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Novel Pyrimidinethione Hydrazide Divalent and Trivalent Metal Complexes for Improved High-Performance Antimicrobial and Durable UV Blocking Cellulosic Fabric

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Abstract: Ultraviolet (UV)-protective and antimicrobial cotton fabrics are necessary for the protection of our skin. In this article, a pyrimidinethione hydrazide (PTH) derivative ligand was complexed with Mn, Co, Ni, Cu, Zn, and Cd as divalent metals and Fe and Cr as trivalent metals to prepare highly antimicrobial and UV-blocking metal–pyrimidinethione hydrazide-modified cotton fabrics (M-PTH-C). The cotton sample treated (M-PTH) was found to show improved efficiency over pyrimidinethione hydrazide-modified cotton (PTH-C). Cadmium-PTH-C showed the highest performance of antimicrobial action against *Staphylococcus aureus* (Gram-positive bacteria), *Escherichia Coli* (Gram-negative bacteria), and *Candida albicans* (fungi) with zones of inhibition 31 mm, 18 mm, and 27 mm, respectively. Furthermore, all M-PTH-C samples showed no effect against *Candida albicans*, except Co, Ni, and Cd pyrimidinethione hydrazide-modified cotton with inhibition zones of 16 mm, 27 mm, and 22 mm. In addition, no compounds showed any activity against *Aspergillus flavus* except Cd-PTH-C, which gave an excellent performance, with a 33 mm inhibition zone. Furthermore, most modified cotton fabrics have excellent UV protection. Fe-PTH-C showed 113.3 as the highest Ultraviolet protection factor (UPF) compared to the other modified samples. The tensile strength test of all samples was also investigated. The values of tensile strength for the treated cotton samples are slightly affected compared to the untreated ones.

Keywords: pyrimidinethione; hydrazide; antimicrobial; modified cellulose fabric; UV protection

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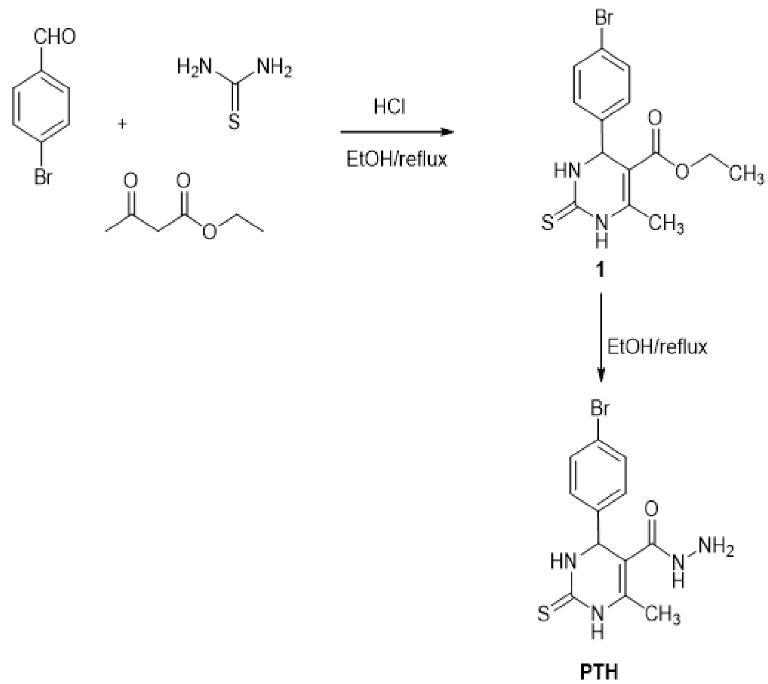
1. Introduction

Countries and communities that have adopted cotton growing have made obvious socioeconomic improvements [1]. Cotton, as one of the most important natural fibres, has several advantages, including high abundance, outstanding mechanical characteristics, and robust biodegradability, giving rise to its wide use in home decoration, packaging, industrial goods, and clothing [2]. The cellulose content in cotton fabric is about 95%. Cotton also contains 5% noncellulosic constituents such as proteins, pectin, waxes, inorganics, and other substances [3]. Antimicrobial textiles have seen a high growth in recent years. Consumer demand for clean, hygienic clothing has driven this growth [4]. Metal salts, organic metallics [5,6], quaternary ammonium salts [7], formaldehyde, amines, urea [8], phenols [9], and antibiotics [10] can interrupt microorganism metabolism and inhibit growth, giving cellulosic fabrics antibacterial and antifungal properties [5]. Antimicrobial fabrics have garnered attention for their potential to prevent pathogenic microbe transmission in medical and healthcare settings [11,12]. Wound dressings, hospital textiles, bed linens, towels, filters, and other medical supplies can be made from textiles treated with antimicrobials [13]. Metal complexes of various organic ligands are intensively studied and used for this purpose [14]. Cotton modification because of growing consumer demand for improved functions of textile products [15]. Cotton fibres are nutritious and hydrophilic, making them ideal for bacterial and fungal growth, and they do not block UV radiation effectively, especially when undyed or dyed in light colours [16]. Today, it is very important to protect people's skin from UV radiation, which can be harmful. Since the ozone layer is becoming thinner, more UV light is reaching the ground. Long-term exposure to UV light can cause many skin diseases, such as skin that ages faster and even skin cancer [17,18]. The UV protection of a fabric depends on the type of fibres it is made of, how it is woven, what dyes are used, and how it is finished. Excellent UV protection for cotton fabrics should be between 40 and 50+. Based on these factors, blank cotton fabric does not protect against UV rays for people who wear it outside [19]. Pyrimidine-based heterocyclic compounds have excellent pharmacological activity [20], and the fluorescent aromatic compound 4-(2,4-dichlorophenyl)-6-oxo-2-thioxohexahydropyrimidine-5-carbonitrile is utilized for the preparation of durable cotton fabrics that are fluorescent, antimicrobial, and UV-protective [21]. 2,4,6-trichloropyrimidine, 2,4-dichloro-5-methoxypyrimidine, and 2-amino-4,6-dichloropyrimidine were used to modify cotton fabrics [22]. The results demonstrated that chloropyrimidine compounds were successfully grafted onto the surface of cotton fabric, resulting in excellent and long-lasting anti-pilling activity of grades 3–4, even after several washing cycles [22,23]. Hydrazide ligands with the general formula R-CO-NH-NH_2 have attracted attention in the literature due to their ease of coordination to several transition metals via various active potential donor sites (C=O, NH, and NH_2), increasing free ligand biological activities [24,25]. Cu(II)–hydrazide complexes were created and demonstrated significant intrinsic DNA binding as well as anti-inflammatory activity [26]. Macrocyclic Ni(II) and Co(II) complexes were synthesized and successfully used as CO_2 reduction catalysts [27].

The aim of the present work, we prepared 4-(4-bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carbohydrazide as a ligand as the previously described method [28] (Scheme 1). The ligand and different divalent and trivalent metals used in modification of cotton fabrics (Figure 1) to acquire highly antimicrobial properties and UV protection. Several techniques, including X-ray diffraction (XRD), Fourier transform-infrared analysis (FTIR), and scanning electron microscopy (SEM) with an attached energy dispersive X-ray spectrometer (EDX), have been used in order to evaluate the prepared cotton fabrics before and after treatment.



Scheme 1. Preparation of pyrimidinethione hydrazide derivative.

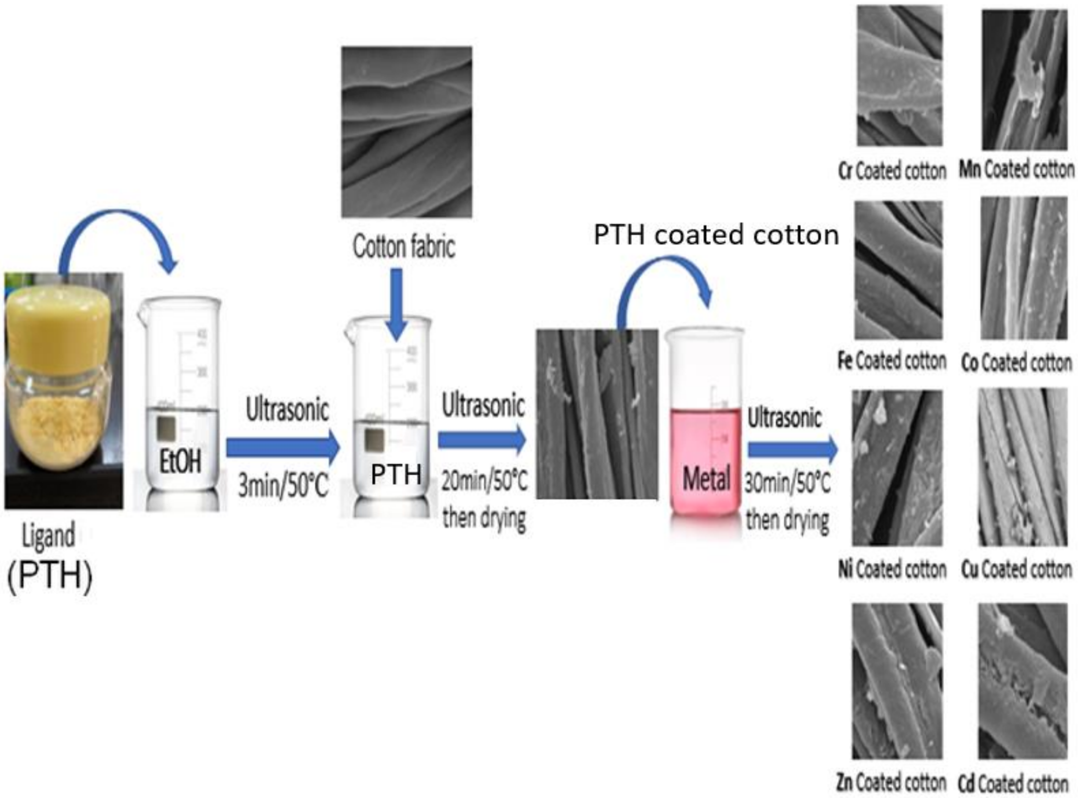


Figure 1. The graphical method of modification of cotton fabrics.

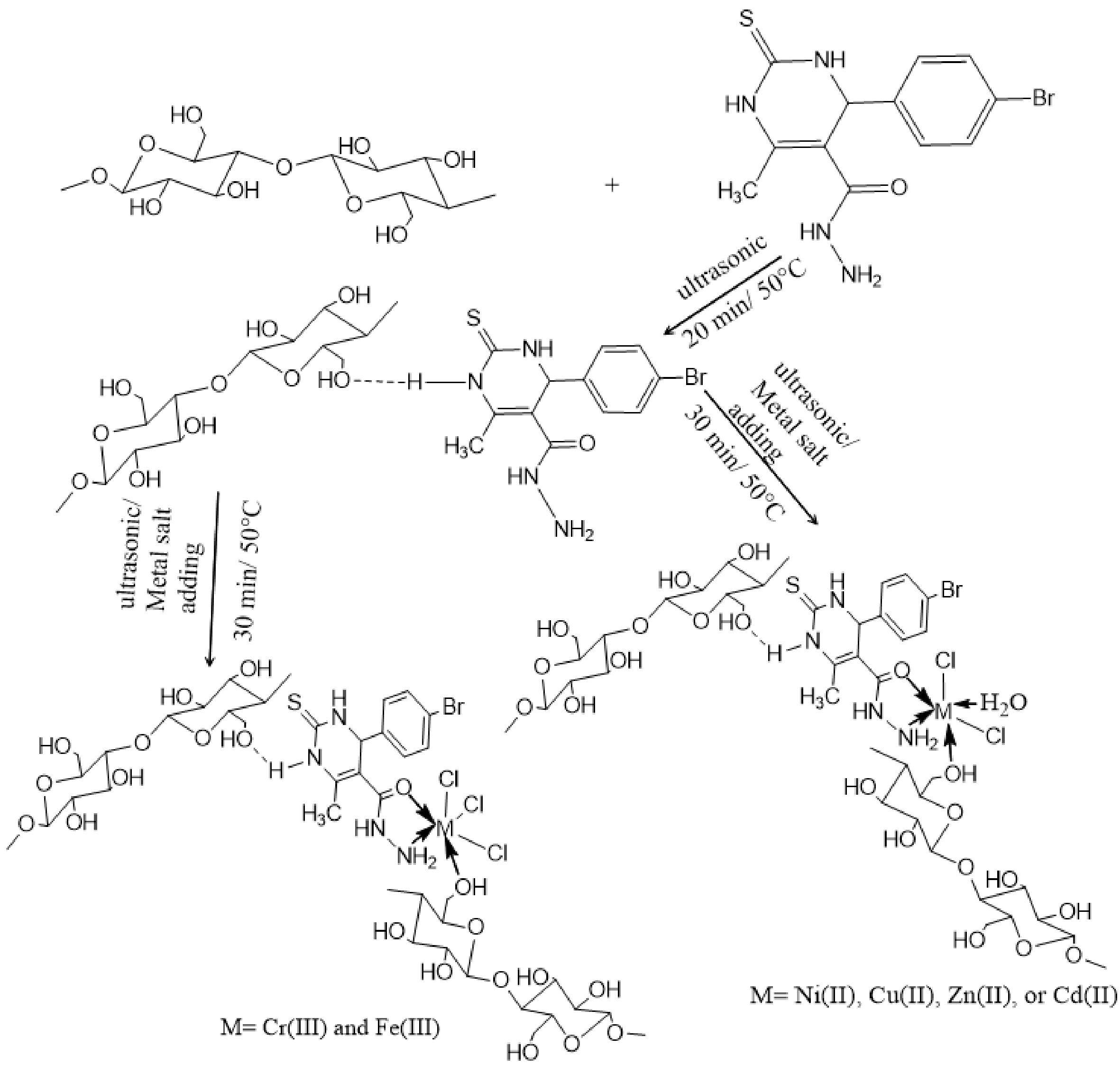
2. Results and Discussions

2.1. Mechanism of Coating Cotton Fabric

Scheme 2 demonstrates the suggested mechanism for the interaction between the cellulose structure and the pyrimidinethione hydrazide (PTH) complex. The interaction between PTH and cotton (C) is based on the hydrogen bonding interaction between the NH_2 group of the ligand and the OH groups of the cotton structure. Upon complexation with different metal ions, the participation of the C=O, NH_2 of the ligand, and OH groups of (C) chains in binding to the metal ions. Intra- and inter-bonds are formed between the OH groups of cellulose chains and metal ions. As a result, a stable complex formed between the metal ion and PTH, impeded in the cellulose chain via intra/inter-bonds.

2.2. FTIR Analysis

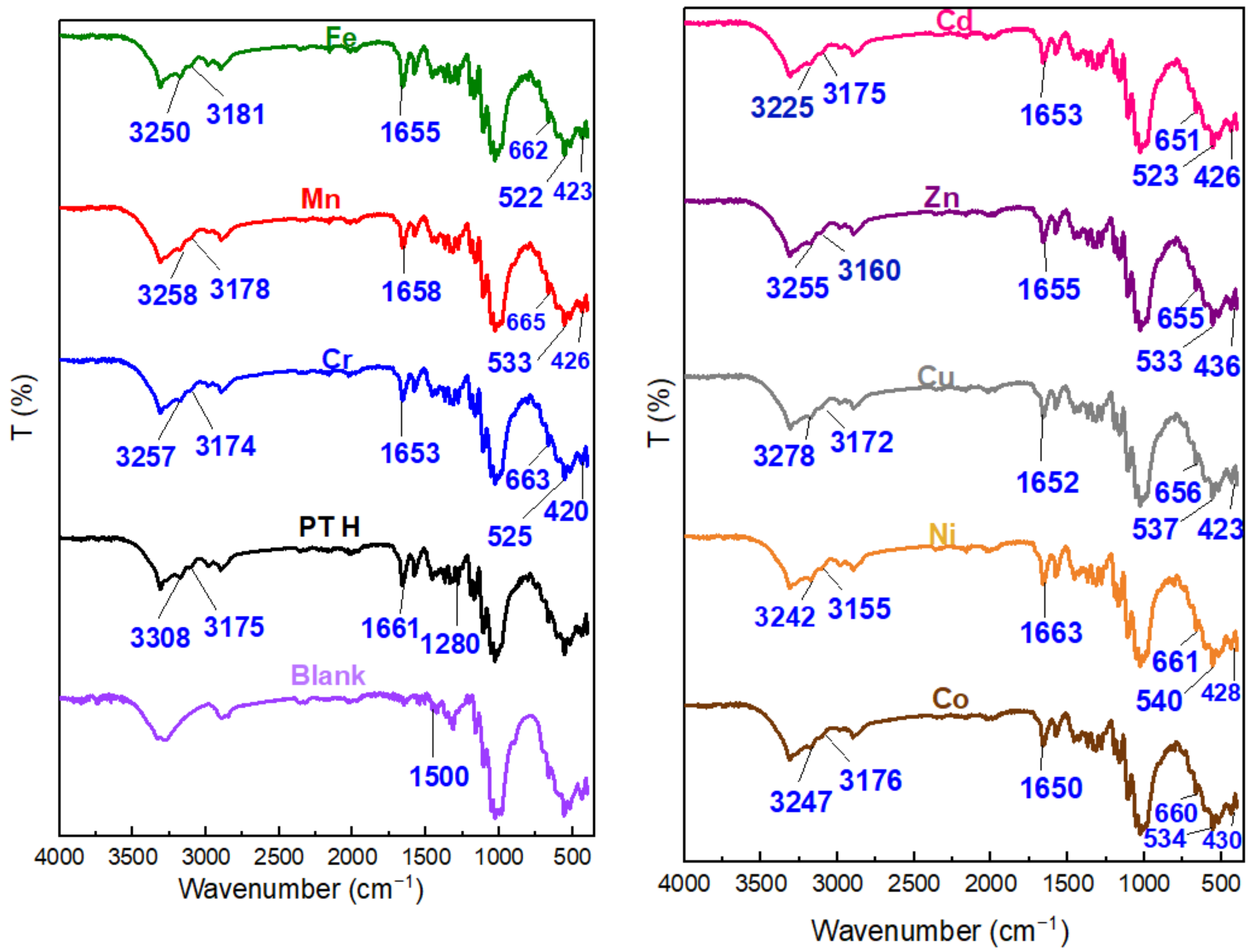
Figure 2 shows the FTIR spectra of blank cotton fabric and the treated samples. As shown in Figure 2a, the untreated cotton has a band that appeared at 3150–3520 cm^{-1} that was assigned to the stretching of O–H. The bands in the range of 1400–750 cm^{-1} are assigned to C–H, C–O, O–H, and C–O–C vibrations of the cellulose structure [29]. New peaks appeared in the PTH-C, indicating the presence of new functional groups at 3308 cm^{-1} and 3175 cm^{-1} for NH_2 and NH, at 1661 cm^{-1} for C=O [30], and at 1280 cm^{-1} for C=S [31]. Compared with the spectra of metal complexes, there is a shift in the intensity of all peaks that appeared, indicating that the formation of metal complexes is successfully deposited on the cellulose chains. Furthermore, weak peaks in the range of 420 cm^{-1} to 660 cm^{-1} could be corresponding to M-Cl, M-N and M-O in the metal complexes.



Scheme 2. The suggested mechanism of the metal complexes bonding with cotton fabrics.

2.3. XRD Analysis

Figure 3 demonstrates the XRD measurements used to analyse the cellulose crystalline structure before and after modification by ligand and ligand metal complexes. Cellulose polymorphs can be classified based on the locations and relative intensities of diffraction peaks [32]. As described in Figure 3, The crystalline structure of cellulose generates sharp diffraction peaks at 14.7°, 16.4°, 22.6° and 34.4° in the XRD patterns [33]. As shown in Figure 3a,b, the treatment of cotton with ligand and its complexes treated affected the lattice and changed the crystallinity of the cotton, as shown from the new peak, which is reasonable for lowering the peak intensity. One new peak appeared for PTH-C at 2θ = 20.8°, Co-PTH-C at 2θ = 21.1°, and Zn-PTH-C at 2θ = 26.04°. However, there are two new peaks for Cr-PTH-C at 2θ = 20.6° and 25.8°, Mn-PTH-C at 2θ = 20.9° and 26.06°, Fe-PTH-C at 2θ = 15.6° and 26.2°, Ni-PTH-C at 2θ = 21.08° and 25.6°, Cu-PTH-C at 2θ = 20.9° and 26.1°, and Cd-PTH-C at 2θ = 20.6° and 25.8°. The absence of these peaks in the blank cotton fabric may indicate that the cellulose chains successfully interacted with the PTH ligand and M-PTH complexes.



(**a**) (**b**)

Figure 2. FT-IR spectra of (**a**) Blank cotton, PTH-C, Cr-PTH-C, Mn-PTH-C, and Fe-PTH-C; (**b**) Co-PTH-C, Ni-PTH-C, Cu-PTH-C, Zn-PTH-C, and Cd-PTH-C.

2.4. SEM/EDX Analysis

The deposition of PTH with its metal complexes on the surface of cellulose fabric was confirmed by using SEM and EDX analysis. SEM images appeared the morphological properties of uncoated and coated surfaces of fabrics. Figure 4 illustrates SEM images of the blank cotton fabric and M-PTH-C complexes. The blank cotton surface was very smooth and clear with characteristic parallel grooves, as shown in Figure 4a. In contrast, the sample coated with PTH in Figure 4b shows a rough surface coating layer of PTH on the surface of the fabric rather than a surface that is clear, smooth, and streamlined. In addition, some granules, agglomerated particles, and pores are found on the surface of the fabric for all samples coated with pyrimidine hydrazide–metal complexes. As can be seen in Figure 5, the EDX data also provided some very useful information confirming the SEM findings. The elemental analysis of the coated fabric was strengthened by the EDX spectra. The EDX results of blank cotton showed only carbon and oxygen. The presence of new elements (Br, N and S) in the PTH-C sample is an indication of its successful treatment with the ligand. In addition, the presence of the used metal element in Figure 4c–j is an indication of the successful treatment of the cotton samples with the metal.

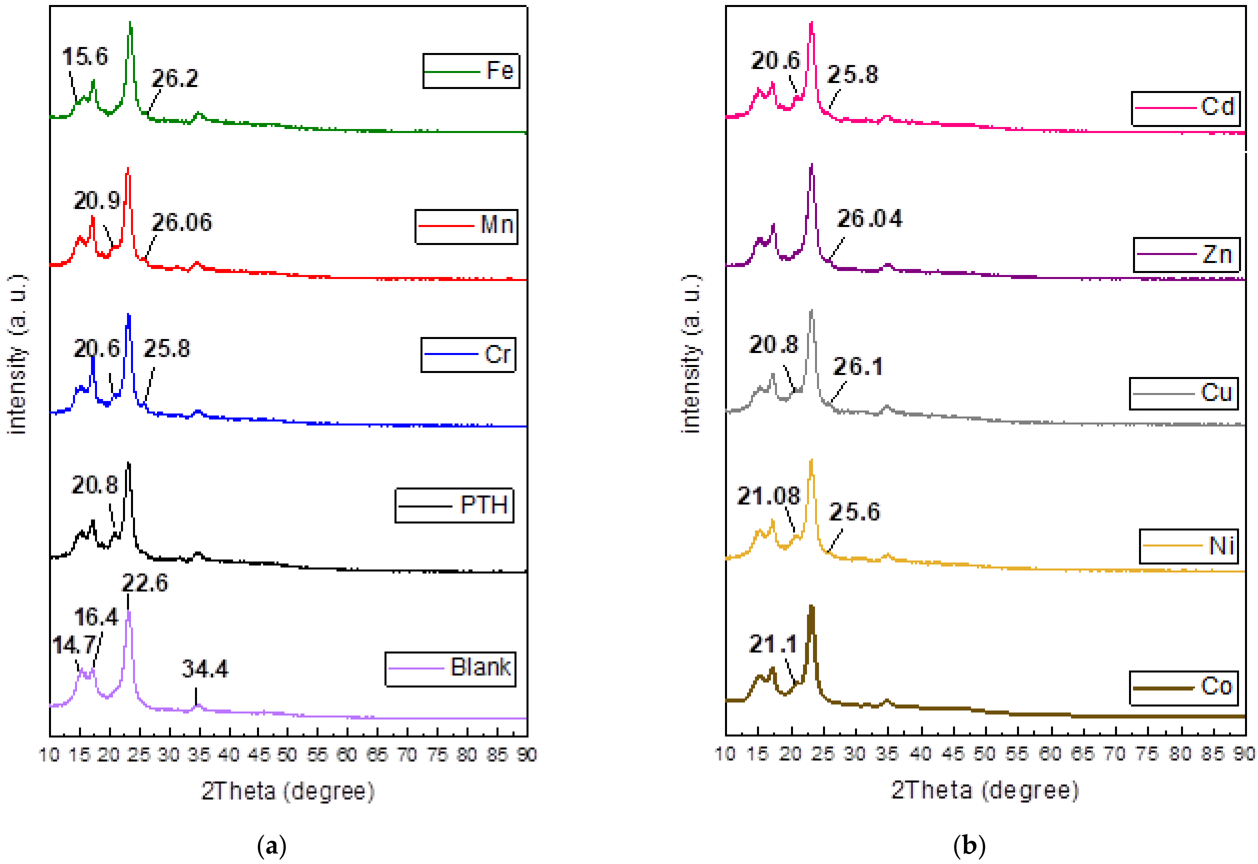


Figure 3. XRD of (**a**) Blank cotton, PTH-C, Cr-PTH-C, Mn-PTH-C and Fe-PTH-C; (**b**) Co-PTH-C, Ni-PTH-C, Cu-PTH-C, Zn-PTH-C and Cd-PTH-C.

2.5. Antimicrobial Activity

The antimicrobial activity is summarized in Table 1 and Figures 6–9. A screening test for possible antibacterial and antifungal activity was applied to pyrimidinethione hydrazide-modified cotton (PTH-C) and metal–pyrimidinethione hydrazide-modified cotton (M- PTH-C). As shown in Table 1, the results showed that the modified cotton fabrics have larger inhibition zones against the two types of bacteria than the fungi used. All modified cotton fabrics with ligand–metal complexes have antibacterial activity ranging from moderate to higher inhibition zones values. Moreover, Cd-PTH-C-modified fabric has the largest inhibition zone (31 mm) for Gram-positive bacteria (*S. aureus*) Figure 6 and 18 mm for Gram-negative bacteria (*E. coli*) Figure 7. Modified samples have greater antibacterial efficiency against Gram-positive bacteria than Gram-negative ones. This may be due to the difference in cell membranes between different types of bacteria [34]. Compared with antibacterial activity, modified fabrics have no activity against fungal strains, except Co-PTH-C, Ni-PTH-C, and Cd-PTH-C, which showed antifungal activities Figures 8 and 9. The outstanding antimicrobial activity of the metal–PTH-C over those of the ligand can be explained by the overtone concept and chelation theory [35]. Due to the overlap of the ligand orbital and the partial sharing of the positive charge of the metal ion with the donor groups, chelation will result in a greater reduction in the polarity of the metal ion [36]. These metal complexes inhibit protein synthesis, which is essential to an organism's development, by interfering with the cell's respiration process. The permeability of the cell membrane or the ribosome differences of microbial cells determines the extent to which ligand and metal complexes differ in their activity. The donor atoms of the ligand may also inhibit the enzyme activity that depends on these groups and appear to be especially susceptible to deactivation by metal ions upon chelation [37].

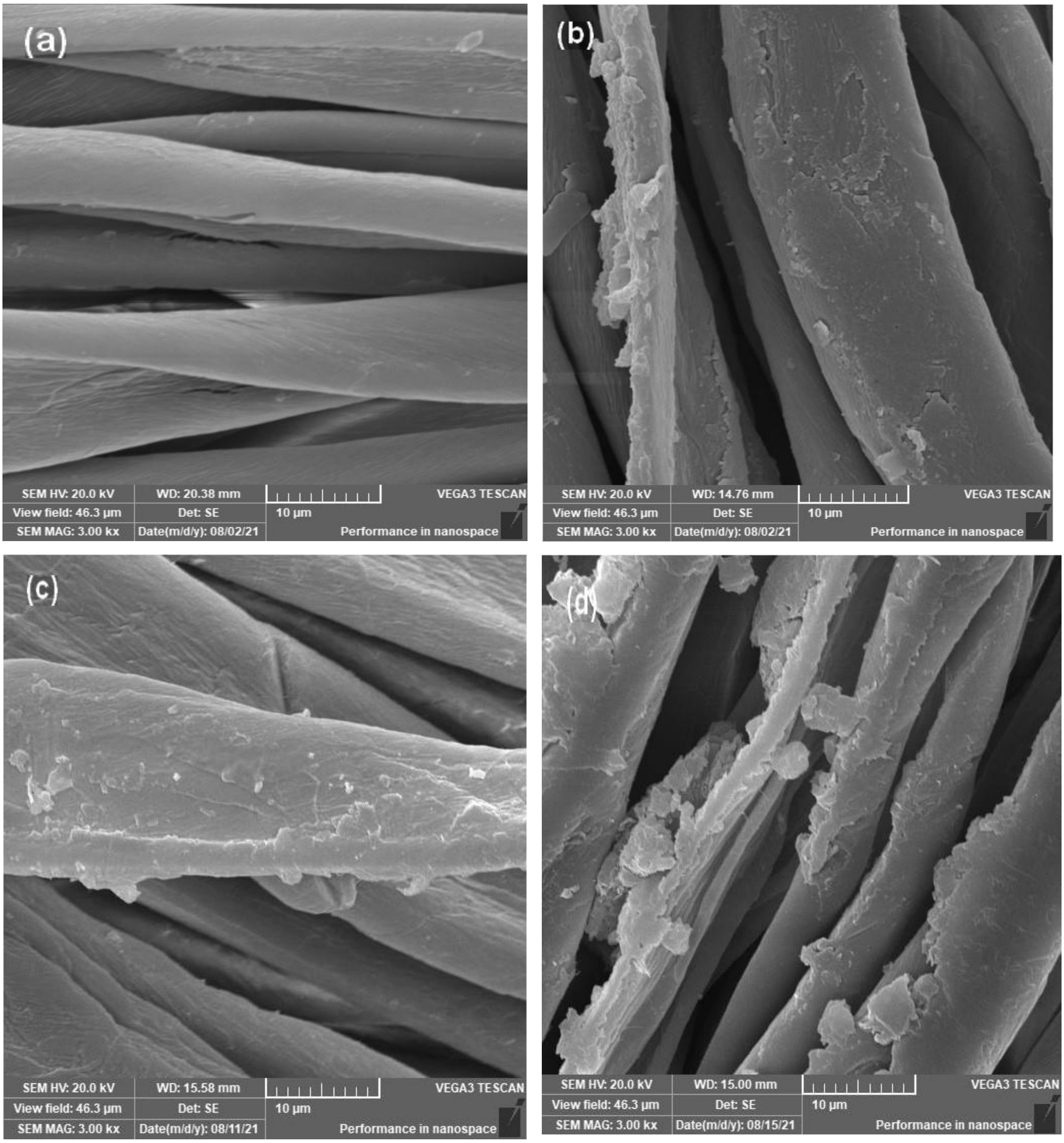
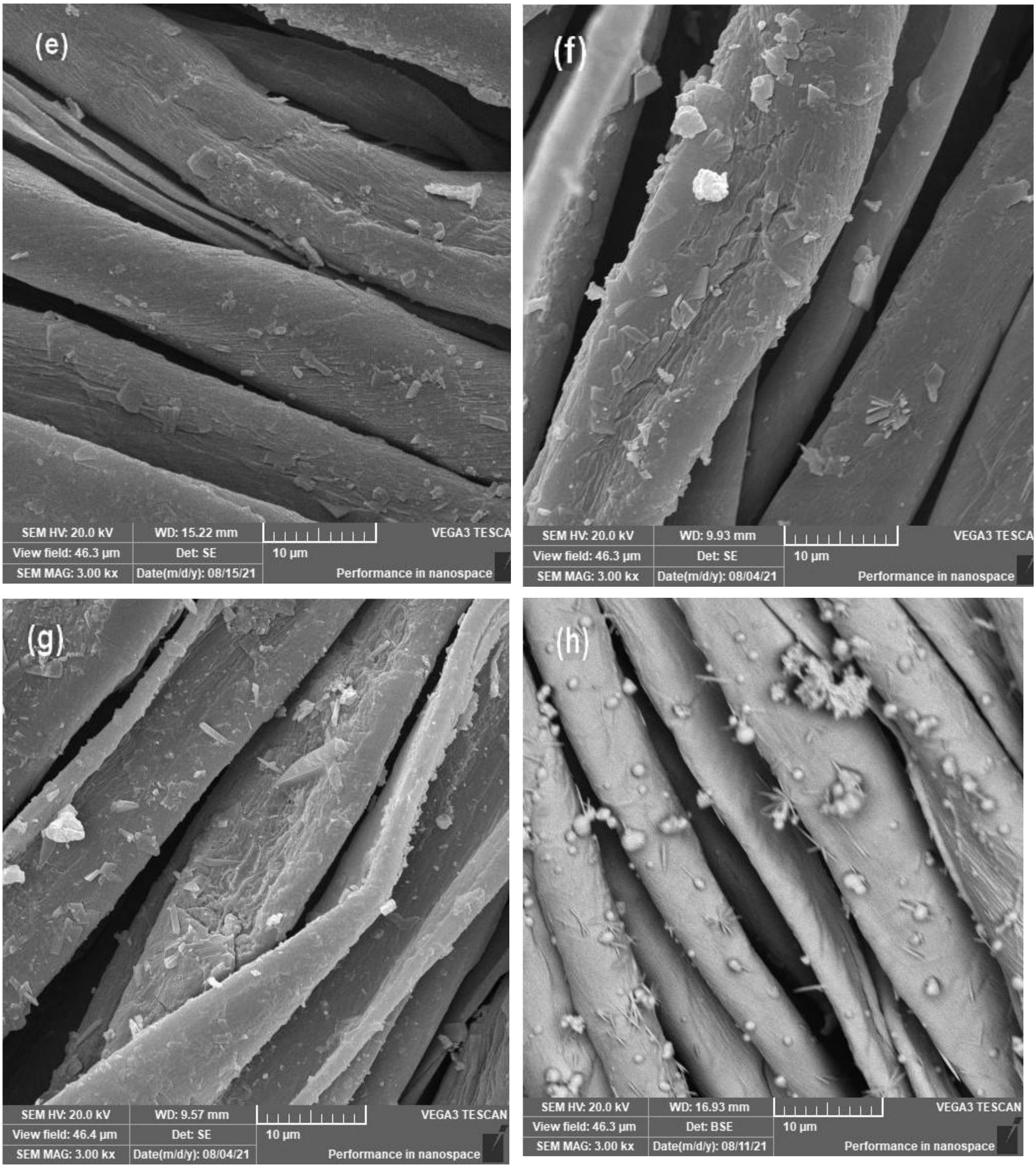


Figure 4. *Cont*.



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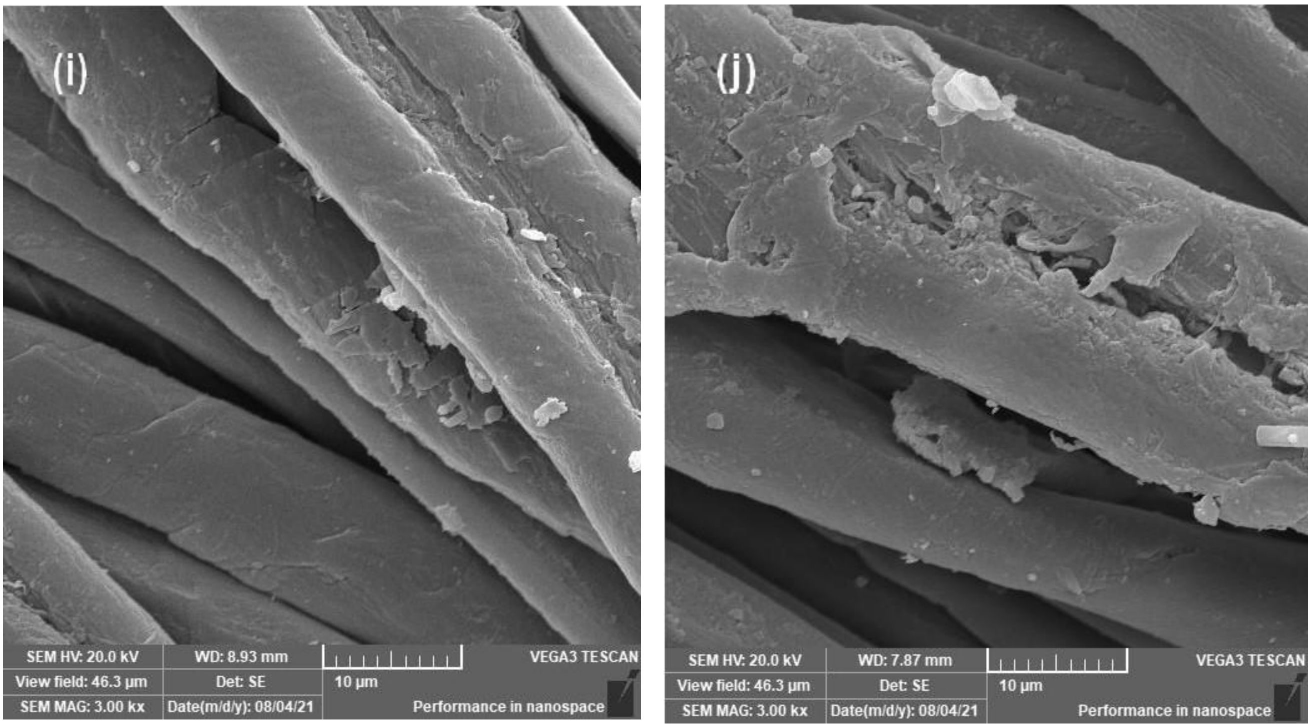
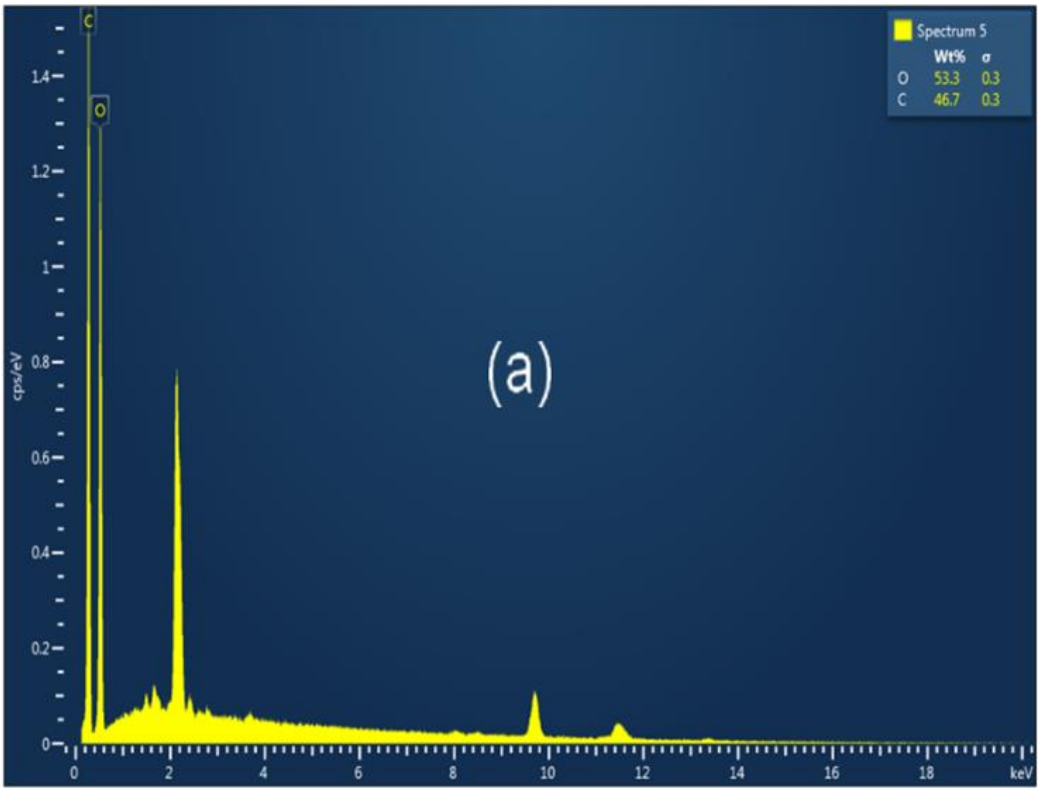


Figure 4. SEM images of (**a**) Blank cotton, (**b**) PTH-C, (**c**) Cr-PTH-C, (**d**) Mn-PTH-C, (**e**) Fe-PTH-C, (**f**) Co-PTH-C, (**g**) Ni-PTH-C, (**h**) Cu-PTH-C, (**i**) Zn-PTH-C, and (**j**) Cd-PTH-C.



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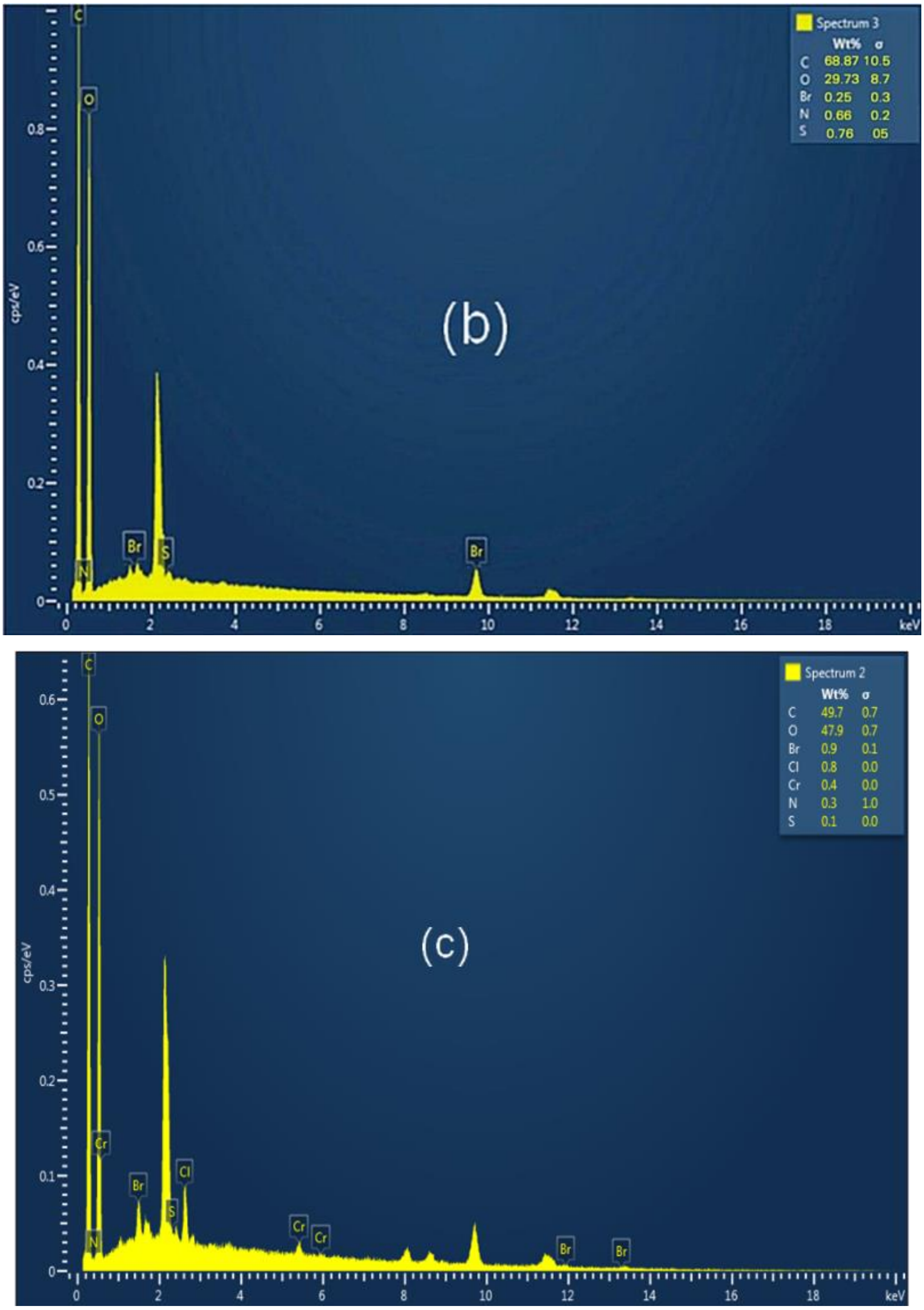

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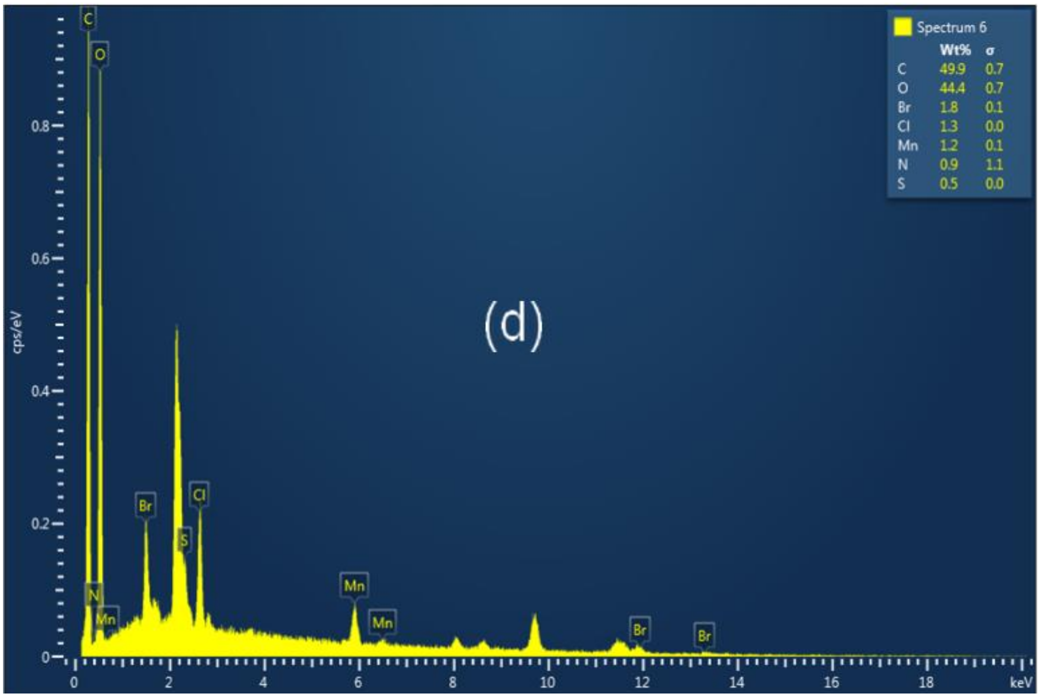

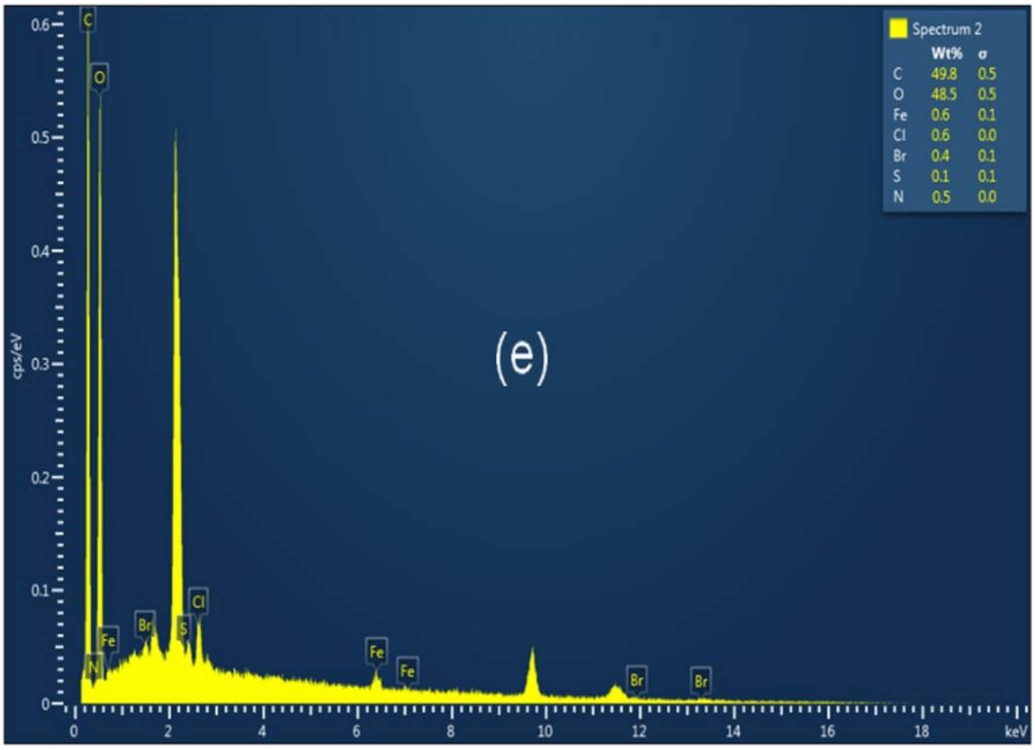

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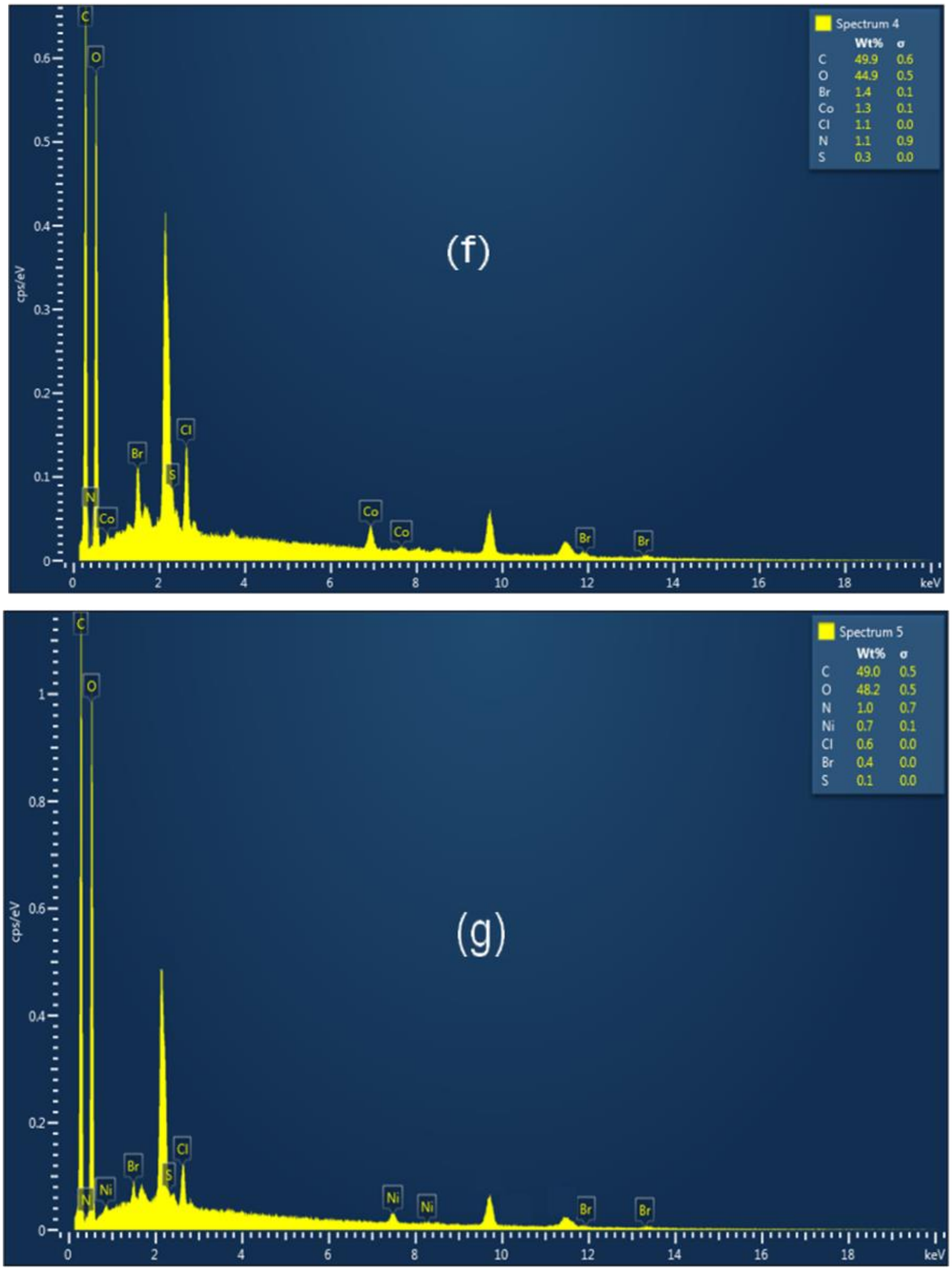

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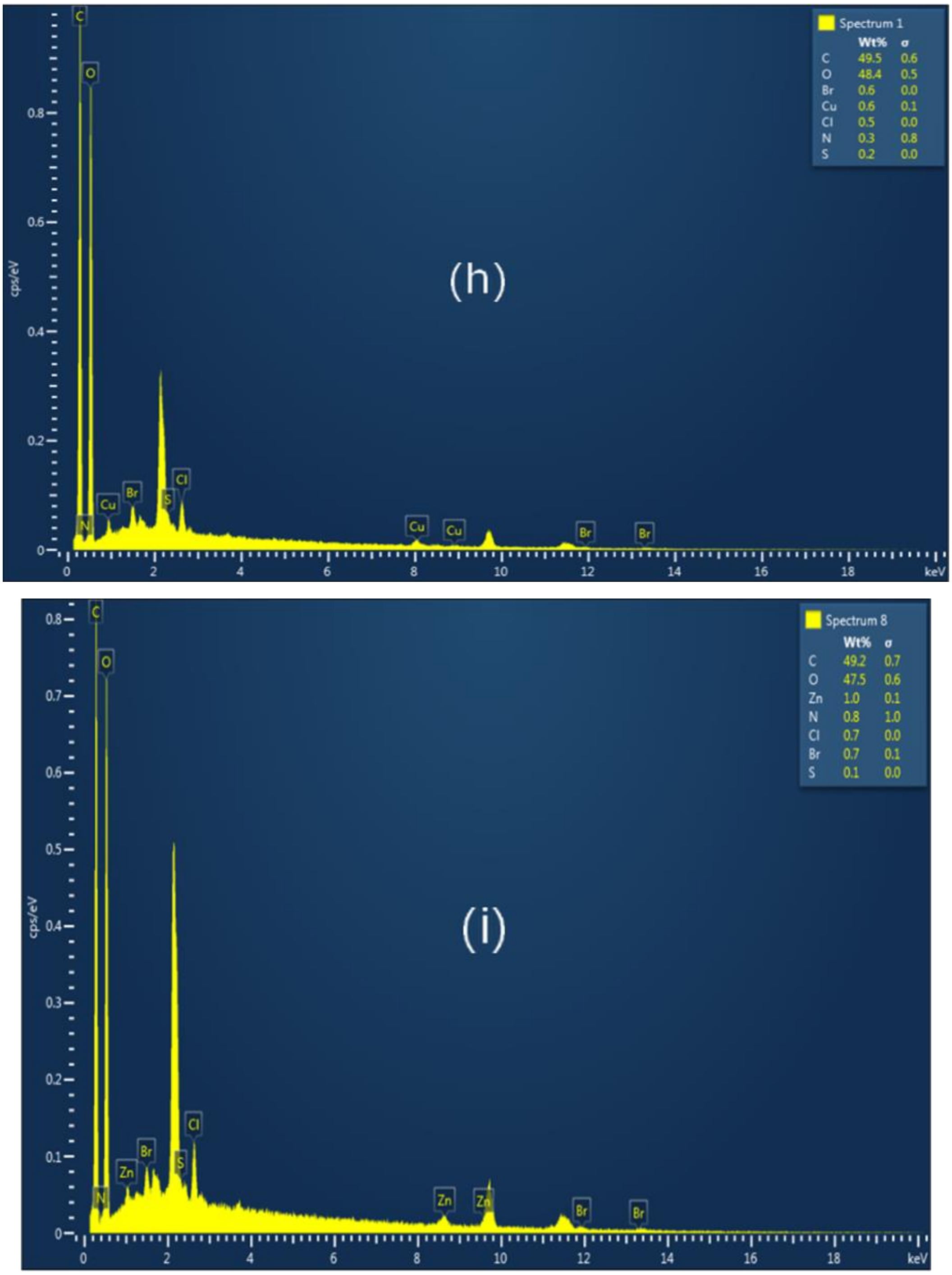

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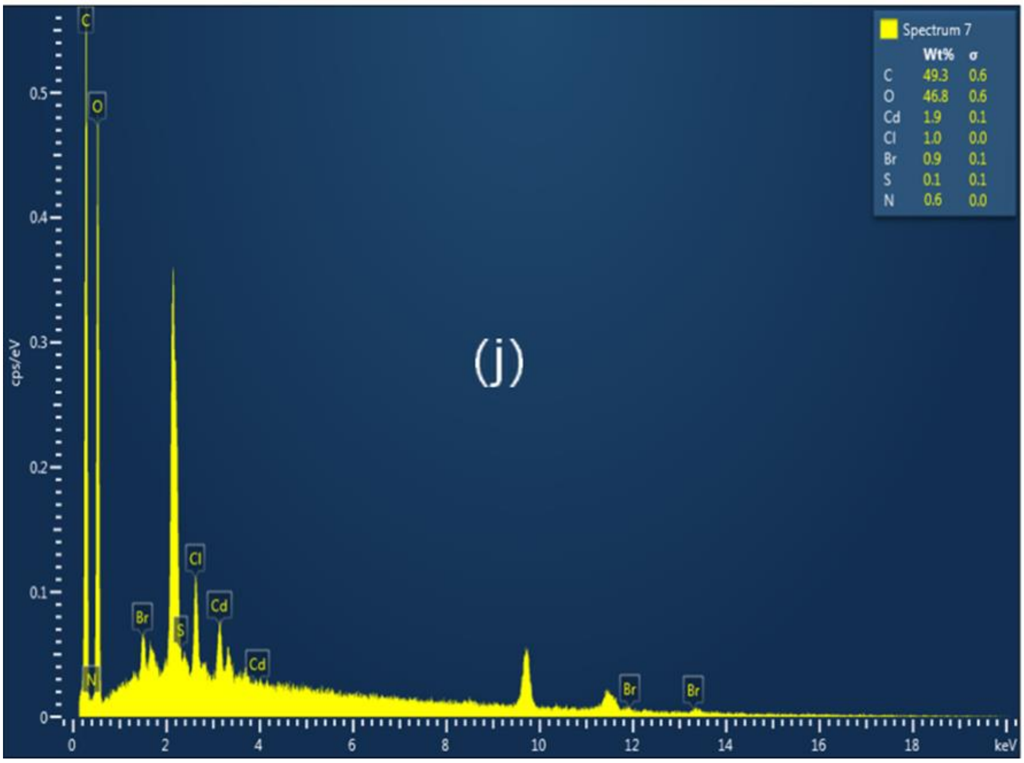

Figure 5. EDX spectra of (**a**) Blank cotton, (**b**) PTH-C, (**c**) Cr-PTH-C, (**d**) Mn-PTH-C, (**e**) Fe-PTH-C, (**f**) Co-PTH-C, (**g**) Ni-PTH-C, (**h**) Cu-PTH-C, (**i**) Zn-PTH-C and (**j**) Cd-PTH-C.

Table 1. Antimicrobial activity of PTH-C and M-PTH-modified fabric.

Treated Sample	Inhibition Zone Diameter (mm/cm Sample)			
	Fungal Species		Bacterial Species	
	Candida albicans	*Aspergillus flavus*	*Escherichia coli(G−)*	*Staphylococcus aureus (G+)*
Blank cotton fabric	0	0	0	0
PTH-C	0	0	0	0
Cr-PTH-C	0	0	12 ± 0.24	12 ± 0.23
Mn-PTH-C	0	0	11 ± 0.3	12 ± 0.26
Fe-PTH-C	0	0	13 ± 0.31	16 ± 0.13
Co-PTH-C	16	0	17 ± 0.22	25 ± 0.4
Ni-PTH-C	22	0	14 ± 0.37	22 ± 0.42
Cu-PTH-C	0	0	16 ± 0.32	15 ± 0.28
Zn-PTH-C	0	0	20 ± 0.29	21 ± 0.33
Cd-PTH-C	27	33	18 ± 0.25	31 ± 0.5

Figure 6. Images of the activity of B (Blank cotton), the modified cotton with PTH or different metal complexes against *S. aureus*.

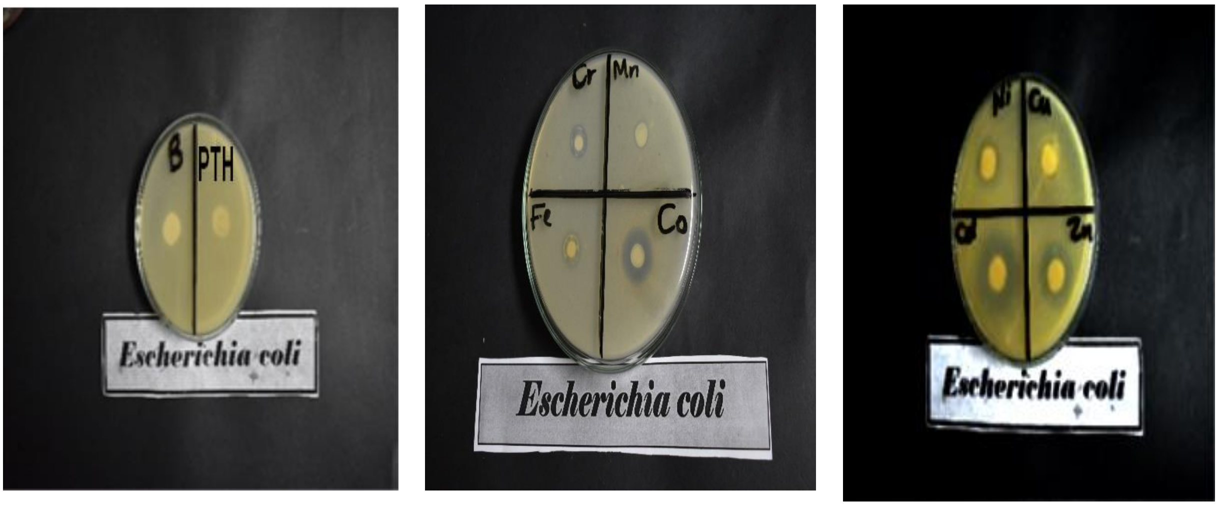

Figure 7. Images of the activity of B (Blank cotton), the modified cotton with PTH or different metal complexes against *E. coli*.

Figure 8. Images of the activity of B (Blank cotton), the modified cotton with PTH or different metal complexes against Candida albicans.

Figure 9. Images of the activity of B (Blank cotton), the modified cotton with PTH or different metal complexes against *Aspergillus flavus*.

2.6. UV Protection

Table 2 displays the UV protection factors (UPF) of both untreated and modified cotton fabrics. The unmodified cotton sample has a UPF of 5.4, while the modified samples that have been treated with ligands and their metal complexes have UPF values that range from 41.1 to 113.3. According to Table 2, the PTH-C sample was found to have a UPF of 41.1. After the metal complexes are deposited on the surface of cotton fabric, the measured UPF values raise noticeably. The sequence of metal complexes in cotton fabric modifications is:

Table 2. UPF values of treated samples.

Sample Name	UPF	UV Transmittance		UPF after 10 Washing Cycles
		UV-A	UV-B	
Blank cotton fabric	5.4 ± 0.20	25.1	17.1	4.2 ± 0.42
PTH-C	41.4 ± 0.10	10.4	1.9	37.3 ± 0.18
Cr-PTH-C	55.0 ± 0.50	8.1	1.4	48.4 ± 0.32
Mn-PTH-C	47.1 ± 0.20	8	1.7	44.5 ± 0.22
Fe-PTH-C	113.3 ± 0.25	1.2	0.9	105.2 ± 0.3
Co-PTH-C	68.2 ± 0.20	6.8	1.1	61.5 ± 0.40
Ni-PTH-C	65.5 ± 0.30	8.3	1.1	57.2 ± 0.35
Cu-PTH-C	59.9 ± 0.34	2.6	1.5	56.1 ± 0.27
Zn-PTH-C	39 ± 0.15	10	2.1	33.7 ± 0.32
Cd-PTH-C	50.6 ± 0.18	9.4	1.5	46.6 ± 0.40

Fe-PTH-C > Co-PTH-C > Ni-PTH-C > Cu-PTH-C > Cr-PTH-C > Cd-PTH-C > Mn-PTH-C > Zn-PTH-C.

The improved UV protection performance of for the PTH-C (pyrimidinethione ligand-treated cotton) and M-PTH (M-ligand treated cotton fabric) may be explained by the π–π* and n–π* transitions of a conjugated system [38]. Also Table 2 represents the durability after 10 washing cycles which supports the successful adherence between the metal complexes and the cotton fiber.

2.7. The Add-On (%) Loading and Tensile Strength

Table 3 shows that the amount of chemicals deposited on the surface of cotton fabric presented as the values of add-on measurements. In addition, Table 3 represents the tensile strength of modified cotton fabric. As presented in Table 3, the add-on values varied between 1.58% and 4.30%. Moreover, a slight decrease in the tensile strength values is also noticeable. This may be attributed to the various modifications to the cotton fabric [39,40].

Table 3. Add-on calculations and tensile strength values of samples.

Treatment	Add-On (%)	Tensile Strength (kg f)
Blank cotton fabric	–	54.7 ± 0.25
PTH-C	1.58 ± 0.1	51.8 ± 0.23
Cr-PTH-C	2.93 ± 0.2	49 ± 0.12
Mn-PTH-C	3.61 ± 0.4	47.2 ± 0.2
Fe-PTH-C	4.04 ± 0.06	48.5 ± 0.41
Co-PTH-C	4.22 ± 0.7	48.2 ± 0.45
Ni-PTH-C	3.4 ± 0.05	48.7 ± 0.3
Cu-PTH-C	4.30 ± 0.04	49.8 ± 0.15
Zn-PTH-C	1.87 ± 0.02	50.7 ± 0.37
Cd-PTH-C	4.25 ± 0.3	48.9 ± 0.11

3. Materials and Methods

3.1. Materials

The fabric of 100% bleached cotton (138 g/m^2) was supplied by the Misr Company for Spinning and Weaving in Mehalla El-Kobra, Egypt.

3.2. Chemicals

All solvents were purchased from Fisher Scientific, Loughborough, UK. 4-bromobenzaldehydes, ethyl acetoacetate, and thiourea were obtained from Sigma Aldrich; hydrochloric acid and hydrazine hydrate were obtained from Loba Chemie. Metal chlorides were purchased from Loba Chemie.

3.3. Methods

4-(4-bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5 carbohydrazide (PTH) was used as a ligand in the modification of cotton fabric to produce PTH-modified cotton (PTH-C). Then, salts of $CrCl_3{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $ZnCl_2$ dry, or $CdCl_2{\cdot}2.5H_2O$ were added to the ligand-modified cotton fabrics to form metal-PTH-modified cotton (M-PTH-C).

3.3.1. Preparation of the Ligand

The ligand was prepared in two steps as the previously described method [28]. The 1st step is the preparation of ethyl 4-(4-bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Scheme 1; structure 1). Hydrochloric acid (36%, 3–4 drops) was added to a solution of 4-bromobenzaldehydes (2 mmol), ethyl acetoacetate (2.5 mmol), and thiourea (2 mmol) were mixed in ethanol (30 mL) and the mixture was refluxed for 6 h. The solvent was largely removed to one-third of its original amount and then left to stand at room temperature for 2 h. The formed precipitate was filtered, washed with methanol, and recrystallized from ethanol to obtain the ester (Scheme 1; structure 1).

The 2nd step is the preparation of the ligand "4-(4-Bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carbohydrazide".

To a solution of the substituted pyrimidine ester **1** (5 mmol) in absolute ethanol (25 mL), hydrazine hydrate 99% (6 mmol) was added, and the reaction mixture was heated under reflux for four hours. The solvent was largely removed under reduced pressure and left to stand at room temperature for 3 h. The obtained precipitate was filtered, dried, and crystallized from ethanol to obtain the pyrimidinethione hydrazide (PTH) ligand (Scheme 1) as yellow crystals.

3.3.2. Coating of Cotton Fabric with Metal–Ligand Complexes

As shown in Figure 1, in a 100 mL beaker, we added 1 mmol (0.34 g) of the ligand to 30 mL ethyl alcohol. After that, it was put in the ultrasonic water bath for 3 min at 50 °C until the ligand dissolved, followed by immersing the fabric in the prepared mixture for 20 min at 50 °C, then dried in the oven at 60 °C for 10 min to produce PTH-modified cotton (PTH-C). The ligand–cotton fabric was immersed in a beaker of 30 mL EtOH; then, we added 1 mmol of $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$ or $CdCl_2 \cdot 2.5H_2O$. The beaker was put in a water bath ultrasonic device for 30 min at 50 °C, after that, the textile was dried at 60 °C for 10 min to produce metal–pyrimidinethione hydrazide-modified cotton (M-PTH-C).

3.4. Instruments

The FTIR spectra of pyrimidinethione hydrazide-modified cotton (PTH-C) or metal–pyrimidinethione hydrazide-modified cotton (M-PTH-C) complexes and the cotton fabric samples were measured using an Agilent spectrometer (Cary 600 FTIR, Santa Clara, CA, USA), which was operated in the wavenumber range of 4000–400 cm^{-1}. A Rigaku XRD diffractometer was used to measure the samples' XRD patterns (Ultima IV, Tokyo, Japan) using Cu Kα radiation (λ = 1.54180 Å). Scanning electron microscopy (SEM) (Tescan Vega3) with an attached energy dispersive X-ray spectrometer (EDX) was conducted. SEM images of treated and untreated samples were prepared on an appropriate disk and coated with gold to make the samples conductive to electrons.

3.5. Antimicrobial Test Method

Antibacterial and antifungal activities of treated cotton fabric were examined using the disc diffusion method. The bacterial species include Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) species. *Candida albicans* and *Aspergillus flavus* were used as fungal species.

3.6. Tensile Strength

The ASTM (D-1682-94 test method) was used to test the cotton samples' tensile strength.

3.7. The Add-On (%) Loading

The add-on was calculated according to Equation (1):

$$Add - on(\%) = \frac{W_2 - W_1}{W_1} \times 100 \tag{1}$$

where W_1 and W_2 are the weights of the cotton samples before and after treatment, respectively.

3.8. Ultraviolet Protection Factor (UPF)

A UV Shimadzu 3101 Spectrophotometer (Shimadzu, Japan, Kyoto) was used to calculate the ultraviolet protection factor with a scan range of 200–400 nm. The Australian/New Zealand Standard (AS/NZS) 4399:1996 describes UV protection and classification. To calculate the UPF, a fabric's direct and diffuse transmission across the UVB (290–315 nm) and UVA (315–380 nm) wavelength ranges are measured. The following equation is used to determine the UPF:

$$UPF = \frac{\int_{290}^{400} E_\lambda S_\lambda d_\lambda}{\int_{290}^{400} E_\lambda S_\lambda T_\lambda d_\lambda}$$

where λ is the wavelength (nm); E_λ is relative erythemal effectiveness;

S_λ is the solar UV spectral irradiance; T_λ is the spectral transmittance of the fabric; and d_λ is the wavelength increment (nm).

3.9. Statistical Analysis

The results of each sample were collected three times and expressed as the average value with its standard deviation (average $\pm$ S.D.).

4. Conclusions

In conclusion, a simple method was developed for fabricated antimicrobial and UV-protected cotton fabric. The modified cotton fabric was obtained by the uniform deposition of 4-(4-bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carbohydrazide ligand and metal complexes on the surface of the cotton fabric. The modified samples were characterized via FTIR, XRD, EDX, and SEM. According to the results of the antimicrobial test, the modified cotton fabrics have the highest efficiency against Gram-positive and Gram-negative bacteria, especially the Cd-PTH-C and Zn-PTH-C sample, while only Cd-PTH-C gives excellent results against fungi. In the UV protection calculations, Fe-PTH-C demonstrated an outstanding performance with a UPF value of 113.3 compared with the other complexes. Mechanical properties expressed as tensile strength values of treated samples showed an insignificant decrease in comparison with untreated cotton samples. In general, we obtain excellent antimicrobial results, as well as excellent results in most of the modified cotton fabrics in terms of UV protection. This study, which combines antimicrobial properties with UV-blocking cotton fabric, is expected to contribute to applications in the field of packaging or home decorations.

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References

1. Kobenan, K.C.; Bini, K.K.N.; Kouakou, M.; Kouadio, I.S.; Zengin, G.; Ochou, G.E.C.; Boka, N.R.K.; Menozzi, P.; Ochou, O.G.; Dick, A.E. Chemical Composition and Spectrum of Insecticidal Activity of the Essential Oils of *Ocimum gratissimum* L. and *Cymbopogon citratus* Stapf on the Main Insects of the Cotton Entomofauna in Côte d'Ivoire. *Chem. Biodivers.* **2021**, *18*, e2100497. [CrossRef] [PubMed]
2. Li, Z.-F.; Zhang, C.-J.; Cui, L.; Zhu, P.; Yan, C.; Liu, Y. Fire retardant and thermal degradation properties of cotton fabrics based on APTES and sodium phytate through layer-by-layer assembly. *J. Anal. Appl. Pyrolysis* **2017**, *123*, 216–223. [CrossRef]
3. Hsieh, Y.-L. Chemical structure and properties of cotton. In *Cotton: Science and Technology*; Woodhead Publishing: Sawston, UK, 2007; pp. 3–34.
4. Mirjalili, M.; Yaghmaei, N.; Mirjalili, M. Antibacterial properties of nano silver finish cellulose fabric. *J. Nanostructure Chem.* **2013**, *3*, 1–5. [CrossRef]
5. Burniston, N.; Bygott, C.; Stratton, J. Nano technoology meets titanium dioxide. *Surf. Coat. Int. Part A Coat. J.* **2004**, *87*, 179–184.

6. Gómez, E.M.P.; Silva, O.F.; Der Ohannesian, M.; Fernández, M.N.; Oliveira, R.G.; Fernández, M.A. Micelle-to-vesicle transition of lipoamino Gemini surfactant induced by metallic salts and its effects on antibacterial activity. *J. Mol. Liq.* **2022**, *353*, 118793. [CrossRef]
7. Liu, Y.; Ma, K.; Li, R.; Ren, X.; Huang, T. Antibacterial cotton treated with N-halamine and quaternary ammonium salt. *Cellulose* **2013**, *20*, 3123–3130. [CrossRef]
8. Osman, E.M.; Khalil, A.A.; El-Shrbini, M.H.; Reda, L.M.; Shaaban, A.F. Characterization and evaluation of phosphorus/nitrogen-containing polymer as a durable flame retardant for cotton fabrics. *J Appl Chem Sci Int* **2015**, *3*, 39–52.
9. Alihosseini, F. Plant-based compounds for antimicrobial textiles. In *Antimicrobial Textiles*; Elsevier: Amsterdam, The Netherlands, 2016; pp. 155–195.
10. Eid, B.M.; El-Sayed, G.M.; Ibrahim, H.M.; Habib, N.H. Durable antibacterial functionality of cotton/polyester blended fabrics using antibiotic/MONPs composite. *Fibers Polym.* **2019**, *20*, 2297–2309. [CrossRef]
11. Elnaggar, M.; Emam, H.; Fathalla, M.; Abdel-Aziz, M.; Zahran, M. Chemical synthesis of silver nanoparticles in its solid state: Highly efficient antimicrobial cotton fabrics for wound healing properties. *Egypt. J. Chem.* **2021**, *64*, 2697–2709. [CrossRef]
12. El-Sayed, S.S.; Alhakimi, A.N. Synthesis, characterization of Lanthanum mixed ligand complexes based on benzimidazole derivative and the effect of the added ligand on the antimicrobial, and anticancer activities. *J. Qassim Univ. Sci.* **2022**, *15*, 35–53.
13. Gulati, R.; Sharma, S.; Sharma, R.K. Antimicrobial textile: Recent developments and functional perspective. *Polym. Bull.* **2022**, *79*, 5747–5771. [CrossRef] [PubMed]
14. Staneva, D.; Atanasova, D.; Nenova, A.; Vasileva-Tonkova, E.; Grabchev, I. Cotton fabric modified with a PAMAM dendrimer with encapsulated copper nanoparticles: Antimicrobial activity. *Materials* **2021**, *14*, 7832. [CrossRef] [PubMed]
15. Tausif, M.; Jabbar, A.; Naeem, M.S.; Basit, A.; Ahmad, F.; Cassidy, T. Cotton in the new millennium: Advances, economics, perceptions and problems. *Text. Prog.* **2018**, *50*, 1–66. [CrossRef]
16. Čuk, N.; Šala, M.; Gorjanc, M. Development of antibacterial and UV protective cotton fabrics using plant food waste and alien invasive plant extracts as reducing agents for the in-situ synthesis of silver nanoparticles. *Cellulose* **2021**, *28*, 3215–3233. [CrossRef]
17. Alebeid, O.K.; Zhao, T. Review on: Developing UV protection for cotton fabric. *J. Text. Inst.* **2017**, *108*, 2027–2039. [CrossRef]
18. Lee, S. Developing UV-protective textiles based on electrospun zinc oxide nanocomposite fibers. *Fibers Polym.* **2009**, *10*, 295–301. [CrossRef]
19. Abidi, N.; Hequet, E.; Tarimala, S.; Dai, L.L. Cotton fabric surface modification for improved UV radiation protection using sol–gel process. *J. Appl. Polym. Sci.* **2007**, *104*, 111–117. [CrossRef]
20. Emam, H.E.; El-Shahat, M.; Hasanin, M.S.; Ahmed, H.B. Potential military cotton textiles composed of carbon quantum dots clustered from 4–(2, 4–dichlorophenyl)–6–oxo–2–thioxohexahydropyrimidine–5–carbonitrile. *Cellulose* **2021**, *28*, 9991–10011. [CrossRef]
21. Emam, H.E.; El-Shahat, M.; Hasanin, M.S.; Ahmed, H.B. Potential Military Cotton Textiles by Carbon Quantum Dots. *Cellulose* **2021**. [CrossRef]
22. Dong, X.; Xing, T.; Chen, G. Durable antipilling modification of cotton fabric with chloropyrimidine compounds. *Polymers* **2019**, *11*, 1697. [CrossRef]
23. Hu, Q.; Wang, W.; Ma, T.; Zhang, C.; Kuang, J.; Wang, R. Anti-UV and hydrophobic dual-functional coating fabrication for flame retardant polyester fabrics by surface-initiated PET RAFT technique. *Eur. Polym. J.* **2022**, *173*, 111275. [CrossRef]
24. Karami, K.; Jamshidian, N.; Zakariazadeh, M.; Momtazi-Borojeni, A.A.; Abdollahi, E.; Amirghofran, Z.; Shahpiri, A.; Nasab, A.K. Experimental and theoretical studies of Palladium-hydrazide complexes' interaction with DNA and BSA, in vitro cytotoxicity activity and plasmid cleavage ability. *Comput. Biol. Chem.* **2021**, *91*, 107435. [CrossRef] [PubMed]
25. Alhakimi, A.N.; Shakdofa, M.M.; Saeed, S.; Shakdofa, A.M.; Al-Fakeh, M.S.; Abdu, A.M.; Alhagri, I.A. Transition Metal Complexes Derived from 2-hydroxy-4-(p-tolyldiazenyl) benzylidene)-2-(p-tolylamino) acetohydrazide Synthesis, Structural Characterization, and Biological Activities. *J. Korean Chem. Soc.* **2021**, *65*, 93–105.
26. Katouah, H.A.; Al-Fahemi, J.H.; Elghalban, M.G.; Saad, F.A.; Althagafi, I.A.; El-Metwaly, N.M.; Khedr, A.M. Synthesis of new Cu (II)-benzohydrazide nanometer complexes, spectral, modeling, CT-DNA binding with potential anti-inflammatory and anti-allergic theoretical features. *Mater. Sci. Eng. C* **2019**, *96*, 740–756. [CrossRef] [PubMed]
27. Alkhamis, K.; Alkhatib, F.; Alsoliemy, A.; Alrefaei, A.F.; Katouah, H.A.; Osman, H.E.; Mersal, G.A.; Zaky, R.; El-Metwaly, N.M. Elucidation for coordination features of hydrazide ligand under influence of variable anions in bivalent transition metal salts; green synthesis, biological activity confirmed by in-silico approaches. *J. Mol. Struct.* **2021**, *1238*, 130410. [CrossRef]
28. Saeed, S.; Alomari, B.A.; Alhakimi, A.N.; El-Hady, A.; Alnawmasi, J.S.; Elganzory, H.H.; El-Sayed, W.A. Pyrimidine hydrazide ligand and its metal complexes: Synthesis, characterization, and antimicrobial activities. *Egypt. J. Chem.* **2022**. [CrossRef]
29. Abd El-Hady, M.; Sharaf, S.; Farouk, A. Highly hydrophobic and UV protective properties of cotton fabric using layer by layer self-assembly technique. *Cellulose* **2020**, *27*, 1099–1110. [CrossRef]
30. Al-Hakimi, A.N.; Alminderej, F.; Aroua, L.; Alhag, S.K.; Alfaifi, M.Y.; Mahyoub, J.A.; Elbehairi, S.E.I.; Alnafisah, A.S. Design, synthesis, characterization of zirconium (IV), cadmium (II) and iron (III) complexes derived from Schiff base 2-aminomethylbenzimidazole, 2-hydroxynaphtadehyde and evaluation of their biological activity. *Arab. J. Chem.* **2020**, *13*, 7378–7389. [CrossRef]
31. Büyükkidan, B.; Büyükkidan, N.; Aslı, A. New schiff bases derived from 3, 4-diamino-1h-1, 2, 4-triazole-5 (4h)-thione: Synthesis and characterization. *J. Sci. Rep.-A* **2022**, *2687*, 25–41.

32. Kafle, K.; Greeson, K.; Lee, C.; Kim, S.H. Cellulose polymorphs and physical properties of cotton fabrics processed with commercial textile mills for mercerization and liquid ammonia treatments. *Text. Res. J.* **2014**, *84*, 1692–1699. [CrossRef]
33. Ahmad, I.; Kan, C.-w.; Yao, Z. Photoactive cotton fabric for UV protection and self-cleaning. *RSC Adv.* **2019**, *9*, 18106–18114. [CrossRef] [PubMed]
34. Lee, M.-J.; Kwon, J.-S.; Jiang, H.B.; Choi, E.H.; Park, G.; Kim, K.-M. The antibacterial effect of non-thermal atmospheric pressure plasma treatment of titanium surfaces according to the bacterial wall structure. *Sci. Rep.* **2019**, *9*, 1938. [CrossRef] [PubMed]
35. El-Sayed Saeed, S.; Al-Harbi, T.M.; Abdel-Mottaleb, M.S.; Al-Hakimi, A.N.; Albadria, A.E.; Abd El-Hady, M.M. Novel Schiff base transition metal complexes for imparting UV protecting and antibacterial cellulose fabric: Experimental and computational investigations. *Appl. Organomet. Chem.* **2022**, *36*, e6889. [CrossRef]
36. Al-Amiery, A.A.; Al-Majedy, Y.K.; Ibrahim, H.H.; Al-Tamimi, A.A. Antioxidant, antimicrobial, and theoretical studies of the thiosemicarbazone derivative Schiff base 2-(2-imino-1-methylimidazolidin-4-ylidene) hydrazinecarbothioamide (IMHC). *Org. Med. Chem. Lett.* **2012**, *2*, 4. [CrossRef] [PubMed]
37. El-Afify, M.E.; Elsayed, S.A.; Shalaby, T.I.; Toson, E.A.; El-Hendawy, A.M. Synthesis, characterization, DNA binding/cleavage, cytotoxic, apoptotic, and antibacterial activities of V (IV), Mo (VI), and Ru (II) complexes containing a bioactive ONS-donor chelating agent. *Appl. Organomet. Chem.* **2021**, *35*, e6082. [CrossRef]
38. Saeed, S.E.-S.; Al-Harbi, T.M.; Alhakimi, A.N.; Abd El-Hady, M. Synthesis and Characterization of Metal Complexes Based on Aniline Derivative Schiff Base for Antimicrobial Applications and UV Protection of a Modified Cotton Fabric. *Coatings* **2022**, *12*, 1181. [CrossRef]
39. Tawiah, B.; Yu, B.; Yang, W.; Yuen, R.K.; Fei, B. Facile flame retardant finishing of cotton fabric with hydrated sodium metaborate. *Cellulose* **2019**, *26*, 4629–4640. [CrossRef]
40. Sahito, I.A.; Sun, K.C.; Arbab, A.A.; Qadir, M.B.; Jeong, S.H. Integrating high electrical conductivity and photocatalytic activity in cotton fabric by cationizing for enriched coating of negatively charged graphene oxide. *Carbohydr. Polym.* **2015**, *130*, 299–306. [CrossRef]