Achieve Authenticity Using Scanning Electron Microscopy and Infrared Analysis, Applied on an Islamic Book.

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Abstract

The process of falsifying old documents and manuscripts of questionable authenticity is a significant problem in the field of forgery. The aim of this study is to reduce forgery and fakes in a scientific and secure manner. To achieve this; it is necessary to understand and study the compounds involved in distinguishing between old paper and modern paper using techniques such as Fourier transform infrared spectroscopy and scanning electron microscopy **(FTIR and SEM)**. Initially, **SEM** is used to identify the surface of the sample and compare it with both old and forged samples. This helps to observe the differences and determine if there are any time-based characteristics specific to the samples. One advantage of using **SEM** is that it requires minimal processing, except in the case of powder samples, where the soft material tends to aggregate to reduce its chemical energy. Secondly, **FTIR** is used to study the internal compounds of the samples and track the time factor's impact on the functional groups. The results clearly demonstrate a distinction between the fake samples and the original ones. This difference becomes apparent through the analyses and examinations conducted. For example, **SEM** reveals the presence of dust and other particles that are not visible to the naked eye in the applied samples due to the accumulation of dust over time. On the other hand, **FTIR** analysis demonstrates the presence of alkane groups responsible for energy storage, which explains the tendency of old paper to burn more quickly. Additionally, the group responsible for the presence of gelatin in the original samples only appears due to past manufacturing techniques. Lastly, the group responsible for carbonyl appears in old paper due to its complete drying process after losing a hydrogen atom, unlike modern forged paper. As a result of this study, we want to establish the idea of detecting forgery with easy-to-apply scientific evidence.

Keywords

Manuscripts, Fake, Forgery, Authenticity, FTIR, SEM.

1. Introduction

In previous studies; Ultraviolet and infrared radiation **(UV & IR)** were used in examining forged manuscripts by revealing the hidden layers after photographing them using infrared or ultraviolet photography [Julio.M.-2016, Noshi W.-2020]. As for our study, we used the scanning electron microscope to generate a current of high energy electronics from (0.5: 40) kV. So, the current clashed

with the sample, the sample image reflected clearly and accurately up to (10) nm. Thus, the electronic microscope features that the samples do not need much of the processing except in the case of the powder sample that is the soft material in a state of agglomeration to reduce its chemical energy. So, this problem can be solved by adding some acetone to the sample to reduce its energy without aggregation. As the scanning electron microscope is used to picturing the structure of the sample with a clear and high magnification [Gambaro. A.-2009, Othman, E.-2014]. So, the analysis by **(SEM)** helped to distinguish between the original and fake manuscript by studying the dating of the manuscript and the technology of the pulp industry. So, the comparison is between the image of the used compounds historically with the image of the Samples to be examined. As for Fourier transforms infrared spectroscopy **(FTIR),** is a non-destructive method [Bicchieri.M.-2013]. It is used to illustrate the chemical properties of manuscript and document surfaces. It analyzes a sample of 1-4 cm. **FTIR** is also used to identify functional groups of cellulose in each sample and to detect the vibration and dysfunction of functional groups [Liang C. Y. -2009]. These differences help to discriminate natural and industrial or fabricated aging. As well as to determine the chemical composition of the additives during the preparation of the pulp for each sample paper. Besides, it also distinguishes between the paper by identifying the raw materials used and the additives in the industry paper which determines the method of making the pulp, if it is from the chemical or quasi-chemical pulp [Doumenq. P.-2015, Puică, N-2006].

2. Materials and Methods

2.1. Historical Samples

Manuscript of the Islamic era named **(Al-Hawi Lilmsael Al-Nfais)**, written by **(Refaa Al-Tahtawi and Mostafa Al-Zrabi)**. Located at a Special library in upper Egypt. Manuscript dimensions are **(24x 19 cm)** 288 pages. The binder is made of textile which is dyed in green color. The manuscript relates to three-piece sutures, has no tongue and printed with black ink by **(Dar- Al-Tebaa)** dating **(1865 AD)** *(fig: 1)*.

Figure 1. *Applied Manuscript of the Islamic era.*

2.2. Experimental Samples

2.2.1. Analysis (SEM + ED-X) of the Applied Sample

The analysis and examination *(figures :2,3,4)* were done, to do the corresponding experimental samples by the laboratory of the Egyptian General Authority for Mineral Resources in the Ministry of Petroleum and the characterization of the scanner electron microscopy used as follows: (Model Quanta 250 FEG + ED X Unit with accelerating Voltage 30 K.V. magnification14x, and up to 100000 resolution)

Figure 2. *A place of a sample of an applied manuscript by circle red color.*

Examine and analyze the manuscript paper using (SEM + ED-X):

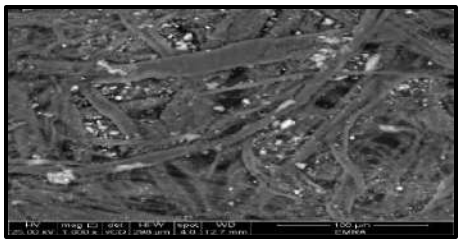

Figure 3. *Paper under 100x*

The fibers used are cotton fibers.

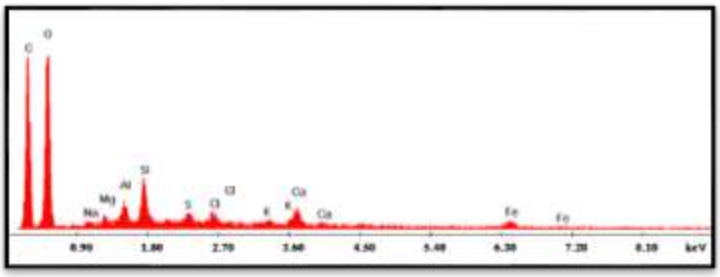

Figure 4. *The analysis of the manuscript paper using (ED-X) The components of cellulose are shown next to the elements of the additives (S, Al, Si) with the presence of (Na, Fe).*

2.2.2. Paper Samples

Based on the examination and analysis of the applied manuscript, it was discovered that the paper pulp consisted of cotton in addition to the additive materials used in the pulp, namely rosin, kaolin, gypsum, and gelatin. [Derrick. M.-1999]. The samples were prepared by hand mill to soften the ingredients and remove the undesirable materials *(fig:5)*, (90% cotton, 10% additives) [Wahba. W.-2017].

Figure 5. *The experimental samples were prepared based on the analysis and tests of the applied manuscript by " Rakta" Company in Alexandria.*

2.2.3. The Aging of Paper

Thermal ageing of the experimental samples was *(fig :6)* under 90 ° C for 500 hours in the presence of a source of moisture and based on the scientific specifications of the measurements (TAPPI T 453) [Zervos. S.-2010] with a 90 ° pattern for 72 hours equal to 25 years old. Using a Thermal oven was (Nabertherm – Model L N31 P) in the laboratory of the Department of Conservation - Faculty of Fine Arts - Minya University. So, the sample is analyzed after every 100 hours by FTIR & SEM components to choose the appropriate sample to compare [Borrego. S.-2016, Thompson. J. M.-2012].

Figure 6. *The experimental samples after aging.*

2.2.4. Experiment for Authenticity

It has been done by devices for authenticity **(Scanning Electron Microscope, SEM)** in the laboratory of the Egyptian General Authority for Mineral Resources in the Ministry of Petroleum, Fourier transform infrared spectroscopy, **(FTIR)** Device in analysis laboratory of precision in the sector of Archaeological projects in Cairo.

3. Results

3.1. Analysis using Fourier transform infrared spectroscopy (*FTIR).*

3.1.1. Analysis of Aging Experimental Samples Using Fourier Transform Infrared Spectroscopy (FTIR).

An experimental aging sample analyzed by Fourier transform infrared spectroscopy **FTIR** after every **(100 hours)** five times to select the nearest to the applied manuscript. So, the five experimental aging samples have been compared (**sample every 100 hours)** with the experimental sample before the aging and the differences between them were monitored.

First step: Comparison of the five experimental aging samples **(sample every 100 hours)**: A comparison of five aging samples at **(100/200/300/400/400/500 hours)** was conducted to monitor the differences between the five samples to select the best. The second step compares them with the experimental and applied samples using **FTIR** *(fig: 7-12)*.

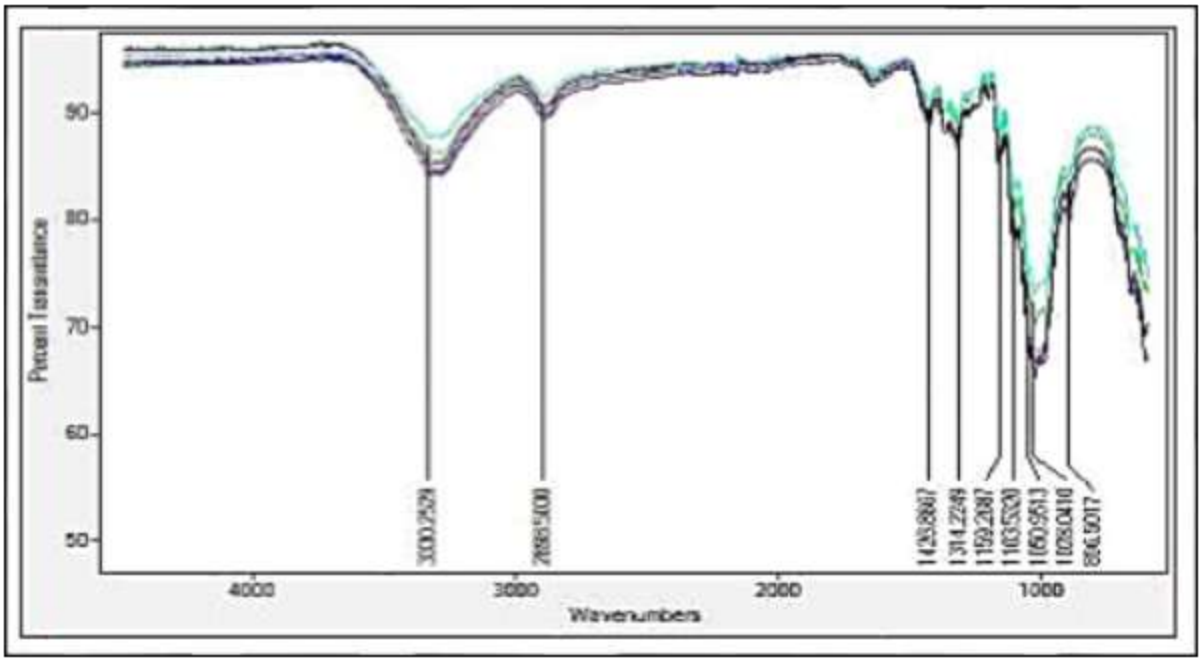

Figure 7. *The analysis pattern is illustrated using FTIR Transmittance and comparison of the five samples.*

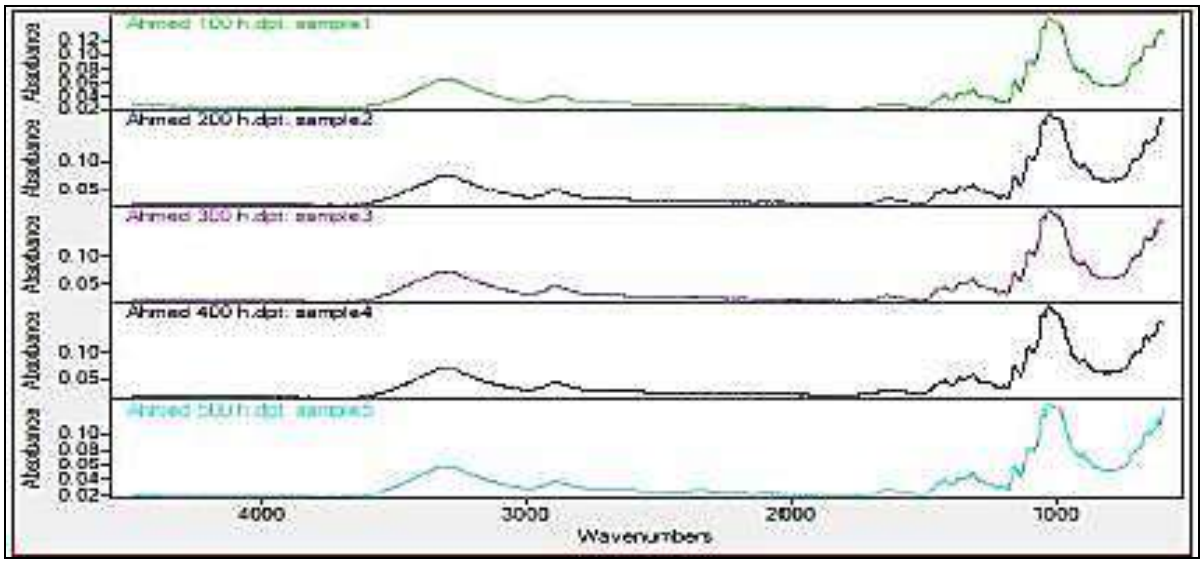

Figure 8. *The pattern of analysis is illustrated using FTIR Absorbance and comparison of the five samples.*

Note, there is no significant difference between the five samples so indicating that the heat does not affect experimental paper compounds. The fifth sample was the most aging sample and therefore it was used in the following comparisons.

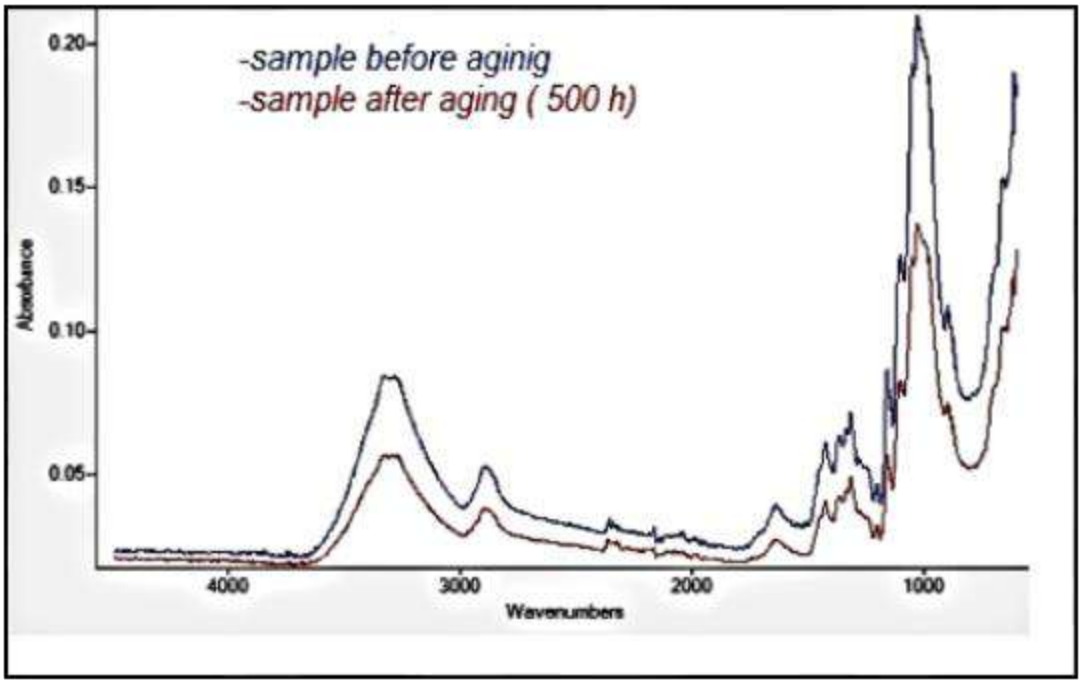

Figure 9. *The applied sample, the experimental sample after the aging (500 h) and the experimental before the aging using FTIR.*

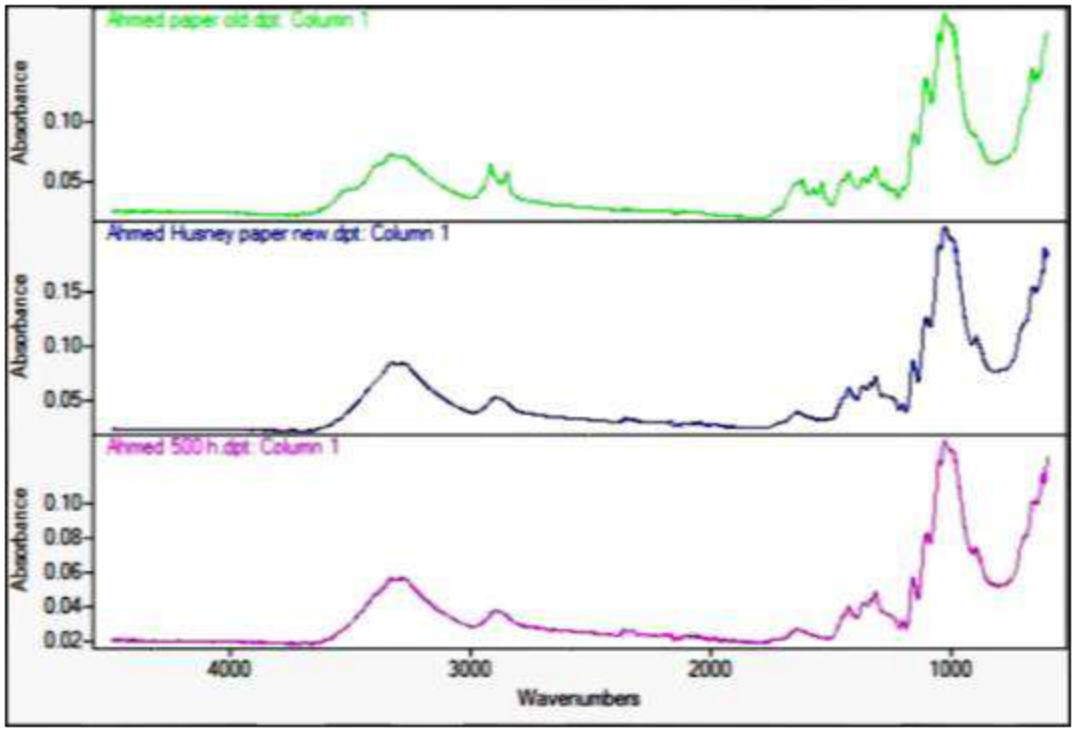

Figure 10. *Pattern analysis is illustrated using FTIR Absorbance, Comparison of the experimental sample prior to aging.*
and the experimental sample after aging.

After comparing the experimental sample before the aging and the experimental sample after the aging within **500** hours, it became clear that the difference between them is nonexistent and negligible *(fig 9)*. As for the comparison explained between the experimental samples before, and after the aging **(500 h)** and the applied sample with the functional groups, there is no significant difference between the experimental sample before the aging and the experimental sample after

the aging **(500 h)**, but the difference was between applied sample and both of samples before & after aging *(fig10)*.

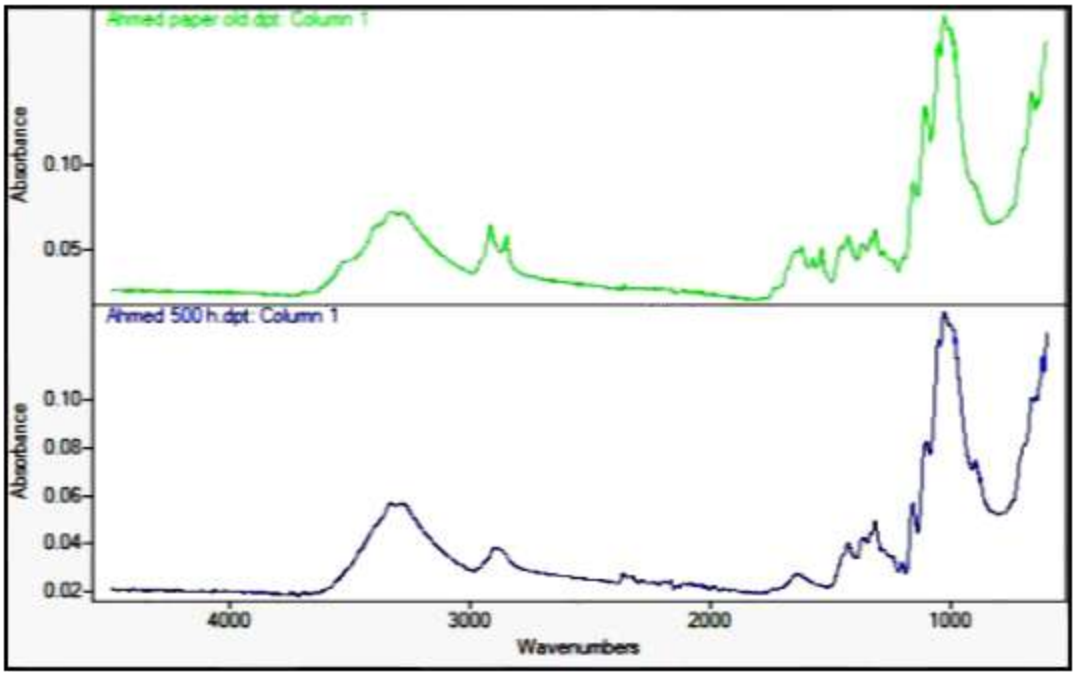

Figure 11. *Applied Sample and Experimental Sample After aging (500 h) Using FTIR.*

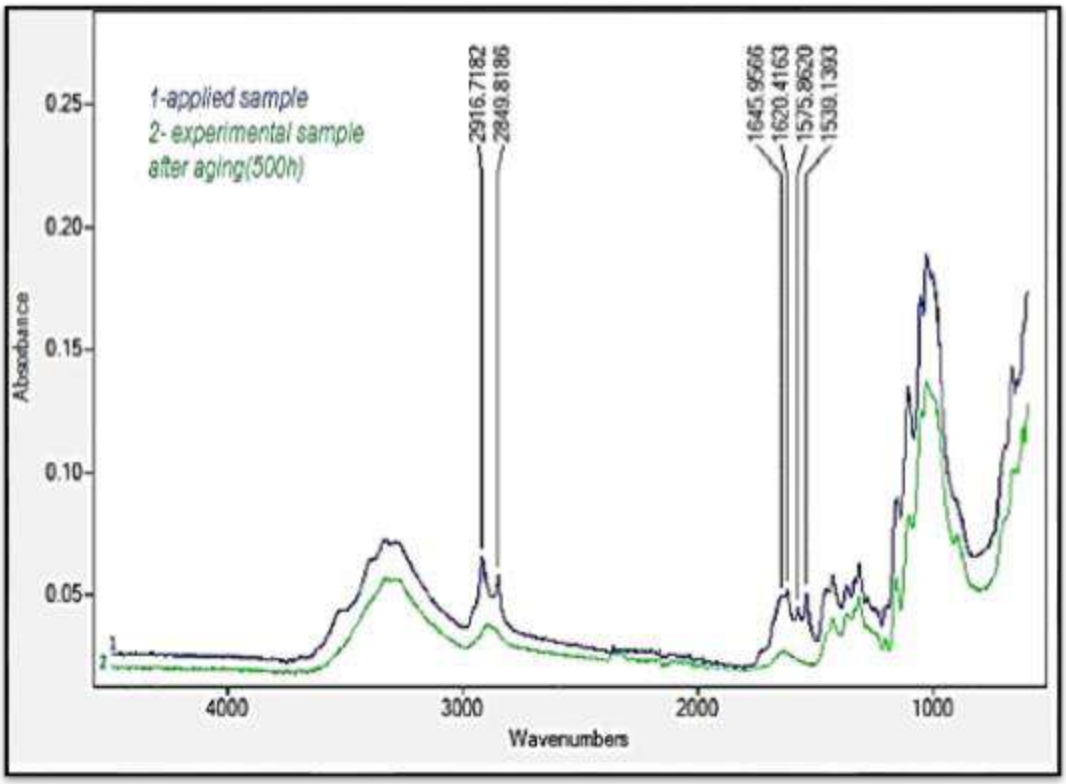

Figure 12. *The applied sample and the experimental sample after the aging (500 h) using FTIR.*

3.1.2. The Comparison

Showed the following differences in the applied sample *(fig 11,12):*

a- Appearance of:

- The group of (C-CH3) at (2916 Cm-1)

This group represents the group of hydrocarbons **(alkanes)** especially **(methyl)** which is responsible for storing energy in the old paper and this explains the speed of ignition of old paper.
b- Appearance of:
- (C-C) group at (1620 Cm^{-1}).
- (C-N-H) group at (1575 Cm^{-1}).
- (C-H) group at (1539 Cm^{-1}), (2889 Cm^{-1}) [7].

These gelatin groups which appeared more densely in the applied sample than the experimental sample were due to the less developed industrial method as well as the treatments for the gelatin ore in the applied sample which made it retain its density.
c- Appearance of:
-The carbonyl group (C = O) at (1645 Cm^{-1})
It is a component of cellulose, and it is noted that there is a double bond of the carbonyl group which appeared only in the applied sample.

3.2. Examine Using Scanning Electron Microscopy (SEM)

The comparison showed that the applied fibers of the manuscript are spread by the dust grains that are diffused and cause the white spots along the fibers. This is not found in the experimental sample *(fig :13,14)* [Hajji. L-2015].

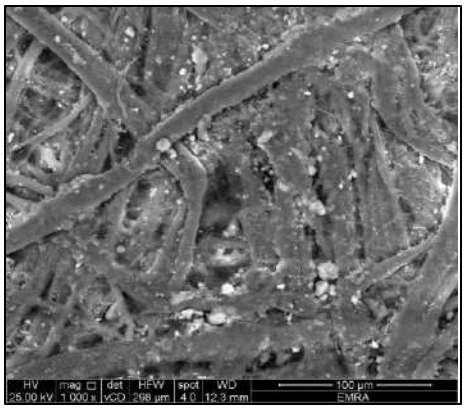

Figure 13. *Applied sample under (SEM) 1000 x.*

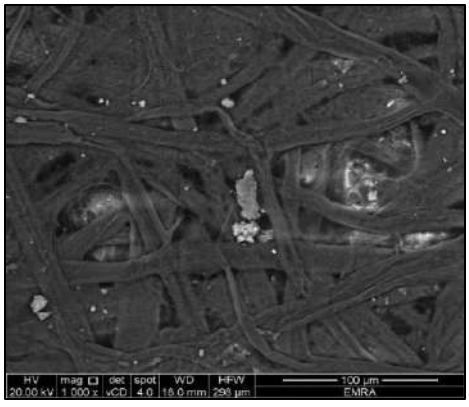

Figure 14. *Experimental sample under (SEM) 1000 x.*

4. Discussion

4.1. Comparison of Surface Appearance Using (SEM) of the Applied Sample and the Experimental Sample:

It is noticed from the comparison between the modern experimental sample and the original old sample that there are clear differences that were accurately recorded by the used device. The differences were in clear physical phenomena such as the reason for the appearance of dust in the

old sample, as well as the reason for the appearance of a group of alkanes in the old sample and not appearing in the modern sample. These differences have been monitored and the phenomena explained in the following tables (table 1 and table 2) for ease and clarification.

Table 1. *Comparison of surface appearance using (SEM) of the applied sample and the experimental sample.*

	Applied Sample	Experimental Sample	Interpretation
SEM	The applied fibre is permeated by the dust particles that are permeable and cause white spots scattered all over the surface of the applied manuscript.	There is no dust and granules.	The manuscript was exposed for a long time to dust, which enabled it to penetrate.

4.2. Comparison of Functional Groups Using FTIR for the Applied Sample and the Experimental Sample

Table 2. *Comparison of surface appearance using (FTIR) of the applied sample Paper and the experimental sample Paper.*

Functional Groups	Applied Manuscript	Experimental Sample	Interpretation
C-CH3	Appear	Do not appear	This group represents hydrocarbons that appear over time (alkanes), especially methyl, which is responsible for storing energy in the old paper and this explains the speed of ignition of old paper.
C-C C-N-H C-H	Appear	Do not appear	These gelatine groups, which appeared more densely in the applied sample than the experimental sample, were due to the less developed industrial method as well as the treatments for the gelatine ore in the applied sample, which made it retain its density.
C=O	Appear	Do not appear	It is considered a component of cellulose, it is noted that there is a double bond of the carbonyl group, which appears only in the applied sample, whose hydroxyl content (OH) has been dehydrated. The hydrogen (H) is moving, and the oxygen atom (O) is bound to the bond with the naturally occurring carbonyl (CO) In

			cellulose, the bond became binary (C = O).

5. Conclusion

The scanning electron microscopy **(SEM)** examination showed that the applied sample paper and experimental sample paper have a clear difference in the penetration of dust in the fibers of the manuscript paper. The Fourier Transform Infrared Spectroscopy **FTIR** analysis showed differences in the appearance of functional groups such as alkenes and functional groups representing gelatin. As well as the emergence of the carbonyl group in the old sample due to complete dehydration which did not occur in the modern sample. Finally, both of FTIR & SEM were important tools to detect forgery and fakeness.

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