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Analytical Techniques used for Condition Assessment of the Historical Prints from Belzoni's Atlas entitled "Plates Illustrative of the Researches and Operations of G. Belzoni in Egypt"

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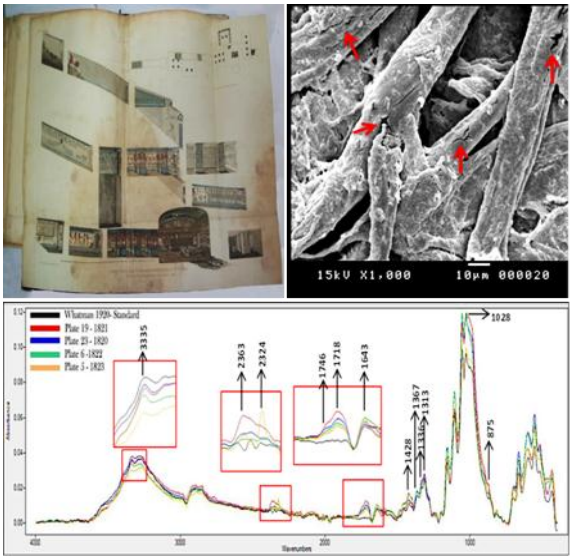
HIGHLIGHTS

- The state of preservation of the historical printed plates from a rare nineteenth-century Belzoni's Atlas was studied.
- Some analytical techniques were used for condition assessment used for the historical plates studied.
- Results showed that the historical prints studied suffered from deterioration caused by a variety of factors.
- The presence of both gelatin and calcium salts in the historical papers plays a positive role in limiting its deterioration.

GRAPHICAL ABSTRACT



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ABSTRACT

The studied historical printed plates, are dated back to the 19th century, and they are from an illustrating atlas of Belzoni's explorations and operations in Egypt. The Belzoni's Atlas is one of the outstanding pictorial records of Egyptology at this period. The aim of this study is to assess the rate of deterioration of rare historical printed plates, using different analytical techniques; pH values, color change measurements, isolation and identification of microorganisms (fungi and bacteria), investigation of the surface morphology by a scanning electron microscope (SEM),

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and determination of paper crystallinity by X-ray diffraction analysis (XRD). In addition, Attenuated total reflection – Fourier transform infrared (ATR-FTIR) spectroscopy was used to detect the changes in cellulose molecules of the paper samples. Based on the results of the analytical techniques mentioned above, the historical printed plates are suffering from deterioration. The pH value of the historical plates ranged between 5.08 and 5.98. Microorganism testing proved the presence of *Aspergillus sp.*, *Penicillium sp.*, *Streptococcus sp.* and *Bacillus sp.* The crystallinity index of cellulose in the historical plates decreased; indicating the degradation of cellulose. The ATR-FTIR spectrum proved that the historical plates had undergone destructive hydrolysis and oxidation processes of cellulose. The SEM investigation showed the effect of the natural ageing and surrounding environmental conditions on the surface morphology of the fibers. This mainly may be due to the preservation of the historical plates in poor storage conditions, which played an important role in the deterioration process.

1. Introduction

Egyptian libraries are abounded with many valuable historical books, manuscripts, etc., such as the Egyptian National Library and Archives, the Library of Alexandria, Al Azhar Library, Rifa'a Al-Tahtawi Library and the heritage libraries in some Egyptian universities. Among these libraries are the heritage libraries of the Faculty of Arts and the Faculty of Archeology at Sohag University, Egypt, which contain valuable historical books, and among these books is the Giovanni Belzoni's atlas dating back to the 19th century AD (1820). It is considered one of the very rare books. The importance of Belzoni's atlas narrative is due to the fact that it is one of the greatest pictorial records of Egyptology at this period. It includes plates simulating some murals in the tomb of Seti I in Luxor, known as KV17. The tomb of Seti I was discovered in 1817 by Giovanni Battista Belzoni, since that time, it is known as the most famous burier in the Valley of the Kings (Beban el Molouk) at Luxor, Egypt. It contains the most beautiful wall decorations and writings [1]. In addition, these plates were made using ancient printmaking techniques, where both lithography and etching were used. A print is in essence a pictorial image that has been produced by a variety of printing techniques [2, 3]. Printing is strictly defined as the transferring of ink from a prepared printing surface (wood, metal, stone or other printing surfaces) to blank paper or other material [4-8]. There are four traditional divisions of printmaking, which are still currently in use; and they are relief, intaglio, planographic and stencil [7, 9-11]. These are general categories and each of these has many variations, depending on the materials and tools used, and the way they are printed [10]. Paper is the most common material in library collections, which a large portion of our cultural heritage is within illustrated printings, sketches, and drawings on paper, etc. Although these printings and manuscripts are not life forms, they are symbols and signs of life, so they are vibrant [12, 13]. Paper artworks are the most susceptible to deterioration due to their organic and inorganic components (cellulose fibers, sizing material, fillers, inks and pigments) and are in poorly controlled storage conditions, which make them difficult to handle and cannot be circulated [12, 14-16]. Paper is mainly composed of cellulose fibers, which are linear polymers of glucose monomers linked together in long chains through β-1,4-glycosidic bonds. Therefore the presence of acidic substances leads to the hydrolysis of cellulose which appears in the shortening of its chains, along with a lower content of the crystalline form. Gradual fragmentation of the chains leads to the brittleness of paper, resulting in increasing weakness and yellowing [17]. The overall behavior of printed papers (chemical and mechanical properties, stability, degradation, etc...) is strongly dependent upon the nature, origin, and characteristics of their components as well as their interactions. The structure of printed papers and their properties depends on both the paper manufacturing process and the different printing processes, which greatly differ, impacting on their durability and susceptibility to agents of deterioration [18]. It was found that one of the reasons for the deterioration of printed papers is correlated to certain stag-

es in the printing process, such as wetting the paper before printing [19]. The degradation of cellulose occurs primarily due to various factors that contribute to the deterioration of printed materials, such as a chemical attack by acidic hydrolysis, oxidative agent, light, temperature, humidity and moisture, air pollution, dust particles, biological attack due to the presence of microorganisms such as bacteria and fungi, insects and human factors [13, 18-21]. The degradation of printed papers results from the interaction of the object with the above-mentioned factors, resulting in an undesirable change in the original state of the materials. The undesirable effects of deterioration may appear in the form of wear and tear, shrinkage, cracks, brittleness, discoloration, abrasion, dust, and dirt accumulation, etc… [18].

This study aims to examine and analyze the state of the deterioration of historical plates from the atlas of "Plates illustrative of the researches and operations of G. Belzoni in Egypt". Some analytical techniques mentioned below were used for condition assessment of the historical plates studied.

2. Materials and Methods

2.1. Materials

2.1.1. Description of Atlas studied

The investigated atlas volume entitled "Plates illustrative of the researches and operations of G. Belzoni in Egypt", contained printed plates, and was issued accompanying Giovanni Battista Belzoni's book which was known as "Narrative of the operations and recent discoveries within the pyramids, temples, tombs, and excavations in Egypt: And of a Journey to the Coast of the Red Sea in Search of the Ancient Berenice, and Another to the Oasis of Jupiter Ammon". It was printed and published in London in 1821. The plates within the atlas volume are divided into two sets, each with its own title and index; **The first set**, dated back to 1821, consisted of 44 plates printed on 34 large folio sheets (some folded). The plates were numbered in the index with Latin numbers, while inside the plates are numbered with English numbers. By comparing the plates with the index, it was found that there are four missing plates, which were plates with numbers (3, 36, 37, and 38). Most plates are lettered with title and numbered. Many plates are lettered with name(s) of artist(s). Each page is lettered variously with the publisher's name and address. **The second set** dated back to 1822 consisted of six plates that were numbered in the index with Latin numbers, while inside the plates they are not numbered - they were printed on 6 large folio sheets (some folded). The dimensions of all the plate sheets range from approximately (45.7 × 56.3 cm) to (45.7 × 73.7 cm).

The plates were printed in a variety of printmaking techniques: lithographs, etchings and aquatints. Most of the Plates within the atlas were hand-colored after printing. These plates were drawn on nature by Giovanni Battista Belzoni, Mrs. Sarah Belzoni and Alessandro Ricci. The printmaking processes were done by Charles Joseph Hullmandal, Agostino Aglio and John Heaviside Clark.

2.1.2. Aspects of deterioration

The historical plates suffered from several forms of damage such as: yellowness of some parts of the paper, fungal spots (Fig. 1-a), improper restoration represented by the Adhesive tapes used to repair some holes and missing parts in some plates (Fig. 1-a), yellowing, brittleness and splitting of paper edges in most plates (Fig. 1-b), dust accumulations (Fig. 1-c), bleeding of printing ink on the back side (verso) of the plates (Fig. 1-e), pencil writings on the back of one of the plates (Fig. 1-f). It was also noted that the original plates were used as holders for other plates, as the remains of the four corners of these extraneous plates are still present (Fig. 1-d).

2.1.3. Samples

The measurements of pH and color changes, were done directly on the background of

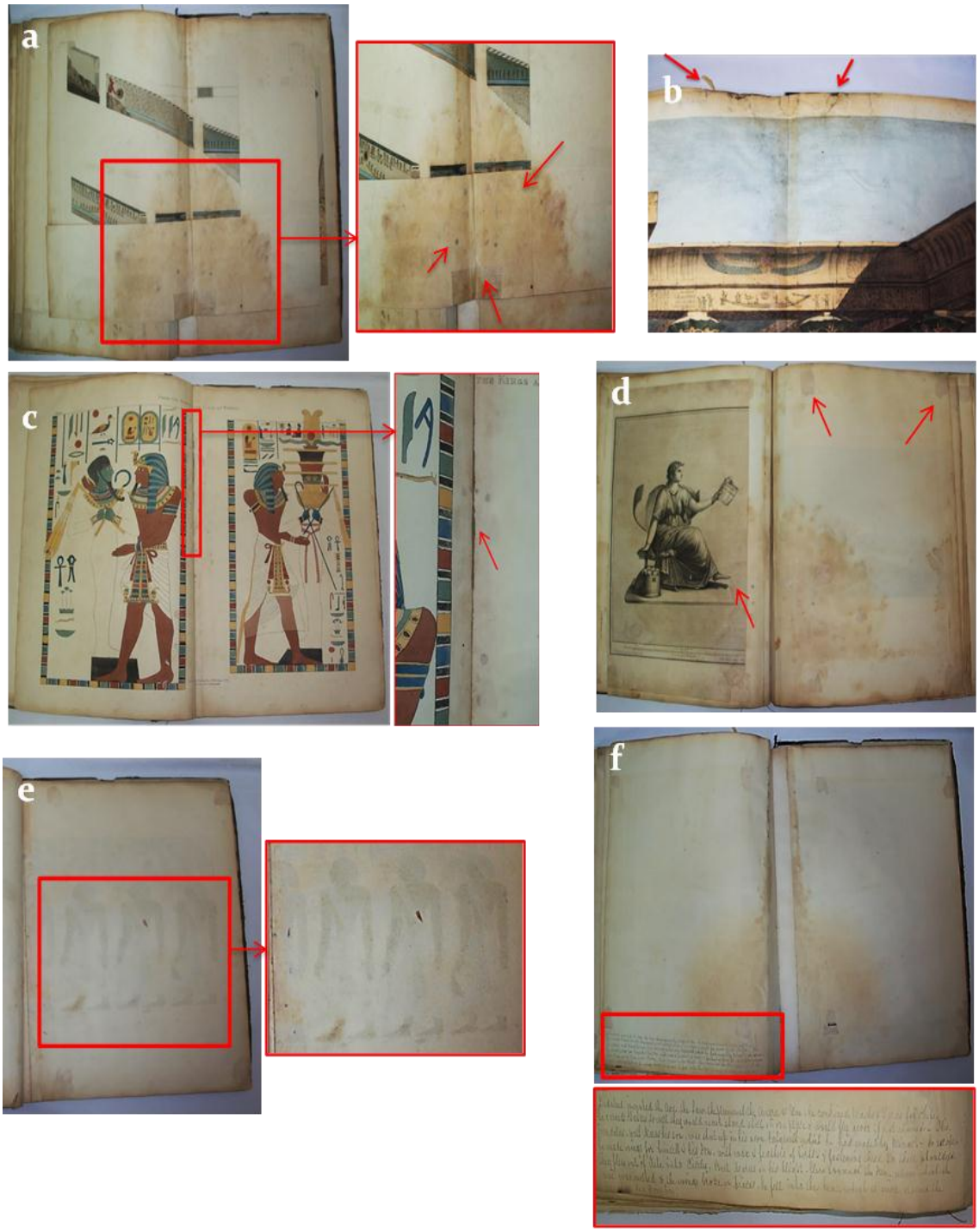

Fig. 1. Aspects of deterioration of the historical plates; (a) yellowness of paper, fungal spots and adhesive tape on tears, (b) fragility and splitting of the edges, (c) dust accumulation, (d) strange plate affixed to the original plate, (e) bleeding of printing ink, (f) pencil writings.

the plates. For XRD, ATR-FTIR, SEM analyses, minute samples (about 100 μg) were collected from only four plates of atlas (two plates from the first set No. 19 and 23, two plates from the second set No. 5 and 6).These plates were selected because of the presence of the watermarks. When water marks became clear on all plates, they were printed on Whatman paper, which dated back to 1820, 1821, 1822, and 1823 (Fig. 2).

For microbial isolation, due to the similarity of the spots, it was performed only on some spots of some historical plates, taking into consideration the different color spots during isolation. In addition to, the pH measurement, XRD, and ATR-FTIR analyses were also carried out on hand-made Whatman paper, dating back to 1920 from Vintage Paper Co at United Kingdom, which is similar to the same type of paper in which the historical plates were printed on. Therefore, it was used to be compared with the studied historical plates in order to observe, how the difference in preservation and storage conditions affect the paper's stability and durability.

2.2. Methods

2.2.1. pH measurement

The pH measurement of the paper, was carried out according to the standard T 529 om-04. The HQ11D Portable pH Meter was used with Intellical™ PHC729 Laboratory Surface Measurements RedRod Refillable Glass pH Electrode. The flat electrode was placed on a drop of distilled water, which was added to the surface of the plates, and the pH value was read after being constant for 30 seconds [22]. The measurement was performed at the organic monuments restoration laboratory in the Faculty of Archaeology at Sohag University, Egypt.

2.2.2. Isolation and identification of fungi and bacteria

Microbial samples using sterile cotton swabs, were collected from areas contaminated with colored spots on the surface and background of the some plates; to isolate the microorganisms. The microbial Swabs were cultivated in Potato dextrose Agar (PDA) medium, consisting of 4 g Potato Starch, 20 g Dextrose, 15 g Agar, and 1000 ml of distilled water in Petri dishes. Fungi isolated in the culture medium, were incubated at a temperature of between 25°C for 5-7 days (performed in the organic monuments restoration laboratory at the Faculty of Archaeology, Sohag University) [23-27]. The fungal species were identified, based on their morphological characteristics, and microscopic analysis in the Microbiology Department at the Faculty of Science, Sohag University, Egypt. The microbial swabs were also cultured on the nutrient agar media (10 g Beef extract, 10 g Peptone, 5 g Sodium chloride, 15 g Agar and 1000 ml of distilled water in Petri dishes), and were incubated at a temperature of (28-30°C) for a period ranging from (3-21) days [28]. After the incubation period, the bacterial growths that appeared in the dishes, were isolated for purification and identification. The bacterial species were isolated, purified, and identified based on their morphological characterisics in the Microbiology Laboratory, Conservation Center at the Grand Egyptian Museum, Egypt.

2.2.3. Investigation of the surface morphology by SEM

Scanning electron microscope (JEOL-JSM-5400LV) was used for the investigation of the surface morphology of the plates. The fine gold coating (JEOL-JFC- 1100E) was used. SEM was performed at the Scanning Electron Microscope Laboratory, The central Laboratory unit, Assiut University, Egypt.

2.2.4. X-ray diffraction analysis for the determination of the paper crystallinity

Bruker D8 Advance equipment at the X-ray diffraction Unit in the Faculty of Science at Sohag University Egypt, was used for determining the crystallinity of cellulose. The crystallinity index is calculated according to the Segal peak height method a maximum intensity value I_{002} is found between the scattering angles of 2θ=22° and 23°. The minimum value I_{am} is taken using a minimum in the data, typically between 2θ=18° and 19°. The sample crystallinity (usually referred to as the crystallinity index) is then calculated as the following equation [29-34]:

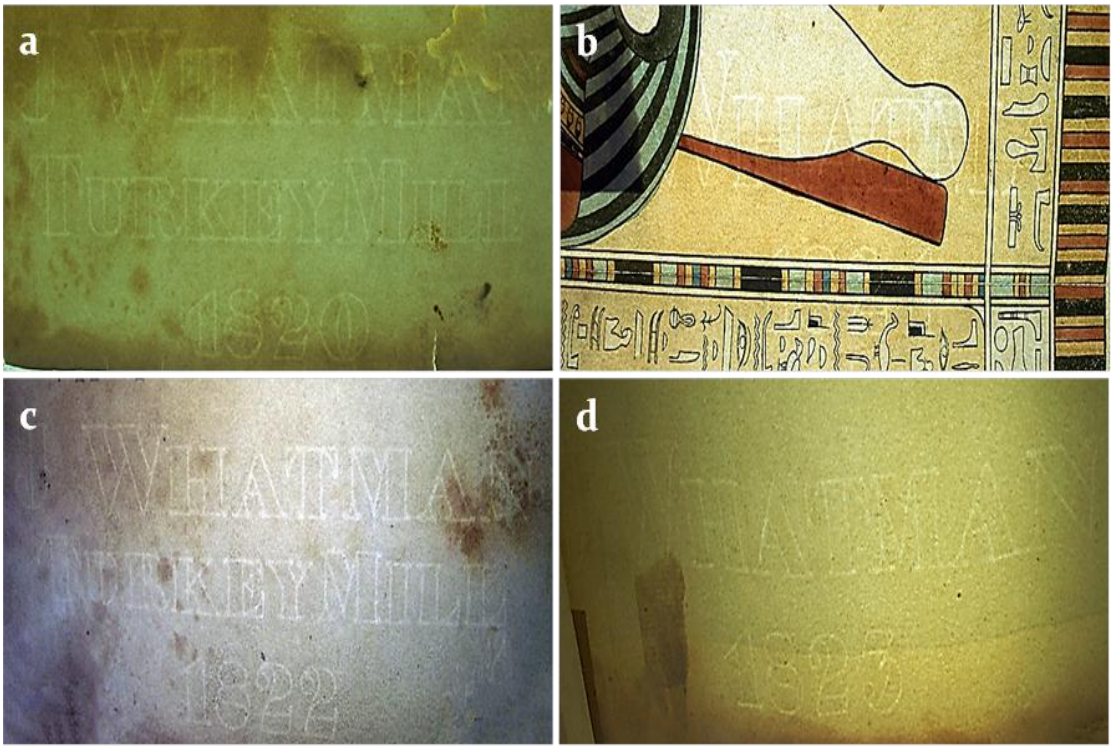

Fig. 2. Watermarks on the historical plates, (a & b) watermarks from the first set; a. plate 23 (J Whatman Turkey Mill 1820), b. plate 19 (J Whatman 1821), (c & d) watermarks from the second set; c. plate 6 (J Whatman Turkey Mill 1822), d. plate 5 (J Whatman 1821).

$$CrI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100$$

2.2.5. Color Change Measurements

Molecular modifications in the cellulose polymer caused by degradation can outcome in chromatic changes [35]. The measurement of values of color changes in the paper of some plates was carried out by the CIE $L^*a^*b^*$ system. The total chromatic change ΔE was calculated according to the following equation: [36, 37]

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

Colorimetric measurements CIE $L^*a^*b^*$ for plates, were performed using a portable colorimeter PCE-CSM 7, in the D65/10 mode at the organic monuments restoration laboratory in the Faculty of Archaeology at Sohag University, Egypt.

2.2.6. ATR-FTIR spectroscopy.

ATR-FTIR spectra were obtained using Bruker ALPHA FT-IR spectrometer with the Platinum diamond ATR crystal, in the frequency range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}, in the absorbance mode. The procedure was carried out at the Microchemical Analysis Unit at Faculty of Science, Sohag University, Egypt. Five samples were used for this analysis (i.e. four paper samples from four plates, and a modern sample of whatman paper). The purpose of this analysis is to evaluate the extent to which historical plates are degraded compared to the standard sample by the characteristic functional groups responsible for the degradation of cellulose.

3. Results and Discussion

The reasons and mechanism of deterioration of the historical plates, were explained through the results of the investigations and

analyses, that were carried out on the historical plates, in addition to the previous investigations and analyses conducted by the authors in previous research to identify the type and components of paper of the printed plates. From the analysis and investigation, it was clear that the type of paper in the printed plates was from Whatman paper, handmade of rags (a mixture of cotton and linen fibers). It was sized with gelatin and alum ($KAl(SO_4)_2 \cdot 12H_2O$) solution. It also contained calcium carbonate arising from calcium hydroxide (lime), which was added to the rags, during the beating process [38].

3.1. pH measurement

The results of paper pH value measurement showed that, the studied plates were with moderately to slightly acidic properties on the surface, and it was ranging between 5.08 -5.98 (Table. 1) [39, 40].

It was clear that the pH of the plates was moderate acidic. A decrease in the pH value may have been caused by the occurrence of acid hydrolysis or oxidation of cellulose, as a result of the presence of alum in paper. On the other hand, the presence of gelatin and calcium salts in the paper, has slowed down the decreasing of pH value caused by alum. Calcium carbonate acts as a buffer against the acids produced during natural paper aging [41-43].

Table 1. pH values of some historical plates compared to Whatman paper (1920)

Samples	pH
Whatman paper (1920)	6.47
Plates from First set	
Title page	5.98
Plate 2	5.38
Plate 7	5.43
Plate 11	5.49
Plate 19	5.84
Plate 23	5.70
Plate 29	5.58
Plate 33	5.21
Plate 40	5.33
Plate 42	5.40
Plate 44	5.15
Plates from second set	
Plate 1	5.08
Plate 5	5.24
Plate 6	5.21

3.2. Identification of fungi and bacteria

The results of this study showed the presence of the following genera on historical plates: *Aspergillus, Penicillium, Streptococcus, Microbacterium, Micrococcus, Bacillus, Staphylococcus and Kocuria*. *Aspergillus terrus* was the most dominant fungal species, followed by *A. flavus* and *A. niger, then Penicillium purpurogenum*. As for bacterial species, *Streptococcus spp.* was the dominant species, followed by *Bacillus subtilis* and *Bacillus megaterium*, and then *Micrococcus luteus, Staphylococcus spp. and Kocuria turfanensis* (Table 2, Figs. 3 and 4).

According to the identification of microorganisms, the prevailing fungal genera isolated from the surface of the historical plates, were *Aspergillus* and *Penicillium.* Regarding the isolated bacteria, it was observed that the Gram-positive bacteria genera were dominant in the historical plates. The presence of these microorganisms may be due to the unsuitable environmental conditions in which the historical Atlas was previously stored in, such as extreme dampness, fluctuations in relative humidity, large variations in day and night temperatures, dust and dirt. These conditions promoted the growth of microorganisms on the plates inside the studied Atlas. In addition to, the adhesives that were used to stick the plates in the spine of the book (Atlas) also helped in the growth of fungi and bacteria, by noting that most of the microbial growth inside Atlas is concentrated in the spine of the book from the inside. Furthermore, the isolated fungal species caused aesthetic and structural damage to the historical plates, through their production of acids, cellulolytic enzymes and their secretions of different pigments on the paper [44- 46].

3.3. SEM investigation

Investigation of the surface morphology of historical plates using SEM, (Fig. 5) revealed the effect of natural aging on the paper fibers.

Table 2. Identified Fungi and Bacteria From some infected historical plates

Identified fungi and bacteria			
Plates from First set			
11	1	*Aspergillus flavus*	*Streptococcus spp.*
19	2	*Aspergillus terreus, Aspergillus niger*	*Micrococcus luteus*
	3	*Aspergillus terreus, Aspergillus flavus, Aspergillus niger*	-
23	4	*Aspergillus terreus, Aspergillus niger*	*Streptococcus spp., Bacillus subtilus*
	5	*Aspergillus terreus, Aspergillus flavus*	-
29	6	*Aspergillus terreus*	*Streptococcus spp.*
33	7	*Penicillium purpurogenum, Aspergillus terreus*	*Staphylococcus spp.*
40	8	*Aspergillus terreus, Aspergillus flavus, Aspergillus niger*	*Kocuria turfanensis*
42	9	*Aspergillus terreus*	*Streptococcus spp.*
Plates from second set			
5	10	*Aspergillus terreus, Aspergillus flavus*	*Bacillus megaterium*
6	11	*Aspergillus terreus, Aspergillus flavus, Aspergillus niger*	-
	12	*Penicillium purpurogenum*	*Streptococcus spp.*

The results showed fiber deterioration as evidenced by the appearance of broken fibers, cracks in some fibers (Fig. 5-a, b), and lots of particles covering the fibers, that obviously are showed in (Fig. 5-c). These particles may be due to dust and dirt found on the surface of the plates. SEM images also showed fungal contamination in the paper, through the spores and fungal hyphae that cover the paper fibers, (Fig. 5-d, e, and f). As it is clear from (Fig. 5-f) that the fungal contamination caused the erosion of the surface of the fibers.

3.4. XRD analysis for determination of the paper's crystallinity

The results of the XRD analysis revealed that, the crystallinity index of the cellulose in the whatman paper 1920s, as a standard sample was 86%, while in the historical paper samples was 63%, 62%, 51% and 48% respectively (Fig. 6).

It was clear from the results obtained that, the aging caused a decrease in the cellulose crystallinity, which means changes in the crystalline phase in all the analyzed papers [47]. The cellulose chains have a strong tendency to aggregate into highly ordered structures. Due to the regularity of chains, cellulose fibers are characterized by a relatively high degree of crystallinity. The strength of paper is determined by the intrinsic strength of fibers and by the strength of interfiber bonding [48]. The presence of crystallinity in cellulose contributes significantly to its mechanical, physical and chemical properties.

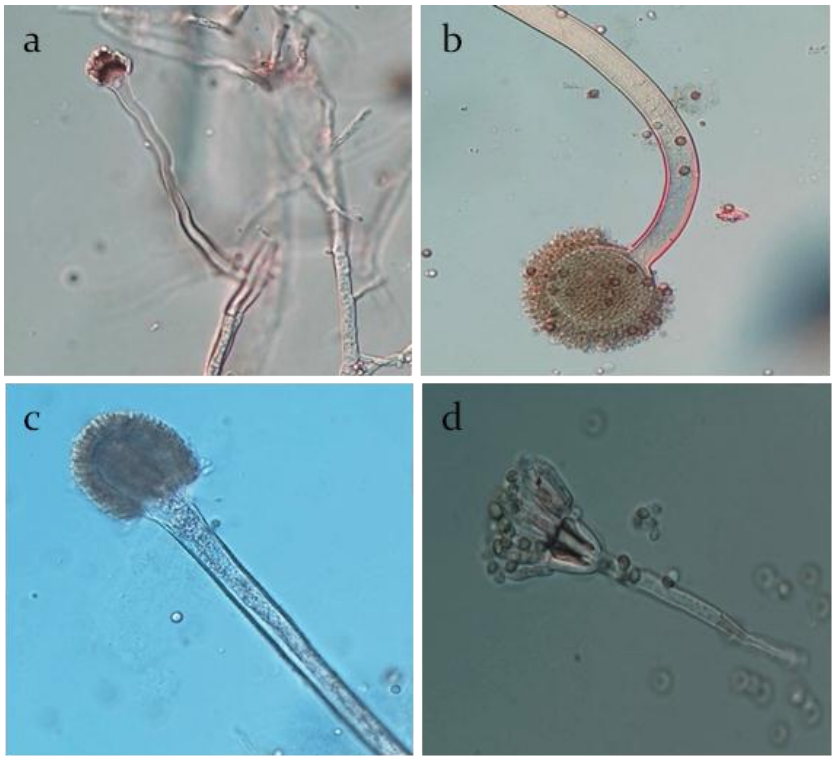

Fig. 3. Microscopic photos of identified Fungi at 400× magnification: a. *Aspergillus terreus*, b. *Aspergillus niger*, c. *Aspergillus flavus*, d. *Penicillium purpurogenum*

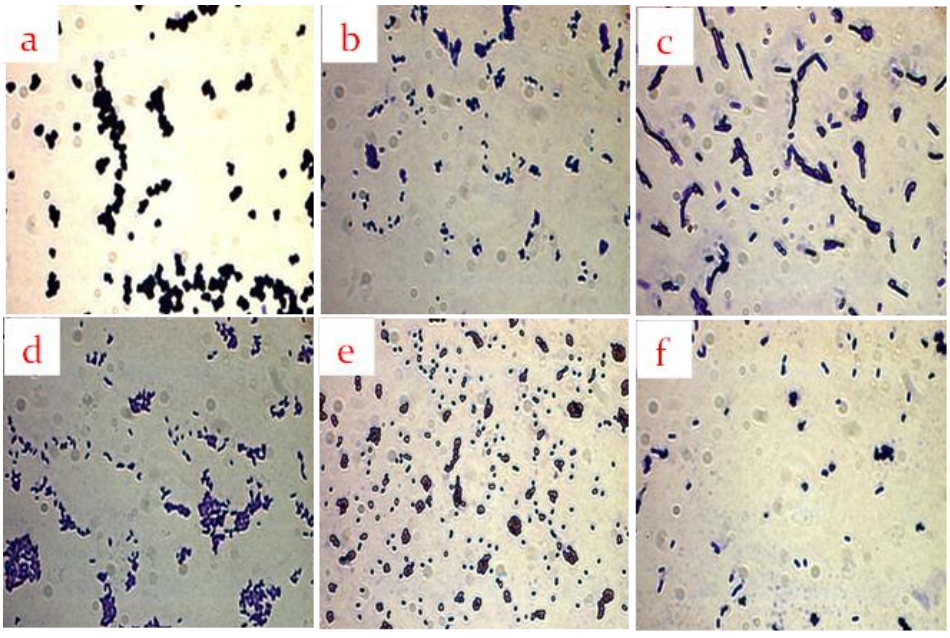

Fig. 4. Microscopic photos of identified Bacteria species at 1000× magnification: a. *Streptococcus spp.*, b. *Micrococcus luteus*, c. *Bacillus subtilis*, d. *Staphylococcus spp.*, e. *Kocuria turfanensis*, f. *Bacillus megaterium*

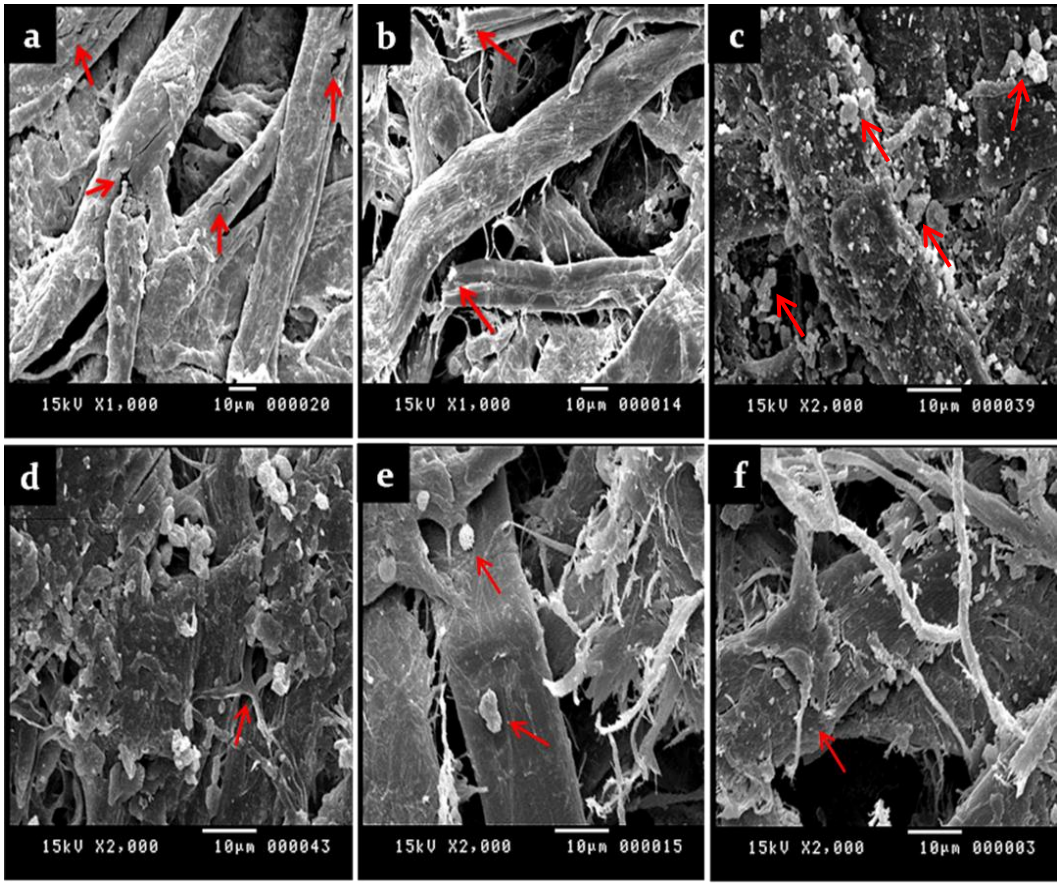

Fig. 5. SEM images of the historical plates show natural ageing effects on the cellulose fibers, (a) Cracks, (b) broken fibers, (c) Particles cover the surface of the paper fibers, (d, e) Spores and fungal hyphae cover the paper fibers, (f) Erosion on the surface of the fibers as result fungal contamination.

The crystallinity index of the cellulosic material has an influence on the strength of the material [49]. Thus, a low crystallinity index of the cellulose indicates a decrease in the strength of the paper, as a result of the degradation of cellulose [50]. Degradation of cellulose can destroy the strong intermolecular bonding, resulting in a change in the chemical structure of cellulose compound as well as the decrease in its crystallinity. Due to different natural degradation mechanisms such as oxidation, hydrolysis and photolysis, etc., the crystalline region of cellulose structure began to undergo chemical changes. Additionally, the destruction of the crystalline cellulose structure can be attributed to the destruction of hydrogen bonds between the cellulose chains. The breaking of the hydrogen bonds leads to the cleavage of glycosidic linkages that shortened chains, leading to the decrease of crystallinity [51]. In addition, the contamination of historical plates with fungi contributed significantly to the low crystallinity index of cellulose. As the fungi lead to the decomposition of cellulose through their enzymatic attack and secretion of acids and pigments as a result of their metabolic activity, leading to a decrease in the crystallinity of cellulose [52]. It is well known that the degradation pathways occur first in the amorphous phase of cellulose and only in the second stage, the crystalline phase is attacked [53]. Therefore, cellulose becomes increasingly amorphous with the gradual degradation of cellulose and the crystallinity index decreases [54].

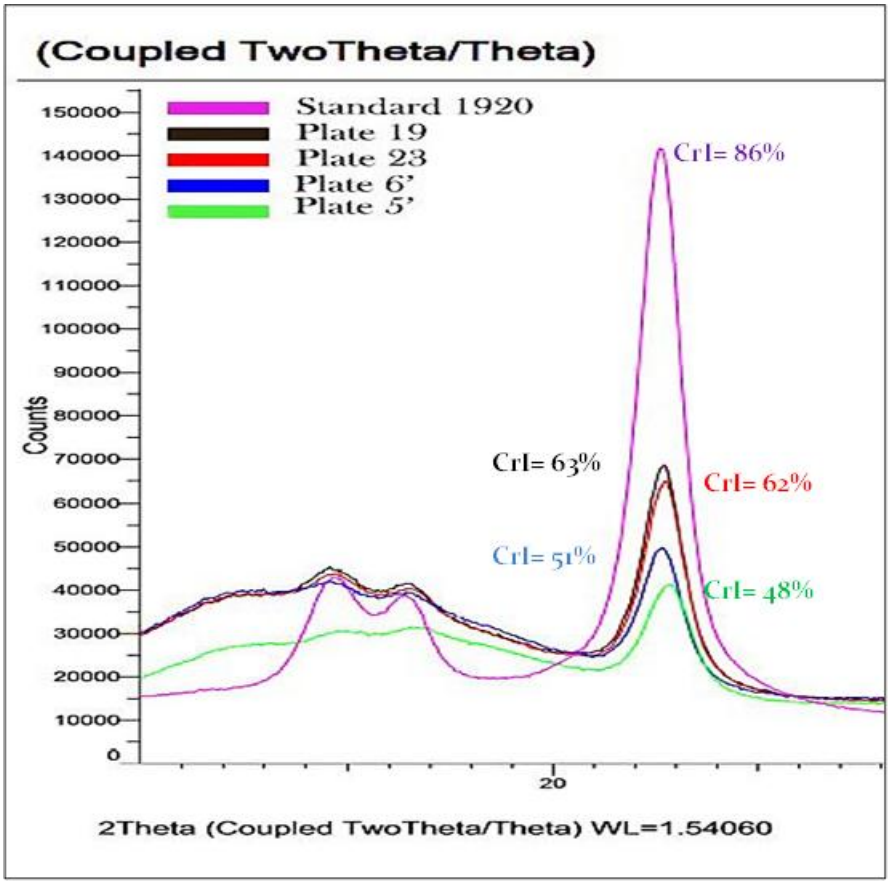

Fig. 6. Shows X-Ray diffraction analysis for determination of paper crystallinity for some historical plates compared to Whatman paper (1920s).

3.5. Color Change Measurements

The results obtained from the change of color measurement, are correspondant to the visual observations. The values of the L^*, a^*, and b^* color coordinates, in addition to the total color difference ΔE, between the browning and non-browning areas in the historical plates, which are shown in (Table 3) can be discussed as follows:

Lightness axis (L^* value): The results showed a significant decrease in the L* (Lightness) values for all samples, so as a result paper has become darker.

Red–green axis (a^* value): The results showed an increase in the (a^*) values for browning areas compared to the non-browning areas on paper, and consequently tends to be redder.

Yellow–blue axis (b^* value): The results showed a significant increase in the b* values for all studied plates, which corresponds to the visually observed yellowing. In comparison to the all studied plates, the changes in the values Δb^* were accompanied by significant changes in the ΔL^* values, corresponding to a more yellow but darker appearance.

Total color difference (ΔE): The results proved that the total color difference between browning and non-browning areas in the all historical studied plates, increased significantly, where their values on some plates exceeded 12.

Some natural changes in the coloration of paper can result from the physico-chemical transformations of their components on ageing [55]. This discoloration can be attributed

to the presence of chromophores found in some of the products formed from the degradation of one or more components of paper. Paper of historical plates is composed of cellulose, sizing agents, and pigments. The oxidative reaction of these components can produce colored degradation products containing carbonyl (C=O) groups [56].

Fungal growth is another cause of colorimetric alterations in paper. A fungus' staining activity is considered to be the result of the synthesis of pigments and/or from the Maillard reaction of by-products of the fungal metabolism such as organic acids, oligosaccharides and protein compounds, which react together chemically with the material under certain conditions. Therefore, produces brown products and oxidative reactions, possibly resulting in the production of melanoidin and the subsequent formation of foxing-type spots [55]. In addition, Gelatin sized papers have generally an accrued tendency to yellow upon aging. In general, metallic components or impurities (iron, copper, and aluminum) could trigger discoloration in paper or gelatin. In particular, alum enhances the discoloration of gelatin/alum sized papers upon aging [57]. Thus, the significant chromatic changes in the color of the paper, which appeared on most of the plates in the form of large brown spots or stains, resulted from a combination of destructive factors, including fungal growth, moisture, oxidation, etc.

3.6. ATR-FTIR Spectroscopy.

The results obtained from the ATR-FTIR spectrum (Fig. 7) of the historical paper samples compared to newer paper of the same type (Whatman paper dated back to the 1920), proved that the historical plates suffered from deterioration. The degradation of cellulose was determined by the appearance of the characteristic bands between (1710–1740 cm^{-1}) corresponding to the carbonyl groups (CO, CHO, and COOH), because one of the most obvious effects of the aging processes is the formation of the carbonyl groups in the cellulose chain, and thus the loss of paper strength [54].

The deterioration of cellulose results from both acid hydrolysis and the oxidation process together [40]. Acid hydrolysis causes chain scission of cellulose macromolecules and generates carbohydrates fragments. These fragments are oxidized to carboxylic acids, which generate an oxidation and hydrolysis cycle [58], thus causing autocatalytic degradation for paper [59]. In the acid hydrolysis process, hydroxyl groups in the actual cellulose structure are oxidized to carbonyl and/or carboxyl groups, weakening the glycosidic linkages in their vicinity [40]. As for oxidation of the cellulose polymer, it results in side groups of aldehydes and ketones, which make the molecule more easily hydrolyzed. As a result of this hydrolysis, hydrogen bonds are changed, which influences the bending vibrations of CCH, COH, OCH, and HCH [21].

The FTIR spectrum of historical samples can be explained in the following points:

- A decrease in the band intensity at 3335 cm^{-1} for historical samples compared to the newer sample was noticed. This band is considered a characteristic of the stretching vibration of the hydroxyl group (OH) in cellulose, and therefore the change in the intensity of this band could reflect the changes in the -OH environment and may vary due to the moisture content of the sample. Therefore, the decrease in the intensity of this band may be related to the acidity in historical samples [60, 61].
- A band appeared at 2363 cm^{-1} in historical samples. This band indicates the presence of, adsorbed carbon dioxide (CO_2) from the atmosphere. The increase in the intensity of absorption in this band in historical samples, could be due to the increased activity of paper surfaces to adsorb CO_2 from the environment during ageing [60, 62].
- Increasing absorption in the spectral region between 1800 and 1500 cm^{-1} in the historical samples was also noticed. This spectral region is considered a characteristic of the degradation products of aged cellulose, where the products of cellulose hydrolysis and partial oxidation appear in the form of various carbonyl groups [63-65]. The following observations were noticed:

a) The spectrum of historical samples, showed new peaks at approximately 1746 cm^{-1} and at 1718 cm^{-1} compared to the

control sample. The band at 1746 cm^{-1} is corresponding to the vibrations of various carbonyl group forms, specifically Carboxyl groups (–COOH) [63, 66, 67].

Table 3. Color change values of some plates paper (verso)

Plates No.	*Non-browning area in paper*			*browning area in paper*			*ΔE**
	L*	a*	b*	L*	a*	b*	
Plates from First set							
Plate 11	92.68	-1.01	16.32	87.52	4.08	25.04	11.34
Plate 23	92.69	-1.42	16.75	85.76	5.60	24.59	12.60
Plate 29	92.40	1.13	16.87	86.63	5.10	22.58	9.04
Plate 33	92.52	0.45	18.33	88.14	4.72	24.74	8.86
Plate 39	92.14	1.35	19.19	85.09	6.25	26.65	11.37
Plate 40	92.68	1.04	18.24	85.82	6.33	26.77	12.16
Plate 42	92.24	0.48	18.17	85.91	5.76	25.20	10.83
Plates from second set							
Plate 5	92.02	1.00	19.12	85.91	5.76	25.20	9.85
Plate 6	92.58	1.50	19.71	86.00	5.79	25.51	9.76

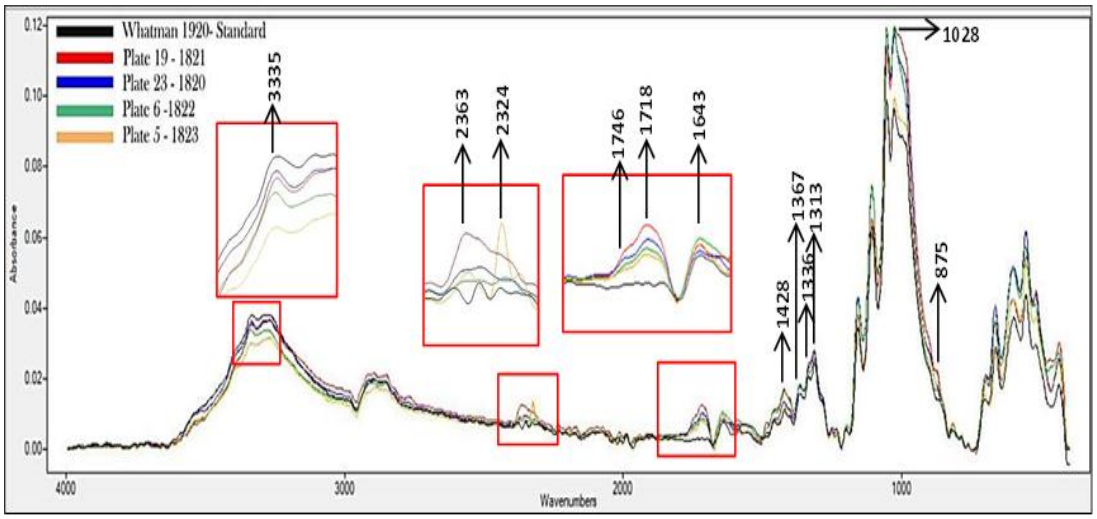

Fig. 7. ATR-FTIR spectrum of the historical samples compared with Whatman paper (1920s).

The absorption band at 1718 cm^{-1} is assigned to (–C=O) stretching vibration of aldehyde groups [68, 69]. All the possible oxidized functionalities appearing after the oxidation reaction (aldehyde, ketone, and carbonyl) absorb in a very narrow region of the spectrum, between 1700 and 1750 cm^{-1}. The carboxyl vibration at 1746 cm^{-1} representing the final oxidation stage of carbon atoms in glucopyranose rings, while carbonyl bands at 1718 cm^{-1} arise from the oxidation intermediates stage [69]. Increasing the intensity of absorption in this region can be assigned as arising from the hydrolysis of hemiacetal bonds, which may eventually generate aldehyde groups on opening the terminal rings [67].

b) The absorption band at 1643 cm^{-1} is commonly assigned to absorbed water (hydrogen-bonded). The increase in absorption of this band in the spectrum of historical samples, indicates an increase in the conjugate carbonyl groups (–CO) that were formed within them during aging [63, 66, 67, 70-72].

- Also, the absorption bands at 1428, 1367, 1336, 1316 and 1028 cm^{-1} belong to stretching and bending vibrations of -CH2 and -CH and -OH bonds in cellulose [61]. Small changes in the intensity of absorption are observed in the bands at 1428, 1336 and 1313 $cm^{-1,}$ due to the natural ageing of cellulose. The 1428 cm^{-1} band is due to H-C-H and O-C-H in-plane bending vibrations, while the 1336 and 1313 cm^{-1} band are due to C-O-H and H-C-C bending vibrations [73].
- Moreover, in all the spectra, it is clearly visible the presence of carbonates, whose bands are at 1428 and 875 cm^{-1} [14]. A broad peak at 1428 cm^{-1} includes -CH2 and CH bond vibrations coming from cellulose as well as the vibration of C = O bonds in the carbonate ion (CO_3^{2-}). The weak intensity peaks at 875 cm^{-1} also belong to C=O bonds in the carbonate anion [61]. These carbonates are found as a result of calcium oxide or calcium hydroxide, which was used in the manufacture of handmade paper. These materials are known to be effective in neutralizing the acidic products of the hydrolysis of paper [14, 74].

4. Conclusions

Fine art printed paper, has received a limited amount of attention in literature, discussing the diagnosis of the condition of paper-based objects; therefore, this study is significant. The historical printed plates in Atlas entitled "Plates illustrative of the researches and operations of G. Belzoni in Egypt" were selected for their historical value, since they are dated back to 1820 A.D. and, are associated with the discoveries of Giovanni Battista Belzoni in the tombs and temples of Luxor. This study proved that the studied historical plates suffered from deterioration, which was caused by the surrounding environmental conditions. The pH values of the historical plates ranged from 5.08 to 5.98. According to the SEM results, the fibers are shown to be damaged in some areas, due to natural aging. The fungi and bacteria isolated from historical plates were identified as *Aspergillus* spp., *Penicillium* sp., *Streptococcus*, *Micrococcus*, *Kocuria*, *Staphylococcus* and *Bacillus* spp. The surrounding environmental conditions of these historical printed plates, played an important role in the growth of fungi and bacteria. XRD results showed a decrease in the crystallinity index of the cellulose in the historical plates compared to the newer papers of the same type, as a result of the deterioration process. ATR-FTIR results of the paper of the historical plates proved that the deterioration mechanism by hydrolysis or oxidation processes, caused changes in the cellulose molecules. And finally, it is imperative to determine the condition of the object in order to choose the appropriate treatment.

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