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Characterization of a Historical Leather Cover of Manuscript 'Ensaan Elaauon fe sert Elameen Elmaamon', Al-Azhar Library, Eygpt

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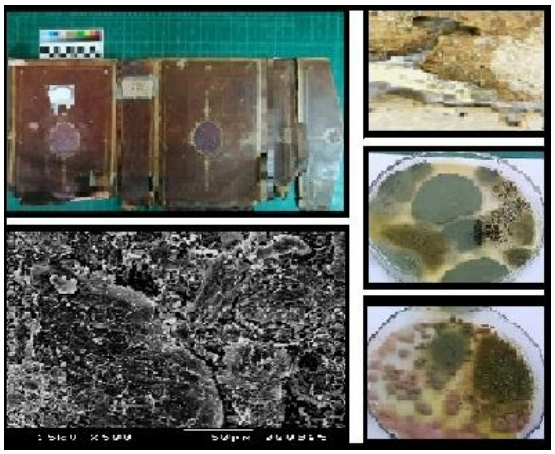
HIGHLIGHTS

- The historical leather cover of manuscript from Al-Azhar Library, Egypt was studied.
- Some aspects of deterioration were noticed such as brittleness, cracks, Wrapping, tears and etc.
- Analytical techniques (SEM, ATR-FTIR, amino acids, pH. etc. were used to study the characterizations of the historical leather cover of manuscript.
- The results proved that the historical leather cover suffers from deterioration caused by different factors.

GRAPHICAL ABSTRACT



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ABSTRACT

This study focuses on a historical leather cover of a manuscript dating back to the 10th A.H century from Al-Azhar Library. The study aims to use analytical techniques to identify the components of the historical leather cover of the manuscript, and to explain its deterioration process. Analytical methods used in this study were visual assessment, investigation of the surface morphology by a digital microscope and a scanning electron microscope (SEM), Attenuated total reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), amino acid analysis, identification of fungi, and measurement of pH.

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The results revealed that the leather suffered from brittleness, white stain, dust, fungal stains, cracks, in addition to missing and burnt parts. The results of SEM revealed that goatskin was identified as the animal skin of the historical leather cover of the manuscript. ATR-FTIR analysis revealed the degradation of chemical composition of the historical leather cover of the manuscript. The amino acid analysis stated that the chemical composition of historical cover of the manuscript suffered from deterioration through oxidation and hydrolysis mechanisms. *Aspergillus sp*, *Chaetomium sp*, *Penicillium sp*, and *Fusarium sp* were the most dominant fungi found. All analytical techniques used in this study proved that the historical leather cover of the manuscript is in urgent need of conservation.

1. Introduction

Leather artifacts are found in many places in Egypt (museums, libraries, etc.), but in some of these places, international standards of conservation are not applied. The leather itself represents a very complex material composition. Its surroundings are, likewise, a very complex and dynamic dimension constantly varying in terms of quantity and degree of their interaction with each other. The most common aspects of artifacts' deterioration are due to poor handling, poor storage methods, and inappropriate display methods, wear due to repeated use, chemical changes in the materials making of the leather objects, chemicals in contact with the leather objects, and a combination of any or all of these aspects, and chemical changes caused by atmospheric pollutants. The historical leather cover of the manuscript exposed to air and light exhibited a great content of sulphuric acid originating from the polluting atmosphere. Degradation induced by the absorption of airborne SO_2 is commonly known as the "red rot", which mainly affects the vegetable tanned leather. Sulfur trioxide, which reacts with air humidity and forms sulphuric acid, is an aggressive leather aging agent. Sulphuric acid breaks down the polypeptide chains to amino acids and ammonium salts. Paper of the manuscript, are subject to various forms of deterioration; initially, the paper may be strong and white, but in due course of time, on account of physical, chemical, and biological factors, their properties undergo changes and they deteriorate and get damaged. Besides natural causes like climate, light, fungi and insects, there are several man-made factors that cause damage to the paper and added materials such as ink and hand-coloring with pigments or dyes. Deterioration of paper-based materials is mainly due to the degradation of cellulose caused by many factors, such as chemical attack due to acidic hydrolysis, oxidative agent, light, air pollution, and biological attack and the presence of microorganisms like bacteria and fungi [1, 2].

Because of the importance of these leather artifacts in general and the historical leather cover of the manuscripts and historical books especially, of religious, cultural, historical, civilization, and artistic values, the role of restoration and conservation is to reveal, highlight and preserve these values. In this study, a historical leather cover of the manuscript [2, 3], which displayed common forms of deterioration found in historical leather covers of the manuscripts from the collection of Al-Azhar Library was selected .

Analysis and investigations are considered important tools for evaluation of the environmental conditions of all components of the historical leather cover of the manuscript [4].

Visual assessment by digital camera and Auto CAD [5], investigation by Digital and Scanning electron microscopy (SEM) are always used to identify the type of animal skin and to reveal different aspects of deterioration found on the surface of the leather artifacts [6-8].

Fourier Infrared spectroscopy (FTIR) was performed to identify the change in the chemical composition [9], and amino acids analysis is used to identify the changes and breakdown of amino acids [10].

The measurement of leather pH reveals the state of preservation of leather at different locations (museums, storages, libraries, etc.) or in storage. Microbiological studies and investigation of the surface morphology are also very important for the estimation of the

deterioration process of paper and leather [1, 11].

This study aims to apply some analytical techniques to identify, the components of the historical leather cover of the manuscript, determine the deterioration of its paper inner lining, and to explain its deterioration process.

2. Materials and Methods

2.1. Materials

2.1.1. Object

The historical leather cover of the manuscript "Ensaan Elaauon fe sert Elameen Elmaamon" belongs to its author (Ali bin Ibrahim bin Ahmed Al-Halabi). This historical leather cover of the manuscript dates back to the 10th century A.H. [12]. The historical leather cover of the manuscript is preserved at Al-Azhar Library - Al-Azhar Sheikhdom. It was registered under general No. 83649, special No. 9036. The historical leather cover of the manuscript consists of five pieces. The size of the first board was 31 cm×17.5 cm, the spine of historical leather cover of the manuscript was 31 cm×5 cm, the size of the second board was 31 cm×17.5 cm, the spine of the flap was 31cm×5 cm, and the flap 31cm×7 cm.

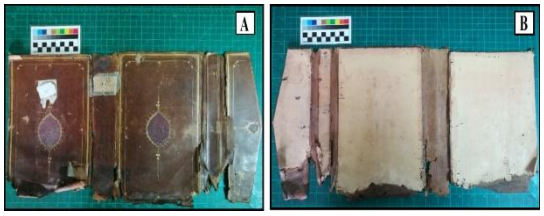

Fig.1. The historical leather cover of the manuscript: (A) Front Cover, (B) Back Cover.

2.2. Methods

2.2.1. Visual assessment by the digital camera and Auto CAD

The authors performed a visual assessment to describe the aspects of deterioration found on the surface of the historical leather cover of the manuscript. This method is very effective because aspects of deterioration can be easily seen [1]. To show the changes found on the surface of the historical leather cover of the manuscript, a high-resolution digital camera image (Kodak Easy Share M1033, 10mp, 3×Optical zoom) was used. AutoCAD 2018 program was also used for this purpose. A map of the aspects of deterioration was documented using CAD.[10]

2.2.2. Digital Microscope

Investigation of the surface morphology of the historical leather cover of the manuscript was carried out using a small handheld U500X Digital Microscope at the Conservation Department, Al-Azhar library. The microscope was made in China with a maximum magnification up to 500x, focus range from 15mm to 40mm, image capture resolution 640 x 480pixels.[6]

2.2.3. Investigation of the surface morphology by Scanning Electron Microscope (SEM)

A scanning electron microscope, JEOL JSM S400LV EDX Lin l ISIS-Oxford "high vacuum", was used for the investigation of the surface morphology of the historical leather cover of the manuscript and paper inner lining. SEM was used to scan and identify the types of skin and paper fibers [13, 14]. SEM was carried out at the Scanning Electron Microscopy Laboratory, The Central Laboratory Unit, Assiut University, Assiut, Egypt.[8] .

2.2.4. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)

ATR-FTIR was used for monitoring the existence and position of functional groups of the samples in the wave number region from 4000 to 400 cm^{-1} on a (JASCO FT-IR 6100, made in Japan). This method of analysis was used in accordance with some authors [9,15,16]. A significant advantage of the ATR technique is that the leather sample does not require any preparation, thereby minimizing possible damage to the sample. FTIR analyses have been performed at the Laboratory of IR, Central Services Laboratory, National Research Centre, Cairo, Egypt.

2.2.5. Amino acid analysis

The amino acid analysis is considered an important quantitative analysis to detect the

stability or changes that occurred in the chemical composition of amino acids .

Acid hydrolysis was carried out according to the method of Larsen [17]. Two samples from new goat skin, that were used as a reference, and goatskin from the historical sample were analyzed. From each dry skin sample, 0.1 g was defatted using diethyl ether and (0.4 g) of hydrochloric acid at 110°C for 24 hrs. At the end of the period, the hydrolysate was evaporated to dryness at 50-60°C in a water bath. Distilled water (5 ml) was added to the hydrochloric acid and then further addition of distilled water till complete removal of excess hydrochloric acid and samples were dried till the dry film was obtained. The obtained dry film was dissolved in a known volume of sample dilution buffer (0.1 N sodium acetate buffer, pH 2.2) and the solution was filtered through (0.45 mm) membrane filter and the samples stored frozen in sealed vials until fractionation of the amino acids by the amino acid analyzer (LC 3000 Eppendorf, Central Lab of Desert Research Center, Cairo, Egypt).[17]

2.2.6. Microbiological Examination

Isolation, culturing and identification of these separated fungal species were carried out at the Laboratory No. 519, Microbial Chemistry Department, National Research Centre (NRC), Dokki, Giza, Egypt.

2.2.6.1. Samples collection for the identification of fungi

Fungi were isolated from the historical leather cover of the manuscript using the following method: sterile cotton swabs were wiped across fungal colonies then transferred to the laboratory in sterile tubes and used for fungal isolation.[19 ،18]

2.2.6.2.Isolation and identification

All samples were transferred to the laboratory on the same day of collection and immediately processed. Each swab of fungal growth was immersed in a sterile glass vial containing 5 ml of sterile distilled water and shaken for 2hr on a reciprocal shaker. Aliquots (100 µ) of spore suspension were spread on each 9 cm Petri dishes (3 plates per sample) containing Czapek-Dox agar medium (g/l): sucrose (30), $NaNO_3$ (3), $MgSO_4.7H_2O$ (0.5), KCl (0.5), $FeSO_4.7H_2O$ (0.001), K_2HPO_4 [1] and agar [20]. This medium was supplemented with the antibacterial agent (Streptomycin, 0.1%) and Rose Bengal [20] to limit the fungal growth.

The most common fungal strains isolated from the historical leather cover of the manuscript were picked up and identified by the traditional method, by studying their morphological appearance on plates and under the microscope. The identification of fungi was carried out based on their macro and microscopically characteristic sporulation according to some references [21-24].

2.2.7. Measurement of pH value

The measurement of the pH value of the sample was done by Orion multi-channel benchtop meter ion analyzer equipped with a ROSS combination electrode. The measurement was carried out according to Kočar et al; ISO: 6588-1[25, 26]. The measurement was performed at the Dyeing, Printing, and Textile Auxiliaries Department, Textile Research Division, National Research Centre (NRC), Dokki, Giza, Egypt.

3. Results and Discussion

3.1. Visual assessment by the digital camera and Auto CAD

The state of preservation of the historical leather cover of the manuscript was, quite poor and fairly homogenous due to their shared history of storage, handling, and environmental conditions. However, diverse degrees of deterioration could be distinguished which depended on various factors. The size of the books makes them difficult to handle and produces important problems of mechanical stability .

Other factors determining their deterioration were inadequate storage and mishandling, which led to numerous tears and damage to the supports of the leather covers of the manuscripts .

The following aspects of deterioration were noted (Figs. 2- 4):

•Dust and label stains (Fig. 2A).

•Brittleness and embrittlement of some parts and some cracks (Fig. 2B).

•Scratching in the surface layer. (Fig. 2B).
•Erosion and tears at the edges of the binding (Fig. 2C).
•Loss of tanning material and missing parts (Fig. 2D).
•Some holes and tunnels (Fig. 3B).
•Missing parts (Fig. 3C)
•Wrapping and tears in the edges (Fig. 3D)

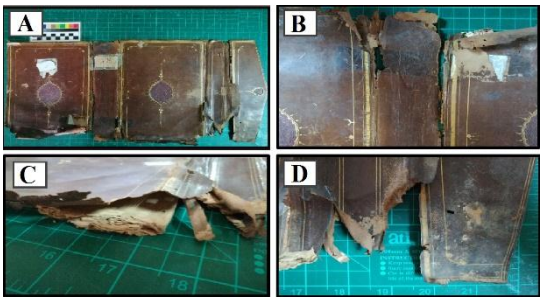

Fig. 2. (A-D) Documentation of deterioration aspects of the historical leather cover of manuscript

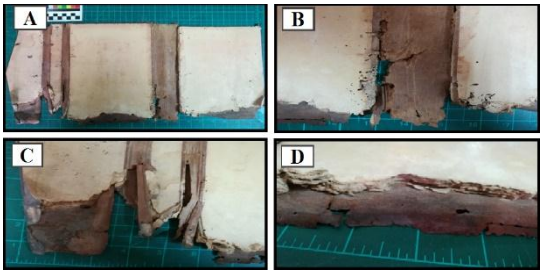

Fig. 3. (A-D) Documentation of deterioration aspects of the historical leather cover of manuscript

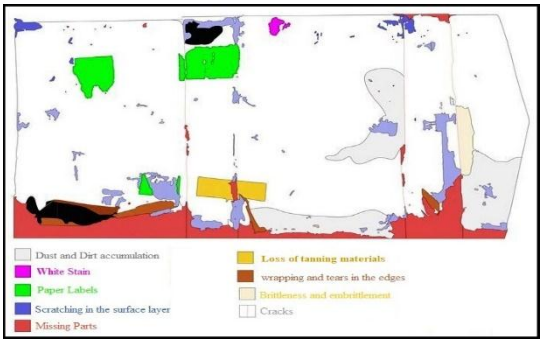

Fig. 4. AutoCAD for documentation of deterioration aspects of the historical leather cover manuscript

3.2. Digital microscope

The digital microscope was also used to register the aspects of deterioration on the historical leather cover of the manuscript such as: flaking of the surface layer of leather, missing parts and holes caused by insects, weakness, and erosion of fibers, loss of tanning material, white hard crust and cracks (Fig. 5A -5 F).

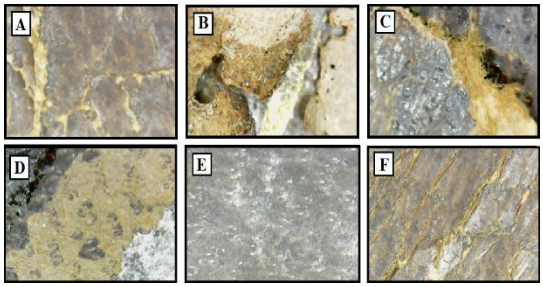

Fig. 5. Aspects of deterioration of the historical leather cover manuscript by Digital microscope 500X: (A) Flaking of the surface layer of leather (B) Missing of parts and insect holes, (C) Deterioration, weakness and erosion of fibers, (D) Loss of tanning material, (E) white hard crust (F) Cracks.

3.3. Investigation of the surface morphology by Scanning Electron Microscope (SEM)

SEM images in (Fig. 6A) reveal the damages and changes in the fiber structures. The surface of the new leather sample was smooth, and the grain surface pattern was easily recognized. The historical leather cover sample (Fig. 6B) suffered from deterioration, since random distribution of the fiber structure was noticed, the grain surface pattern cannot be recognized and this indicated that the leather surface was exposed to the destruction caused by a combination of factors from surrounding environmental conditions (physical, chemical, biological and human factors).[27-29]

SEM was used to investigate the surface morphology of the historical paper inner lining (Fig. 7), which showed that small amounts of filler materials appeared between the fiber structures. Paper is a non-homogenous material and gaps can be found between the structure of the fibers, and the tearing of paper fibers and deformation of the paper appearance was also noted [1, 30].

SEM was also used to identify the type of animal skin used for the historical leather

cover of the manuscript. It was clear by a study of the grain surface of the leather according to Haines [13], and from investigation of the surface morphology of the leather that the type of skin used very similar to the new sample form for goatskin, so it is maybe that the historical skin used was goatskin (Fig. 6). The study was made between two samples: new leather sample of goatskin and the other from the historical leather cover of the manuscript. The leather surface was smoothed and the coarse follicles were in the form of groups. There was a wide and smooth surface between these groups. The grouping of course and fine follicles was easily recognized [1]. The SEM was also used to identify the kind of fibers used for the paper inner lining. It was clear by a study of the surface morphology that the cotton fibers appeared polished and accurate. This study was made between two samples: a new sample of cotton fibers [14], and the other from the historical paper inner lining. So, from SEM investigation of the surface morphology, it was clear that the historical paper's inner lining used was similar to the new sample made form cotton fibers, so it is probable that the historical paper's inner lining was cotton fibers (Fig. 7).

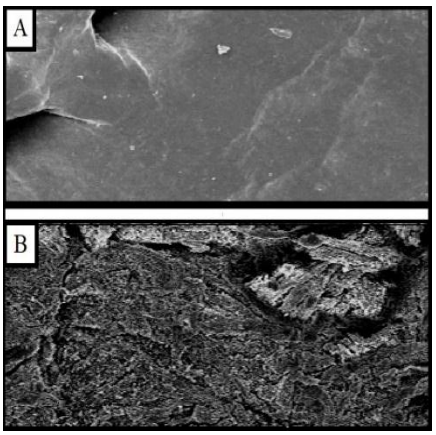

Fig. 6. Investigation of the surface morphology by SEM (A) New leather sample of goatskin (B) Historical leather cover sample

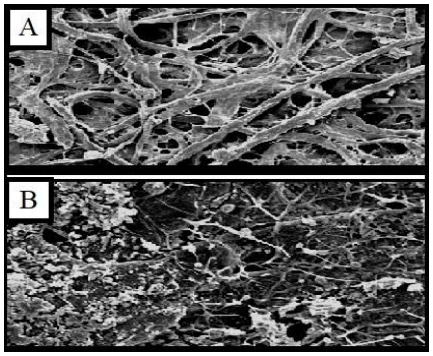

Fig. 7. SEM Investigation of the paper inner lining: (A) New paper sample (B) Historical paper inner lining

3.4. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR)

FTIR analysis indicated the changes in the collagen structure of the leather at the molecular level. The spectra of the new leather sample and historical leather cover sample are shown in (Fig. 8).

It is observed that the relative intensity of amide A in the new leather sample decreased and the historical leather cover sample absorption peak shifted to the higher frequency from 3295.9 cm^{-1} to 3434 cm^{-1}. The intensity change of amide A was associated with the intermolecular and intermolecular hydrogen bonds, which suggests that NH group of a peptide should be involved in hydrogen bond [31]. The result showed that the hydrogen bond within the new sample is stronger than that of the historical leather cover sample.

Also, from the result it was observed that the relative intensity of amide I, amide II and amide III bands for the new leather sample all increased with relative intensity, compared with historical leather cover sample which could be attributed to the partial changes of C − O group into C = O group [23-33].

The peak at 1034 cm^{-1} in new leather sample was more clearly than the historical leather cover sample, which can be assigned to aromatic C–C vibrational modes in tannins, suggesting the forming of cross-linking of collagen and tannins, which were taken as an indication of the extent of collagen degradation in historical leather cover sample.

All the changes in the collagen structure of the leather at the molecular level indicates collagen degradation, which is due to poor storage conditions and the impact of deteriorated leather by hydrolysis and oxidation, El-Moselhy.[34]

For the paper inner lining (Fig. 9), it is observed that the relative intensity of O-H stretching in the new paper sample increased and the paper inner lining sample absorption peak shifted to the lower frequency from 3643.1cm^{-1} to 3441 cm^{-1}, and the relative intensity of O-H bending in the new paper sample increased and the paper inner lining sample absorption peak shifted to the lower frequency from 1677.8cm^{-1} to 1661 cm^{-1}. This may be due to the partial loss of the water content of the deteriorated paper inner lining and the occurrence of dehydration in it.

Also, the result observed that the relative intensity of C-H stretching and C-H bending for the new paper sample were all decreased with relative intensity, compared with paper inner lining sample which could be attributed to the partial changes of C-H, where the intensity of this band slightly decreased due to cellulose oxidation.

The absorption band of C-O stretching in the new paper sample was recorded at 1134.5 cm^{-1} while, in the historical sample it shifted in the baseline to a lower wavenumber 1107 cm^{-1}. This may be due to the fact that the deteriorated paper inner lining has been exposed to strong oxidation .[35]

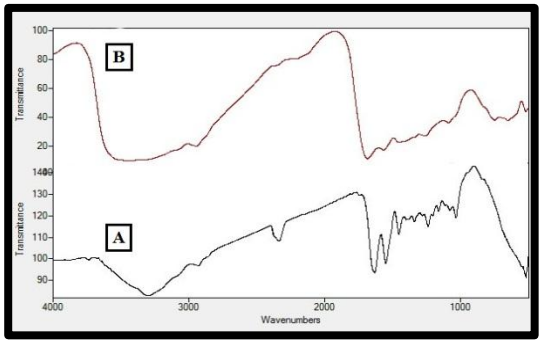

Fig. 8. (ATR-FTIR) analysis: (A) New leather sample, (B) Historical leather cover sample.

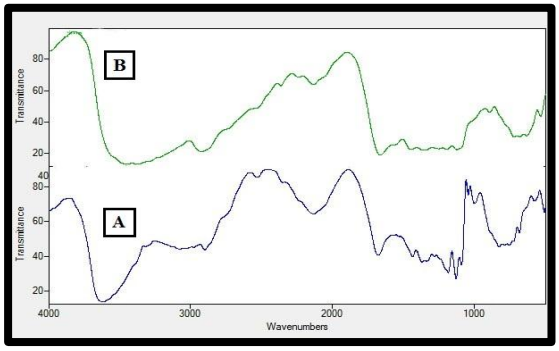

Fig. 9. (ATR-FTIR) analysis :(A) New paper sample, (B) cotton fibers from the paper inner lining of the historical leather cover.

3.5. Amino Acid analysis

The method of amino acid analysis is particularly useful to detect the deterioration mechanism of collagen in leather cover corium [5]. The results of the amino acid analysis of the sample taken from both the new leather sample and the historical leather cover sample (shown in Fig. 10 and Table 1) revealed that the basic amino acid lysine in the historical leather cover was (3.1%) lesser than its percentage in the new sample, which was (5.3%). The value of the basic amino acid arginine in the historical sample was (6.4%), while its value in the new leather sample was (7.6%). A similar trend was noted for the basic amino acid histidine. Its value was (1.9%) for the historical leather cover and was (3.1%) for the new leather sample. It can be explained by the fact that the oxidative decomposition of the side chains of amino acids forms ammonium (NH4+) ions. The basic amino acids lysine and arginine are particularly sensitive to oxidation and the results reflect this [10]. The historical leather cover sample showed that ammonium content was (5.8%) while its value in the new leather sample was (4.3%). The acidic condition of the historical leather cover sample may lower the value of the basic amino acids and increase the value of ammonium (NH4+) ions. This also indicated that acid hydrolysis may also have occurred in the historical leather cover sample. It was noticed that with an increase in NH4+ ions, there was a clear tendency for the lower value of serine (3.0%) in the historical sample and (3.2%) in the

new leather sample. It was also noticed that there was a lower value of threonine in the historical sample (2.3%) compared to the new leather sample (2.5%). The results showed lower value of glutamic acid in the historical sample (12.7%) than the new leather sample (13.1%). The results also showed increases in the value of aspartic acid in the historical leather cover sample (9.4%) than the new leather sample (8.0%), with the increase of hydrolysis in the historical leather cover sample.

3.6. Identification of fungi

The results stated that most of the fungi species identified from the leather cover and the paper inner lining are hydrolysis for proteins and cellulosic materials protease protein and paper [40 ،39]. The most dominant fungi for the leather cover (Fig. 11A ~ D) were: *Fusarium sp.* (A), *Penicillium sp.* (B), *Aspergillus niger* (C), and *Aspergillus flavus* (D).

Most dominant fungi found on the paper inner lining (Fig.12 A ~ D) were: (A) *Aspergillus niger*, (B) *Penicillium sp*., (C) *Aspergillus flavus*, . (D) *Chaetomium sp.* and *Aspergillus fumigatus*. A genetic analysis (DNA) to accurately identify the types of microorganisms and determine the best antimicrobial is recommended for future studies .

Fungi cause severe deterioration of the manuscripts and historical leather [36, 37]. Azab [38] reported that the most dominant fungi isolated from Egyptian books are *Aspergillus* sp. Abdel-Maksoud [1] said that the most dominant fungi on a historical leather cover of a manuscript were *Penicillium oxalicum*, *P. rubrum*, *P. funiculosum*, *A. fumigates*, *A. niger*, *A. flavus*, *A. versicolor*, *A. Wentii*, and *Fusarium sp.*, whereas the most dominant fungi found on papers of the manuscript were: *Penicillium restrictum*, *P. spinulosum*, *P. rubrum*, *P. chrysogenum*, Aspergillus *fumigates*, *A. niger*, *A. flavus*, *A. ustus*, *A. terreus*, and *Chaetomium sp.*

3.7. Measurement of the pH value

The pH value of the historical leather cover of the manuscript was (5.6). This means that the pH value was in the normal level, which is (4-6) [5]. On the other hand, the pH value of the paper inner lining of leather cover was (6). This indicates a little decrease in the pH value of the paper. The reduction in the pH value may be due to the effect of acidic air pollution gases [27]. pH measurements indicated hydrolysis and acidic degradation of the leather [41].

Conclusion

The current work proved that the historical leather cover of the manuscript suffers from deterioration caused by surrounding environmental conditions through characterization using different techniques. Visual assessment, AutoCAD documentation, and investigation of the surface morphology by digital microscope showed many aspects of deterioration on the surface of the leather cover such as brittleness and embrittlement of some parts, white stains, holes caused by insects, wrapping, loss of tanning material, and missing parts. The investigation of the surface morphology by a scanning electron microscope investigation of leather contents proved that the goatskin was most probably the animal skin used for the leather and the paper inner lining may have been made from cotton fiber .

FTIR results showed that there are significant spectral changes in functional groups of the chemical composition of leather cover and paper inner lining, which indicated that deterioration had occurred. The amino acid analysis showed a decrease in the levels of lysine, arginine, and histidine in the historical leather cover, which indicated oxidation breakdown. The high value of the NH4+ ions and aspartic acid in the historical leather cover indicated the presence of hydrolysis breakdown .

The most dominant fungi on the historical leather cover were: *Fusarium sp*., *Penicillium sp.*, *Aspergillus niger*, and *Aspergillus flavus*. The most dominant fungi found on the paper inner lining were: *Penicillium sp*., *Aspergillus flavus*, *Aspergillus niger*, *Chaetomium sp*., and *Aspergillus fumigatus*.

The pH value of the historical leather cover was at a normal level, but there was a little reduction in pH value. The pH of the paper inner lining was lower than reference sample.

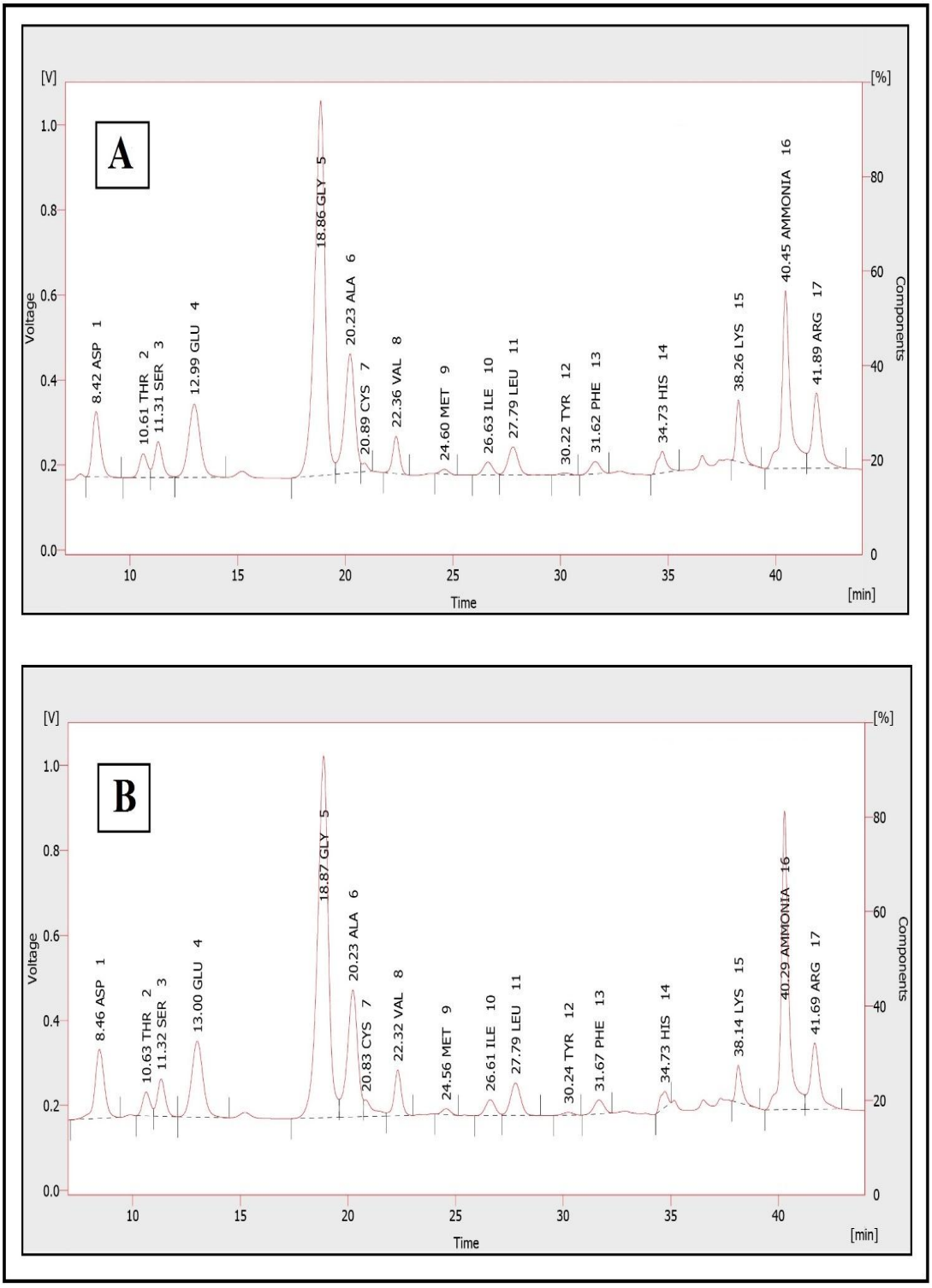

Fig. 10. Identified amino acids: (A) New leather sample, (B) Historical leather cover.

Table.1. Amino acids of new r and historical leather cover samples

Amino acid	Acid type	New goat skin		Historical leather cover		The per-centage change in amino acids
		Concentration of amino acids	Percentage	Concentration of amino acids	Percentage	
Aspartic acid	**Acidic**	**32.93**	**8.00**	**42.85**	**9.4**	**117.5+**
Glutamic acid	**Acidic**	**54.11**	**13.1**	**57.49**	**12.7**	**96.9-**
Threonine	**Neutral**	**10.20**	**2.5**	**10.22**	**2.3**	**92.0 -**
Serine	**Neutral**	**13.23**	**3.2**	**13.82**	**3.00**	**93,7-**
Histidine	**Weak bases**	**12.89**	**3.1**	**8.66**	**1.9**	**61.2-**
Lysine	**Bases**	**21.81**	**5.3**	**14.05**	**3.1**	**58.4-**
Ammonium **(NH4+)**	**Bases**	**17.76**	**4.3**	**26.36**	**5.8**	**134.8+**
Arginine	**Strong bases**	**31.18**	**7.6**	**28.90**	**6.4**	**84.2-**

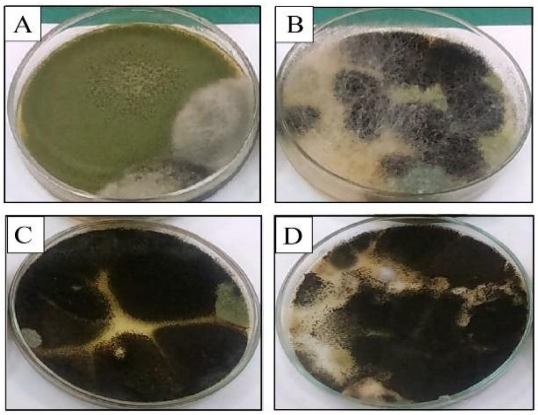

Fig. 11. (A-D) Different fungal colonies grown on (PDA) plates of the historical leather cover were: (A)*Fusarium sp.*, (B) *Penicillium sp.* (C) Aspergillus niger, and (D) *Aspergillus flavus.*

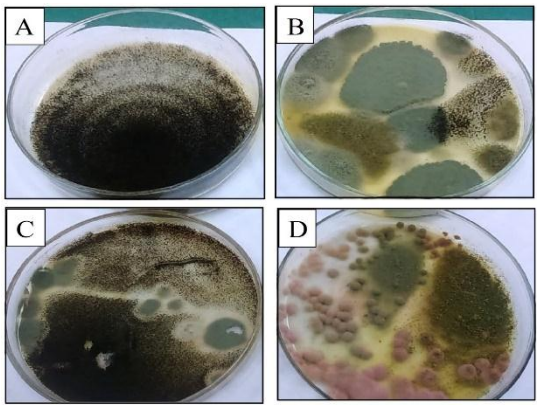

Fig. 12. (A-D) Different fungal colonies grown on (PDA) plates of the paper inner lining was: (A) *Aspergillus niger*, (B) *Penicillium sp.*, (C) *Aspergillus flavus*, (D) *Chaetomium sp.* and *Aspergillus fumigatus.*

This may be due to the effect of acidic air pollution gases, as the paper is inherently alkaline.

Analytical methods used in this study proved that the historical leather cover of the manuscript revealed that it suffered from adverse deterioration, and authors recommend the necessity of a conservation treatment.

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