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AN ANALYTICAL STUDY OF HISTORICAL LEATHER BINDING FOR MANUSCRIPT "EXPLANATION AND INTERPRETATION OF AL-SAFARI" BACK TO 1499 A.D , THE LIBRARY OF ALAZHAR AL-SHARIF MOSQUE.

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Abstract:
The main goal of the current study is a detection of the degrading mechanisms of historical leather binding of a manuscript from at Al-Azhar Al-Sharif Library in Cairo; by using various analytical techniques to map the conservation steps in shades of these mechanism data The used analysis included visual assessment, investigation of the surface using a digital microscope and a scanning electron microscope (SEM), Attenuated total reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), identification of fungi, and measurement of pH. The results revealed several aspects of deterioration in the historical leather object such as erosion, brittleness, white stains, dust, fungal stains, and cracks, tears, peeling of the outer layer, missing and burnt parts, adhesive residue, holes, insect tunnels, and abrasion. Furthermore; by the analysis of the grain pattern by digital microscope. We observed that the leather tanned from goat skin, Results of pH showed that the acidity of the leather remained in its typically state and the leather binding did not exhibit any hydrolysis nor oxidation. The SEM results showed that the grain layer of the leather surface has been completely destroyed in some parts of leather furthermore advanced erosion fibers, ATR-FTIR analysis revealed degradation in the chemical composition of the historical leather binding. Aspergillus niger and yeast fungi were found to be the most dominant fungi. Overall, all the analytical techniques used in this study confirmed that the historical leather bookbinding of the manuscript is in urgent need of conservation.

1. Introduction

Leather is a sheet material with the area of each piece ranging from tens of square centimeters to seven or more square metres depending on; the animal from which it was obtained. It is a sheet material derived from the dermis layer of the skin, with sizes varying depending on the animal used [1]. Throughout human history, leather products have been valuable materials. Many leather objects hold historical significance and pose challenges for preservation in museums and private collections. Tanning has been recognized as one of the earliest manufacturing processes, with evidence of its use in ancient Egypt [2]. Due to its widespread use across societies and social classes, leather provides a unique insight into and grounds for comparison within and between cultures. By analyzing leather objects, we can gain information about their former owners and the cultures they belonged to [3]. Methods of preparing and working with leather follow cultural traditions influenced by material availability and local economies [4]. Tanning serves several purposes and is the primary process in leather production. The finished leather should possess resistance to rotting when wet, strength and flexibility when dry, and the ability to retain these properties even after exposure to moisture and subsequent drying. The deterioration of leather is a complex chemical process influenced by various factors. Environmental conditions greatly impact leather deterioration, with factors such as moisture, heat, light, pollution, oxygen, and heavy metals being absorbed into the leather and causing harm. Many researchers are concerned with the deterioration of the collagen - tannin complex [5,6]. They attribute the deterioration of leather to two main processes; oxidation or hydrolysis mechanism. These mechanisms do not only occur in tanning materials but extend to peptides and amino acids. They report that all environmental factors involve leather degradation as well as free metal ions. The end result is the formation of oxidative lipids and the breakdown of tannins or amino acids for vegetable-tanned leather, deterioration can be categorized into hydrolysis and oxidation,

with all the aforementioned factors playing a role. Deterioration affects the collagen's amino acids and peptides, as well as the chemicals used in tanning and treatment. This chemical deterioration gradually weakens the structural integrity of the leather, making it brittle, stiff, and prone to distortion or loss of shape [1]. In extreme cases, deteriorated leather can experience flaking and material loss. Additionally, deteriorated leather has a lower shrinkage temperature, meaning it shrivels up and shrinks irreversibly when exposed to moisture. In environments with high pollution levels, red rot can occur, leading to the crumbling of leather into an orange-red powder [7]. Leather is resistant to bacterial attack but susceptible to fungal growth [2]. Fungal attacks are a common and severe problem in museum storage rooms. Fungi contribute significantly to the deterioration of cultural heritage due to their enzymatic activity and ability to decay various organic materials, including leather [8]. The study and analysis of archaeological leatherwork provide insights into its origin, date, and the culture and economic background it represents. Understanding the original leather processing methods is crucial in this line of inquiry [9]. However, analyzing historical or cultural materials presents challenges in terms of sample size and material heterogeneity. Limited quantities of material often allow for only one measurement, and the heterogeneity of the material prevents correlation of results obtained from different analysis methods [4,10]. Analysis and investigation are vital in the field of conservation, as they elucidate degradation mechanisms and the state of preservation of historical leather bindings. This information helps conservators develop conservation treatment plans or preventive conservation strategies [11]. This study aims to assess the degradation process of historical leather bindings from the Library of Al-Azhar Al-Sharif Mosque collections. Various investigation and analytical techniques, such as attenuated total reflection-Fourier transforms infrared spectroscopy (ATR-FTIR), visual assessment, digital microscopy, scanning electron microscopy (SEM), pH measurement, and microbiological studies, will be employed to understand the chemical structure, composition, and deterioration mechanisms of the leather object materials.

2. Materials and Methods

2.1. *Historical background*

The leather binding is one of the most important leather artifacts that dates back to the Turkish corridor in Al-Azhar Mosque, which was later transferred to the Al-Azhar Library. It is characterized by the sunken letters on the outer leather. The historical leather binding is a cover of the manuscript which entitle "Explanation and Interpretation of Al-Safari" belongs to its author, Muhammad bin Abd al-Rahman bin Abdullah al-Hasani, famously known as al-Safarii n Al-Azhar Al-Sharif Library, the leather of the cover is reddish-brown, which is the common color for leather of that historical period. the data of this the man-uscript are listed in tab. (1).

Table (1) the data of leather bookbinding

Public number	85830
Special number	3018
Library name	Turks
Art	collections of manifestation in the interpretation or interpretation of Al- Safavi
Number of volumes	1
Number of leave	257 leaves
The author	Muhammad bin Abd al-Rahman bin Abdullah al- Hasani, famously known as Al-Safavi
Title	Explanation and Interpretation of Al-Safavi
Length	22 cm
Width	16 cm
date	1499 A.D

2.2. *Visual examination*

The authors performed a visual assessment to detect the degrading aspects found on the surface of the historical leather bookbinding. Visual assessment is very effective because aspects of deterioration can be easily seen. To show the changes found on the historical leather, a high-resolution digital camera image, Kodak EasyShare M1033 10.0MP, was used. Also, an advanced AutoCAD 2018 program was used to map the aspects of deterioration.

2.3. *Digital microscope examination*

A digital microscope (model: NO.9595 60.x made in China) is used to study the surface of the object which cannot be seen with the naked eye [12,13].

2.4. *Scanning electron microscope examination*

Scanning electron microscope was used to examine the surface appearance and identify the shape of the fibres that make up the leather and to know the signs of damage on the leather manuscript because it has a very high magnification power [14] SEM investigation was carried out using (JEOLISMS400 LV EDX link ISIS – Oxford. High vacuum)

2.5. *pH value*

pH, is one of the most important analyses in the field of conservation [15], 0.25 gm from fallen residue of historical leather was cut into small slices & dissolved in 50 ml distilled water, then measured by the device 04, JENWAY 3510 PH meter) [16].

2.6. *Biological investigation*

This test was done to identify the different types of fungi and/or bacteria present on the leather object. the study was conducted in the Microanalysis Center, Faculty of Science, Cairo University. The fungi were isolated by rubbing the swabs gently on a culture medium of Czapek-Dox Agar/ 1 Liter composed of 41 g K_2HPO_4, 30 g sucrose, 0.5 g magnesium sulphate, 3.0 g sodium nitrate, 0. 5g potassium chloride, 0.01 g Iron (II) Sulphate, 17 g agar, pH = 5.5-6, at 25 °C for 1-3 weeks. Inoculated Petri dishes with fungi were incubated at 25±2 °C for 7 days. Resultant cultures were purified using the hyphal tip and/or a single spore technique. The preparation method of the sample in a Petri dish was achieved by adding about 1 g of the tested sample in a sterilized Petri dish, then adding about (20-25 ml) of dissolved agar to the sample and mixing well. Let the mixture solidify on a flat surface, the temperature of the dissolved agar should be about (45) degrees Celsius before pouring it into the sample, then it was placed in an incubator for (10) minutes to solidification, after that the number of viable cells is checked after 24 hours and 48 hours at (37-35) degrees Celsius for the bacterial counting and (5-3) days at (27 -25) degrees Celsius, for the counting of the fungi [17].

2.7. *FTIR*

FTIR analysis was used to evaluate changes in the functional groups of the historical leather object [18] by comparing the results with the standard leather sample [19]. The analysis was carried out using the device (ATR-FTIR. Bruker Vertex 70 spectrometer at the Molecular Modeling).

3. Results

3.1. *Visual assessment by digital camera and Auto-CAD*

We can observe by the digital camera and Auto CAD program that leather binding was, stained, worn and cracked, as shown in figs. (1 & 2). The following aspects of deterioration were as the following: **a)** Dust and label stains, fig. (1-a), **b)** brittleness & some cracks, fig. (1-b). **c)** tears and erosion, fig. (1-b & c) **d)** fading and missing parts, fig. (1-b).) **e)** some holes missing parts and tunnels, fig. (1-b, c & d), **f)** wrapping, scratching in the surface layer, and tears in the edges, fig. (1-b & c).

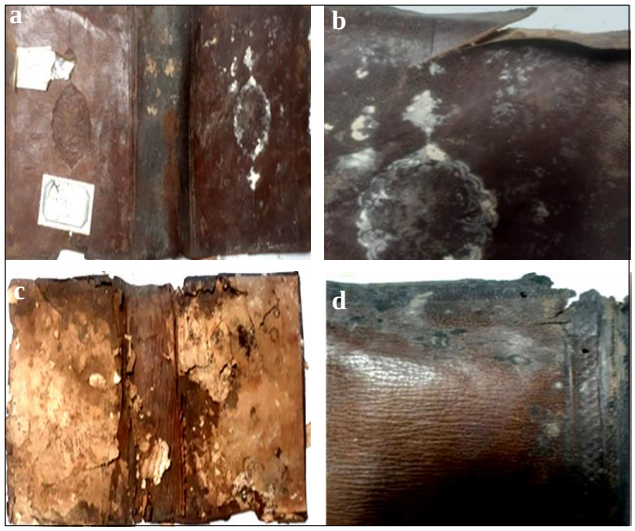

Figure (1) the leather binding; **a.** the leather cover from the inside, **b.** the aspects of damage to the cuticle; cracks and separation at the edges the **c** leather cover from the outside, **d.** holes spotted edges; cuts in the leather cover

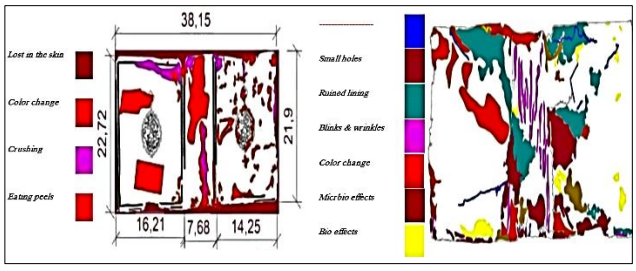

Figure (2) documenting the aspects of damage affected the leather binding using *AutoCAD*

3.2. *Digital microscope results*

The examination with a digital microscope revealed many deterioration aspects of the historical leather object as shown in fig. (3) such as the presence of fine cracks, areas of brittle limbs, the separation of the surface layer, As well as the presence of sticky residue on the surface of the leather erosion, insect tunnels and wrinkles. This phenomenon of damage could be caused by the effect of the uncontrolled surrounding environment of the leather object in the library [20,21].

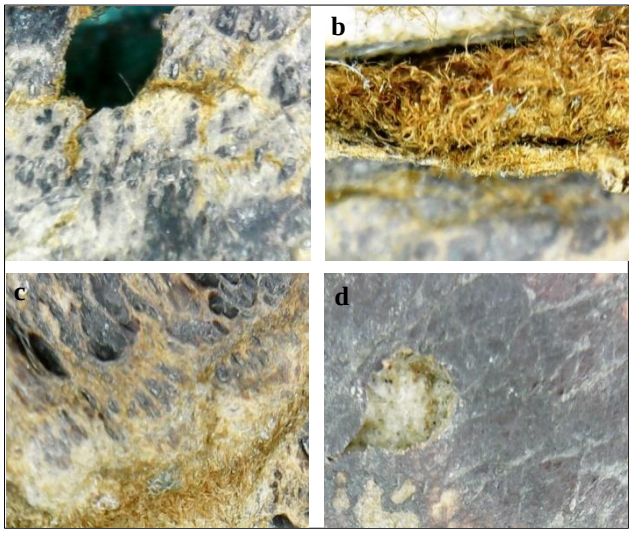

Figure (3) digital microscope examination shows aspects of degrading of leather bookbinding; **a.** wrinkling& Surface cracking, **b.** advanced erosion on the surface, **c.** complete destruction of leather fibers, **d.** advanced erosion, white spots on the, and insect holes in the grain layer.

Scientifically, various morphological methods had throughout time been used for species identification of leather. The most method is based on a morphological investigation of the hair, grain layer and as well as the collagen fibrils and fibre bundles characteristics examined under light microscope [22]. By studying the granular layer of the skin under study and comparing it with standard samples of different types of skins, it was found to be identical to the granular layer of goat skins, which proves that the leather cover was tanned from goat skin, fig. (4).

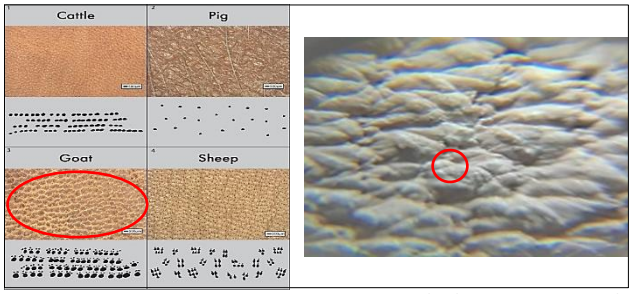

Figure (4) comparing between the grain pattern of references leather (left) & and leather binding (***right***) the ***left*** image (*After: Ebsen et al., 2019*). the figure shows a clear match between the historical sample and the goat skins.

3.3. *SEM examination*

The aim of scanning electron microscope using is the detection of changes in the anatomical structure of the leather binding caused by various factors of degradation [23], the surface layer of the leather has undergone large stresses, and there is significant erosion in the leather in addition to traces of fungal damage and insect holes, according to the

results of the electron microscope examination Scanner of the historical leather sample, as shown in fig. (5) Furthermore, Advanced erosion of leather fibers can be observed, in addition to cracks between the fibers and fibrous bundles. Through microscopic examination, we find that the grain layer of the leather surface has been destroyed totally in some areas.

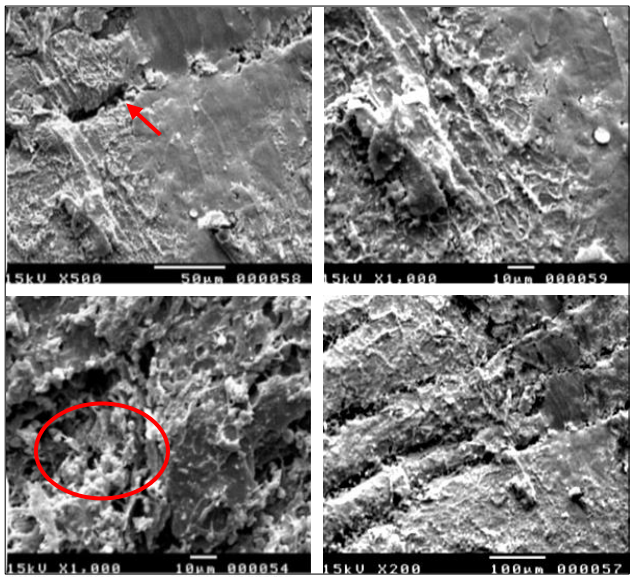

Figure (5) SEM photomicrographs of the historical leather; **a.** destroyed of bundles of leather, **b.** erosion, **c.** & **d.** cracks, **e.** Insect holes, **f.** roughness of leather surface.

3.4. *pH results*

The pH value of the leather binding studied was 4, which indicates that the leather is acidic. The pH value of natural leather after tanning directly ranges from 3-5, and some references have indicated a pH range of 3-6. Based on these results, the studied leather is at a normal level of acidity compared to the acidity of the leather after tanning. However, it is less than the value of 5 which may be attributed to, exposure to various degrading factors and poor storage.

3.5. *Microbiological results*

Two swaps were obtained from the leather bookbinding, tab. (2) & fig. (6) one swap from the surface of the cover of the historical manuscript, and the other from the area between the heel and the leather of the manuscript, to determine the type and counting of fungi that damage the leather, which indicates to the degree of the leather infection. Fungal identification was done on the purified fungal species which were identified by the microscopic and culture characteristics according to standard keys of *Aspergillus spp*. [24]. The most dominant detected fungi of the leather object such as *Aspergillus niger* and yeast fungi and it was noticed that these fungi contributed significantly to the deterioration and disintegration of the leather.

Table (2) isolated fungi from the leather object.

Samples	Fungal count	Fungi types
Leather swap (1)	1 Uncountable	*Aspergillus Fungi* *Yeast*
Leather swap (2)	Uncountable	*Yeast*

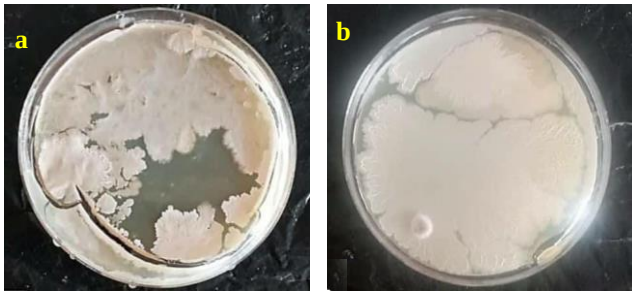

Figure (6) & different fungal colonies grown on (PDA) plates of the historical leather cover were: **a.** *Aspergillus niger*, **b.** *Yeast.*

3.6. *FTIR results*

By comparing the spectra of the historical leather with the spectra of the standard new sample, it was found that the characteristic functional groups of leather's collagen have some notable differences between them. The shift in the absorption band of the function groups, fig. (7). Amine (I) at 1690 cm^{-1} [25] from its original position to higher wave numbers of 1704.76 cm^{-1} for the historical sample, while in the standard sample the absorption bands (NH curvature and (CN repulsion) (Amine (II)) at 1480 cm^{-1} were shifted -1575 cm^{-1} to the lower wave number of (NH bending) (Amine (II) and was placed at 1563.99 cm^{-1}, this indicates the deterioration of the historical sample caused by the influence of different degrading aspects, or perhaps due to the wrong handling. Without a doubt, environmental factors such as humidity, temperature, and air pollution, in addition to two main processes, oxidation and hydrolysis can transform the leather into powder [26].

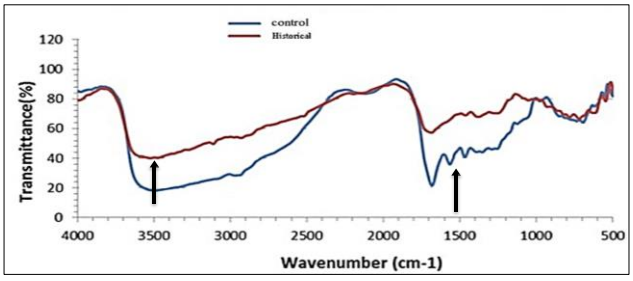

Figure (7) results of infrared spectroscopy of a sample of historical leather compared to a sample of standard leather.

4. Discussion

4.1. *Visual assessment*

From fig. (1) we can observe the areas have cuts and tears. This may be the result of the influence of various degrading factors, including impact of temperature, relative humidity, pollution, poor control storage, and poor ventilation. Also, improper handling of the manuscript may have a significant impact. There are many missing places in the leather and at the edges. Furthermore; the inner lining and epidermis are covered with tunnels of insects due to the leather itself is suitable food source for microorganisms and insects, separated from inconvenient environmental conditions. In terms of change in temperature and relative humidity, the monthly poor preservation places, this has led to the activity of insects

and the presence of holes in the leather and the inner lining. Also, we can see fragility and wear on all sides of the leather, which may be a result of the environment in which it is damaged and the effect of changes in temperature and humidity that destroy it. Perhaps this is due to the presence of many stored manuscripts on the metal shelves, which causes more friction during dealing with the ancient manuscript in the library. due to their history of storage, handling, and environmental conditions. However, diverse degrees of deterioration could be distinguished which depended on various factors. For example, the size of the books makes them difficult to handle and produces problems of mechanical stability. Other factors determining their degrading were inadequate storage and mishandling which led to numerous tears and damage to the supports of the leather

4.2. *Digital microscopy*

Through digital microscopy, some signs of damage were identified, such as cracks and tears, which may be attributed to fluctuations in temperature. The presence of adhesive residues was also observed, along with surface peeling on the historical leather. The examination also revealed the presence of precise insect holes that were not visible to the naked eye, possibly due to moisture. Microscopic examination also identified the presence of deteriorated and acidic lining residues inside the historical leather cover [27]. Microscopic examination revealed that the leather suffers from obviated dryness, fragility in the fibrous structure, and loss of elasticity, which may be due to the lack of fat in the decomposed leather [28]. All of these phenomena are closely related to thermal decomposition resulting from uncontrolled storage conditions. The steps of thermal damage can be explained as follows Supplying external heat to a chemical compound, is simply transferring kinetic energy to it; this externally applied energy causes an increase in molecular motion which increases the rate of collision between adjacent molecules which in turn increases the rate of reaction. In a polymer like leather the heat increases the molecular motion until it is so extreme that the bond holding the chain together can no longer resist the movement and finally break. The three protein chains in a triple helix can separate under impact the thermal degradation such as is found in collagen; an example is the proteins denaturation of using thermal effect to determine the shrinkage temperature. It is a sudden reaction and can be compared to a zipper breaking all at once heat and the moisture content of materials and the air around them are interconnected from the air; after many fluctuations the leather loses its regain ability and becomes hard and brittle. The internal chemical compounds become concentrated because of the reduced amounts of water present. When leather loses or gains moisture a rapid change in the internal temperature of leather will occur due to the latent heat of vaporization [29].

4.3. *SEM*

Upon careful monitoring of the scan images, we find clear erosion and advanced destruction of the leather's fibers and fibrous bundles. Collagen fibril formation relies on the behavior of self-assembly to triple-helical structure of collagen. Besides, molecules of collagen align in a parallel and ordered manner through terminal-to-terminal combination accompanied by a quarter staggered arrangement between the head and tail [30,31] (Resulting in a D-periodic banding space due to hydrophobic and electrostatic interactions but under impact of various damage factors such as humidity and temperature these bundles gradually become more dispersed and irregularly distributed. This can be clearly observed in the scanning images of the historical sample, which supports the effect of the leather binding due to the effect of high temperature and fluctuations in humidity. Additionally, we can observe there was evidence of pore closure on leather's surface, fig. (5-b) In some areas we notice tiny gaps that may be caused by shrinkage of collagen bundles, fig. (5.a). Furthermore, erosion in the leather was observed, as well as significant dust and dirt accumulation, and the spread of fungal hyphae within protein cells as the circle indicates in the fig. (5-c). These may be attributed to significant fluctuations in temperature and humidity, high pollution levels in the surrounding environment of the manuscript, and high moisture levels reaching over 60%, especially in winter. Poor ventilation plays a significant role in fungal deterioration and can also act as a carrier for iron and copper components, converting gases into harmful acids for the historical manuscript [32,33].

4.4. *pH value*

The pH value of the leather under study recorded 4. Acidity of leather after tanning ranges from 4 to 6 [34]. therefore, the leather is relatively acidic by nature after tanning, as some weak acids These include hydrochloric, sulphuric, sulphonic, oxalic, sulphureous, formic, lactic, acetic, ellagic, gallic, and carbonic are used in the tanning preparation processes [35] to reduce the swelling of the hides after soaking in lime and also to make the hide fibers accept the tanning process [36]. The literatures report that the tan liquor acidity was considered to be the result of hydroxyl groups of the hydrolysable tannins and possibly from catechol tannins, phenolic hydroxyl groups of the pyrogallol and catechol tannins and lignins, and this natural acidity due to lactic, gallic, acetic, oxalic, citric, tartaric, carbonic and phosphoric acids present in tannins, uronic acid and pectins, added formic, boric, sulphureous and sulphuric acid. How many of these end up in the leather is an unrecorded totally [37]. Although the historical leather recorded a value in the normal range for tanned leather, it is the lowest in this range, indicating a high pH in the leather sample which may indicate that the leather has been exposed to acid decomposition, which may be limited but present. In general, the chemical deterioration of vegetable-tanned leather is caused by acid hydrolysis and oxidation due to environmental deteriorative factors like air pollutants, heat and light. In addition, the type of tannin material influences the rate of deterioration. The degree of degrading can be measured by the fall in the shrinkage temperature of the leather. pH data shows that,

although environmental factors have a generally larger impact on the deterioration, the average degree of oxidation is greater in older leathers and it significantly influences the Ts in these materials. Moreover, it is also shown that acid pollution is indicated in the relation between the sulphate content and pH measured in the leathers although ammonia is released by oxidation of amino acids and may influence the pH value in acid-damaged leathers. Leather like other proteins, is an ionic species containing amino groups and carboxyl groups on its terminal amino acids. It also contains a variety of other acidic and basic groups on the side chains of its non-terminal amino acids. The effect of pH on the degrading of casein reflects the ionization of the acidic and basic groups in its structure. At high pH, leather will have a negative charge due to the ionization of its acidic side chains CO_2. The form of deterioration known as red rot is considered to be caused by the action of strong acids on vegetable-tanned leathers especially on those processed with condensed tannins. These strong acids, particularly sulphuric acid, could have been added to the leather during processing or have been formed in situ from sulphur dioxide absorbed from polluted atmospheres. Several analytical methods have been developed to determine the amount of strong acid present in leather. However, it has been found empirically that if a standard extract from vegetable-tanned leather has a pH over 3.2 it is unlikely to contain damaging quantities of strong acids. Leather having a pH of 2.8 or less, the deterioration perhaps due to the effect of acids produced by insects and bacteria, or perhaps due to the effect of air pollution in the surrounding environment.

4.5. *Microbiological analysis*

Through fungal examination, the most prevalent fungi were identified, such as Aspergillus niger and yeast fungi. It was clear that these fungi significantly contributed to the deterioration and disintegration of the historical leather cover. Fungal growth processes are affected by temperature changes in storage environments, in addition to a significant rise in temperature to approximately 30 ºC, especially in the summer, as well as pollution levels in the environment surrounding the manuscript, as well as the degree of humidity, it almost reaches more than 60%, especially in the winter season. Poor ventilation plays an important role in the fungal damage. It can also act as a carrier of iron and copper components or both. Which helps in converting gases into harmful acids in the ancient leather [38,39]. During monsoon season, the temperature and humidity conditions are most congenial for optimum fungal growth and activity. The atmosphere during this period is replete with innumerable number of fungal spores. The aerial fungal flora has played vital role in the degradation of exposed leather. The pattern of fungal attack is, however determined by climatic effect coupled with actinic effect and the effect of atmospheric chemicals It is clear that the uncontrolled preservation conditions in the library, which lack good ventilation and control of temperature and humidity during the summer and winter, were the reason for the spread of these aerial fungi that are widespread in the air [40].

4.6. *FTIR*

When comparing the spectra of the historical leather with the spectra of the standard sample (new leather), noticeable differences were found in the distinctive functional groups of collagens in the leather [41]. The shift in the absorption range of functional groups was most evident. The wavelength of the N-H stretching in the standard sample was 3481 cm^{-1}, but it was shifted to lower wave numbers (3320) in the historical skin sample. The absorption range of the extended C=O (amide I) shifted from its original position at -1690 cm^{-1} to higher wave numbers, reaching 1704.76 cm^{-1} for the historical skin sample. In the standard sample, the absorption ranges of the bending N-H and stretching C-N (amide II) were found at 1480-1575 cm^{-1}, but they were shifted to a lower wave number of the bending NH (average amide II) and placed at 1563.99 cm^{-1}. Based on the above, it can be concluded that the collagen-related ranges indicated the severe deterioration in the historical skin sample compared to the standard sample, whether in terms of the disappearance of some ranges, the shift of wave numbers to lower values, or the intensity of absorption ranges, which was higher in the standard sample compared to the historical sample. This indicates the severe deterioration in the historical leather [42,43]. Furthermore, 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. The band of H-C-H deformation slightly decreased and the same behavior was undertaken to α-helix H-CH_2 at 1334 cm^{-1}. Accordingly, the amide III was dramatically affected at 90˚C, while chains of aliphatic side remained stable. the amide I and amid III (1300-1400 cm^{-1}) increased significantly in all leather types, causing the first step of the denaturation; where the helices begin to unfold. This phenomenon works to disrupt the secondary and sometimes triangular structure of the protein [8].

5. Conclusion

The studied historical bookbinding had been investigated using different analytical techniques, visual assessment, isolation and identification of fungi, pH measurements, SEM and FTIR spectroscopy, to understand deeply the nature and mechanics of degradation of this artifact. The conclusions that can be reached from this research can be summarized as follows: ****)*** *Many aspects of deterioration were noted on the surface of the leather bookbinding, such as holes caused by insects, wrapping, and erosion of tanning material and missing parts. The most dominant fungi were Aspergillus and yeast.* ****)*** *It is clear that the uncontrolled preservation conditions in the library, which lack good ventilation and control of temperature and humidity during the summer and winter, were the reason for the spread of these aerial fungi that are widespread in the air.* ****)*** *Through digital microscopy, some signs of damage were identified, such as cracks and tears, which may be attributed to fluctuations*

in temperature. The presence of adhesive residues was also observed, along with surface peeling on the historical leather. ****)*** *The pH values of leather bookbinding were equaled their normal value because this manuscript was damaged by alkaline environmental conditions.* ****)*** *The results of the scanning electron microscope showed erosion and weakness of the leather body under the influence of natural aging and bad storage.* ****)*** *The result of FTIR showed that the hydrogen bond within the new sample is stronger than that of the historical leather 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 furthermore the amide I and amid III (1300-1400 cm^{-1}) increased significantly in all leather types, causing the first step of the denaturation*

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