





Research Article

Characterization of Two Historical Postage Stamps Made from Cotton Fibers and Their Restoration Trials Based on the Experimental Studies

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Ancient stamps are suffering from the destructive effects of different kinds of inks that were prepared from different ingredients. Two Egyptian historical postage stamps printed in blue and red printing inks were evaluated and examined for their composition using a light microscope, SEM-EDS, FTIR, and Raman spectroscopic analyses. Mechanical, chemical, and deacidification treatments were done for the two stamps. Model stamps were made from the cotton pulp in the book house to simulate historical stamp paper with an average thickness of 11 microns. The unprinted and printed paper samples with printing inks that aged and unaged were treated with 0.7% Klucel G, 0.2% TiO₂ NP, or a mixture of 0.7% Klucel G + 0.2% TiO₂ NP, and the color change was measured and compared with the blank samples. The two stamps are suffering from high pH, where the margin color of the stamps changed to yellow-brown with weakness of the stamp paper. By SEM examination, stamps have suffered from fibers' weakness and dryness resulting from the self-oxidation reactions. EDS elemental composition of the red stamp showed the presence of C, O, Na, Al, Si, Mg, S, Ca, Ba, and Fe, while in the blue stamp, it was C, O, Na, Al, Si, P, S, Cl, and Ca. Raman spectrometer wavelengths turn out that the blueprinting ink of the stamp was characterized with spectra of ultramarine blue (lazurite), while hematite was characterized by the red stamp. FTIR analysis for the printing inks identified that gum Arabic sample and linseed oil were the binding and color medium, respectively. From the model trials, it was observed that the treatment of a mixture of Klucel G and TiO₂ NP had the best properties for the consolidation of stamps. The two historical stamps were documented through different spectroscopic analyses, and from the restoration trials, it was observed that the mixture of 7% Klucel G + 0.2% TiO₂ NP appeared to be a new and effective method for recovering the historical postage stamps.

1. Introduction

Libraries and archives include historical objects such as manuscripts, documents, and ancient envelopes with their stamps suffering from damage resulting from the destructive

effects of different kinds of ink that were prepared from different ingredients [1–4], causing acidic hydrolysis and catalyzed oxidation of cellulose [5–8]. It is very important to determine the chemical component of the inks of historical paper objects for possible development of an effective

method for conservation [9–11]. Subsequently, the paper should be reserved in safe conditions to avoid the acidity [12, 13].

Inks used for printing basically consist of a carrier medium (e.g., water, solvent, or oil), binder (resin), and colorant agent (pigment or dyestuff) [14]. These compositions can be inedited using different spectroscopic analyses, such as Raman spectroscopy, SEM-EDS, XRD, and FTIR [3, 15–17].

Several consolidation materials have been recommended to be used for consolidation of archaeological objects or paper sheets, such as hydroxypropyl cellulose (Klucel G), chitosan or Paraloid B-72 combined with nanoparticles (NPs) from Ag, ZnO, or cellulose [18–21], chitosan [22], or using nanocomposite materials [23–25]. Consolidation and protection of stamps are a general and comprehensive expression that indicates the restoration of natural properties, resistance to damage factors, and the stabilization of the surrounding conditions for the stability of the state of the paper.

Deacidification process of historical paper can be achieved by using different materials such as $\text{Ca}(\text{OH})_2$ in the form particles or NPs [26, 27], $\text{Mg}(\text{OH})_2$ NPs [28], mass deacidification [29–31], or by natural plant extracts [7]. The success of the deacidification process does not depend only on the composition of the solution used, but on the application method used as well, as the pH rise of the paper depends on the homogeneous and good distribution of the alkali granules in the internal composition of the paper fibers [32].

This process aims to stabilize the state of the stamp paper and improve its mechanical properties, while leaving an appropriate alkaline precipitate in the stamp material to offset any future acidity resulting from air pollution, oxidation, or decomposition of stamp compounds [33], but the alkaline percentage should not exceed the limit. Excess alkalinity may lead to a change in some colors and has a destructive effect on paper fibers [34], as the medium acidity environment (pH 6) is an encouraging factor for fungal growth, which then raises the acidity of the paper to a higher degree. According to TAPP standard T529, the optimum pH values for paper are 6.5–8.5 [35]. Studies have shown that cellulose is unstable and susceptible to damage when pH = 5.5–6, and that the paper's durability and its good condition is linked to a pH higher than 7.5 and an alkaline reserve of at least 2% [36].

Therefore, this study aimed to provide description and documentation of two Egyptian historical postage stamps using several spectroscopic analyses and possible conservation methods based on the model experimental study.

2. Materials and Methods

2.1. Description, Documentation, and Registration of the Egyptian Stamps. The first Egyptian stamp (Arabic and French in languages) with a value category of five-tenths of piaster (5 m) dates back to 1888 AD, with red printing ink (Figure 1(a)). The stamp was designed at the Egyptian Mail press and issued by Delray Press, England, as a fifth edition

made from cotton fibers. This edition is known to have been used for 26 years, the longest period of any previous or later Egyptian edition. The thickness of the stamp paper (Figure 1(b)) was measured ($11\ \mu\text{m}$) in order to choose the thickness of the paper suitable for various repairs and conservations.

The red postage stamp was drawn and formed as follows: in the center of one of the pyramids and the right of the pyramid from the bottom of the head of the sphinx in an oval frame and on the edges decoration surrounded by all directions, outside the frame of the left stamp (five-tenths of the piaster_5-5) (cinq millièmes) and below (postes Egyptiennes_5-5) within the oval and top (Egyptian post) within the oval frame. The dimension of the stamp is $2.5 \times 2\ \text{cm}$, with the margin serration size of 14. The watermark was designed as a crescent in the middle of a star [37, 38] during preparation of the paper pulp (Figure 1(c)).

The second Egyptian stamp was printed in blue color (Arabic and French in languages)—category 1 piaster—and the year of issuance was 1884 AD (Figure 1(d)). The designer is post office with the fourth edition, when four denominations of the fourth group stamps were reprinted in 1879 AD, Del Rey Press, England. The stamp dimensions was $2.5 \times 2\ \text{cm}$ and thickness was $11\ \mu\text{m}$ (Figure 1(e)) with the margin serration size of 14. The postage stamp was drawn and shaped as follows: in the center is one of the pyramids, and to the right of the pyramid is the Sphinx, in an oval frame and on its edges is surrounded by decoration from all directions. From outside the frame written (Egyptian Post—One piaster) POSTES EGYPTIENNES-UNE PIASTRE-1-1-1-1. The watermark is also designed as a crescent moon with a star in the middle, during the paper pulp preparation (Figure 1(f)).

2.2. Photographic Registration and Visual Documentation. The stamps were photographed to show the general conditions of what they were before the process of treatment and restoration. Also, to document the manifestations of damage to the nature such as cuttings, fragments, and missing parts as well as characterization during the restoration process and after completion.

2.3. Examination and Analysis

2.3.1. Optical Microscope. The stamp samples were examined using (Leica EZ4) Stereo Microscope and Canon EOS 4000D/Rebel T 100 Digital SLR Camera.

2.3.2. ESEM-EDX Measurements. Stamps' surfaces were examined using an environmental scanning electron microscope with energy-dispersive spectroscopy ESEM-EDS (Quanta FEG250, with tungsten electron source, at 20 KV) [39]. The shape and weakness of fibers as well as the distribution of binding medium were observed by ESEM. Different spots from the stamps were chosen for the analysis by ESEM-EDS. The relative proportion of elements distribution was recorded.

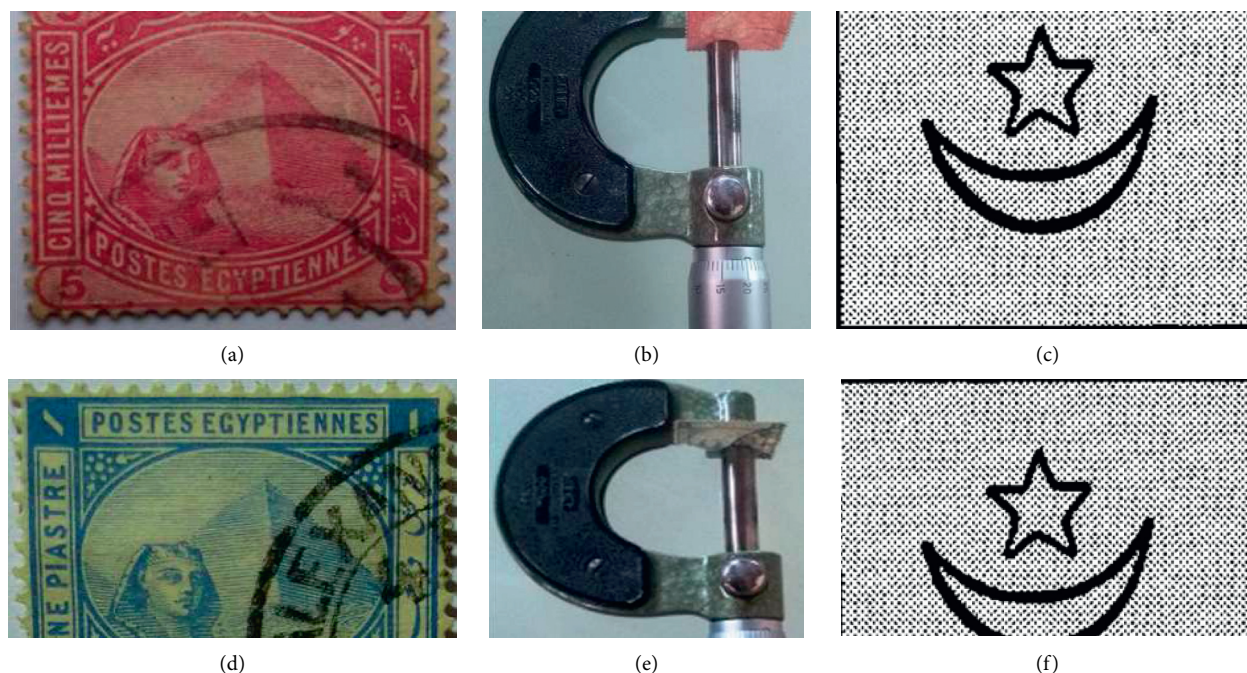


FIGURE 1: The stamp form. Red color and shape (a), blue color and shape (d), measurement of the stamp thickness (b, e), and the stamp watermark (c, f).

2.3.3. pH Measurement of Stamps. The pH value of the stamp papers was measured using flat electrode-pH meter, a direct nondestructive method, where a drop of distilled water is placed on the surface of the stamp, the acidity of the surface paper is dissolved in the water drop, and the flattening instrument is placed on the drop [40]. The device is given a direct reading from different places of the surface of the stamp, and the average readings were recorded.

2.3.4. Raman Spectroscopy. This technique is considered one of the nondestructive techniques used in the study of colored materials, in which a laser beam with a length of between 2 and 8 μ passes through the microscope, and is focused on the grains of the colored material of the sample. By measuring the scattering caused by monochromatic light when it falls on the sample, we can identify the organic and inorganic materials by referring to research and scientific references. Raman spectra of the pigments were collected using Senterra spectrometer (Bruker, Type Senterra Ex Laser 1064 nm) coupled to a confocal Raman spectroscopy (20x–100x objective lens), operating at near-IR laser diode emitting at 785 nm. The average spectral resolution in the Raman shift range of 100–2000 cm^{-1} was 4 cm^{-1} . The spectral compounds were identified by comparing them to reference spectra [11, 15, 41].

2.3.5. FTIR Spectroscopy Analysis. The IR spectra of identifying the adhesive and the printing media linseed oil and gum Arabic samples were measured using Nicolet 380 (FTIR) spectrometer mode having a zinc selenide crystal, in the range of wavelength 600–4200 cm^{-1} . The IR absorbance frequencies for the samples under test were recorded with an

average of 128 scans using a resolution of approximately 4 cm^{-1} [11].

2.4. Manufacturing of Model Stamp and Treatments

2.4.1. Materials and Tools Used for Preparing the Experimental Samples. Paper samples were made from cotton pulp in the book house to simulate stamp paper with an average thickness of 11 micron. Pebeo brand oil color as printing ink was used. For red printing ink, hematite (Fe_2O_3) was used. While for blue printing ink, ultramarine blue ($\text{SiO}_2\text{Al}_2\text{O}_3\text{Na}_2\text{OS}$) was used. Linseed oil as a medium for printing ink was used. Some tools such as rubber cladding, rubber roller to straighten the ink, and a piece of glass to spread the ink on it were used.

2.4.2. Preparation of Unprinted and Printed Paper Samples with Printing Inks. The unprinted paper samples made from the cotton pulp paper made in Dar al-Kutub, Cairo, Egypt, were cut into 6 cm \times 6 cm. The prepared printed paper samples with cotton pulp paper were printed with 2 different colored materials, blue and red, as shown in Figures 2(a) and 2(b), respectively, by the (cliché or rubber cladding) typograph, in which linseed oil was used as a chromatic medium, as the results of the analysis showed. However, due to the lack of homogeneity in the eclectic editions, a rubber roll was used to spread the ink on the glass plate, and then the same rubber roll was used to print the paper, as it gave a homogeneously printed rectangular area of 6 cm \times 6 cm, which was cut after drying into 18 pieces of 2 cm \times 2 cm to be used in experimental works.

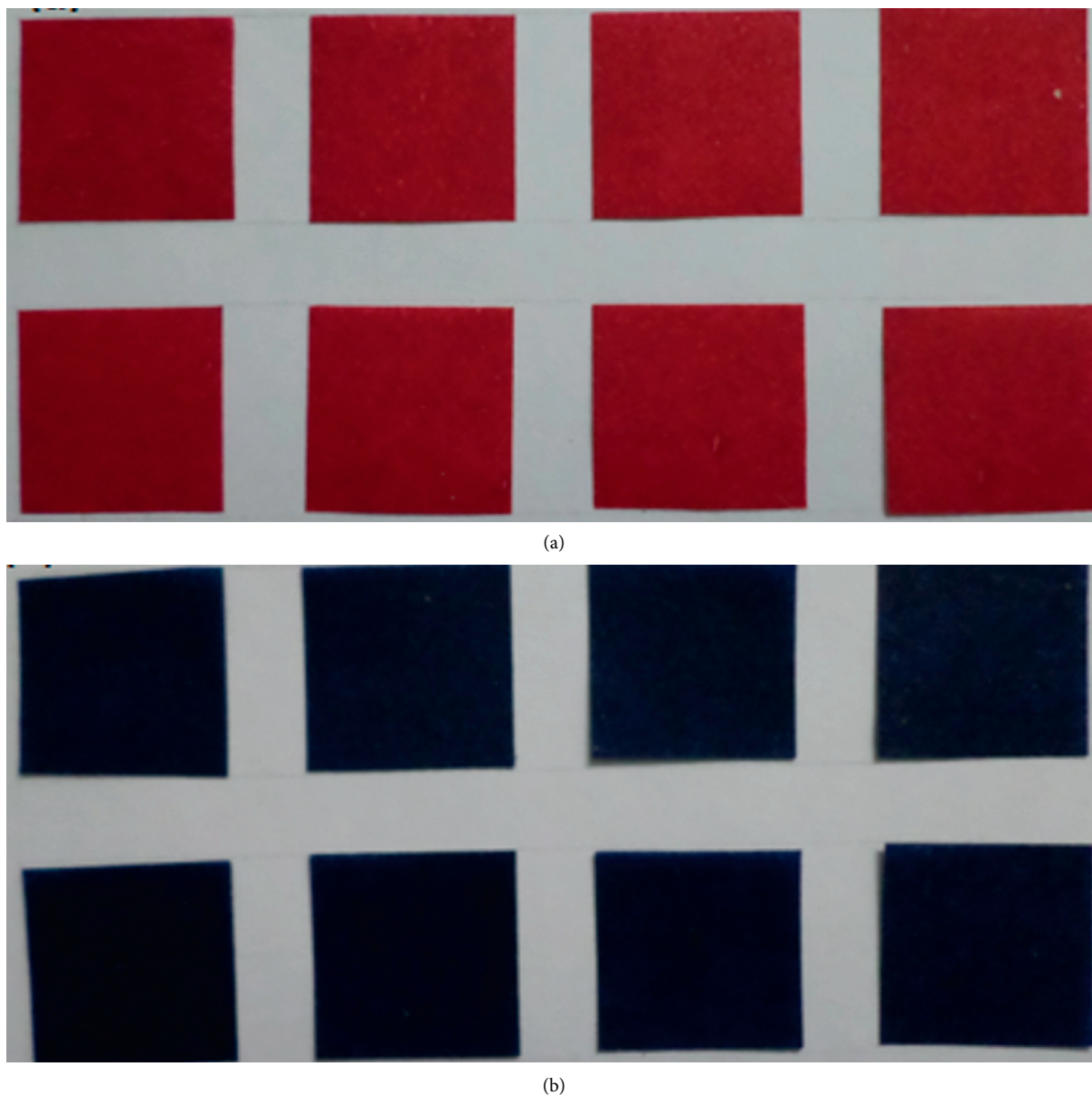


FIGURE 2: The samples printed with red printing ink (a) and with blue printing ink (b).

2.4.3. Consolidation, Strengthening, and Protection of Experimental Postage Stamps. Hydroxypropyl cellulose (Klucel G, CTS Srl, Altavilla Vicentina, Italy) and TiO_2 nanoparticle (NP) (Aldrich, Darmstadt, Germany) were chosen as consolidates. The effectiveness of Klucel G was used to strengthen and enhance the durability of postage stamp papers and its role in improving the mechanical properties of paper and improving the optical properties of ink, while TiO_2 NP was used to insulate postage stamps and protect them from ultraviolet rays, irreversible damage, photofading, and color fading. Also, these materials were studied for their effects on stamp colors.

Klucel G solution was prepared at 0.7%, and this was done by dissolving 0.7 g of Klucel G in 100 mL ethanol. TiO_2 NP solution was prepared at 0.2% by dispersing 0.5 g of TiO_2

in 250 mL ethanol using an ultrasonic device for 5 min [42]. Also, the mixture of them was used, where 0.2% TiO_2 NP solution was dispersed in 0.7% Klucel G solution. Application of consolidation, strengthening, and protection materials to experimental samples that mimic the composition of postage stamps were processed by immersion in the treatment solution for 5 min.

All paper samples were divided into the following groups: first group: unprinted samples that have not been subjected to ageing (UPUA); second group: unprinted samples that have been subjected to photoaging (UPPA); third group: printed samples that have not been aged (PUA); fourth group: printed samples that have been aged (PA). All paper group samples were treated as shown in Table 1.

TABLE 1: Treatments used for the four paper samples.

Blank samples	Treatment		
	0.7% Klucel G	0.2% TiO ₂ NP	Mixture of 0.7% Klucel G + 0.2% TiO ₂ NP
UPUA	UPUA	UPUA	UPUA
UPPA	UPPA	UPPA	UPPA
PUA	PUA	PUA	PUA
PA	PA	PA	PA

2.4.4. Light Exposure for the Ageing Test. All untreated and treated paper samples were subjected to photoaging, in which a light fastness tester-Microscal Ltd, England, was used. This device contains 2 UV lamp 40 W, for 250 h at a temperature of $20 \pm 2^\circ\text{C}$, and a relative humidity of $50 \pm 5\%$ so that the samples were placed at an appropriate distance from the light source. It was observed that the color of all paper samples changed to darkening and yellowing, especially the untreated paper sample.

2.4.5. Measurement of Optical Properties. To evaluate the effect of treatment materials on the color change of printed and unprinted paper samples, the values of brightness, whiteness, and yellowness were set for all treated and untreated samples before and after photoaging using (HunterLab LabScan 600 spectrophotometer, version 3.0; Hunter Associates Laboratory Inc., Reston, VA, USA), and the color change (ΔE) was measured using the following formula [43–46]:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}, \quad (1)$$

where $(\Delta L)^2$, $(\Delta a)^2$, and $(\Delta b)^2$ are the differences between the values of the color indices before and after ageing for all treatments and compared to blank samples.

2.5. Conservation Procedure for the Historical Stamps

2.5.1. Mechanical Cleaning. The dust and dirt deposited in the front and back sides of the stamps were cleaned using different types of soft brushes with natural hair; then, the brushes, spatula, and scalpels were used to remove the outstanding sticks and dirt (Figure S1).

2.5.2. Chemical Cleaning. First, the stamp was separated from the paper part that was affixed to it, which became clear from the examination that it suffers from a very high pH. The separation process was carried out using warm water and ethyl alcohol at a ratio of 1 : 3. From the back of the stamp, blunt brushes were gently used without damaging the stamp (Figure S2).

To remove and clean the stains that remained after mechanical cleaning, distilled water and ethyl alcohol were used after testing their effect on the inks, which gave good results, taking into account that water was not used on the back of the stamp to preserve the original glue of the stamp, and the use of organic solutions and solvents in cleaning operations in case of necessity and on a small scale.

2.5.3. Deacidification of Stamps. The method of immersion of the stamp in the alkaline solution was used for 5 min, until the reaction between the alkali and acids in the stamp was neutralized, leaving an alkaline precipitate of $\text{Ca}(\text{OH})_2$ NP to act as a pH regulator inside the fibers if acidity occurred in the future (Figure S3). Then, the stamp was lifted from the treatment solution and left to filter in the air after treatment, and the calcium hydroxide was converted into calcium carbonate during the interaction with atmospheric carbon dioxide, and before it completely dried, it was placed between blotting papers and pressed under a press to straighten it and dry it well. It was found that this method gave a homogeneous treatment and gave the treated paper a good resistance to resist future deterioration factors [47].

2.6. Manual Restoration for Consolidation and Protection of Stamps. To stick the torn parts and assemble the separated parts and assemble the separated parts, the manual restoration process was carried out using the optical restoration table and magnifying lenses, where the pieces were restored using Japanese paper (9 g) and HPC (0.7%) with the use of thermal spatula as a source of heat necessary for the gluing process. The edges of the torn parts were glued with a brush, and the repair paper was fixed on it using Klucel G; then, the rest of the repair paper was removed.

This stage was carried out based on the results of the experimental study and the recommendation for using TiO₂ NP as a protective coating for preserving paper artworks [42], where the process of strengthening and isolation was carried out together by immersion in a composite mixture of a solution of TiO₂ NP (0.2%) and HPC (0.7%) in ethanol for 10 sec and then filtered, and before the completion of the drying process, the process of drying was carried out. The paper was placed between two sheets of polyethylene and pressed for a day under a hydraulic press to straighten the stamp and give it a smooth and homogeneous shape. The nonaqueous method was used to remove the nonaqueous deacidification of the stamp paper to avoid the difficulties resulting from water treatments. Although the stamp is printed with printing inks that are not affected by water, the adhesive substance on the back of the stamp represented by gum Arabic is affected by water, and this method does not affect the printing inks [27], where the alkaline solution was prepared with a concentration of 0.05% of $\text{Ca}(\text{OH})_2$ NP, which was prepared immediately before use by adding 0.05 g of the substance in 100 mL of

methyl alcohol, and the solution was prepared by dissolving it on a warm water bath and the dissolution continued for a long time and then the mix was filtered until the solution is ready for use, after which the clear solution is used.

3. Results and Discussion

3.1. Visual and Optical Microscope Observations of the Stamp. For the visual observation (Figure S4), after examining the stamps, they turned out that they were suffering from high pH, as evidenced by the change of paper color (margin) to yellow-brown, in addition to the very weakness of the stamp paper. Also, the stamp is suffering from yellowness and brittleness in the papers, presence of dust, presence of water and fungi spots, and erosion at the ends of the stamp (serrated margins).

By sign of the light microscope and at magnification 10X (Figures 3 and 4) and 50X (Figures 5 and 6), paper tearing, weakness of the outer part (serrated margins), and breaks of the fiber were observed.

3.2. pH Measurement. The readings were taken for different points on the surface of the stamp. The average pH values 5 and 6 were measured for red and blue stamps, respectively. These readings indicate that the acidity of the stamp paper is not high at a high rate, and this may be due to the fact that the stamp contains a high percentage of alkaline CaCO_3 added to the paper core, as a filler during the manufacturing process [48–51]. This reading indicates that the paper has the average acidity due to the poor preservation and also because the paper contains a percentage of the additives, causing acid damage to the stamp paper ($\text{Al}_2(\text{SO}_4)(3 \times 18 \text{H}_2\text{O})$). In the final stages of the paper industry, these additives considered to be one of the main sources of acidity due to partial or total degradation [52–54], where it was used as a crystalline stabilizer in the process of volatilization on cellulose fibers [55, 56]. The chlorine residues in paper used to whiten the old rags interact with the similarity to form hydrochloric acid, resulting in the acidity of the paper [57–60].

3.3. EDX Analysis. Elemental analysis of the stamps with the EDX unit was done to identify the paper components and the red and blue printing inks (Figure 7).

From the first spot of front side of red stamp (Figure 7(a)), the presence of elements carbon, oxygen, sodium, aluminum, silica, magnesium, sulfur, carbonate, calcium, and iron was shown. In the second spot of front side (Figure 7(b)), the elements of carbon, oxygen, iron, aluminum, silica, sulfur, calcium, and barium were found. In the back side (Figure 7(c)), the following elements were identified: carbon, oxygen, sodium, silica, potassium, sulfur, chloride, and calcium. From the red stamp, the colored material for the red printing ink is likely to be mars red synthetic iron(III) oxide (hematite) Fe_2O_3 due to the presence of iron and oxide elements.

At the beginning of the 19th century, barium on the form of BaSO_4 , an inorganic pigment, was used as colorant material for the stamps; also in some cases, its presence beside calcium and iron was found to identify the white areas of several stamps [16].

From the first spot of blue stamp, the front side showed the presence of elements C, O, Na, Al, Si, P, S, Cl, and Ca (Figure 7(d)). In the second spot, the elements of C, O, Na, Al, Si, P, S, and Ca were found (Figure 7(e)). In the back side (Figure 7(f)), the following elements were identified: C, O, Na, Al, Si, and Ca. The colored material for the blue printing ink is likely to be ultramarine blue (lazurite) $\text{SiO}_2\text{Al}_2\text{O}_3\text{Na}_2\text{OS}$ due to the presence of elements Si, Al, Na, and S in different proportions [61–65].

The presence of Cl is likely used as a bleaching agent for the paper pulp from which the stamp paper is made by the chemical method [66–68]. The presence of Na suggests the use of NaOH in the manufacture of paper [69, 70]. The presence of Al and Si, which is likely to use kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) as a filler during the paper industry [71–73]. Also, the presence of Ca in a high percentage indicates the use of CaCO_3 as a filler during the paper industry [71–73], as a result of the use of chalky paper in the manufacture of that period. Additionally, Ca-C-O-rich phase (e.g., CaCO_3) that appeared to be a binder for the other particulate [74]. P and Al were presented, which suggests the use of AlPO_4 to adjust the pH value of the printing ink [75].

3.4. SEM Examination of Stamp Samples. The scanning electron microscopy (SEM) of red stamp was done on the studied stamp made from the cotton fiber. SEM images with different magnification showed a barium-sulfur-rich phase (Figure 8), probably BaSO_4 —white [16].

Previously, a barium-sulfur-oxygen-rich phase (BaSO_4) was identified in an incant stamp; also the presence of aluminum-silicon-oxygen-rich phase was suggested as a mineral filler [74].

The SEM examination showed that the red stamp suffers from weakness and dryness of the fibers involved in the composition of the paper resulting from the self-oxidation reactions [76]. Photos in Figure 9 show how the red stamp is suffering from severe damage in printing ink (Figures 9(a) and 9(b)) and fiber breakage with the presence of some fungal infections and the damage and cracks caused in the colored layer and inks (Figures 9(c)–9(e)). Furthermore, the shape of the red stamp with cotton fibers and their interlocked is shown in Figure 9(f).

The blue stamp was photographed with SEM to identify the type of fibers was made of cotton fibers (Figure 10(a)). It was also used to know the damage caused to the layer of colors and inks from deterioration and cracks. Through examination, it was found that it suffers from severe damage, breakage of the fibers and the presence of some fungal infections through the growth of fungal spores (Figures 10(b)–10(d)). Also, calcium-carbon-oxygen-rich phase (calcium carbonate) appeared to be a binder for the other particulates [74].

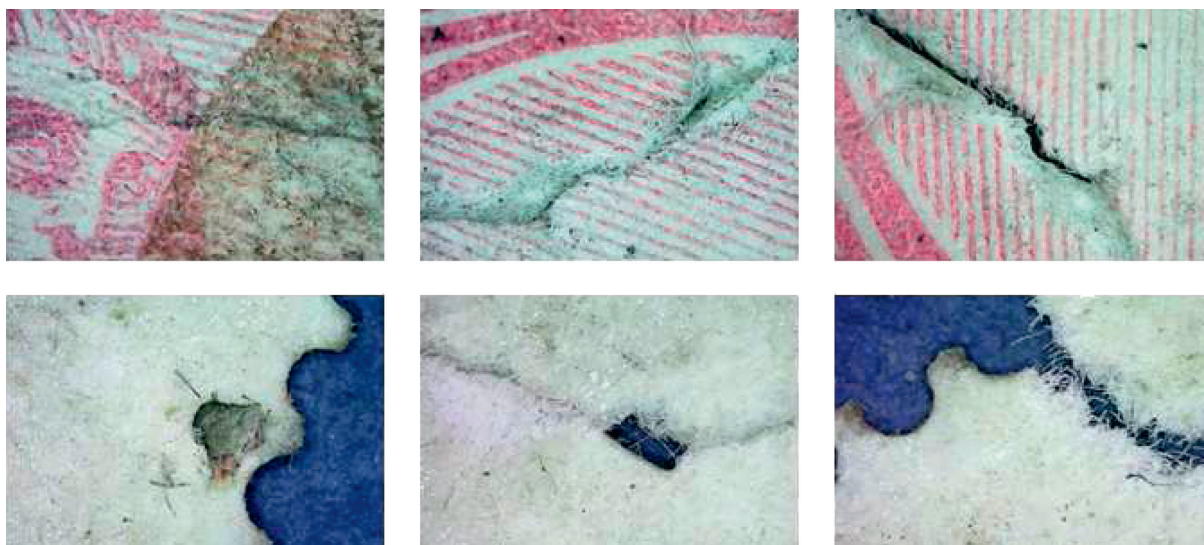


FIGURE 3: Various tears and spots on the red stamp and the weakness of the outer part (serrated margins) at 10X.

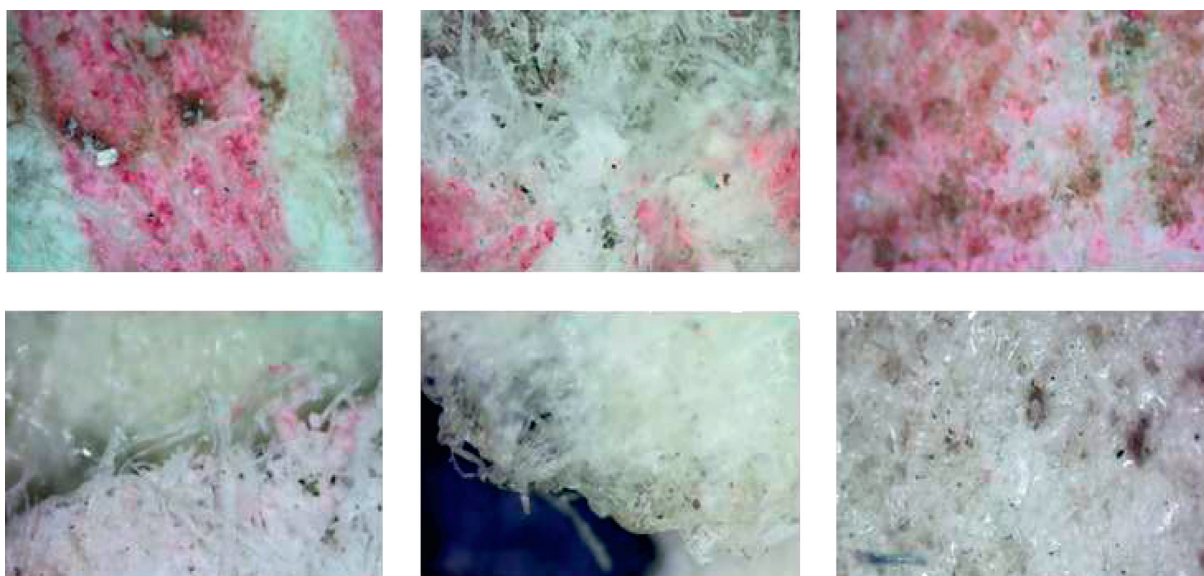


FIGURE 4: Various tears and spots on the blue stamp and the weakness of the outer part (serrated margins) at 10X.

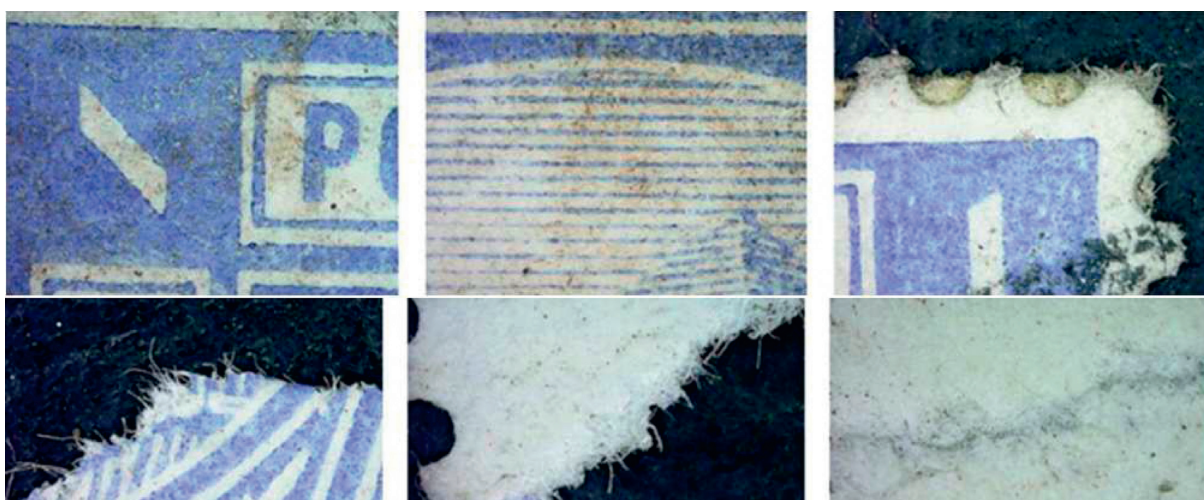


FIGURE 5: Various defects in red stamp fibers at 50X.

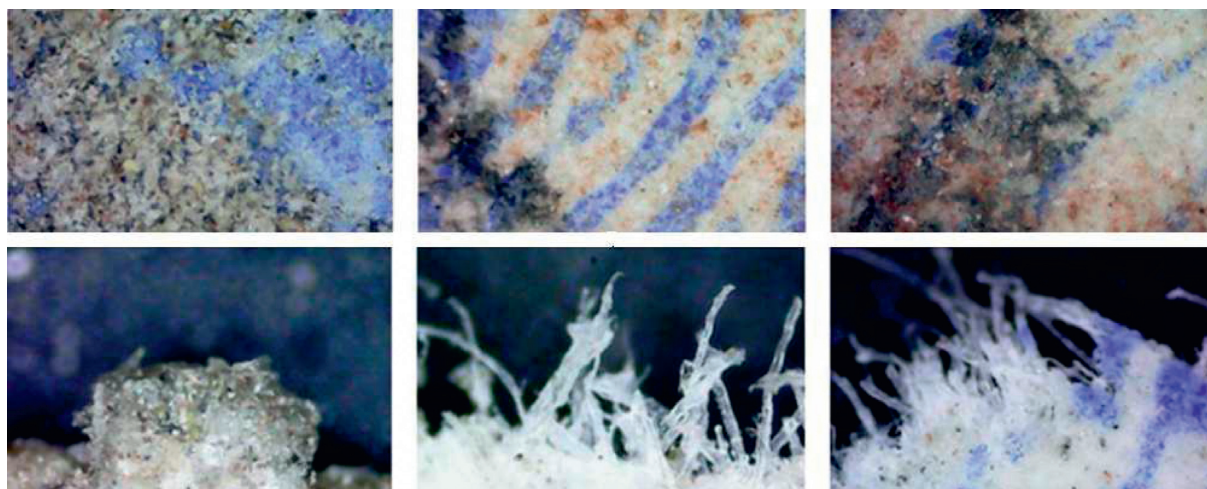
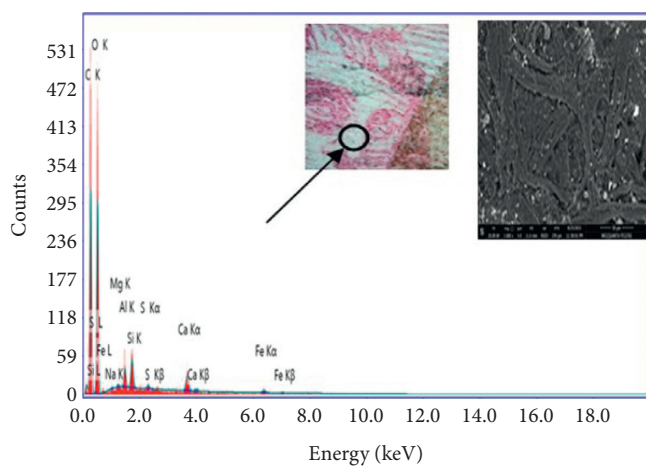
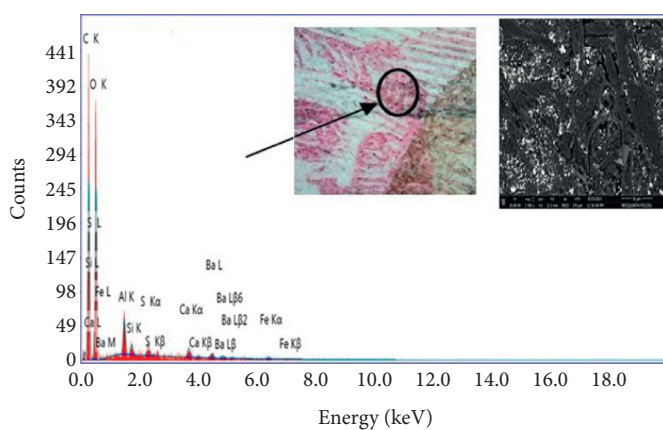


FIGURE 6: Various tears and spots on the blue stamp and the weakness of the outer part (serrated margins) at 50X.



Element	Weight%	%	Net Int.
C	46.23	45.62	152.55
O	48.54	43.05	152.1
Na	0.3	0.18	2.16
Mg	0.24	0.14	3.35
Al	1.03	0.54	18
Si	1.38	0.7	28.14
S	0.19	0.08	3.59
Ca	1.53	0.54	19.37
Fe	0.58	0.15	3.35

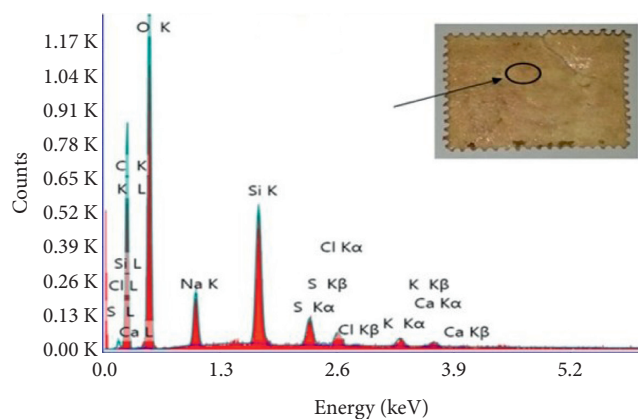
(a)



Element	Weight%	%	Net Int.
C	46.11	55.02	124.28
O	47	42.67	126.45
Al	2.05	1.09	29.63
Si	0.52	0.27	8.72
S	0.73	0.33	11.72
Ca	0.98	0.35	10.44
BaL	1.5	0.16	4.78
Fe	0.48	0.12	2.33

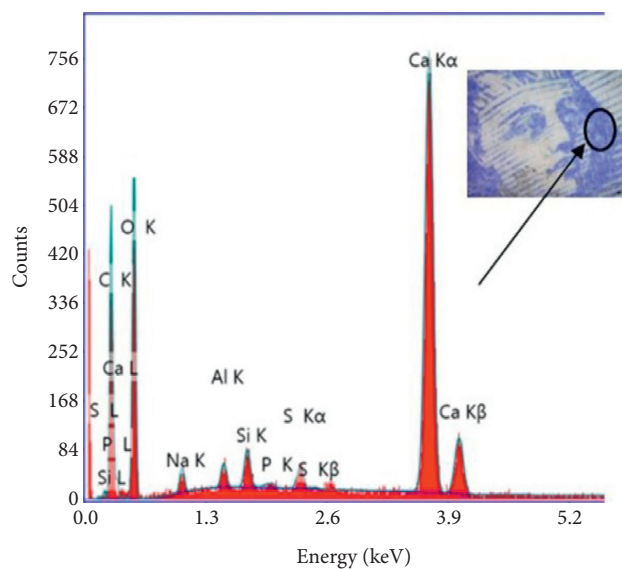
(b)

FIGURE 7: Continued.



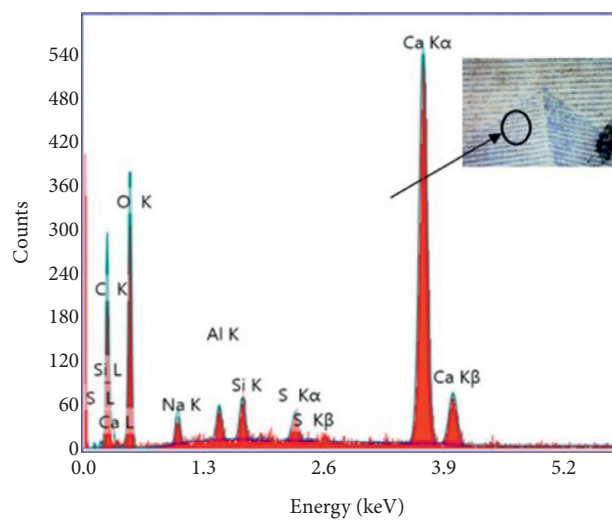
Element	Weight%	%	Net Int.
C	37.58	46.82	25.98
O	48.9	45.74	54.92
Na	4.77	3.11	11.62
Si	5.63	3	36.47
S	1.36	0.64	8.02
Cl	0.78	0.33	4.26
K	0.58	0.22	2.71
Ca	0.4	0.15	1.59

(c)



Element	Weight%	%	Net Int.
C	23.34	34.57	15.1
O	45.47	50.57	23.26
Na	1.6	1.24	2.38
Al	0.8	0.53	2.93
Si	1.08	0.69	4.8
P	0.16	0.09	0.62
S	0.75	0.42	3.3
Ca	26.81	11.9	77.95

(d)



Element	Weight%	%	Net Int.
C	20.56	31.31	8.52
O	44.95	51.4	15.91
Na	2.53	2.01	2.61
Al	1.27	0.86	3.21
Si	1.39	0.91	4.21
S	1.15	0.66	3.48
Ca	28.15	12.85	56.55

(e)

FIGURE 7: Continued.

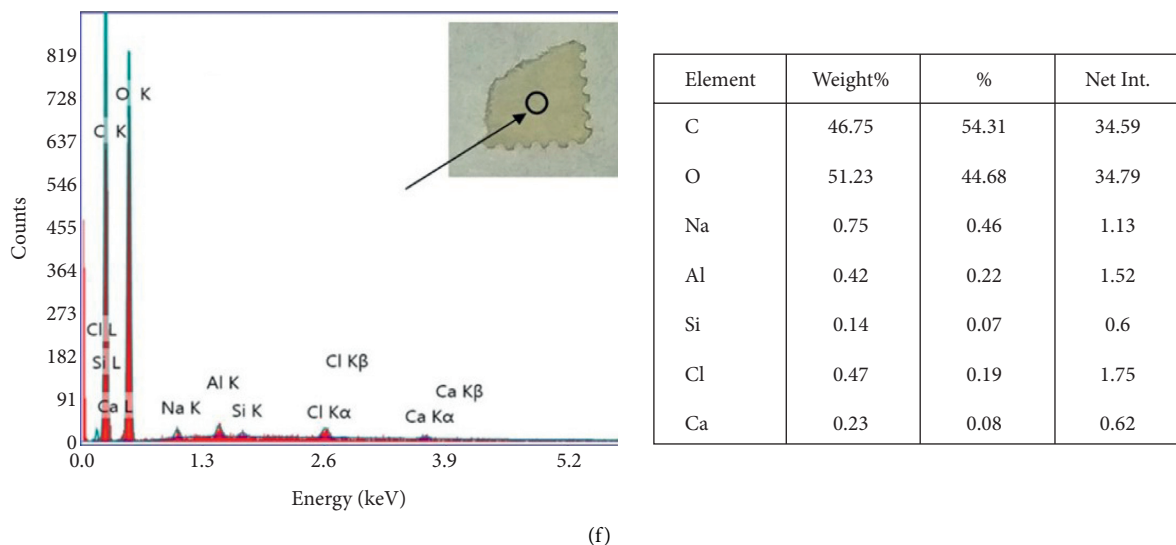


FIGURE 7: EDX analysis of stamp surface (front and back sides). Measurement of two spots from the stamp front side ((a, b) from red stamp, (d, e) from blue stamp) and one spot from the back side ((c) from red stamp; (f) from blue stamp).

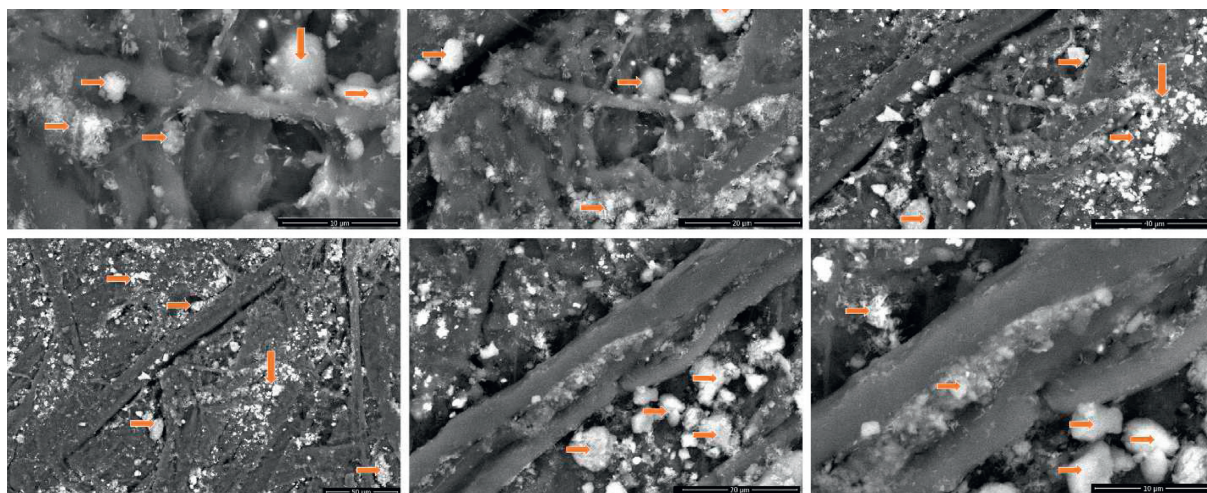


FIGURE 8: SEM images showing the distribution of barium sulfate (BaSO_4 —white).

3.5. Raman Spectral Analysis. By studying the wavelengths of the reflections of the Raman spectroscopy (Figure 11(a)) and comparing them with the reference samples of blue stamp [15], it turns out that they are the characteristic spectra of each of ultramarine blue, which is likely to be used as a blue printing ink for the stamp, CaCO_3 , and kaolinite, which are likely to be used as a filler during the manufacture of stamp paper, while linseed oil is likely to be used as a medium for printing ink (Table 2) [77].

Raman spectra for blue stamp (Table 2) showed spectrum at 548 cm^{-1} , which reflected to Al and assigned to lazurite and 713 cm^{-1} for Ca, which assigned to calcite, also, 396 cm^{-1} for Na and 390.5 cm^{-1} for Si [78]. Bands at 1086, 713, 283, and

156 cm^{-1} are referring to the presence of calcite in natural pigments [78]. Characteristic band at $\sim 547\text{ cm}^{-1}$ by Raman spectroscopy showed the presence of ultramarine [79].

From the studied wavelengths of Raman spectroscopy of red stamp samples and their comparison with the reference samples (Table 3 and Figure 11(b)), iron(III) oxide (hematite) or $\alpha\text{-Fe}_2\text{O}_3$ was characterized for the red color [15]. The Raman bands appear at 225, 245, 290–300, and 412 cm^{-1} are attributed to the hematite based on the characteristic spectral features of the Fe–O group located at $630\text{--}430\text{ cm}^{-1}$ and appeared at 498 and 614 cm^{-1} [80, 81]. A band with maximum at 1079 cm^{-1} , strong and broad, most probably belongs to Si–Al–O asymmetric stretching vibration of ultramarine [82].

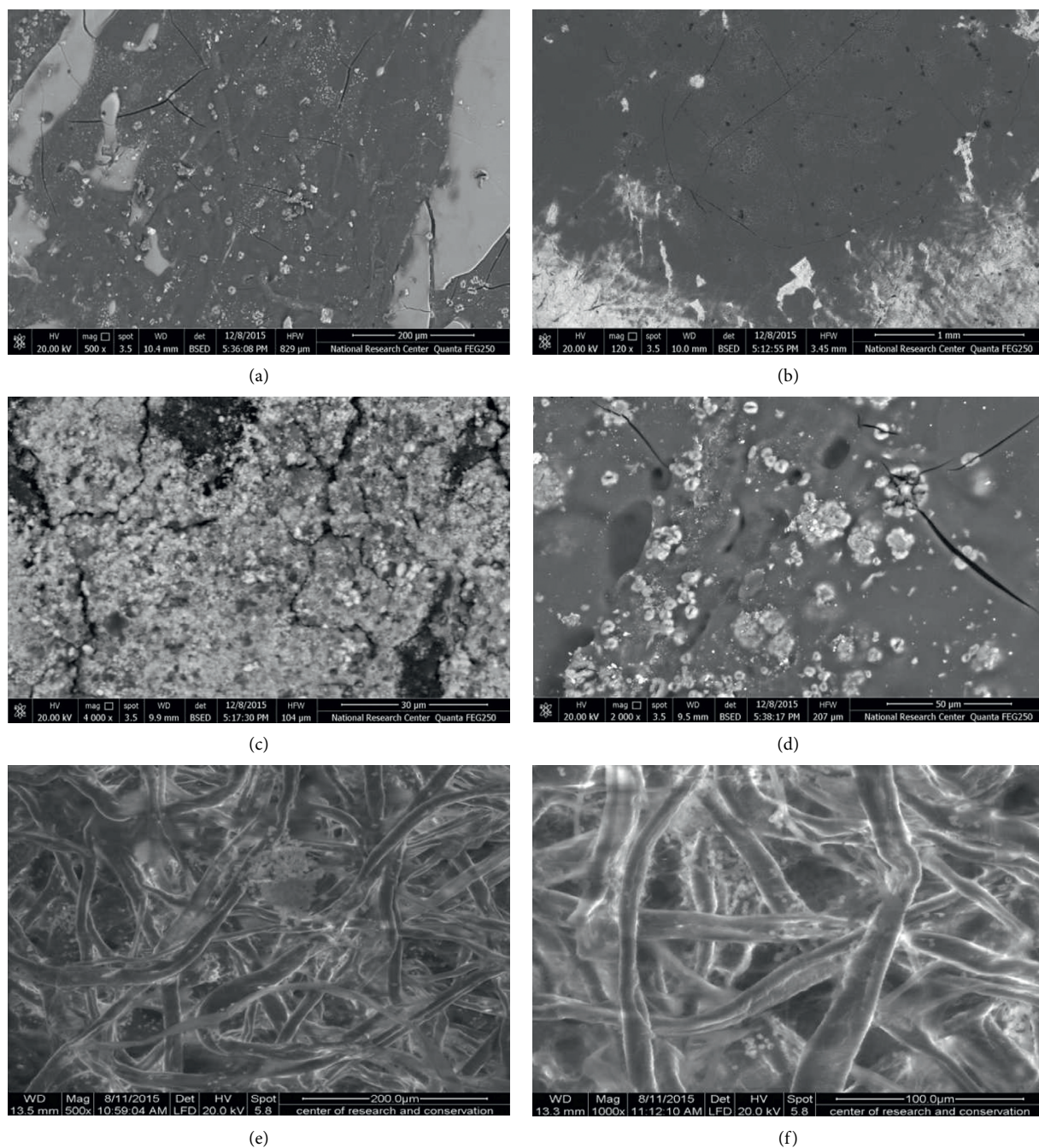


FIGURE 9: The cracks in the printing ink layer of red stamp at 500X magnification power (a). The printing ink layer at 120X magnification (b). The growth of fungi on the paper fibers at 4000X magnification (c). The cracking of the color layer and the growth of fungi on the printing ink at 2000X magnification (d). The erosion of the stamp fibers showing their attack by fungi at 500X magnification (e). The shape of the stamp fiber paper, which shows that it is made of cotton pulp at a magnification of 1000X (f).

The presence of the element Ba suggests the use of BaSO_4 as stretcher and extenders, which can be mixed with Cr_2O_3 to reduce ink absorption of the oil medium and to dry the ink [16, 83–85].

3.6. *Fourier Transform Infrared Spectroscopy (FTIR)*. FTIR analysis was carried out to identify the adhesive and the printing media (Table 4). It was clear from the functional

groups infrared analysis of the stamp back side by comparing the results that the color medium for the printing ink is flaxseed oil for blue stamp (Figure 12(a)) and red stamp (Figure 12(b)). Linseed oil was widely used as binder for pigments and ink used with old printing plates and stamps [86].

From the FTIR spectra for the printing ink (Figure 12), some main characteristic peaks of linseed oil were identified in our historical sample. The identification of the historical

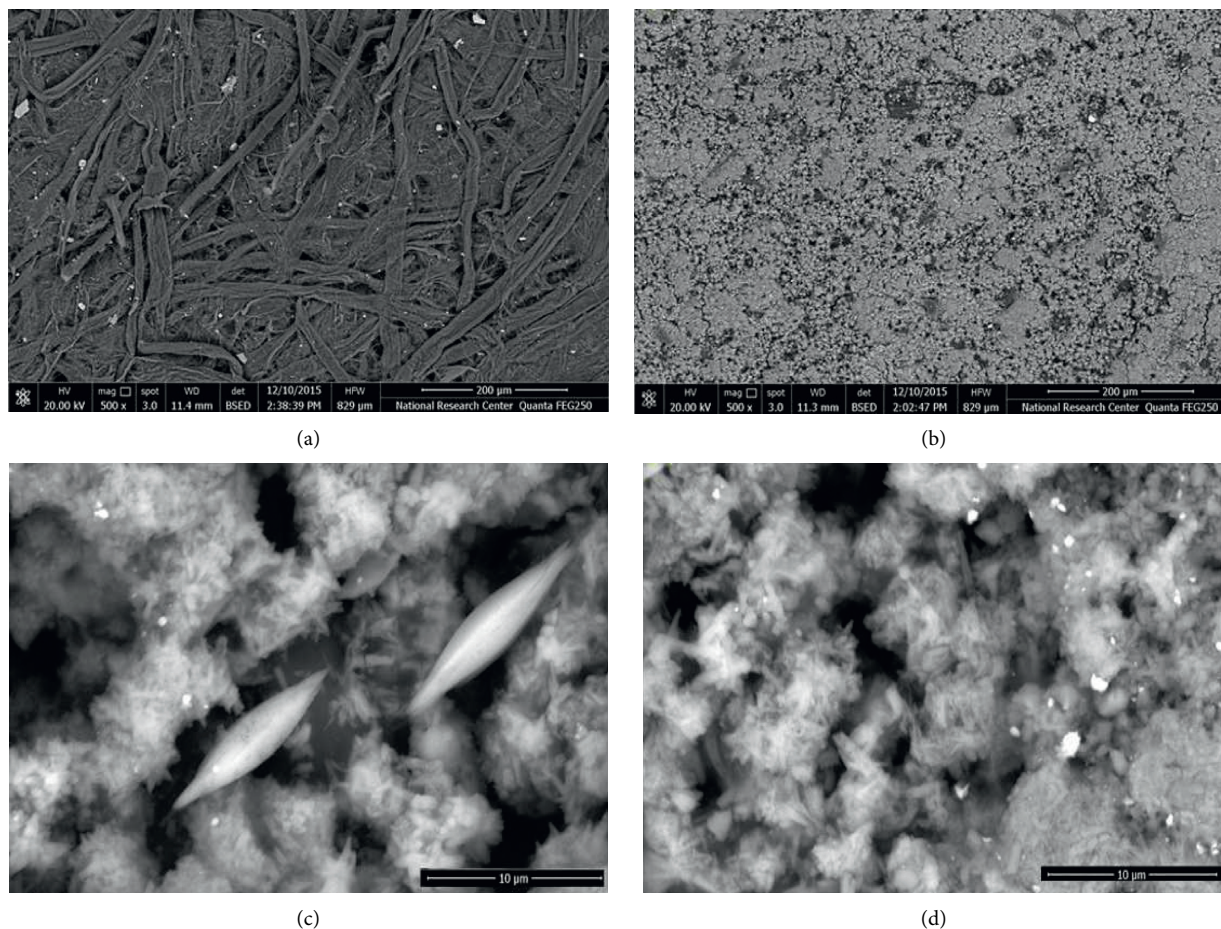


FIGURE 10: The shape of the blue stamp fiber paper, which shows that it is made of cotton pulp at a magnification of 500X (a). Printing ink granules with cracking in the color layer and growth of fungi at 500X magnification (b). (c) Amount of stamp fibers frayed using SEM (12000X magnification). The effect of fungal growth on the erosion of the fibers of the stamp paper (12000X magnification) (d).

binder was performed according to de Viguierie et al. [17], where the main characteristic beaks of linseed oil in our historical sample were detected as follows: $\nu(\text{OH})$ stretching (hydroxyl and hydroperoxides) at 3281 cm^{-1} , C-H stretching band at 2920 cm^{-1} , C-H bending at 2851 cm^{-1} , $\nu(\text{C}=\text{O})$ at 1789 cm^{-1} , weak *cis* C=C at 1643 cm^{-1} , C-H bending at 1406 cm^{-1} , and $\nu(\text{C}-\text{O})$ at 1003 cm^{-1} . Linseed oil spectra showed ester and carboxylic acids at 1735 cm^{-1} and 1710 cm^{-1} , respectively [87]. Also, free acids can appear at 1703 cm^{-1} [88]. Sharp bands at 2924 and 2853 cm^{-1} in linseed oil were associated with methyl and methylene groups in triacylglycerol molecules and by the band at 1738 cm^{-1} ascribed to the carbonyl bond in the ester groups of triacylglycerol molecules [88].

By analyzing the adhesive material on the back side of the blue and red stamps (Table 5), it was found that it is gum Arabic in blue stamp (Figure 13(a)) and red stamp (Figure 13(b)). An infrared analysis of the adhesive found on the back face of the stamp composed of a gum Arabic resin.

The data obtained from FTIR spectra (Figure 13) for the adhesive material found on the back of stamp showed the characteristic beaks of gum Arabic. The identification of Arabic gum was done in accordance with Vetter and

Schreiner [89]; Hassan [90]; and Boyatzis et al. [91], where O-H stretching band was detected at 3281 cm^{-1} , C-H stretching band at 2923 cm^{-1} , O-H bending band at 1603 cm^{-1} , the C-H bending band at 1415 and 1395 cm^{-1} , and very strong band at 1016 cm^{-1} due to C-O stretching band. The carboxylates, hydroxyls, and amines are from the characteristic functional groups of gum Arabic [92]. Bands identified in the spectra at 779.2 cm^{-1} may be assigned to 1–4 linkage of galactose and 1–6 linkage of mannose [94]. Galactan can be associated at 1072.32 cm^{-1} and 884.67 cm^{-1} in the spectrum [95]; also, peaks at 1027.62 cm^{-1} and 844 cm^{-1} may be associated with arabinogalactan. Pyranose rings bands are lying between 700 cm^{-1} and 400 cm^{-1} [96].

3.7. Color Change

3.7.1. Unprinted Paper Sample. Table 6 presents the color change (ΔE) measurements of aged and unaged paper for colored stamps. It was clear from the results that the unprinted paper sample tends to be darker in color. The sample treated with Klucel G + TiO_2 NP gave the best results

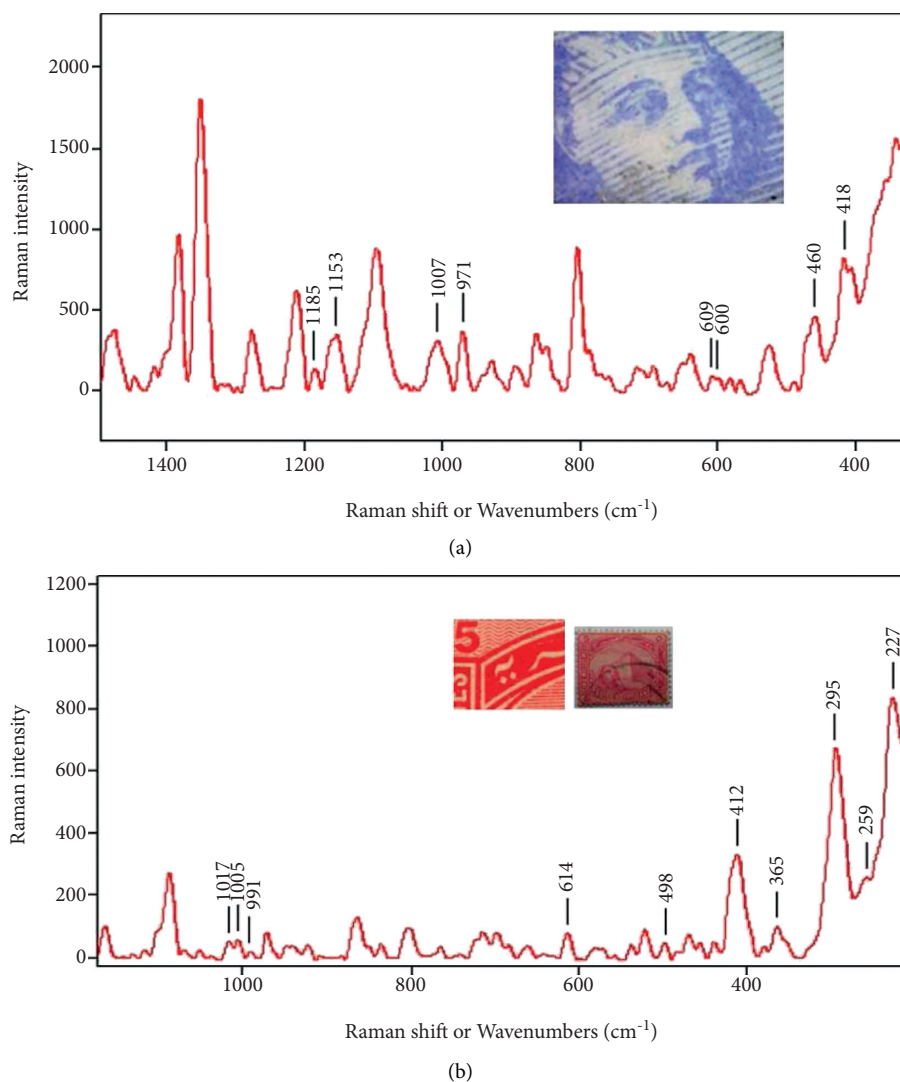


FIGURE 11: The reflections of the Raman spectroscopy for the blue printing ink in the stamp (a) and red printing ink in the stamp (b).

TABLE 2: Raman spectra of the blue stamp components.

Compound	Raman shift/wavenumbers (cm^{-1})	
	Reference sample*	Stamp sample
Ultramarine blue	352, 378, 549	346, 377, 546
Calcium carbonate	283, 713, 1087	280, 712, 1088
Kaolinite	120, 145	121, 147
Flaxseed oil	865, 1076, 1302, 1443	869, 1070, 1307, 1438

*Data are from [11, 15, 41].

TABLE 3: Raman spectra from the reference and red stamp samples.

Compound	Raman shift/wavenumbers (cm^{-1})	
	Reference sample*	Stamp sample
Barium sulfate	454, 464, 989	458, 460, 992
Calcium carbonate	283, 713, 1087	1017
Kaolinite (silica)	145	147
Flax seed oil	865, 1076, 1302	864, 1447
Hematite	225, 245, 294, 290–300, 412	295, 227, 412

*Data are from [11, 15, 41, 80].

in terms of the lowest color darkening ratio that reached -0.02 , while the TiO_2 NP-treated sample gave color darkness that reached -0.03 . The Klucel G-treated sample gave acceptable results where the color darkness reached -0.51 , while the blank sample gave color darkness that reached -2.31 .

ΔE of red to green in Table 6 showed that the unprinted paper sample tends to be green. The sample treated with Klucel G + TiO_2 NP gave the best results in terms of the lowest percentage of greening tendency, which reached -0.01 , while the sample treated with TiO_2 NP reached -0.02 and Klucel G-treated sample reached -0.21 compared to the blank sample that reached -0.62 .

ΔE of yellow/blue for the unprinted paper sample tends to be yellow. Klucel G + TiO_2 NP-treated papers gave the best results in terms of the lowest tendency to yellow, reaching 2.08, while the sample treated with TiO_2 NP showed tendency for yellowing reached 2.25. Klucel G-treated sample reached 2.39, while the blank sample reached 4.73.

TABLE 4: Similar functional groups to the FTIR spectrum of the blue and red stamps in linseed oil medium sample.

Functional group	Wavenumbers (cm ⁻¹)			
	Standard linseed medium*	Linseed oil reference spectrum**	Blue stamp sample	Red stamp sample
O-H stretching band	3200–3600	—	3281	3305
C-H stretching bands (methyl and methylene groups in triacylglycerol molecules)	2800–3000	2865–2927	2851–2920	2851–1919
C=O stretching (triglycerides (esters, fatty esters and carboxylic acids))	1500–1750	1745	1643–1789	1578–1642
C-H bending bands	1300–1480	1426	1406	1414
C-O stretching bands	900–1300	1168	1003	983–1065
C-H torsion	700–750	727	711	—

*Data are from [17, 86]. **Standard linseed oil.

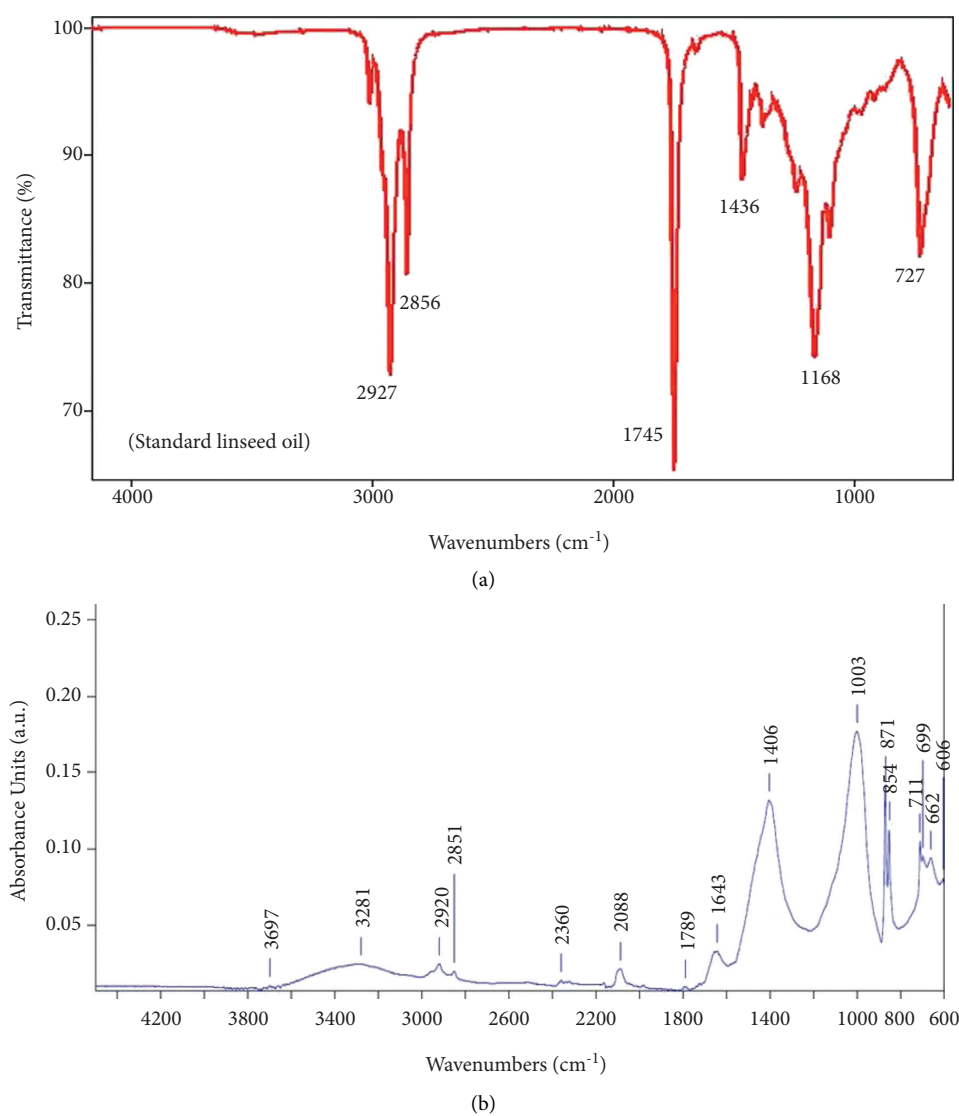


FIGURE 12: Continued.

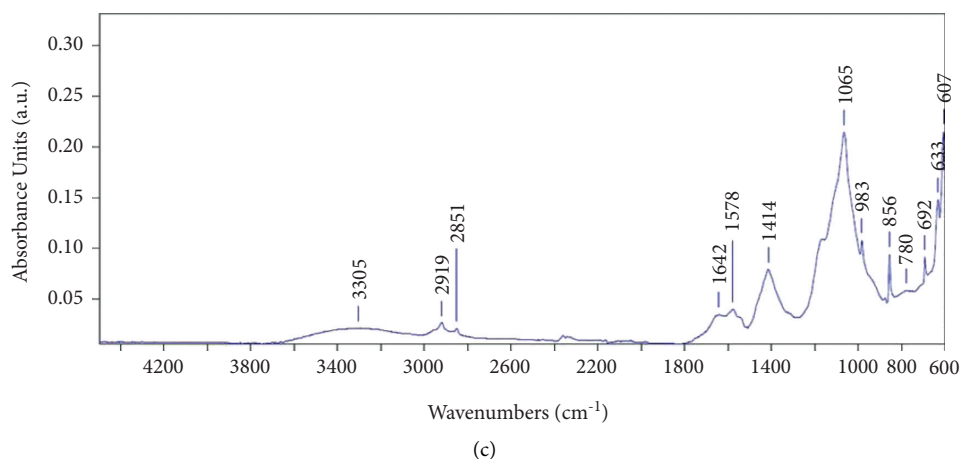


FIGURE 12: The pattern of infrared analysis of flaxseed oil. The color medium of the printing ink blue stamp (a) and red stamp (b).

TABLE 5: The similar functional groups for the FTIR spectrum of the adhesive sample on the back side of the blue stamp, which turned out to be gum Arabic samples.

Functional group	Standard gum Arabic sample*	Wavenumbers (cm ⁻¹)			Characterization
		Gum Arabic reference spectrum**	Blue stamp sample	Red stamp sample	
O-H stretching band	3200–3600	3313	3281	3335	Characteristic of glycosidic ring $\nu(\text{C-H})$ in CH_3 pyranose ring
C-H stretching bands	2800–3000	2925	2854–2923	2850–2920	
C-H bending bands	1300–1480	1425	1311–1415	1414	Carboxylic groups of uronic acid residues of gum polysaccharides
C-O stretching bands	900–1300	1017	1016	1026	Finger print of carbohydrates or polymer backbone

*Data are from previous [89–93]. **Pure gum Arabic.

3.7.2. Printed Paper Sample in Blue Color. The paper samples printed in blue color (Table 6) showed that the sample treated with a mixture of Klucel G and TiO_2 NP had the optimum results in terms of the lowest percentage of brightness color (0.90), while the sample treated with TiO_2 NP gave good ΔE (1.43). Also, acceptable ΔE was found as blue stamp treated with Klucel G (2.64), while the blank sample observed the highest color change (3.21).

Red/green value showed that the paper samples printed in blue color tend to be red. Klucel G + TiO_2 NP treatment showed the best results with the lowest tendency to redness (0.26), while it reached 0.34 with the treatment TiO_2 NP and 0.75 with Klucel G, compared to blank sample (0.95).

Yellow/blue value showed that the paper samples printed in blue color tend to yellow, whereas the sample treated with Klucel G + TiO_2 NP, TiO_2 NP, and Klucel G gave the color change values of 0.43, 0.6, and 1.03, respectively, compared to blank (1.48).

3.7.3. Printed Paper Sample in Red Color. Paper samples printed in red color tend to be darker in color (Table 6). The sample treated with a mixture of Klucel G and TiO_2 NP gave the best results in terms of the lowest percentage of color darkening that reached -0.31 , followed by the sample treated with TiO_2 NP (-1.7), and the sample treated with Klucel G (-2.04), while the blank sample showed color change with color darkness reached -2.48 .

Red/green value showed that the paper samples printed in red color tend to be green. Klucel G + TiO_2 NP-treated sample showed the lowest percentage of greenness (-0.26), followed TiO_2 NP-treated sample (-1.17) and Klucel G-treated sample (-1.42), compared to blank samples (-1.51).

ΔE of yellow/blue value showed that the paper samples printed in red tend to be blue. The sample treated with Klucel G + TiO_2 NP gave the best results in terms of the lowest tendency for blueness (-1.80), while the TiO_2 NP-treated sample gave tendency for blueness reached -2.66 , and Klucel

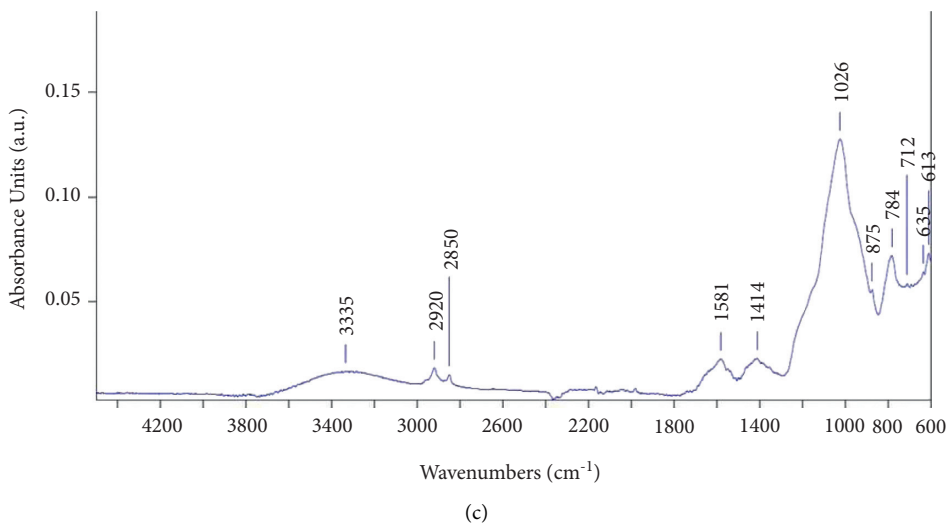
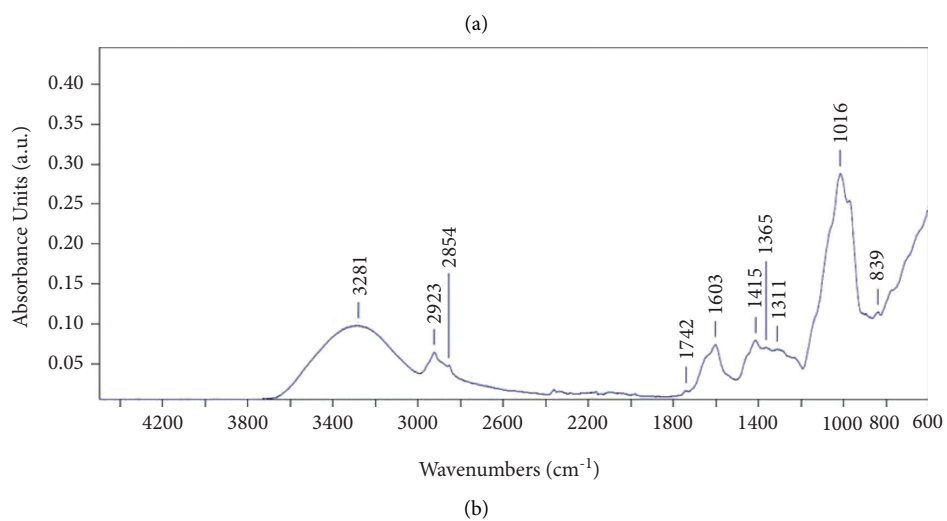
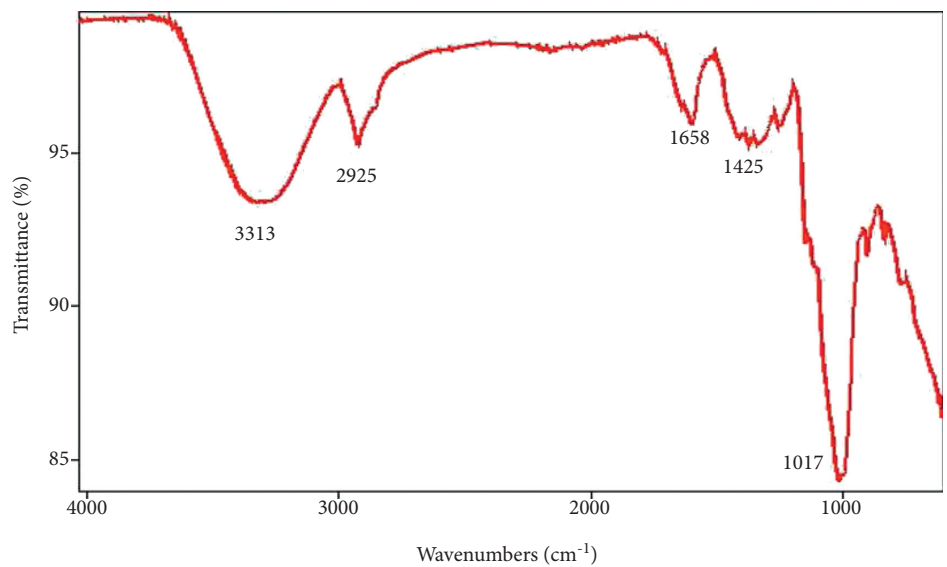


FIGURE 13: The infrared analysis of gum Arabic sample; the adhesive substance on the back side for blue stamp (a) and red stamp (b).

TABLE 6: Color change measurements of blue and red stamps compared with unprinted papers before and after photoaging.

Paper sample	Treatment	ΔL		Δa		Δb		ΔE
		B	A	B	A	B	A	
Unprinted paper samples	Blank	83.91	81.60	0.79	0.17	5.17	9.9	5.30
	TiO ₂ NP	83.94	83.91	0.57	0.52	5.13	7.38	2.25
	Klucel G	87.37	86.86	0.72	0.51	5.11	7.50	2.45
	Klucel G + TiO ₂ NP	87.51	87.49	0.79	0.78	5.44	7.52	2.08
Blue color stamp	Blank	17.11	20.32	0.64	1.59	7.11	8.59	3.66
	TiO ₂ NP	27.05	28.48	1.94	2.28	11.96	12.56	1.59
	Klucel G	19.25	21.89	1.38	2.13	9.85	10.88	2.93
	Klucel G + TiO ₂ NP	20.99	21.89	1.55	1.81	10.21	10.64	1.03
Red color stamp	Blank	36.47	33.99	37.20	35.69	12.53	8.94	4.62
	TiO ₂ NP	36.59	34.89	29.79	28.62	8.44	6.38	2.92
	Klucel G	39.52	37.48	30.94	29.52	9.01	6.39	3.61
	Klucel G + TiO ₂ NP	37.98	37.67	30.68	30.42	6.81	5.01	1.84

B: before ageing; A: after ageing.

G-treated sample reached -2.62 compared to blank samples (-3.59).

Through the results for the chromaticity values, the best result of treatment for resistance is the sample treated with Klucel G + TiO₂ NP, then the treated sample with TiO₂ NP followed by the Klucel G-treated sample, and lastly the blank samples.

3.8. Conservation Trials of the Historical Stamps. The visual observations of the mechanical cleaning, chemical cleaning, and deacidification results of the historical stamps are shown in Figures S5, S6, and S7, respectively. After the completion of those treatments for historical stamps, the manual restoration operations were started as shown in Figures S8 and S9. Finally, the restoration of stamps was done as shown in Figure S10.

4. Conclusions

This study focused on the importance of historical stamps as archaeological artifacts that must be preserved from various factors of damage. It became clear from the study that the type of printing in all the stamps made from cotton is typography, and free from defects, and the printing was done in Del Rey Press in England. Cracks in the ink layer and chromatic medium, loss and shedding of inks, and the mechanical damage caused by fungal damage were observed. The pH values of the stamps did not decrease significantly, as it recorded values ranging between 5 and 6, despite the poor preservation of the stamps, where they contained a percentage of acid-damaging additives, such as alum and chlorine residues. The chemical component of printing inks and paper was determined in order to develop effective methods of preservation, as it became clear from the analysis using Raman and the EDS unit attached to the SEM that ultramarine blue as a blue printing ink and red hematite as a red printing ink were used. The black stamping ink in both printers is carbon ink. Also, the use of barium sulfate as ink extenders was mixed with coloring materials in order to reduce the ink absorption of the oily medium and to speed up the drying process of the ink, in order to prevent the prints from damaging each other on the prints. Calcium carbonate was used

as a filler during the manufacture of paper, as a result of the use of chalky paper in the manufacture of stamps in that period, to improve the surface properties of the paper by giving it a smooth, homogeneous surface suitable for printing. Chlorine, as a bleaching agent, was used for paper pulp made of stamp paper. Kaolinite was used as a filler during the manufacture of stamp paper. Aluminum phosphate was used to adjust the pH value of the printing ink. Aqueous potassium and aluminum sulfate were used in the manufacture of stamp paper. It was also shown by infrared analysis that linseed oil was used as a media for printing ink, and gum Arabic was used as an adhesive in all the stamps subject of the study. Stamps have restored their luster and vitality after carrying out maintenance and restoration operations and giving them a homogeneous and streamlined shape. The mixture of 7% Klucel G + 0.2% TiO₂ NP in ethanol was worked to strengthen the stamps and protect them from ultraviolet rays and give them a homogeneous and streamlined shape. Also, the deposition of a percentage of TiO₂ NP could act as a future antibacterial and a carrier of self-cleaning properties.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

Cleaning of stamps and restoration trials are included as supplementary information. *Figure S1*. The cleaning of stamps from dust and its plankton using different brushes, under the magnifying glass and the front and back sides after

cleaning for (a) blue stamp and (c) red stamp. Cleaning and removing calcifications using scissors and blunt scalpels under the magnifying glass for (b) blue stamp and (d) red stamp. *Figure S2*. The process of removing the stamp and the chemical cleaning process using distilled water and ethyl alcohol and drying with blotting paper for (a) blue stamp and (b) red stamp. *Figure S3*. The removal of acidity from the stamp by immersion in solution of $\text{Ca}(\text{OH})_2$ NP for (a) blue stamp and (b) for red stamp. (c) Drying the stamps with blotting paper and placing it under a weight. *Figure S4*. The general nature status of the red stamp (a) and blue stamp (d) from front side and back side of red stamp (b) and blue stamp (e), and the various damages, and the stamp documentation using of AutoCAD program for red stamp (c) and blue stamp (f). *Figure S5*. The blue stamp (a) and red stamp (b) from the front and back sides after the mechanical cleaning process. *Figure S6*. The blue stamp (a) and red stamp (b) from front and back sides after the chemical cleaning process using distilled water and ethyl alcohol. *Figure S7*. The blue stamp (a) and red stamp (b) from front and back sides after the nonaqueous deacidification method by immersion in $\text{Ca}(\text{OH})_2$ nanosolution. *Figure S8*. Manual restoration of blue stamp, where (a) shows the individual torn stamp fibers using distilled water and alcohol after placing a piece of blotting paper under the stamp to absorb the excess solution, (b) shows the placement of the Klucel G adhesive on the torn edges and assembling the two parts of the stamp using the thermal spatula on the optical table, (c) shows the process of reinforcing the torn part of the stamp from the back using chew and thermal spatula paper, (d) shows the placement of the stamp between two pieces of polyethylene before placing it under a weight. *Figure S9*. Manual restoration of red stamp, where (a) shows the individual torn stamp fibers using distilled water and alcohol after placing a piece of blotting paper under the red stamp to absorb the excess solution; (b) illustrates applying the Klucel G adhesive to the torn edges after unrolling them; and (c) shows the assembly of torn fibers from stamp paper using thermal spatula. *Figure S10*. Blue stamp before restoration (a1) and after restoration (b1). (a2) shows the red stamp before restoration and (b2) after restoration. (*Supplementary Materials*)

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