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Research Article

Preparation of Modified Kaolin Filler with Cesium and Its Application in Security Paper

Houssni El-Said,[1] Samya El-Sherbiny,[2] Omnia Ali,[2] Wafaa El-Said,[3] and Said Rohyem[4]

[1] *Cellulose and Paper Department, National Research Centre (NRC), Dokki, Giza 11622, Egypt*
[2] *Chemistry Department, Faculty of Science, Helwan University, Ain Helwan, Cairo 11975, Egypt*
[3] *National Centre for Nuclear Safety & Radiation Control (NCNSRC), Egyptian Atom Energy Authority (AEA), Nasr City, Cairo, Egypt*
[4] *Research Counterfeiting and Forgery Department, Forensic Medical Authority, Ministry of Justice, Cairo, Egypt*

Correspondence should be addressed to Omnia Ali; omniaibrahim95@gmail.com

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In this study, cesium was added intentionally during paper manufacture for protecting the papers against forgery and counterfeiting by sorbing cesium ions (Cs^+) on kaolin, used as special filler in papermaking. The sorption of cesium from aqueous solution by kaolin was studied as a function of pH, shaking time, cesium initial concentration, and mass of kaolin using batch technique. The results showed that a solution containing 10 mg/L Cs^+ and 250 mg of kaolin at pH 6 can be used to modify the kaolin. Paper handsheets were prepared containing various percentages of the modified kaolin. The mechanical and optical properties of paper handsheets were studied. The prepared paper handsheets were irradiated by gamma irradiation using different doses. Fourier transform infrared (FTIR) spectroscopy was used to study the effect of kaolin modification by cesium and gamma irradiation on paper handsheets properties. The results indicated that modified kaolin enhanced the mechanical and optical properties of paper handsheets. Electron spin resonance (ESR) spectroscopy and laser-induced breakdown spectroscopy (LIBS) were also used. They provided rapid, sensitive and nondestructive techniques in differentiating between different questioned documents. This study presents a new concept in manufacturing security papers and anticounterfeiting applications.

1. Introduction

The examination of questioned documents is an ongoing challenge to forensic science to cope with the modern technology of document manufacturing and the increasingly sophisticated documents forgeries. The many facets of modern documents demand many areas of expertise from forensic specialists in order to identify and authenticate a questioned document. The counterfeiting of banknotes and other financial transaction documents as well as visas, passports, ID cards, and other official government security papers and the pharmaceuticals and brand name products is now becoming one of the world's fastest growing areas of criminal activity [1].

Many techniques have been developed for protecting the documents to prevent counterfeiting or fraudulent use. Techniques such as holograms on credit cards and magnetic coding on various articles have been in use for some time [2, 3]. These prior art techniques have been less than fully effective either because the counterfeiters have found ways to duplicate the label, or the apparatus for detecting the label and verifying its authenticity has been too expensive or unmanageable to be accepted for widespread use. Recently, ink tagged with rare-earth elements has been studied as a reliable method to identify sensitive documents and to extend the scope of age determination. This is due to the fact that the taggants act as a unique identification index to discriminate documents. Rare-earth elements were selected as taggants due to various advantages such as satisfactory sensitivity of analytical determination and their absence in normal varieties of inks [4, 5].

Fluorescence-active pyridinecarbonitriles were prepared and evaluated in the production of functionalized paper

sheets, from nonwood pulps [6, 7]. Fluorescent nanoparticles [8] and Fe_3O_4 nanoparticles [9] were also used as successful methods for anticounterfeiting applications and documents' identification. Bracher represented a method for patterning solids in two dimensions within the bulk of sheets of paper—instead of only on its surface—by generating the solids as precipitates of reactions within the pores of the paper [10]. The method is simple, requires no specialized equipment beyond a color office printer, and should be amenable to scale up in roll-to-roll processes.

The objective of the current work is to tag the kaolin (used as filler in paper making) by cesium as a trace element. Fillers are added to papermaking furnishes to fill the spaces and crevices between the fibres, thus improving brightness, smoothness, and opacity of the paper sheet [11]. Selection of cesium as taggant primarily depends on the absence of natural kaolin from cesium and can be effective in discriminating between papers.

Kaolin is essentially a hydrated aluminum silicate, with the composition $Al_2Si_2O_5(OH)_4$. The most reactive parts of kaolin are the hydroxyl groups. It has been shown that it is possible to bring molecules in between the layers of a kaolin crystal, so called intercalation [12]. Numerous studies of the intercalation of various compounds into kaolin have been reported. Not all compounds intercalate directly into kaolin but are brought into the kaolin layers by displacement of a previously intercalated compound. Previous studies of isotopic exchange on kaolin have been performed using intercalated kaolin [13, 14].

The aim is also to irradiate the prepared paper handsheets by gamma irradiation; then Fourier transform infrared spectroscopy (FTIR), electron spin resonance spectroscopy (ESR), and laser-induced breakdown spectroscopy (LIBS) techniques were used to differentiate between paper samples.

2. Experimental

2.1. Modification of Kaolin with Cesium

2.1.1. Materials and Reagents. The kaolin (china clay) was supplied by Rakta, Alexandria, Egypt. It has a refractive index of 1.56, density of 2.62 g/cm^3, and particle size of 3–8 μm. The kaolin was used as received without further purification. Standard cesium solution (1000 mg/L) was prepared from cesium chloride (Fluka, Germany) by dissolving 1.2670 g in 1-litre distilled water. All other reagents used were analytical reagent grade.

2.1.2. Sorption Experiments. The sorption experiments were studied by batch technique. In the experiments, kaolin was separately shaken with cesium solution at various experimental conditions. Separating of solid phase from liquid was done by centrifuging at 4000 rpm for 15 min. The pH of the solutions was maintained in the range 2–10 using drops of 0.1 M HCl and 0.1 M NaOH. After equilibration, the cesium concentration was determined spectrophotometrically employing atomic absorption spectrometer of type AA-scan-4 (Thermo Jarrell Ash, USA).

2.2. Application of Modified Kaolin in Paper Handsheets

2.2.1. Paper Handsheets Formation. The pulp used throughout the experimental work was bleached wood sulphite supplied from Quena Paper Industry Company, Egypt. Oxidized starch was used as a retention aid and was supplied from Quena Paper Industry Company, Egypt. The pulp was beaten to Schopper-Riegler 35 SR° in L&W laboratory beater, A2-66-1424 according to the Swedish Standard Method (SCA). Paper handsheets of basis weight 60 g/m^2 were formed using Tappi standard (T205 sp-95). Native kaolin and modified kaolin were added at 5%, 8%, 12%, and 15% based on the dry weight of pulp.

2.2.2. Gamma Irradiation of Paper Handsheets. Irradiation of paper handsheets was performed with a dose rate of 0.817 Gy/s using ^{60}Co gamma source cell located at the National Center for Radiation Research and Technology (NCRRT), Nasr City, Cairo, Egypt [15].

2.2.3. Characterization of the Prepared Paper Handsheets before and after γ-Irradiation

Optical and Mechanical Properties. The brightness and opacity of the paper handsheets were measured using integrating refractometer, model JY9800, according to ISO 2470:1999 and ISO 2471:1998, respectively.

The tensile strength and burst strength were determined using Hounsfield H5KS tensile tester (Tappi 404) and Frank GMBH 1882 burst tester (Tappi 807), respectively. A tear tester (L&W 2404) was used according to Tappi 496.

Fourier Transform Infrared (FTIR) Spectroscopy. Infrared spectra were taken on a NEXUS-670 FTIR spectrophotometer (Iclet Co., USA), in the range of the frequencies from 4000 to 400 cm^{-1}. Samples were prepared as a thin film with potassium bromide (KBr disc). The mean hydrogen bonds strength (MHBS) was calculated according to Levdik et al. [16] as the ratio of $A_{\mathrm{OH(str.)}}/A_{\mathrm{CH(str.)}}$, where A is the integral intensity of the stretching vibration bands of the subscript group. The mean hydrogen bonds strength (MHBS) also is the ratio of the absorption band at ~3400 cm^{-1} to the band at ~2900 cm^{-1}.

The crystallinity index (Cr.I) can be calculated by the following equation provided by Nelson and O'Conner [17]:

$$\mathrm{Cr.I} = \frac{A \sim 1370\ \mathrm{cm}^{-1}}{A \sim 2920\ \mathrm{cm}^{-1}}, \quad (1)$$

where $A \sim 1370\ \mathrm{cm}^{-1}$ is the absorbance intensity at 1370 cm^{-1} band associated with symmetric C–H bending from methoxyl group and $A \sim 2920\ \mathrm{cm}^{-1}$ is the absorbance intensity at 2900 cm^{-1} associated with the C–H stretching vibration.

Electron Spin Resonance (ESR) Spectroscopy. The system used in this study was an EMX-BRUKER system (Germany) supplied by a 9.5 QHZ Microwave (x-band) Gum-Oscillator Bridge with automatic tuning capability and a rectangular

4102 ST cavity operating in the TE102 mode. The standard EMX signal channel can be operated at any modulation frequency between 6 KHz and 100 KHz and has unsurpassed phase resolution and stability.

Laser-Induced Breakdown (LIBS) Spectroscopy. A typical LIBS experimental setup, described in detail elsewhere [18], was used throughout the present investigations. Laser-induced plasma was produced by focusing 60 mJ of a Q-switched Nd: YAG laser (Surelite I, Continuum, USA) operating at 1064 nm (pulse duration of 7 ns) on paper samples. An energy meter (Nova 978, Ophir Optronics Ltd., USA) was employed to monitor the shot-to-shot pulse energy at the National Institute of Laser Enhanced Science (NILES), Cairo University, Cairo, Egypt.

3. Results and Discussion

3.1. Sorption Experiments. The parameters which may affect the uptake of cesium by kaolin, such as shaking time, pH, initial concentration of cesium, and kaolin mass were investigated. The results showed that the equilibrium reached to its maximum within 40 min of shaking. Therefore, the sorption experiments were carried out for 40 min. Uptake percentage (%E) was calculated as follows:

$$\%E = \frac{C_o - C_e}{C_o} \times 100, \quad (2)$$

where C_o and C_e are the initial and equilibrium cesium concentrations in the solution (mg/L), respectively.

Figure 1 shows the influence of pH on the sorption of cesium. The data reveal that the sorption increased with increasing pH up to 6, then decreased. Consequently, in the subsequent work, the sorption experiments were carried out at pH 6. Increasing pH of solution resulted in a decrease in H^+ ions leading to less competition for the vacant exchange sites of the kaolin, and hence more Cs^+ ions uptake is occurring. At higher pH values, the dissociation of counter ions in the kaolin matrix may increase resulting in a lower percent sorption of cesium. In contrast, at lower pH values of hydrogen ion strongly compete for the vacant sites in the crystal lattice giving rise to a decrease in the uptake percentage [19].

The sorption of cesium as a function of cesium initial concentration was studied by varying the cesium initial concentration from 10 to 80 mg/L. Figure 2 shows that the uptake percentage decreased with increasing the concentration of cesium ions. This is due to saturation of active sites on kaolin surface with increasing cesium ions concentration. Accordingly, cesium solution with concentration of 10 mg/L was selected in the subsequent experiments.

Effect of kaolin mass on the sorption process of cesium is presented in Figure 3. The experimental results reveal that the sorption of Cs^+ ions slightly increased with increasing the kaolin mass. Although the uptake percentage increased with increasing kaolin mass, 250 mg was chosen to avoid atomic absorption spectrometry problems of cesium determination in case of using large quantity of kaolin.

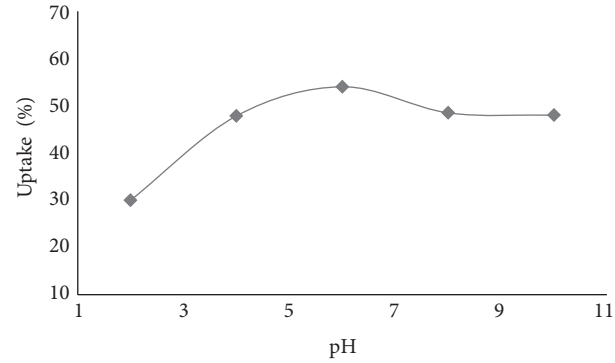

Figure 1: Variation of uptake percentage with pH for cesium sorption on kaolin. Operating conditions: 50 mL solution, [Cs^+] = 25 mg/L, 250 mg kaolin, and shaking time = 40 min.

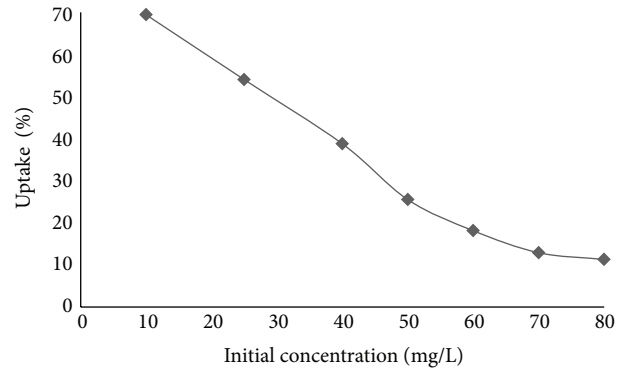

Figure 2: Variation of uptake percentage with initial concentration of cesium for its sorption on kaolin. Operating conditions: 50 mL solution, pH = 6, 250 mg kaolin, and shaking time = 40 min.

From the previous results, it can be concluded that solution containing 10 mg/L Cs^+ and 250 mg of kaolin at pH 6 can be used to modify the kaolin which was used in preparing handsheets.

3.2. Effect of Kaolin Modification on Paper Handsheets Properties before γ-Irradiation. The mechanical and optical properties of paper handsheets loaded by both native kaolin and Cs-kaolin as fillers are summarized in Table 1.

3.2.1. Mechanical Properties. The strength properties (burst, tensile, and tear indexes) of wood paper handsheets having various percentages of fillers using both native kaolin and cesium modified kaolin (Cs-kaolin) are represented in Table 1. The greater the amounts of filler percentages the weaker the paper will be mechanically in respect to, for example, burst, tensile, and tear indexes. It is generally accepted that paper strength is attributed to the fiber strength and the number of inter fiber bonds. Kaolin particles in a handsheet interfere the fiber bonding, which reduce the strength and number of interfiber bonds [20, 21].

The percentage decrease in burst, tensile, and tear indexes reached to 26.8, 34.6, and 14.8 at 15% addition of native kaolin,

Table 1: Mechanical and optical properties of wood paper handsheets loaded with native kaolin and Cs-kaolin.

Wood paper handsheets		Mechanical properties			Optical properties	
		Burst index	Tensile index	Tear index	Brightness	Opacity
	Filler %	Kpa·m^2/g	N·m/g	mN·m^2/g	%	%
Kaolin	0	4.88	46.20	10.25	77.10	76.70
	5	4.19	40.82	9.57	80.50	76.90
	8	4.04	36.44	9.79	81.70	77.10
	12	3.84	32.28	9.43	82.30	78.00
	15	3.57	30.22	8.73	83.30	79.08
Cs-kaolin	0	4.88	46.20	10.25	77.10	76.70
	5	4.32	41.73	10.17	81.60	77.50
	8	4.14	37.28	10.16	82.66	78.00
	12	4.02	35.29	9.71	84.50	78.50
	15	3.70	32.25	9.30	85.60	79.80

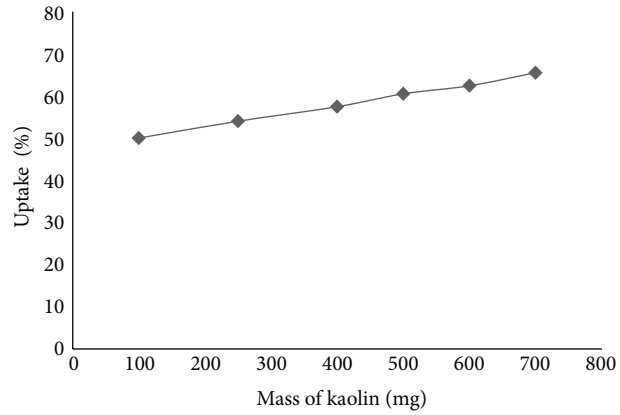

Figure 3: Variation of uptake percentage with kaolin mass for cesium sorption on kaolin. Operating conditions: 50 mL solution, [Cs^+] = 25 mg/L, pH = 6, and shaking time = 40 min.

respectively. The table also shows slight improvements in the mechanical properties of paper handsheets upon using modified kaolin (Cs-kaolin). The increases were 3.6, 6.7, and 6.5% for burst, tensile, and tear indexes, respectively, at 15% addition level of Cs-kaolin. Changing the chemical nature of the native kaolin by modification may lead to increase in kaolin positivity, consequently enhancing the filler-to-fiber bonds [22].

3.2.2. Optical Properties. Table 1 shows the effect of modification of kaolin on the brightness and opacity of the prepared paper handsheets. The results showed that the addition of fillers improved both two properties, increasingly in percentage of 8.04% and 3.1% at 15% addition level of kaolin. The same behaviour was obtained with using Cs-kaolin, and the increase reached to 11.02% and 4.04% for brightness and opacity, respectively.

The brightness and opacity of paper depend on the number of individual particles in the sheet structure, the grammage, the number of surfaces in the structure, and on the differences in refractive index between the particles and the surrounding medium. Adding fillers to paper sheet improves optical properties including both the opacity and brightness due to the higher light scatterings of filler than fibers, which has the linear relationship of the following form:

$$S_{\text{sheet}} = S_{\text{unfilled sheet}}\,(1 - L) + LS_{\text{filler}}, \quad (3)$$

where S is light scattering coefficient and L is the filler loading amount.

The results also indicated that the brightness and opacity improved upon using modified kaolin (Cs-kaolin) filler. This may be due to the adsorbed Cs on kaolin increased the particle size of the native kaolin, consequently increasing the voids between the fibres [23, 24].

3.3. Effect of Kaolin Modification on Paper Handsheets Properties after γ-Irradiation. Table 2 shows the effect of ^{60}Co γ-irradiation by various radiation doses (3, 6, 9, 12, and 15 KGy) at a dose rate 0.817 Gy/s on the mechanical and optical properties for wood paper handsheets (without kaolin, 12% kaolin, and 12% Cs-kaolin).

3.3.1. Mechanical Properties. From Table 2, it is observed that with increasing γ-irradiation doses the mechanical strength (i.e. burst, tensile, and tear indexes) of wood paper handsheets is slightly decreased.

The percentage decrease in burst, tensile, and tear indexes reached to 8.7, 14.5, and 2.2% at a 15 KGy dose of γ-irradiation in the case of wood paper handsheets loaded with 12% kaolin, respectively. But in the case of wood paper handsheets loaded with 12% Cs-kaolin, the percentage decrease in burst, tensile, and tear indexes reached to 7.6, 11.8, and 2.6, respectively. It can be concluded that the effect of γ-irradiation on mechanical properties for prepared paper handsheets loaded with 12% Cs-kaolin was less than the effect of γ-irradiation on mechanical properties for prepared paper handsheets loaded with 12% kaolin.

3.3.2. Optical Properties. The effect of γ-irradiation on optical properties of wood handsheets is represented in Table 2. γ-irradiation slightly decreased brightness and opacity of the prepared handsheets. There is no significant effect on

Table 2: Mechanical and optical properties of γ-irradiation wood paper handsheets: without kaolin, 12% kaolin, and 12% Cs-kaolin.

Wood paper handsheets		Mechanical properties			Optical properties	
		Burst index	Tensile index	Tear index	Brightness	Opacity
	Radiation dose (KGy)	Kpa·m^2/g	N·m/g	mN·m^2/g	%	%
Without kaolin	0	4.57	43.24	9.93	77.10	76.70
	3	4.50	42.52	9.90	76.80	76.50
	6	4.46	41.63	9.87	76.50	76.50
	9	4.41	40.40	9.79	76.00	76.30
	12	4.35	39.52	9.70	75.90	76.50
	15	4.32	38.81	9.66	75.70	76.30
12% kaolin	0	3.84	32.28	9.44	82.30	78.00
	3	3.76	31.36	9.38	82.00	77.90
	6	3.69	30.64	9.33	81.80	78.20
	9	3.61	29.54	9.29	81.10	78.24
	12	3.56	28.66	9.25	80.70	78.30
	15	3.51	27.59	9.23	80.50	78.10
12% Cs-kaolin	0	4.02	35.29	9.71	84.50	78.50
	3	3.94	34.57	9.66	84.10	78.40
	6	3.87	33.76	9.61	83.80	78.51
	9	3.82	32.64	9.57	83.20	78.60
	12	3.77	31.86	9.52	83.00	78.80
	15	3.71	31.13	9.46	82.80	78.70

Table 3: Mean hydrogen bonds strength (MHBS) and crystallinity index (Cr.I) for wood paper handsheets before and after γ-irradiation.

Paper handsheets	Nonirradiated paper		γ-irradiated paper	
	MHBS	Cr.I	MHBS	Cr.I
Without kaolin	1.505	1.030	1.314	1.010
12% kaolin	1.349	0.942	1.276	0.830
12% Cs-kaolin	1.375	0.955	1.282	0.994

brightness and opacity of paper handsheets loaded with 12% kaolin and Cs-kaolin after γ-irradiation at a dose of 15 KGy.

3.4. FTIR Spectra. Figures 4 and 5 show the IR spectra for three nonirradiated paper handsheets: paper without kaolin, paper loaded with 12% kaolin, and paper loaded with 12% Cs-kaolin from wood pulps before and after γ-irradiation. Table 3 illustrates the mean hydrogen bonds strength (MHBS) and crystallinity index (Cr.I) for wood paper handsheets before and after γ-irradiation.

3.4.1. Effect of Kaolin Modification on Paper Handsheets before γ-Irradiation. Figure 4 along with Table 3 shows that the MHBS and Cr.I decreased upon the addition of filler, either native or modified kaolin (Cs-kaolin). The results also illustrated that Cs-kaolin had lower effect than native kaolin. This may be due to the modification of kaolin with cesium enhancing its cationic charge creating more and stronger bonds with anionic cellulosic fibres. The improvements in MHBS led to an increase in crystallinity of the cellulose.

It can be concluded that the increasing of MHBS and Cr.I can explain the improvement in the mechanical properties of wood and bagasse paper handsheets prepared with modified kaolin (Cs-kaolin).

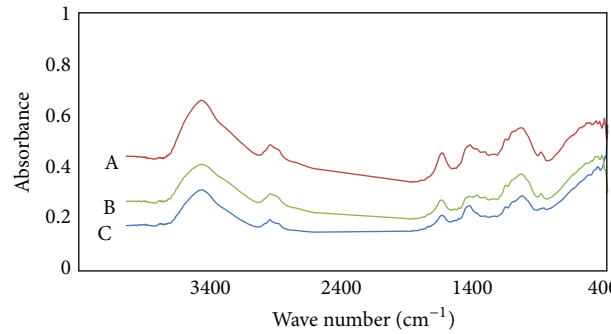

Figure 4: FTIR spectra for three nonirradiated wood paper handsheets. A: paper loaded with 12% kaolin, B: paper loaded with 12% Cs-kaolin, and C: paper without kaolin.

3.4.2. Effect of Kaolin Modification on Paper Handsheets after γ-Irradiation. Figure 5 and Table 3 show that both MHBS and Cr.I decreased after γ-irradiation. The results indicated that the resistance of paper handsheets loaded with Cs-kaolin toward γ-irradiation at 15 KGy dosage was higher than the resistance of paper handsheets loaded with native kaolin. These results confirmed the high mechanical properties of γ-irradiated paper handsheets loaded with Cs-kaolin.

3.5. ESR Spectra

3.5.1. Effect of Modification of Kaolin on Paper Handsheets before γ-Irradiation. In order to study the effect of modification of kaolin with cesium, ESR spectra of three different nonirradiated samples: paper sample without kaolin, paper sample containing 12% kaolin, and paper sample containing 12% (Cs-kaolin) were determined. Figure 6 shows that in the case of addition of kaolin, large numbers of peaks appeared compared to peaks of paper without kaolin. It is also obvious

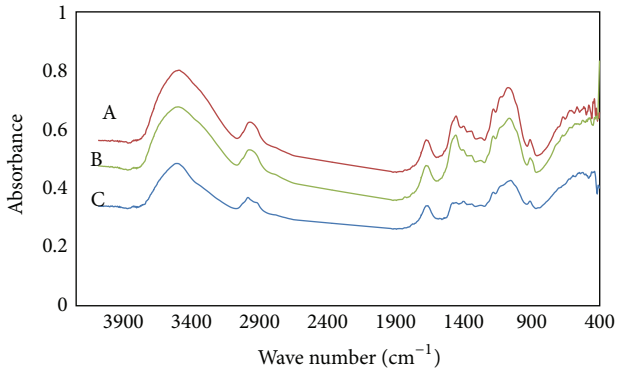

Figure 5: FTIR spectra for three γ-irradiated wood paper handsheets: A: paper loaded with 12% kaolin, B: paper loaded with 12% Cs-kaolin, and C: paper without kaolin.

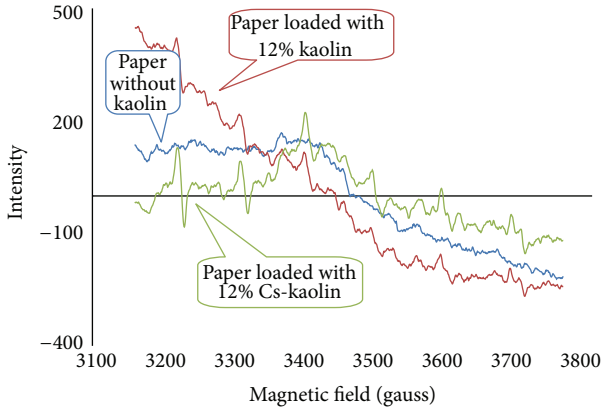

Figure 6: ESR spectra for nonirradiated wood paper handsheets (without kaolin, 12% kaolin, and 12% Cs-kaolin).

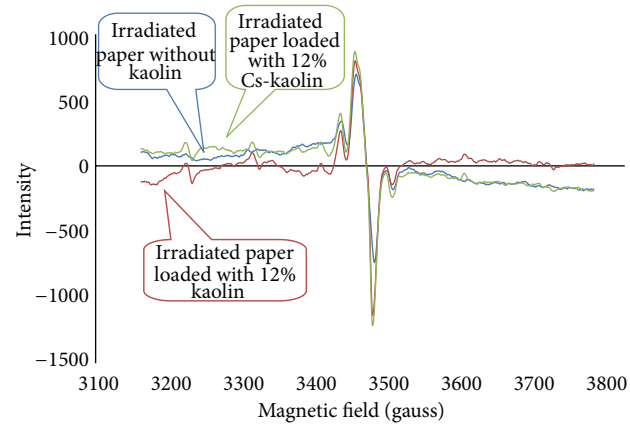

Figure 7: ESR spectra for irradiated wood paper handsheets (without kaolin, 12% kaolin, and 12% Cs-kaolin).

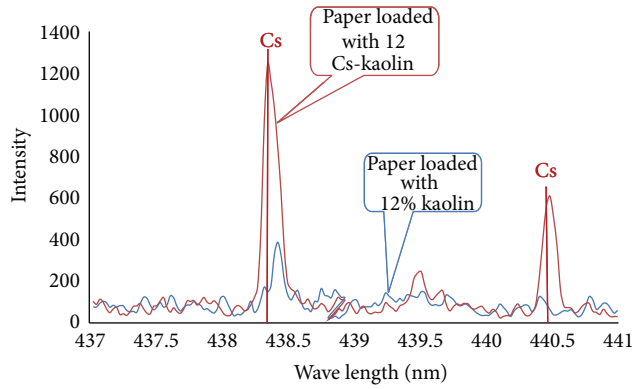

Figure 8: LIBS spectra for wood paper handsheets loaded by 12% kaolin and 12% Cs-kaolin.

that the effect of addition of cesium is very clear since the peaks are more sharper in presence of cesium and the peaks intensities are larger than those of kaolin without cesium as well. These results revealed that it is easy to differentiate between two papers containing native kaolin and modified kaolin with cesium, respectively.

3.5.2. Effect of Kaolin Modification on Paper Handsheets after γ-Irradiation. ESR spectra of three different samples: paper sample without kaolin, paper sample containing 12% kaolin, and paper sample containing 12% (Cs-kaolin) after irradiation exposing to γ-irradiation were determined. It is noticed from Figure 7 that the ESR spectra of the three samples are to some extent similar, the intensity of free common radicals and have maximum peak around 3460 G. The paper handsheet containing 12% modified kaolin (Cs-kaolin) slightly increased after the γ-irradiation than that of native kaolin. This is also noticed in ESR spectra for γ-irradiated wood paper handsheets loaded with 12% (kaolin and Cs-kaolin); some splitting peaks around 3220 G, 3310 G, and 3340 G disappeared in the γ-irradiated wood paper handsheets without kaolin.

3.6. LIBS Spectra. LIBS is a relatively new technique which offers significant advantages in speed, sensitivity, nondestructive, and cost effectiveness over other processes such as X-ray florescence (XRF), scan electron microscope (SEM), and mass spectrometry. It uses a high-intensity pulsed laser focused on the sample to create a tiny plasma of vaporized matter which emits an atomic spectrum of the constituent elements of the sample—providing a material "fingerprint." A database of emission lines provides automatic identification and labeling of elements present.

The LIBS spectra in Figure 8 show the presence of two prominent peaks for cesium around 438.3 nm and 440.5 nm in the case of paper handsheets loaded with 12% Cs-kaolin, but on the other hand there is no peaks in the case of paper handsheet with native kaolin indicating the absence of cesium in paper handsheets loaded with native kaolin.

4. Conclusions

This work represents a new concept and nondestructive methods in authenticating the documents. Kaolin (used as filler in papermaking) was modified chemically by ion exchange with cesium ion. The modification was carried out

to change the nature of the native kaolin. The results of this study led to the following conclusions.

(i) Sorption studies on kaolin proved that a solution containing 10 mg/L Cs^+ and 250 mg of kaolin at pH 6 can be used to modify the kaolin which was used in preparing paper handsheets.

(ii) Modified kaolin with cesium enhanced the mechanical and optical properties of paper handsheets.

(iii) FTIR studies showed that MHBS and Cr.I increased upon the addition of modified kaolin compared to native kaolin, and the resistance of paper handsheets loaded with Cs-kaolin toward γ-irradiation was higher than that of those loaded with native kaolin.

(iv) ESR spectroscopy and LIBS provided rapid, sensitive, and nondestructive techniques in differentiating between the paper handsheets containing native kaolin and those having modified kaolin with cesium.

(v) The ESR spectra of γ-irradiated paper handsheets containing both native and modified kaolin showed slight difference.

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