organic matter decomposing; it dissolves easily in water and produces alkaline solutions. Other gases react with it to create salts that deposit on surfaces and alter the local acidity (Puică and Ardelean, 2008).

Determination of paper crystallinity with X-ray Diffraction:

The paper crystallinity was measured using a small X-ray diffractometer (PW 1840 - Analytical Equipment - Philips- Eindhoven, the Netherlands; CU Ka radiation with Ni-filter). The formula used to determine the crystallinity index was ICrys = (I002 - Iam)/(I002) 100. where I 002 = intensity at roughly 2θ = 22.6°, Iam = intensity at roughly 2θ = 19°, and ICrys = crystallinity index. And in terms of the relative ranking of cellulose/crystallinity, this method is just as effective as any other (Atalla, 1989; Atalla and Vanderhart, 1984; Kataoka and Kondo, 1996). The Segal equation was also used to estimate the crystallinity index of cellulose using X-ray diffraction. Where (Cr) denotes

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the crystallinity of cellulose, (I002) denotes the peak's highest intensity at (2θ = 22–24°), and (I am) denotes the intensity of noncrystalline cellulose's diffraction at (2θ = 18°). A comparison of the historical paper sample's cellulose crystallinity revealed a decline in the crystalline index. According to the results, the crystallinity index of cellulose has significantly decreased, indicating that the chemical and mechanical properties of the cellulose molecule have significantly changed (Table. 8 - 11) (Fig. 11a,12b).

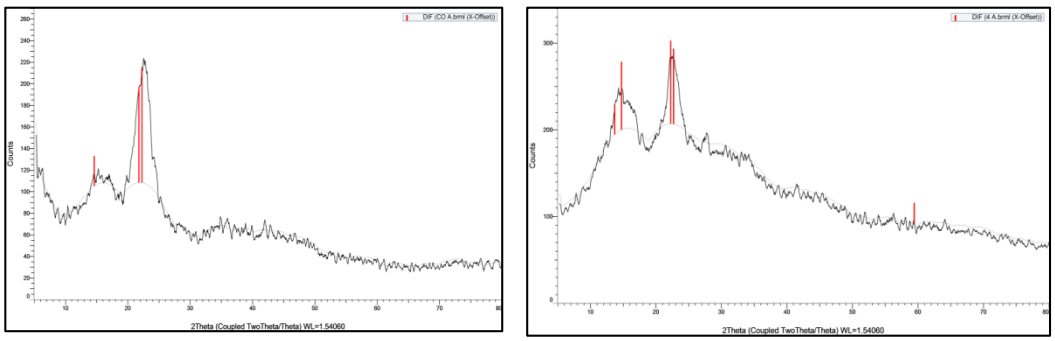

Fig. 11 a. X-ray diffraction pattern of the old paper manuscript

Table.8 Ranking of cellulose crystallinity

Index	Angle	d Value	Intensity	Rel. Intensity
1	14.615 °	6.05611 Å	27.6	25.7 %
2	21.783 °	4.07675 Å	88.7	82.6 %
3	22.274 °	3.98795 Å	107	100.0 %

Table.9 Ranking of cellulose crystallinity

Index	Angle	d Value	Intensity	Rel. Intensity
1	13.711 °	6.45315 Å	34.5	35.9 %
2	14.746 °	6.00270 Å	78.5	81.9 %
3	22.260 °	3.99048 Å	95.9	100.0 %
4	22.703 °	3.91354 Å	86.9	90.6 %
5	59.424 °	1.55414 Å	24.9	26.0 %

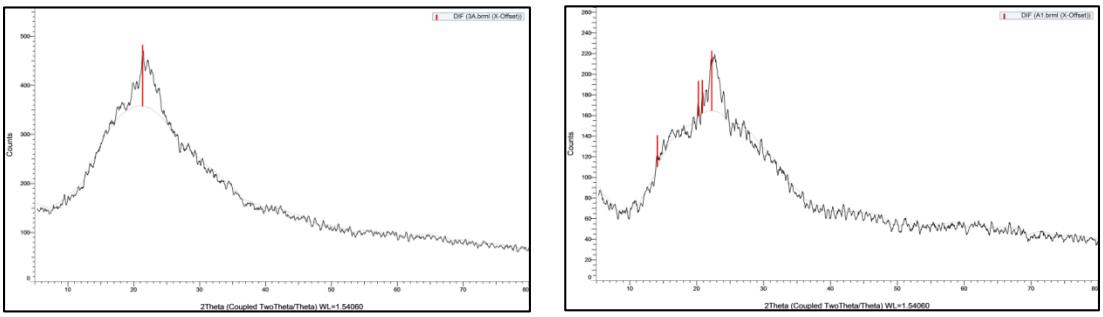

Fig. 12b. X-ray diffraction pattern of the paper manuscript

Table.10 Ranking of cellulose crystallinity.

Index	Angle	d Value	Intensity	Rel. Intensity
1	21.356 °	4.15726 Å	125	100.0 %

Table.11. Ranking of cellulose crystallinity

Index	Angle	d Value	Intensity	Rel. Intensity
1	14.130 °	6.26284 Å	30.7	52.9 %
2	20.273 °	4.37686 Å	34.3	59.0 %
3	20.854 °	4.25630 Å	32.4	55.7 %
4	22.260 °	3.99047 Å	58.1	100.0 %

Treating of the Manuscript by Antimicrobial activities of the natural extracts

Each papers manuscript were washed with the *Pinus rigida* extract using Spraying, a solution of each prepared concentration of extracts from 2 - 4 %. This method of cleaning was repeated several times and then papers were air dried for 24 h. As future protection against biological damage.

CONCLUSIONS

This study examined a historical manuscript in the Al-Azhar Library in Cairo using several experimental approaches; the leather and paper used were manufactured from goat skin and cotton fibers, respectively. Inspecting the old paper using SEM, FTIR, EDXS, and X-ray diffraction studies to determine paper crystallinity, measuring pH, separating and identifying fungi, following is a summary of the conclusions that may be drawn from this research: The surface of the old paper had several signs of deterioration, including holes from insects, packing, and missing pieces. *Aspergillus terreus Ate456, Aspergillus niger Ani245, and Fusarium culmorum Fcu761* were the three most prevalent fungi. Environmental factors harmed the manuscript; consequently, the ancient paper had higher pH values than it should have been. Cotton from rags was used to make the old paper that was used for writing materials. In order to choose the finest procedures and resources for conservation, it is crucial to analyze the manuscript that needs restoration.

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تقييم حالة المخطوطات التاريخية (المطول للقزوينى) التى تعود للقرن الرابع عشر الميلادى المحفوظ بمكتبة الأزهر بمصر – دراسة حالة

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الملخص

تهدف هذه الدراسة إلى تقييم حالة المخطوطة المحفوظة بمكتبة الأزهر الشريف تحت عنوان " شرح المطول للقزويني" وهي مخطوطة نادرة ترجع إلى القرن الثامن الهجري / الرابع عشر الميلادي. وذلك باستخدام تقنيات الفحص والتحليل المختلفة لمكونات المخطوط والتي تشمل الورق والجلد المستخدم في عملية التجليد من أجل التعرف على هذه المواد التي صنعت منها هذه المخطوطة ومناقشة وتقييم حالة التلف التي وصلت لها من خلال الفحص والتحليل باستخدام SEM-EDAX و FTIR و X.R.D.، حيث أظهرت النتائج أن جلد الماعز استخدم في صناعة الجلود المستخدمة في تجليد المخطوط كما أن لب الورق التي استخدم في صناعة المخطوط كان من القطن فى هذه الفترة . كما تقدم هذه الدراسة مثالاً على الإجراءات العلمية الفعلية التي تم استخدامها لفحص المخطوطة الورقية التالفة باستخدام SEM-EDAX وFTIR وحيود الأشعة السينية لتحديد مكونات الورق وجوانب التلف المختلفة لها، مع استخدام هذه النتائج لوضع خطة علمية لترميم وصيانة المخطوطات داخل المكتبات من التلف .

بيانات المقال

تاريخ المقال
تم الاستلام في ١٢ فبراير ٢٠٢٣
تم استلام النسخة المنقحة في ٢٠ اكتوبر ٢٠٢٣
تم قبول البحث في ٢٨ اكتوبر ٢٠٢٣
متاح على الإنترنت في ٢١ يناير ٢٠٢٤

الكلمات الدالة

مخطوط،
مكتبة،
تلف،
تحليل ،
فحص.

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