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Treatment of cotton and wool fabrics with different nanoparticles for multifunctional properties

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Abstract

ZnO, TiO2, and CuO nanoparticles were immobilized onto the cotton and wool fabrics at room temperature. The antimicrobial activity of dyed cotton and wool fabrics with reactive dye against S-aureus, E-coli, and C-candida were measured by the optical density method. It was observed that the killing of bacteria and the bacterial cell damage were harmed efficiently. The effect of pre-treatment of cotton and wool fabrics with different NPs metal oxides on the color strength of dyed fabrics was studied. Color strength (K/S) and colorimetric data (L*, a*, and b*) were measured at specific λmax. Besides, washing, rubbing, perspiration, and lightfastness of dyed cotton and wool fabrics were determined. UV blocking and self-cleaning of the treated fabrics were measured accordingly. The obtained results of the pre-treated fabrics with ZnO, TiO2, and CuO nanoparticles would support the current research outputs as a potential production of protective textile.

Keywords: Cotton and wool fabrics, ZnO, TiO2 and CuO nanoparticles, reactive dye, antimicrobial activity, self-cleaning, protective textile

1. Introduction

The technology of nano-science has arisen over the last years as a cutting edge of technology and science. Nanoscience and technology perform a significant change in the industry. It deals with the very tiny structure of materials which shows undoubtedly innovation and enhances biological, chemical, and physical characteristics [1-4].

Nanotechnology known and used in many fields to overcome a problem or to enhance a required property. In textile field, nanotechnology have been used in several processes such as dyeing, [5-10] printing, [6-8, 11-15] and finishing [16-20] to improve their performance. [21-29]

The essential characteristics of nanoparticle are defined by shape, size, structure, morphology, and crystallinity. The nanoparticles (NPs) supply a small size allocation, which is needed to get a regular material reaction. It has been announced that NPs could be made from hydrous solutions by using various methods like sedimentation, micro-emulsion, and hydrothermal ways. The wetted chemical synthesis of nanoparticles is a useful alternative to the traditional method besides gas-phase synthesis using common commercial implementations [23, 24, 30-32].

The NPs have a greater surface area and greater ability that have singular biological, optical, physical, and chemical characteristics. NPs are categorized into organic plus non-organic NPs. Generally, organic NPs are not able to resist severe conditions such as high pressure and temperature. On the other hand, inorganic NPs such as copper oxide, zinc oxide, and titanium dioxide exhibit strong stability in severe conditions; therefore, using inorganic NPs resulting a significant effect in many fields especially in microbial resistance [33-39].

A lot of researches have been made about the application of nanoparticles on textile fabrics to

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produce finely finished textile with various useful functional properties. For instance, nano magnesium is used for obtaining antimicrobial properties, nano titanium dioxide is utilized for obtaining UV protection and self-cleaning properties, while nano zinc oxide is well known for its antimicrobial activity and UV protection **[21, 22, 38-40].** Nano-materials have special optical character properties, for example, a solid reflective property that diverse from much bigger grains for ultraviolet beams and infrared beams. The nano-materials might give great ultraviolet-resistant properties, great resistance against heat, heat protection action, and anti-aging properties in case of adding to textile fabrics.

It is stated that textile fabrics treated with nano-materials show different properties such as tensile strength, flexibility, wear durability, water and oil repellency, light fastness, and heat constancy. The multifunctional properties and the added value of textile fabrics could be created when these nanomaterials with unique characteristics and features are added to the area of functional finishing of textile fabrics [41]. At lower concentrations, metal and metal oxides are poisonous and kill bacteria by binding to intracellular proteins and deactivating them. Due to their antibacterial properties, silver and zinc oxide nanoparticles have been chosen as a practical solution to prevent bacterial infections **[42]**.

As a result of their photocatalytic action within ultraviolet light, inorganic oxides nano-particles of zinc oxide calcium oxide, magnesium oxide have antibacterial action that is due to the production of reactive oxygen species on the surface of these oxides. The antibacterial system of chemical compounds is due to the interaction of the surface of the compound with a micro-organism and the subsequent absorption of the chemical compounds within the micro-organism. The treatment of fabrics with nano-particles may have an impact on other characteristics of the fabric such as coloration, tensile strength, flexibility, air permeability, and rubbing **[43, 44]**.

In all these nano-particles, copper oxide nano-particles resist extreme heat, less expensive than silver, are simply combined with polymers, and fairly constant. The fabrics coated with nanoparticles of CuO demonstrate very good antibacterial action towards both Gram-positive and Gram-negative bacteria. Therefore, the nano-particles of copper oxide are immobilized on fabrics to be used as a smart fabric for UV protection, anti-bacterial, wound healing, self-cleaning, and in different areas where microbes assume a risky job to limit the opportunity of the nosocomial diseases **[45]**.

It was reported that treatment and modification of non-woven textiles using grafted graphene oxide (GO) with different metals nanoparticles such as (Cu, Zn, Ag, Fe,…etc.) and photocatalysts (TiO_2, CdS, MnS_2, etc.) seeming to have very effective antimicrobial resistance Graphene derivatives have been reported to be used as antimicrobial composites with different metals (Cu, Zn, Ag, Fe, …etc.) **[46, 47]**.

Both enveloped and non-enveloped viruses were significantly affected and deactivated when tested against copper and silver nano-based systems loaded on GO **[46, 48]**. It was demonstrated that treatment and loading of many medical protective textiles such as medical gowns, bedsheets, and protective masks with antimicrobial nano metal oxides such as CuO safely reduced the risk of influenza virus environmental contamination, without altering the filtration capabilities of the textile **[49]**.

All types of fabrics are considered to be highly qualified to carry microbes and to serve as a source for the transmission of infection. Hence, Antimicrobial fabrics can help people suffering from immunocompromised infections recover greatly. In the textile industry, nano-technology is currently at the cutting edge and has a great future **[30]**.

In this study, two different types of natural fabrics (cotton and wool) were successfully treated with three different nano metal oxides (ZnO, TiO_2, and CuO) to impart new multifunction properties such as antimicrobial activity, UV protection as well as self-cleaning to the treated fabrics to be utilized as protective textile.

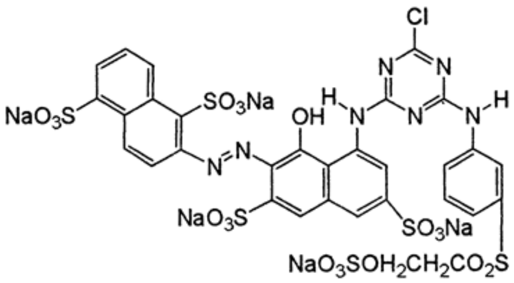
2. Experimental

2.1. Materials

Cotton fabric; scoured cotton fabrics 140 g/m^2 were supplied from Misr for Spinning and Weaving Company, Mahalla El- Kobra., Egypt. Cotton fabric was further treated with a solution containing 2g/L nonionic detergent (Hostapal®CV-Clariant), at 60°C for 30 minutes, then the fabrics were thoroughly rinsed with water and air-dried at room temperature.

Wool fabric; wool fabrics 220 g/m^2 were supplied from Misr for Spinning and Weaving Company, Mahalla El- Kobra., Egypt. Cotton fabric was further treated with a solution containing 2g/L nonionic detergent (Hostapal®CV-Clariant), at 50°C for 30 minutes, then the fabrics were thoroughly rinsed with water and air-dried at room temperature.

TiO_2, ZnO, and CuO nanoparticles were purchased from Sigma Aldrich Co. (Germany), commercially available reactive red 195 dye (see Figure 1) and non-ionic detergent was supplied from a private sector dye house company.



Reactive Red 195

Figure 1: chemical structure of Reactive Red 195

2.2. ***Methods***

2.2.1. Treatment of cotton and wool fabrics by ZnO nanoparticles

The samples were impregnated in a ZnO treatment bath (conc. 0.5- 2 % owf), using a liquor ratio of 1:30, in presence of dispersing agent to suspend the ZnO in water to obtain a homogenous solution. After padding, the samples were squeezed to 80% pick up, then they were dried at 60°C. The treated fabrics were cured at 140°C for 10 min. Finally, treated fabrics were washed at 60°C for 20 min. followed by drying. [50]

2.2.2. Treatment of cotton and wool fabrics by TiO_2 nanoparticles

The fabrics were treated with TiO_2 nanoparticles via the exhaustion method. The fabrics were treated with 4 different percentages of TiO_2 nanoparticles (0.5- 2 % owf) at 80°C for 20 min. in the presence of a wetting agent in the dyeing machine. The liquor ratio of exhaustion bath was 1:10. After 20 min. the treated cotton and wool fabrics were cured at 140°C for 10 min. Finally treated cotton and wool fabrics were washed at 60°C for 20 min. followed by drying.

2.2.3. Treatment of cotton and wool fabrics by CuO nanoparticles

The fabrics were treated with CuO nanoparticles via the exhaustion method. The fabrics were treated with 4 different percentages of CuO nanoparticles (0.5 - 2 % owf) for 20 min. in the presence of a wetting agent in the dyeing machine. The liquor ratio of exhaustion bath was 1:20. After 20 min. the treated fabrics were cured at 120°C for 3 min. Finally, treated fabrics were washed at 60°C for 10 min. followed by drying.

2.2.4. Dyeing Method

The dyeing of cotton and wool fabrics was carried out in a laboratory-scale thermal HT dyeing machine (Roachs Co. England)

Dyeing of cotton fabric was performed by using the (reactive red 195) reactive dye. The dyeing was carried out by dissolving of dye (2% (owf)) in distilled water then 5 g cotton fabrics were added to the dye solution using the material to liquor ratio of 1:50. To this dye bath, 30 g/L sodium sulfate was added at 40°C, and after 30 min, 20 g/L sodium carbonate was drop wisely added. Then the temperature was raised to 60°C and the dyeing process was preceded for a further 60 min. At the end of dyeing, the dyed samples were rinsed with tap water and the samples were soaped in a bath containing 2% nonionic detergent at a temperature of 60°C, then rinsed with water and dried at room temperature.

Dyeing of wool fabric with reactive dye was performed using the (reactive red 195) reactive dye. The dyeing was carried out by dissolving 2% dye (owf) in distilled water then 5 g wool fabrics were added to the dye solution using the material to liquor ratio of 1:50. To this dye bath, 30 g/L sodium sulfate was added at 60°C and after 30 min, the pH was adjusted to 5-6. Then the temperature was raised to 80°C and the dyeing process was preceded for a further 60 min. At the end of dyeing, the dyed samples were rinsed with tap water and the samples were soaped in a bath containing 2% nonionic detergent at a temperature of 60°C, then rinsed with water and dried at room temperature.

2.3. Colorimetric measurements

2.3.1. Color strength (K/S) and Color data CIE LAB space

The color strength (K/S) in the visible region of the spectrum (400-700) nm was calculated based on Kubelkae– Munk equation: [51-61]

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

R = Decimal fraction of the reflectance of PP dyed fabric.

R_0= Decimal fraction of the reflectance of the undyed fabric.

K = Absorption coefficient.

S = Scattering coefficient.

The colorimetric properties of PP dyed fabrics were obtained with Hunter Lab DP-9000 Color-Spectrophotometer.

The total difference CIE (L*, a*, b*) was measured using the Hunter-Lab spectrophotometer (model: Hunter Lab DP-9000).

CIE (L*, a*, b*) between two colors each given in terms of L*, a*, b* is calculated from:

L* value: indicates lightness, (+) if the sample is lighter than standard, (-) if darker.

a* & b* values: indicate the relative positions in the CIE Lab space of the sample and the standard, from which some indication of the nature of the difference can be seen.

2.3.2. Fastness properties

The Colourfastness properties of treated fabrics have been evaluated to observe the enhancement in the treated fabric rather than the untreated one. [54, 55, 59, 62-66]

2.3.2.1. Washing fastness

The colorfastness to washing was determined according to ISO 105-C01:1989 (E) test method [67]. The washing fastness test was conducted in a launder Ometer (ATLAS–Germany) using 5g/L non-ionic detergent at 50°C for 45 min. using liquor ratio 1:50. The composite specimen was removed, rinsed with running tap water, squeezed, then opened and dried in air. It included the test specimen and the two adjacent fabrics in contact with the main sample. A Grayscale was used to assess the color change of the dyed sample and the staining of the two adjacent white fabrics (cotton and wool) [48, 68].

2.3.2.2. Lightfastness

This test was evaluated according to ISO 105-B02: 1988 test method using a xenon lamp. Samples were exposed to continuous light for 35 hours to determine the degree of color resistance to light photodegradation [69, 70].

2.4. Antimicrobial test

The antibacterial and antifungal studies of treated fabrics were accomplished in triplicates using standard methods (AATCC TM100) [71]. Three different microbes were used in this research namely; Gram-positive bacteria: Staphylococcus aureus ATCC 6538; Gram-negative bacteria: Escherichia coli ATCC 8739 and Yeast (is a unicellular fungus): Candida albicans ATCC 10231

The treated fabric (0.5 g) was introduced into 20 ml nutrient broth and inoculated with the respective bacterial strains followed by overnight (24 hrs) incubation at 37°C. Growth of the bacterial strains was determined spectrophotometrically (OD660) in presence of the treated fabric against a blank of un-inoculated sterile medium. Similarly, the fungal strains were inoculated into potato dextrose broth and incubated for 48hrs at 28°C in a shaker incubator followed by measurement of OD450 against a blank of un-inoculated sterile medium. Before recording the OD of the respective media after incubation, the culture tubes were shaken thoroughly to bring microorganisms into suspension. [72-75]

Optical density is directly proportional to the number of microorganisms (bacteria or fungi) in the medium. The percentage of reduction of the microorganisms was expressed as follows.

R = (B - A)/B x100, where; R = percentage of reduction of the microbial population; B = absorbance of the media inoculated with microbes, and A = absorbance of the media inoculated with microbes and treated fabric [3, 61, 76].

3. Results and Discussions

The main goal of the current work is to explore the impact of pretreatment with metal oxides within the nano-form particles in enhancing the dyeability of wool and cotton textile fabrics and improving their antimicrobial properties and ultraviolet resistance. TiO_2, ZnO, and CuO were prepared in the form of nanoparticles as the procedure reported in the experimental part to attain this aim. Scanning Electron Microscopy (SEM) was used to measure the particle size of the prepared metal oxides.

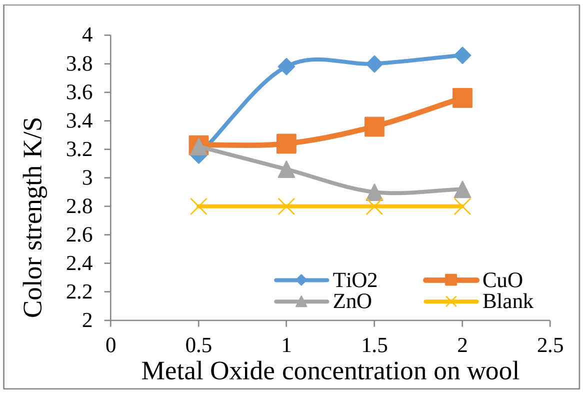
3.1. Color strength and color data of dyed fabrics with reactive dye

Figure 2 shows the impact of pre-treatment of wool fabrics with various NPs metal oxides on the color strength of dyed wool fabrics using reactive dyes. It is obvious from the information in **Figure 2** that the values of color strength of cotton fabrics are based on (a) type of nano oxide utilized, (b) its concentration.

From this figure, it can be observed that pretreatment of wool using different nano-particles leads to increasing the color strength of dyed wool fabrics according to the following order; TiO_2> CuO > ZnO comparing with color strength of the blank (2.8). It is obvious from the information in **Figure 2** that the highest value of color strength was obtained by modifying wool fabrics using TiO_2 nanoparticles (2% owf) compared to the blank, CuO, and ZnO.

Besides, when trying to compare all such values with that of untreated fabrics, it is stated that the integration of TiO_2 nanoparticles into wool fabrics has a noticeable impact on the enhancement of its dyeability. This phenomenon may be attributed to the negative electrons and positive holes formed by titanium dioxide conducting and valence bands, respectively.

Such dynamic species, besides, interact with oxygen and water molecules creating hydroxyl radicals and super-oxide anions which increase the dye reacts with the samples, leading to an increase in the color strength values [1]. **Figure 2** also includes information on the treatment of wool fabrics with four TiO_2 NPs concentrations viz 0.5, 1, 1.5, 2 % owf. As it is obvious from the information that as the concentration of TiO_2 NPs rises, the K/S also increases, i.e., increasing the concentration of TiO_2 from 0.5 to 2 with an improvement of the K/S values from 2.8 (blank sample) to 3.16, 3.78, 3.54 and 3.86 respectively. In other words, when wool fabrics were treated with 2 % owf TiO_2 NPs, the highest K/S value was obtained.



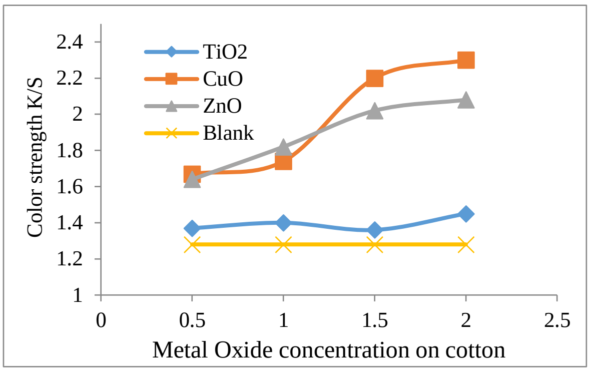


Figure 2: Effect of pre-treatment of cotton and wool fabrics with different NPs metal oxides on the color strength of dyed fabrics with reactive dye

Also, **Figure 2** shows the influence of pre-treatment of cotton fabric with various NPs of metal oxides on the color strength of colored fabric with reactive dye. From this Figure, it can be assumed that pre-treatment of cotton fabric with various NPs leads to increasing the color strength of, CuO, ZnO, and TiO_2 respectively, comparing with the color strength of the blank (1.28).

From **Figure 2**, it can be concluded that at a concentration of 1.5% owf of CuO nanoparticles, the K/S was increased from 1.28 to 2.02. However, raising the concentration of CuO NPs more than 1.5% owf doesn't affect the K/S of the treated sample compared to the untreated one, this implies that treatment of cotton fabrics with 1.5% copper oxide is useful in achieving a significant rising in K/S values. At higher CuO concentration, the color strength value increases, this increase may be caused by the Cu^{+2} ion rule that causes the positive charges to increase, i.e., the reactive anionic dyes attract more ions. Hence optimum conditions for the treatment of cotton fabrics with CuO were found to be at a medium concentration of 1.5 or 2 % owf.

The color data results were listed in

Table 1. The results of L* values indicated that dyed wool fabric becomes darker by increasing the concentration of the CuO and TiO_2 nanoparticles for wool fabrics dyed with reactive dye. Also, the results of a* and b* values for wool fabrics dyed with reactive dye and treated with ZnO are almost the same as the blank in the CIE Lab color space. While wool fabric dyed with reactive dye treated with CuO is shifted in the opposing direction of the red co-ordinate in the red-blue zone of CIE Lab color space and finally, wool fabric dyed with reactive dye treated with TiO_2 is shifted towards the red co-ordinate in the red-blue zone of CIE Lab color space.

The results of L* values indicated that dyed cotton fabric becomes darker by increasing the concentration of the ZnO and CuO nanoparticles for cotton fabrics dyed with reactive dye. Also, the results of a* and b* values for cotton fabrics dyed with reactive dye and treated with ZnO is shifted towards the red co-ordinate in the red-blue zone of CIE Lab color space, while cotton fabric dyed with reactive dye treated with CuO is shifted in the opposing direction of the red co-ordinate in the red-blue zone of CIE Lab color space and finally cotton fabric dyed with reactive dye treated with TiO_2 is almost the same as the blank in the CIE Lab color space.

Table 1: The effect of cotton and wool fabrics pre-treated with various NPs metal oxides on color data of dyed fabrics with reactive dyes

Metal salt concentration		Wool			Cotton		
		L	a*	b*	L	a*	b*
Metal salt	Blank	54.6	37.79	- 7.51	66. 53	31.19	-16.21
ZnO Conc. (%) owf	0.5	53.75	37.83	- 6.94	68. 11	29. 60	-16.22
	1	54.39	37.71	- 6.95	66. 67	31.18	-15.98
	1.5	54. 94	37.34	- 6.83	65. 08	32.77	-16.34
	2	54.77	37.24	- 7.14	63. 89	33.20	-15.41
CuO Conc. (%) owf	0.5	53.31	36.84	- 6.97	65. 40	28.88	-14.90
	1	51.82	32.10	- 6.58	64. 31	29.10	-14.90
	1.5	52.6	33.68	- 6.22	61. 35	25.04	-12.40
	2	50.30	32.34	-6.53	62. 17	26.29	-12.83
TiO_2 Conc. (%) owf	0.5	52.40	39.28	-7.10	66. 65	31. 70	-15. 50
	1	52.15	39.96	-7.56	66. 95	31. 56	-15. 75
	1.5	52.97	39.52	-7. 65	67. 21	31.26	-15. 65
	2	51.70	39.96	-7.10	66. 70	31.45	-15. 62

Table 2 illustrates the colorfastness properties of wool fabrics dyed with reactive dyes. By comparing the colorfastness properties for both pre-treated wool fabrics with different concentrations of NPs and the blank (without using NPs), it is clear that colorfastness to washing and rubbing are improved (from fair and good to very good and excellent) by using NPs as pre-treatment before the dyeing process. While colorfastness to perspiration and light is almost the same (very good to excellent) for both pre-treated wool fabrics with different concentrations of NPs and the blank (without using NPs).

Table 3 demonstrates the colorfastness properties of wool fabrics dyed with reactive dyes. By comparing the colorfastness properties for both pretreated wool fabrics with different concentrations of NPs and the blank (without using NPs), it is clear that colorfastness to washing and rubbing are improved (from fair and good to very good and excellent) by using NPs as pre-treatment before the dyeing process. While colorfastness to perspiration and light is almost the same (very good to excellent) for both pretreated wool fabrics with different concentrations of NPs and the blank (without using NPs).

Table 2: Fastness properties of pre-treated wool fabrics with metal oxides NPs and dyed with reactive dyes

Metal salt concentration		Washing fastness at 60°C			Rubbing Fastness		Perspiration fastness						Lightfastness
							Acidic			Alkali			
		St.*	St.**	Alt.	Wet	Dry	St.*	St.**	Alt.	St*.	St.**	Alt.	
Metal salt	Blank	4	4	4	2-3	3	4-5	4-5	4	4-5	4-5	4	5
ZnO Conc. (%) owf	0.5	4-5	4-5	4	2-3	3-4	4-5	4-5	4	4-5	4-5	4	5
	1	4	4	4-5	3	3-4	4-5	4-5	4-5	4-5	4-5	4	5
	1.5	4-5	4-5	4-5	3	3-4	4-5	4-5	4	4	4	4-5	5
	2	4	4	4-5	2-3	3	4-5	4-5	4-5	4-5	4-5	4	4-5
CuO Conc. (%) owf	0.5	4-5	4-5	4	2-3	3	4	4	4-5	4-5	4-5	4-5	5
	1	4	4	4	2-3	3	4	4	4-5	4-5	4-5	4-5	4-5
	1.5	4	4	4	3	3-4	4-5	4-5	4-5	4	4	4-5	4-5
	2	4-5	4-5	4-5	3	3-4	4-5	4-5	4	4-5	4-5	4	5
TiO_2 Conc. (%) owf	0.5	4	4	4	2-3	3	4-5	4-5	4-5	4	4	4-5	5
	1	4-5	4-5	4-5	2-3	3	4	4	4-5	4	4	4	4-5
	1.5	4-5	4-5	4-5	3	3-4	4	4	4-5	4-5	4-5	4	5
	2	4-5	4-5	4	2-3	3	4- 5	4- 5	4	4-5	4-5	4	5

St.* = Staining on cotton; St.** = Staining on wool; Alt. = alteration in color.

Table 3: Fastness properties of pre-treated cotton fabrics with metal oxides NPs and dyed with reactive dyes

Metal salt concentration		Washing fastness at 60°C			Rubbing Fastness		Perspiration fastness						Lightfastness
							Acidic			Alkali			
		St.*	St.**	Alt.	Wet	Dry	St.*	St.**	Alt.	St.*	St.**	Alt.	
Metal salt	Blank	2-3	2-3	3	4	4-5	2-3	2-3	3	2-3	2-3	3	4
ZnO Conc. (%) owf	0.5	2-3	2-3	3	4	4-5	2-3	2-3	3	3	3	3	4
	1	2-3	2-3	3	4	4-5	2-3	2-3	3	2-3	2-3	2-3	4
	1.5	3	3	3	4	4	3	3	3	2-3	2-3	3	4-5
	2	2-3	2-3	3	4	4-5	2-3	2-3	3	2-3	2-3	3	4
CuO Conc. (%) owf	0.5	2-3	2-3	2-3	4-5	4-5	3	3	3	3	3	3	4
	1	3	3	3	4-5	4-5	2-3	2-3	3	3	3	3	4-5
	1.5	2-3	2-3	3	4	4-5	2-3	2-3	3	2-3	2-3	3	4
	2	3	3	3	4-5	4-5	2-3	2-3	3	3	3	3	4
TiO2 Conc. (%) owf	0.5	3	3	3	4-5	4-5	3	3	3	3	3	3	4
	1	2-3	2-3	3	4	4	3	3	3	3	3	3	4-5
	1.5	3	3	2-3	4	4-5	3	3	3	3	3	3	4-5
	2	2-3	2-3	3	4	4-5	2-3	2-3	3	2-3	2-3	3	4

St.* = Staining on cotton; St.** = Staining on wool; Alt. = alteration in color.

3.2. Antimicrobial activity of dyed fabrics with reactive dyes

The wool samples were treated with diverse concentrations of metal oxides. The absorption of nanoparticles on the wool's surface was proven to increase by increasing the number of metal oxides in the impregnated bath.

As a result, better quality could be achieved with the proposed characteristics. Therefore, the wool surface could absorb higher amounts of metal oxides. Via oxidation processes, the bonding between wool and carboxylic acids is stronger in modified wool compared with raw wool. In other words, wool is not only allowed to obtain greater cross-linking agents through these treatments but also to absorb higher amounts of nanoparticles on the wool's surface, thus allowing for higher proposed characteristics (**Figure 3**). The selected microorganisms for this investigation were E. coli, S. aureus, and Candida albicans that are the most regularly assessed species. E. coli oppose basic antimicrobial agents and cause urinary tract in addition to wound diseases, and S. aureus is the principal reason for cross-disease in medical clinics.

Figure 3 and **Figure 4** expressing the antimicrobial effect of the TiO_2 on the treated fabrics. Generally, TiO_2-NPs produce positive species and it especially increases under UV rays, as its energy level is higher than its bandgap. On the other hand, a photocatalytic effect starts due to the TiO_2 nature, which reacts with negatively charged residues at the bacteria's cell surface leading to leakage of intercellular substance, such substance in a way or another inhibits the normal metabolism of the microorganisms; hence, the death of bacteria is the final result of such effect (**Figure 3**). The cell wall of the *S. aureus* bacterium is thicker than that of *E. coli*; therefore, TiO_2 was not powerful enough to destroy it. Hence, explaining why the antimicrobial activity was not observed in the case of *S. aureus* bacteria as shown in **Figure 3**

Treatment of textiles by exploiting the TiO_2-NPs which possess several advantages as 1) great safety of TiO_2-NPs on the human skin, 2) fast effect to reach the bacteria, only one hour needed to affect the bacteria as compared to 24 hours needed for the antibacterial effect of the silver nanoparticles, 3) maintenance and long term anti-bacterial effect for the TiO_2 NPs could keep its effect semi-permanent, and may not go as far as those other anti-bacterial agents whose effects decrease with the dissolution from the fiber

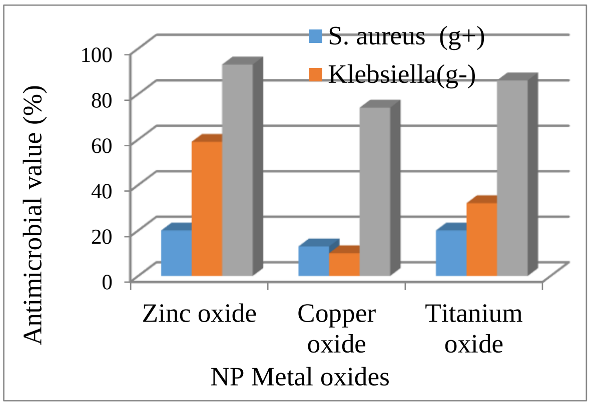


Figure 3: Effect of antibacterial activity for treated wool samples

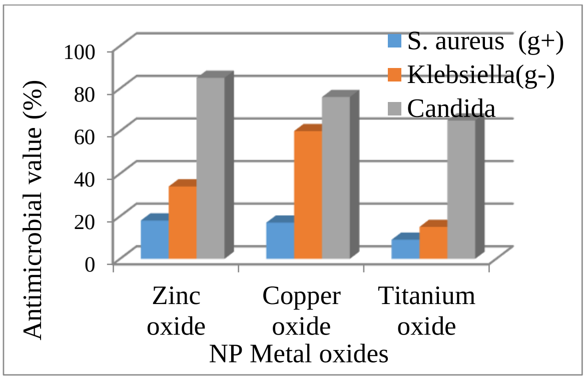


Figure 4: Effect of antibacterial activity for treated cotton samples

3.3. Ultraviolet-Resistance Function of dyed fabrics with reactive dyes

Global warming and overexposure to sunlight are greatly affecting the human skin causing many skin diseases including cancer, such a threat has a great encouraging effect on the scientists searching for different alternatives for UV-resisting textile. Organic UV-resisting agents have been widely used in textile industries on a large scale due to their good UV-resistance; however, it is unfavorable as most of such agents have a high level of toxicity.

Different inorganic metal oxides NPs used as UV-resisting agents have the advantages of chemical stability, odorless, no burning, and non-toxicity. The small size which lies between 20-40 nm and the large specific surface area of different NPs metal oxides can scatter ultraviolet rays at wavelengths of 200-400 nm. When the size of the NPs is one-tenth of the scatter wavelength the scattering effect reaches the optimum to ultraviolet rays. The absorption effects of treated wool and cotton fabrics with different metal oxides NPs such as ZnO, CuO, and TiO_2 could alter the degradation of fiber macro-molecules and decrease the formation of free radicals, and thus the anti-aging effects in sunlight can be achieved. Treatment of wool and cotton fabrics with ZnO, CuO, and TiO_2 NPs has a strong ability to shield UVA（320-400 nm）and UVB（280-320 nm). Consequently, textiles modified with different NPs metal oxides may reduce UV damage on the human body **[40, 77, 78]**.

There are three types of solar UV radiation, UV-C (290–200 nm), UV-B (315–290 nm), and UV-A (400–315 nm). These types of radiations are found in different amounts in the natural sunlight depending on the upper atmosphere filtering activity and local conditions (clouds, latitude, and altitude). Most UV-B and UV-C are filtered by the naturally protective ozone layer. The UV spectra of the untreated and treated fabrics were recorded by measuring the absorbance, transmission and reflection. The untreated cotton doesn't absorb UV rays while untreated wool fabric naturally absorbs UV rays in the UV region ranged from 200 nm to 300 nm. Treatment of cotton and wool fabrics with nanosized ZnO, CuO, and TiO_2 increases the absorption of UV light over the entire investigated UV spectrum. The UPF values given in Table 4 reflect high protection of the treated fabrics against UV rays provided by the ZnO, CuO, and TiO_2 NPs.

The calculated UPF for untreated 100% cotton fabrics are lower than the standard values required for classifying the clothing as UV-protective, such results supports the demand of protection against UV radiation by the treatment of textiles with different UV-resistant nano-sized metal oxides such as ZnO, TiO_2 and CuO. The obtained results show that wool fabrics exhibit better UV absorption characteristics than cotton fabrics due to the better UV absorption characteristics of the wool fabrics. Therefore, it is clear that the application of ZnO, TiO_2 and CuO NPs on cotton fabric increases the UV protection in the region ranged from 300 to 400 nm. The achieved results indicate that the effectiveness in UV shielding characteristics is due to the UV absorption capacity of ZnO, TiO_2 and CuO NPs on the treated fabrics surface.

Table 4: UPF for wool and cotton fabrics treated with ZnO, CuO, and TiO_2 NPs

Sample		AATCC Test Method 183:2010-UPF	
Kind of fabrics		wool	cotton
Blank		482.6	13.0
ZnO Conc. (%) owf	0.5	616.1	14.9
	1	485.2	14.6
	1.5	558.0	17.4
	2	516.0	16.5
CuO Conc. (%) owf	0.5	487.5	18.3
	1	537.6	22.0
	1.5	662.2	16.4
	2	746.8	15.3
TiO_2 Conc. (%) owf	0.5	630.6	15.9
	1	681.0	19.2
	1.5	648.3	16.3
	2	590.6	19.3

3.4. Self-cleaning properties of dyed fabrics with reactive dyes

Several nanoparticles metal oxides such as ZnO, TiO_2 and CuO have a strong photochemical catalysis which can decompose and degrade dirt by exposure to UV. Decomposition of dirt occurs on the surface of the particles in the light. Therefore, cotton and wool fabrics can be treated with different self-cleaning materials such as ZnO, TiO_2 and CuO to create fabrics with self-cleaning properties. The self-cleaning characteristic of TiO_2 and ZnO nanoparticles is predicted to change the traditional washing habits with detergent[25, 79-86]. It was obvious that treatment of cotton and wool fabrics using TiO_2 and ZnO NPs increase the self-cleaning function of the treated fabrics by 85 % while using CuO increase the self-cleaning function of the treated fabrics by 75%.

3.5. Morphological properties of dyed fabrics with reactive dyes

The surface morphology of the treated wool and cotton fabric was examined by scanning electron microscope. **Figure 5** exhibit SEM images of both blank as well as nano-coated wool and cotton fabrics. A well dispersion and deposition of ZnO, CuO, and TiO_2 NPs onto the surface of the treated fabrics were observed. Significant differences between blank and treated fabrics are clearly observed for both wool and cotton samples; the former has a smooth and a uniform surface, while the latter is showing increase in roughness as the concentration of the used nano metals were increased from 0.5-2% conc. (owf), which ascribed to the deposition of ZnO, CuO, and TiO_2 NPs onto the surface of the coated fabric.

4. Conclusion

In conclusion, padding method has been used for treatment of dyed cotton and wool fabrics with ZnO, TiO_2 and CuO to impart functional properties. The treated cotton and wool fabrics with ZnO, TiO_2 and CuO NPs were found to have antimicrobial, self-cleaning, and UV blocking property. The treatment of cotton and wool fabrics with ZnO, TiO_2 and CuO NPs resulted in penetration of smaller particles deeper and adhere strongly into the fabric matrix due to nano-size and hence reduced friction in comparison with its bulk counterpart. Thus, the treatment of cotton and wool fabrics with ZnO, TiO_2 and CuO NPs is proved to have better UV-absorption and 75-85% self-cleaning properties. Also dyed cotton and wool fabrics with reactive dyes and modified by these nano-materials recognized arrange of 10% up to 80% antimicrobial activity against *S-aureus, E-coli and C-candida*. Based on the above results, these pre-treated fabrics could be promising for possible medical and protective purposes.

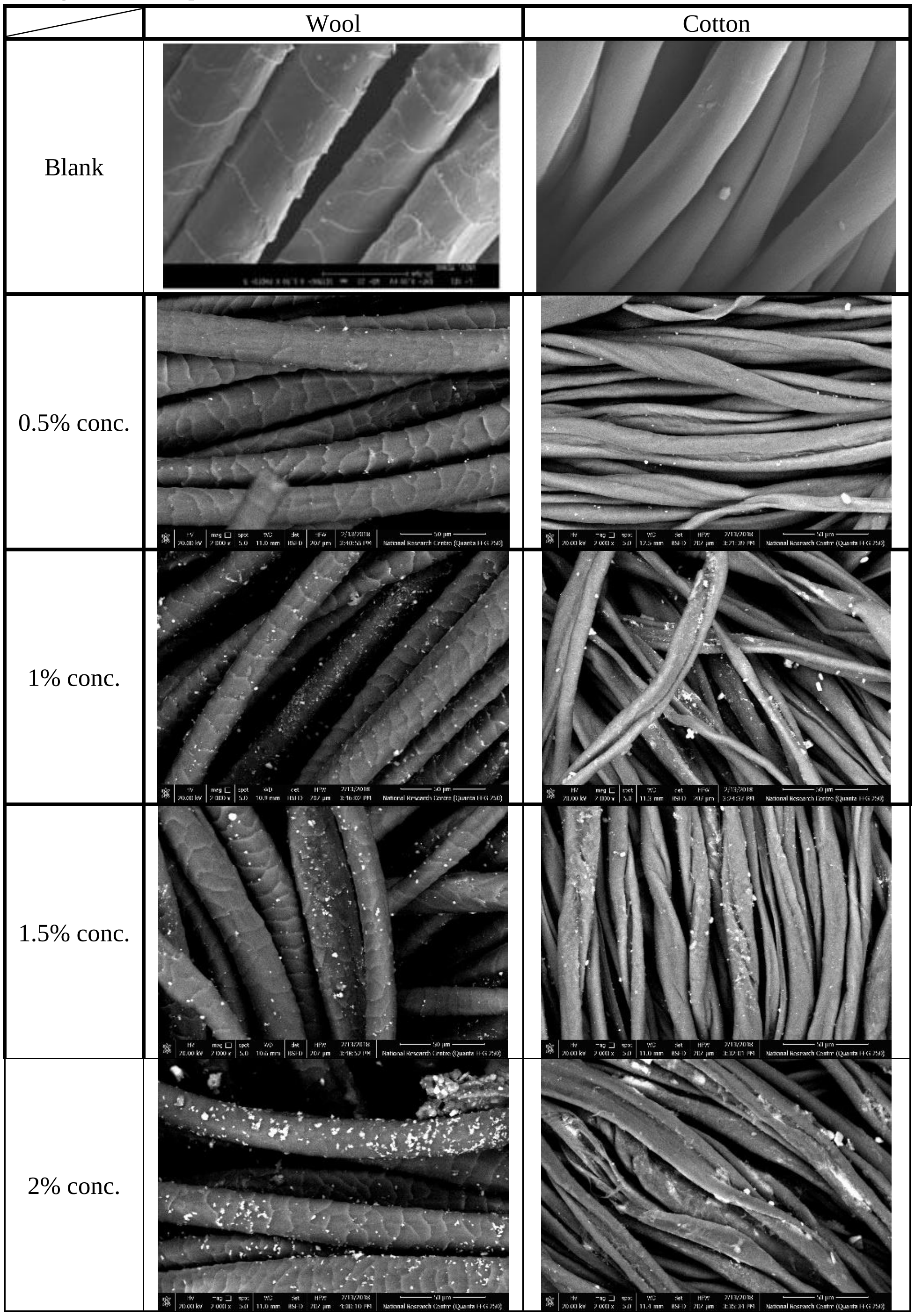


Figure 5: SEM images of wool and cotton fabrics treated with zinc oxides nanoparticles with different concentration

5. Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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