



Surface Functionalization of Printed Natural Textiles for Medical Applications

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Abstract

Nanoparticles of zinc oxide, copper oxide, and titanium dioxide were immobilized on cotton and wool fabrics. The color strength and colorimetric data (L^* , a^* , and b^*) of NPs pretreated cotton and wool samples were measured at normal condition and after 120 hours daylight exposure time. The fastness properties against washing, rubbing, perspiration and light of the NPs pre-treated and printed cotton and wool samples were also evaluated. The UV resistance as well as the microbial resistance of the treated and printed materials against *S. aureus*, *E. coli*, and *C. albicans* was examined using the optical density technique. This would promote the use of recent study discoveries as a revolutionary form of fabric manufacture method for pre-treatment of textile fabrics with ZnO, CuO, and TiO₂ nano-particles for use in medical applications.

Keywords: ZnONPs, TiO₂NPs, CuONPs, nano particles, antimicrobial activity, UPF

1. Introduction

In recent decades, several industrial and scientific initiatives have been made to create new items that would enhance the quality of human existence. This rule also applies to the manufacture of textiles, one of the most significant and rapidly changing industrial sectors in the world. Textiles with antimicrobial qualities are becoming a more enticing industry for both producers and researchers as there is a growing awareness of personal health and cleanliness. [1-8]

Recently, a substantial nanotechnology development was carried out to improve textile functionalization and create smart textile having a high resistance to different microbes, good resistance to stain as well as UV blocking properties. [9-13] The current study is aiming to improve the resistance of cellulosic and proteinic textiles against different microbial infections, UV blocking and stain-resistance through the utilization of metal oxides nanoparticles.

As noted by *Byule et al*, textile finishing was developed using nanoparticles for their unique small size and high surface area to impart one or several protective property to the treated textile to produce materials with novel properties [14]. Nano ZnO has received a lot of attention recently due to their wide range of versatile properties, among these are UV absorption, optical transparency, electrical conductivity, and antimicrobial uses. [15]

Due to its numerous applications in solar cells, optical and electrical devices, medication delivery, cosmetics, sensors, and drug delivery, [16] these nanoparticles possess a broad range of uses. The usage of nanoparticles in antimicrobial applications has significantly risen in recent years since they are one of the potential solutions for preventing antibiotic resistance. A new class of significant materials called nanoparticle metal oxides is being developed more and more in the fields of research and medicine. [17]

The current research has four key goals: (1) application of chemical reduction of TiO₂, CuO, and

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ZnO; (2) surface modification using the ready metal oxide nanoparticles to functionalize and modify cotton and wool textiles; (3) enhancing dye affinity to improve the printability of the treated fabrics; and (4) assessment of the fastness properties, antimicrobial, and UV blocking of the treated textiles with metal nanoparticles.

Experimental

Materials and methods

Materials

A plain-woven, 100% cotton fabric with a surface weight of 140 g/m² that was bleached and unmercerized was employed. It was supplied from Misr for Spinning and Weaving Company, Mahalla El-Kobra., Egypt.

The cotton fabric was then subjected to a second treatment with a 2g/L nonionic detergent solution (Hostapal® CV-Clariant), which was applied at 60°C for 30 minutes. Then the fabrics were rinsed with water and air dried at room temperature.

- nonionic detergent (Hostapal® CV): bring from Clariant company.
- Zinc oxide (in the form of nano-powder <100nm particle size): bring from Sigma-Aldrich company.
- Copper (II) oxide: (in the form of nano-powder <50nm particle size): bring from Sigma-Aldrich company.
- Titanium dioxide (in the form of nano-powder <100nm particle size): bring from Sigma-Aldrich company.

Thickener:

Daico Chemica Industry S.A.E Cairo, Egypt generously donated sodium alginate with a medium viscosity, also known as Daico thickener RE.

Used organisms:

- Staphylococcus aureus (S. aureus) Gram-positive bacteria).
- Escherichia coli (E. coli), Gram-negative bacteria).
- Candida albicans (C. albicans), fungus.

Treatment of cotton and wool fabrics using ZnO nano particles

Cotton and wool samples were soaked in a solution of ZnO of (0.5-2% wof) with 1:30 L/R and addition of wetting agent in order to create a homogeneous solution. Then samples were squeezed to an 80 percent pick-up, and then drying at 60°C. The treated textiles were baked at 140°C for 5 minutes. The treated textiles were then washed and air dried.

Treatment of cotton and wool fabrics by TiO₂ nano particles

TiO₂ nanoparticles were applied to the fabrics using the exhaustion method. (0.5-2% wof) TiO₂ nanoparticles solution were applied to the textiles for 20 minutes at 80°C in presence of wetting agent. using liquor ratio 1:30. The treated wool and cotton materials were then cured at 140°C for 5 minutes. Finally, treated wool and cotton materials were washed and air dried.

Treatment of cotton and wool fabrics using CuO nano particles

Cotton and wool Fabrics were treated with CuO nanoparticles solution using 0.5 – 2% wof for 20 minutes along with a wetting agent, with L/R 1:30. The treated textiles were cured at 140°C for 5 minutes. The treated textiles were then washed and air dried.

Printing Method

Following pretreatment with various concentrations of CuO, TiO₂, and ZnO nanoparticles, both wool and cotton samples were printed using screen printing technique. After that, samples printed with reactive dye was steamed at 100-103°C for 15 minutes. [18]

Preparation of reactive dye printing paste

Reactive printing paste formulation [19-22]

Reactive dye	50 g
Thickener	600 g
Urea	200 g
Resist salt	10 g
Sodium carbonate	20 g
Water	120 g
Total	1000 g

Color strength

The printed samples' colorimetric measurement was carried out using a Hunter Lab ultra-Scan® PRO spectrophotometer. Applying the Kubelka Munk equation, the matching colour strength value (K/S) was calculated as shown below.

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_0)^2}{2R_0}$$

Where, R is decimal fraction of the reflection of the printed fabric, K is absorption coefficient, and S is scattering coefficient

Fastness testing

According to conventional ISO procedures, the coloured samples were exposed to rubbing, washing, perspiration, and light. (ISO 105-X12 (2016), [23] ISO 105-C04 (1989), [24] ISO 105-E04 (2013), [25] ISO 105-B02 (1988) [26] respectively)

CIE Lab Difference

The overall disparity The Hunter-Lab spectrophotometer (model: Hunter Lab DP-9000) was used to measure CIE (L^* , a^* , and b^*).

Calculated from: CIE (L^* , a^* , b^*) between two hues, each provided in terms of L^* , a^* , and b^* . If the sample is lighter than the standard, the L^* value will be higher (+), and if it is darker (-). The relative locations of the sample and the standard in the CIE Lab space are shown by the a^* and b^* values, which provide some insight into the nature of the discrepancy.

Antimicrobial test

Studies on the antimicrobial and antifungal properties of treated materials were carried out in triplicate using conventional techniques (AATCC TM100). [27]

The treated cloth (0.5 g) was added to 20 ml of nutrient broth, where it was infected with the appropriate bacterial strains before being incubated at 37°C for 24 hours. In contrast to a control of uninoculated sterile media, the growth of the bacterial strains was measured spectrophotometrically (OD660) in the presence of the treated cloth. Similar to this, the fungi were inoculated into potato dextrose broth and cultured for 48 hours at 28°C in a shaker incubator before the OD450 was measured against a blank of uncontaminated sterile media. The culture tubes were properly shaken to disperse the bacteria before measuring the OD of the corresponding media after incubation.

The number of microorganisms (bacteria or fungus) in the media directly relates to optical density. The microbes were reduced by the following proportion, which was stated as follows.

$$R = (B - A)/B \times 100$$

where R is the percentage of microbial population decrease, B is the amount of bacteria that can be absorbed by the medium, and A is the combined amount of bacteria that can be absorbed by the media and the treated fabric. [18, 28-40]

Measurement of UPF:

Evaluation of the printed fabric for blocking UV light is given by the ultraviolet protection factor (UPF) value. The measurement of UPF values was performed in UV/Visible Spectrophotometer 3101 PC with a software version, using an integrating sphere loaded with the fabric sample from 290 nm at an interval of 10 nm. [41, 42]

The measurements of the UV- penetration characteristics of the fabrics were achieved in range of 290-400 nm by using the UV penetration and protection measurements system. Before measurements, relative humidity for 24h is done for the sample. During the measurements, four scans were obtained by rotating the sample 90° each time

and the spectral data were recorded as the average of these four scans.

The equation used by the software to calculate the UPF value for a flat, tensionless dry fabric is as follows:

$$UPF = \frac{\sum_{290}^{400} E(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)}{\sum_{290}^{400} E(\lambda) \times T(\lambda) \times \varepsilon(\lambda) \times \Delta(\lambda)}$$

Where $E(\lambda)$ is the solar irradiance ($Wm^{-2}nm^{-1}$) measured; $\varepsilon(\lambda)$ is the arithematic action spectrum; $\Delta(\lambda)$ is the wavelength interval of the measurements; and $T(\lambda)$ is the spectral transmittance at wavelength λ . The percentage blocking of UVA (315-400nm) and UVB(315-290nm) was calculated from the transmittance data [43].

3. Results and Discussions

3.1. Effect of pretreatment of cotton and wool samples

The K/S and colour data of the printed fabrics with reactive dyes are affected by the pretreatment of wool and cotton fabrics with different metal oxides NPs.

The aim of this work is studying the impact of pretreatment of wool and cotton fabrics with nanoparticles to increase the UV and antimicrobial protection, as well as improve the printability of cotton and wool fabrics. TiO_2 , CuO and ZnO NPs were prepared according to the process showed in the experimental part and used for pre-treatment procedure. SEM was used to study morphology of the treated fabrics.

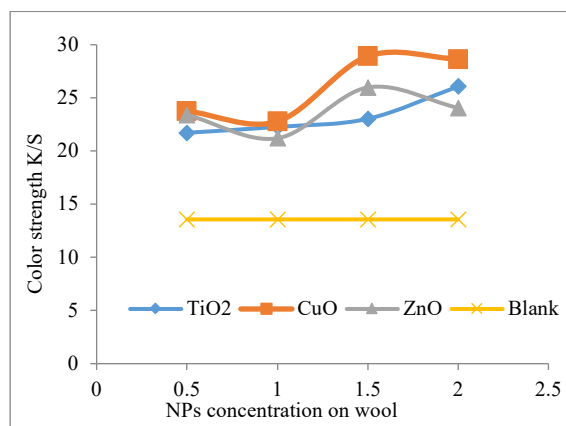


Fig.1: Effect of NPs concentration on the K/S of the printed wool fabrics

Figure 1 makes it obvious that the K/S of wool textiles printed with reactive dyes is affected by the pretreatment of wool fabric with different NPs metal oxides. Figure 1 makes it evident that the type and concentration of the nano oxide affect the color intensity of printed wool garments.

Additionally, according to this figure, pre-treating wool textiles with different nanoparticles improves the color strength of printed wool samples at the sequence in which: $\text{CuO} > \text{ZnO} > \text{TiO}_2$ as compared to the K/S of the blank wool fabric (13.57). Also, figure 1 shows that the significant increase in K/S values was achieved by treatment of wool before printing with CuO nanoparticles (1.5 % owf) compared to the blank sample.

Moreover, when these values are compared to those of untreated examples, it is clear that inclusion of TiO_2 nano particles on the wool fabrics significantly affects improving its printability. This marvel might be because of the negative electrons and positive holes which created in conduction and valence groups of titanium dioxide, separately. These dynamic species thusly react with water and oxygen particles delivering hydroxyl radicals and super oxide anions which increase the fabrics-dye interaction which reflects on the K/S values.

Additionally, Figure 1 details the treatment of wool materials with 0.5, 1, 1.5, and 2 percent owf of TiO_2 NPs. As can be seen from the information, the K/S increases along with an increase in the TiO_2 NP concentration. For instance, the values of K/S increased from 13.57 (obvious example) to 21.72, 22.27, 23.03, and 26.07, respectively, when the TiO_2 concentration increased from 0.5 to 1 to 1.5 to 2. That implies; the maximum values of K/S for the TiO_2 NPs treatment was accomplished at 2 % owf concentration of TiO_2 .

The effect of pre-treating wool fabrics with different NPs on the color strength (K/S) of printed fabrics using reactive dyes is also shown in Figure 1. According to this Figure, it is generally conceived that pre-treating wool textiles with different nanoparticles increases the individual colour strength of CuO, ZnO, and TiO_2 , as well as the contrast and colour strength of the blank (13.57).

Figure 1 demonstrates that the K/S increased from 13.57 to 28.91 at 1.5 percent owf of CuO nanoparticles, but that at 2 percent owf, the concentration of CuO nanoparticles had no influence

on the K/S of treated samples compared to blank sample. This indicates that increasing the K/S of wool textiles by treating them with concentrations of 1.5% CuO is feasible. At larger concentrations of CuO, the K/S value may increase because of the rise in Cu^{+2} ions, this results in more positive charges and more powerful ionic interactions with the reactive dyes. Therefore, medium concentrations of 1.5 % owf were found to be the best conditions for treating wool materials with CuO.

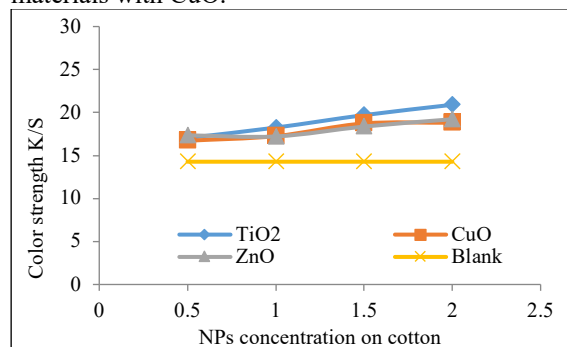


Fig.2: Impact of pretreatment of cotton fabrics with various conc. of NPs on the K/S of printed fabrics

Fig. 2 depicts the effects of pre-treating cotton textiles with different NPs on the color strength of reactively printed cotton fabrics. Figure 2 clearly demonstrates that the K/S values of the printed cotton fabrics rely on (a) the type of utilized NPs and (b) The concentration of the NPs when compared to the color strength of the blank, this figure shows that pre-treating cotton with different nanoparticles boosts the color strength of printed cotton textiles in the following order: TiO_2 , ZnO, and CuO. (14.28).

Figure 2 also demonstrates that the K/S rose from 14.28 to 19.70 at a 1.5% conc. owf of TiO_2 NPs, whereas at a concentration of 2 percent owf of TiO_2 nanoparticles, the K/S increased to 20.9, indicating that the treatment of cotton fabrics with concentrations of 2 percent TiO_2 results in high values for the color strength of the treated samples.

Table 1: The impact NPs on CEI coordinates of the pretreated wool and cotton fabrics

Sample	Wool			Cotton			
	L*	a*	b*	L*	a*	b*	
Blank	33.59	16.14	-2.32	37.65	49.23	0.64	
ZnO Conc. % wof	0.5	18.41	8.36	-1.25	36.59	51.78	4.03
	1	17.38	7.47	-1.16	35.48	51.54	4.86
	1.5	15.25	2.64	-0.41	35.26	50.35	3.66
	2	16.46	5.63	-0.60	35.53	49.50	3.69
CuO Conc. % wof	0.5	19.89	6.49	-0.59	33.18	45.07	-0.76
	1	17.58	7.43	-1.09	31.56	41.99	-2.86
	1.5	15.0	6.28	-0.04	32.12	41.13	-4.22
	2	17.13	6.66	-0.36	29.77	38.7	-3.66
TiO ₂ Conc. % wof	0.5	18.11	8.91	-1.53	35.06	51.65	6
	1	18.41	8.66	-1.16	35.95	52.18	4.37
	1.5	18.18	9.29	-1.26	36.46	52.09	3.44
	2	15.47	5.15	-0.70	36.07	51.98	4.66

While in case of cotton fabrics, the formation of Ti^{+2} ions increases the +ve charges of the reactive anionic dyes which resulting a greater ionic interaction which could explain the raise of K/S value at higher concentrations of TiO_2 . Therefore, at a concentration of 2% owf, ideal conditions for treating cotton textiles with TiO_2 .

The results listed in table 1 indicated that in case of wool fabrics the L^* values showed that, increasing the concentration of CuO, ZnO and TiO_2 nanoparticles causes the printed wool fabric to become darker. Additionally, the results of a^* and b^* values of printed wool fabrics with reactive dye and

treated with ZnO, CuO, and TiO_2 are shifted to the direction the red and blue zone in the CIE Lab colour space.

The L^* measurements demonstrated that the reactive dye-printed cotton textiles got darker when the CuO nanoparticle concentration was increased. In addition, the results of a^* and b^* values for cotton fabrics printed with reactive dye and treated with TiO_2 and ZnO are shifted to the red yellow zone in the CIE Lab colour space. while, the results of a^* and b^* values for cotton fabrics treated with CuO are shifted to the direction of red and blue zone in the CIE Lab colour space.

Table 2: Fastness properties of the pre-treated and printed wool fabrics

NPs concentration	Washing		Rubbing		Perspiration				Light	
	St.	Alt.	Wet	Dry	Acidic		Alkali			
					St.	Alt.	St.	Alt.		
Control sample	3	4	3	3-4	4	4	3-4	4	4	
ZnO Conc. % wof	0.5	4	4-5	3-4	4	4-5	4-5	4	4	5
	1	4	4-5	3-4	4	4-5	4-5	4-5	4-5	5
	1.5	3-4	4	4	4-5	4-5	4-5	3-4	4	5
	2	4	4-5	4	4-5	4-5	4-5	4	4	4-5
CuO Conc. % wof	0.5	3-4	4	3-4	4	4-5	4-5	4	4-5	5
	1	4	4-5	3-4	4	4-5	4-5	3-4	4	4-5
	1.5	4	4	4	4-5	4-5	4-5	4	4-5	4-5
	2	3-4	4	4	4-5	4-5	4-5	3-4	4	5
TiO_2 Conc. % wof	0.5	4	4	3-4	4	4-5	4-5	4-5	4-5	5
	1	4	4-	3-4	4	4-5	4-5	3-4	4-5	4-5
	1.5	3-4	4-5	4	4	4-5	4-5	4	4-5	5
	2	4	4-5	4	4-5	4-5	4-5	4-5	4-5	5

St. Staining on wool, Alt. Alteration in color

Table 3: Fastness properties of the pre-treated and printed cotton fabrics.

NPs concentration	Washing		Rubbing		Perspiration				Light	
	St.	Alt.	Wet	Dry	Acidic		Alkali			
					St.	Alt.	St.	Alt.		
Control sample	4	4	3	3	4	4	3-4	4	4	
ZnO Conc. % wof	0.5	4	4-5	3-4	4	4-5	4-5	4	4	4
	1	4	4-5	3-4	4	4-5	4-5	4-5	4-5	4
	1.5	3-4	4	4	4-5	4-5	4-5	3-4	4	4-5
	2	4	4-5	4	4-5	4-5	4-5	4	4	4
CuO Conc. % wof	0.5	3-4	4	3-4	4	4-5	4-5	4	4-5	4
	1	4	4-5	3-4	4	4-5	4-5	3-4	4	4-5
	1.5	4	4	4	4-5	4-5	4-5	4	4-5	4
	2	3-4	4	4	4-5	4-5	4-5	3-4	4	4
TiO_2 Conc. % wof	0.5	4	4	3-4	4	4-5	4-5	4-5	4-5	4
	1	4	4-	3-4	4	4-5	4-5	3-4	4-5	4-5
	1.5	3-4	4-5	4	4-5	4-5	4-5	4	4-5	4-5
	2	4	4-5	4	4-5	4-5	4-5	4-5	4-5	4

St. Staining on cotton, Alt. Alteration in color

3.2. Fastness properties of pre-treated printed wool and cotton fabrics.

The colorfastness of wool fabrics are shown in Table 2. The colorfastness to washing, rubbing, perspiration, and light was found as fair to good (for the blank), while the results of colorfastness to

washing, rubbing, perspiration, and light for the pre-treated wool fabrics with different concs. of NPs showed very good to excellent.

The data listed in table 3 for the cotton fabrics pre-treated with NPs and printed with reactive dye showed results of good to very good for the colorfastness to washing and rubbing, while the

colorfastness for perspiration and light showed results of very good to excellent when compared to the untreated and printed blank sample which showed fair to good colorfastness results.

3.3. Effect of light exposure time of the pre-treated and printed wool and cotton fabrics on the colour strength and color data.

Table 4 and 5 illustrates the effect of light exposure time of the pretreated and printed wool and cotton fabrics respectively. From the results of table 4 it can be concluded that CuO gives the highest colour strength (K/S) among the used NPs metal oxides. Also, by increasing the light exposure time for the pretreated wool samples (20-120 hours), the lowest change in colour strength was in the presence of ZnO. On the other hand, the highest change in colour strength was witnessed in case of using CuO. For the

L* values all the printed wool fabrics and pretreated with NP metal oxides became lighter by increasing the light exposure time.

While table 5 shows the effect of light exposure time on the pretreated and printed cotton fabrics with ZnO, TiO₂ and CuO NPs metal oxides. It can be summarized that CuO gives the highest colour strength (K/S) among the utilized NPs. Also, by increasing the light exposure time for the pretreated cotton samples (20-120 hours), the lowest change in colour strength was happened in printed sample that pretreated with CuO. Accordingly, the highest change in colour strength was happened in case of treatment with ZnO. For the L* values all the printed cotton fabrics and pretreated with NP metal oxides became lighter by increasing the light exposure time.

Table 4: Effect of light exposure time of the ZnO, TiO₂ and CuO NPs pretreated and printed wool fabrics on the color properties.

Time of exposure to light	NPS	K/S	L	a	b
Without exposure to light	ZnO	25.98	27.50	24.77	-1.95
	TiO ₂	26.07	23.32	17.54	-5.76
	CuO	28.91	28.03	15.54	-4.85
After 20 hours	ZnO	24.91	29.20	15.99	-5.18
	TiO ₂	25.2	33.09	16.86	-5.47
	CuO	26.87	32.09	17.17	-5.75
After 40 hours	ZnO	24.20	31.53	15.89	-4.91
	TiO ₂	24.30	33.41	15.90	-5.11
	CuO	26.11	33.52	15.44	-4.78
After 60 hours	ZnO	23.51	31.77	15.95	-5.18
	TiO ₂	24.20	34.41	14.91	-4.57
	CuO	25.51	34.75	15.24	-4.24
After 80 hours	ZnO	23.11	31.07	18.84	-5.20
	TiO ₂	23.21	35.38	15.86	-4.87
	CuO	24.91	35.19	14.62	-4.16
After 100 hours	ZnO	23.11	32.15	14.54	-4.49
	TiO ₂	22.91	35.76	15.74	-3.94
	CuO	24.81	35.59	16.18	-4.91
After 120 hours	ZnO	22.23	33.85	11.76	-5.10
	TiO ₂	22.31	35.87	14.83	-5.29
	CuO	24.61	36.05	15.03	-4.70

Table 5: Effect of light exposure time of the ZnO, TiO₂ and CuO NPs pretreated and printed cotton fabrics on the color properties.

Time of exposure to light	NPS	K/S	L	a	b
Without exposure to light	ZnO	19.22	25.72	51.54	4.86
	TiO ₂	18.9	24.61	51.98	4.66
	CuO	18.81	24.55	38.7	-3.66
20 hours	ZnO	16.67	25.38	30.10	-1.14
	TiO ₂	15.71	26.72	27.23	-2.01
	CuO	18.46	25.08	28.54	-1.59
40 hours	ZnO	14.82	26.89	25.70	-2.71
	TiO ₂	15.37	27.17	26.13	-2.16
	CuO	17.20	26.64	30.09	-2.57
60 hours	ZnO	14.67	25.75	27.64	-1.76
	TiO ₂	14.28	28.19	28.86	-1.49
	CuO	15.87	26.03	24.95	-1.80
80 hours	ZnO	14.44	27.22	26.81	-1.95
	TiO ₂	14.16	27.14	29.43	-1.06
	CuO	15.71	26.62	26.32	-1.50
100 hours	ZnO	11.34	28.19	29.78	-1.50
	TiO ₂	11.44	29.99	26.12	-1.42
	CuO	15.51	27.15	28.78	-1.28
120 hours	ZnO	10.96	28.22	28.89	-1.10
	TiO ₂	11.04	30.68	27.54	-1.89
	CuO	14.76	30.88	27.56	-2.00

3.4. UPF values for ZnO, CuO, and TiO₂ NPs pretreated and printed cotton and wool fabrics

The threat of various skin diseases, including cancer, brought on by global warming and excessive sun exposure has substantially influenced scientists' search for new UV-resistant textile materials. Due to their excellent UV resistance, organic UV-resisting compounds have been utilized extensively in the textile industry; nevertheless, this is disadvantageous because the majority of these agents have a high degree of toxicity.

Chemical stability, odor lessness, non-burning, and non-toxicity are benefits of several inorganic metal oxide nanoparticles (NPs) employed as UV-resisting agents. Some NPs metal oxides may scatter UV light at wavelengths between 200 and 400 nm because to their tiny size, which ranges between 20 and 40 nm, and high specific surface area. The UV light scattering effect is most pronounced when the NP size is one-tenth of the scatter wavelength. The anti-aging effects of sunlight may be achieved by modifying the breakdown of fiber macromolecules and lowering the production of free radicals, the effects of treating wool and cotton fabrics with various metal oxide nanoparticles (NPs), including ZnO, CuO, and TiO₂. Wool and cotton fabrics may be efficiently protected from UVA (320-400 nm) and UVB (280-320 nm) radiation by using ZnO, CuO, and TiO₂ NPs. As a result, fabrics treated with various NPs metal oxides may lessen UV harm to humans.

Table 6: UPF for ZnO, CuO, and TiO₂ pre-treated and printed cotton and wool fabrics

Metal oxide	Conc. (%)	UPF (AATCC Test Method 183:2010)	
		cotton fabric	wool fabric
Blank		4	32.1
ZnO Conc. % wof	0.5	45.4	94.4 (50+)
	1	77.8 (50+)	119.9 (50+)
	1.5	83.1 (50+)	132.8 (50+)
	2	95.9 (50+)	154.3 (50+)
CuO Conc. % wof	0.5	53.4 (50+)	86.6 (50+)
	1	51.9 (50+)	93.4 (50+)
	1.5	54 (50+)	101.8 (50+)
	2	74.1 (50+)	119.3 (50+)
TiO ₂ Conc. % wof	0.5	58.1 (50+)	86.5 (50+)
	1	65.4 (50+)	93.2 (50+)
	1.5	62.2 (50+)	111.3 (50+)
	2	71.7 (50+)	125.1 (50+)

UV-C (290–200 nm), UV-B (315–290 nm), and UV-A (400–315 nm) are the three wavelengths of solar UV radiation. Depending on the activity of the upper atmosphere's filter and the local circumstances, several types of radiations are present in natural sunshine in varying proportions (clouds, latitude and altitude). The ozone layer's built-in protection filters out the majority of UV-B and UV-C radiation. By measuring the absorbance, transmission, and reflection of the treated and untreated textiles, the UV spectra of each were recorded. Untreated cotton fabric does not naturally absorb UV rays in the UV region between 200 and

300 nm, whereas untreated wool cloth does. The absorption of UV light over the whole studied UV spectrum is increased when cotton and wool materials are treated with nanosized ZnO, CuO, and TiO₂. Different concentration of ZnO, CuO, and TiO₂ NPs treated and printed textiles resulted in a very good to excellent UV protection for the studied concentration as listed in Table 6.

The findings indicate that wool textiles have greater UV absorption features than cotton fabrics, with the following order ZnO, TiO₂ and CuO NPs which gives UV shielding its efficiency. [31, 42, 44-51]

3.5. Antimicrobial resistance of ZnO, CuO, and TiO₂ NPs pretreated and printed wool and cotton fabrics.

Fig. 3 and figure 4 shows the antimicrobial activity of ZnO, CuO and TiO₂ NPs pretreated and printed wool and cotton fabrics, *S. aureus*, *Klebsiella* and *Candida albicans* were chosen as the microorganisms for this study. The two species that are most often assessed are *S. aureus* and *Candida albicans*. While *S. aureus* is the most frequent source of cross-disease in healthcare settings, serious infections of the lungs, bladder, brain, liver, eyes, blood, and wounds can be brought on by *Klebsiella*.

In general, TiO₂-NPs form positive species, which grow under UV light because their energy level is larger than their band gap.

However, due to the nature of TiO₂, which combines with negatively charged residues on the surface of the bacterium, a photocatalytic effect begins. This intercellular material leaking disrupts the microorganisms' regular metabolism in some way. As a result, the effect leads to the death of bacteria. In case of tested the treated samples with CuO it was found unable to destroy the *S. aureus* bacterium because its cell wall is thicker than *Klebsiella*'s.

TiO₂-NPs gave high antimicrobial activity with *S. aureus* bacteria and *Candida albicans* yeast in case of wool fabrics. Treatment of textiles using TiO₂-NPs, which have various advantages, including 1) the high safety of TiO₂-NPs on human skin, 2) fast action against bacteria, requiring only one hour as opposed to 24 hours for TiO₂ nanoparticles to have an antimicrobial impact, 3) long-term anti-bacterial effects of TiO₂-NPs which could be semi-permanent. While ZnO and CuO gave good antimicrobial activity with *S. aureus* bacteria and *Candida albicans* in case of printed cotton fabrics. On the other hand, all metal

oxides NPs didn't give any antimicrobial activity with *Klebsiella* in case of printed wool and cotton fabrics. Also, all metal oxides NPs gave good antimicrobial activity with *S. aureus* in case of printed cotton fabrics.

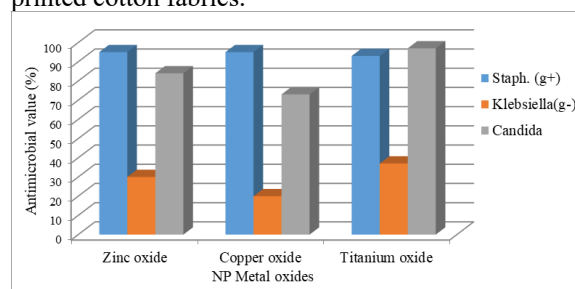


Figure 3: Effect of antimicrobial activity for NPs pretreated wool fabrics

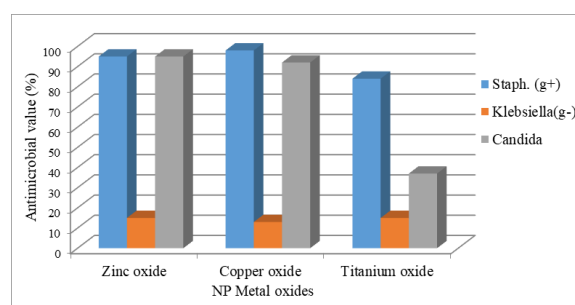


Figure 4: Effect of antimicrobial activity for NPs pretreated cotton fabrics

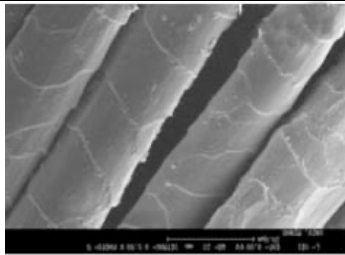
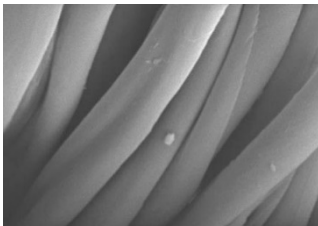
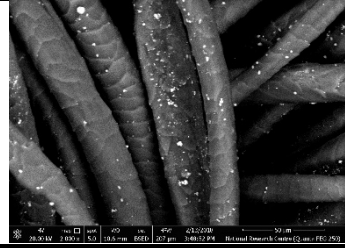
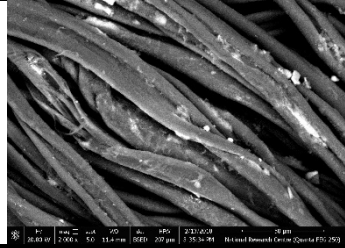
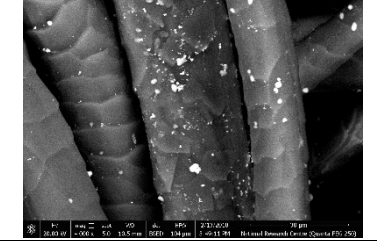
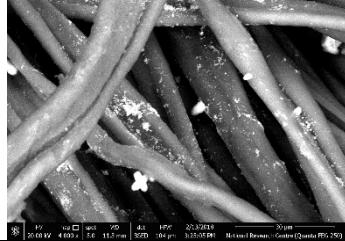
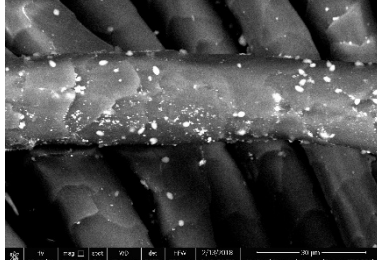
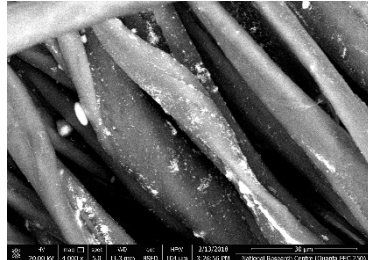
Details of used organisms:

- *Staphylococcus aureus* ATCC 6538, a gram-positive microorganism
- *Klebsiella* ATCC 8739, a gram-negative bacterium
- *Candida albicans* ATCC 10231, yeast that is a single-celled fungus.

SEM images of printed wool and cotton fabrics treated with ZnO₂, CuO, and TiO₂ NPs:

The treated wool and cotton textiles' surface morphology was assessed using SEM of both blank and nano treated textiles. The SEM shown in table 7 illustrates the deposition of ZnO, CuO, and TiO₂ NPs on surface of the treated textile which was evenly distributed according to the concentration (0.5-2% owf) of the different NPs. Both wool and cotton samples clearly show variations between untreated and treated textile.

Table 7: SEM of TiO₂, CuO, and ZnO (@ 1.5 conc.) pre-treated and printed wool and cotton fabrics.

	Wool	Cotton
Blank		
TiO ₂		
CuO		
ZnO		

Conclusion

A simple approach for treatment of wool and cotton fabrics using ZnO, TiO₂, and CuO NPs was utilized. Such pretreatment could impart multifunctional properties of the final printed wool and cotton fabrics. The treated fabrics with different concentration ranging from 0.5-2% owf showed very good to excellent UV blocking properties even with aging under light up to 120 hours as compared to the blank sample. The antimicrobial activity of printed cotton and wool fabrics against S-aureus, E-coli, and C- albicans was enhanced, making these pre-treated materials appropriate for use in medical applications.

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Dedication

The authors are pleased to dedicate this work to the spirit of Professor Dr. Mona Kamel (Professor of Dyeing at the Textile Research and Technology Institute) for her continuous thoughts

with us and her support in our present world. We ask God to have mercy on her and dwell her in his spacious paradise.

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Author Declarations

The authors claim that the paper has the information needed to justify the study's conclusions.

There is no conflict of interest, according to the authors.

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