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Superior Self-cleaning and Antimicrobial Properties on Cotton Fabrics Using Nano Titanium Dioxide along with Green Walnut Shell Dye

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Abstract: In this study, functional cotton fabrics were prepared through applying nano titanium dioxide as photocatalyst and using green walnut shell dye as both natural dye for coloration and agent capable of modifying TiO_2 nanoparticles. Natural dye extract of green walnut shells was used as photo sensitizer to fabricate titanium dioxide nanoparticles. Surface modification and coloration of cotton fabrics were performed by adding modified titanium dioxide nanoparticles in exhaustion bath. Produced cotton fabrics were characterized by field emission scanning electron microscope, energy-dispersive X-ray spectroscopy and X-ray diffraction. Results indicated that all properties such as self-cleaning, antibacterial and antifungal of treated cotton fabric were superior with modified titanium dioxide compared to treated sample with TiO_2 alone. Moreover, the photocatalytic activity of titanium dioxide has no negative effect on fabric color.

Keywords: Titanium dioxide, Walnut shell dye, Cotton fabric, Self-cleaning, Antimicrobial

Introduction

In recent decades, much interest has arisen in developing photocatalyst nanoparticles on textiles due to their potential to utilize in applications such as protective clothing, medical devices, wound dressings and smart textile [1-6]. Titania is the most frequently used photocatalyst for textile finishing. For example, Karimi *et al*. obtained self-cleaning cotton fabric using nano titanium dioxide [7]. Nazari *et al.* synthesized titania on wool fabric and achieved mothproofing fabric with good performance [8]. Montazer *et al*. coated wool fabric with TiO_2 nanoparticles and showed efficient anti-felting and antibacterial properties [9]. Moreover, a chemical coating of wool with titanium dioxide nanoparticles along with flame-retardancy property was reported by Cheng *et al*. [10]. Also, superior UV-blocking and superhydrophobic properties on cotton fabric through applying polyvinylsilsesquioxane and nano-TiO_2 was reported by Chen *et al*. [11].

Although nano titanium dioxide is the most currently applied photocatalyst to finish textile, it demonstrated some drawbacks. Nano-TiO_2 presents photocatalytic activities only under UV rays. Moreover, the high electron-hole recombination rate causes low efficiency of titania [12]. Attempts to overcome these problems have mainly focused on use of second constituent to combine with titanium dioxide. For instance, Karimi and co-workers treated cellulose fabrics with Ag/TiO_2 nanocomposite and reported significant improvement in self-cleaning and antibacterial properties of fabric [13]. Along the same lines, Mahdieh *et al*. obtained self-cleaning polyester/cellulose fabric through *in situ* synthesis of Ag-TiO_2 nanocomposite and proved efficient photocatalytic properties [14]. Derakhshan *et al*. enhanced self-cleaning properties of cotton fabric through application of TiO_2/Pt nanocomposite [15]. Moreover, superior self-cleaning property on wool fabric by adding nano zinc oxide to nano titanium dioxide was reported by Behzadnia and colleagues [16]. Recently, some studies have also focused on the combination of nano titanium dioxide with carbonaceous nanomaterials for producing multifunctional textiles. Superior photocatalytic properties were reported through applying graphene/TiO_2 [17-19], graphene oxide/TiO_2 [20,21], carbon nanotube/TiO_2 [22,23] and carbon black/TiO_2 [23,24] nanocomposites on textiles. However, there are some disadvantages of using noble metals or carbonaceous materials for modification of TiO_2. For example, noble metals like Pt, Au and Ag are expensive and black color of carbonaceous materials is one of the major limitations to extend its usage in fabrics or textiles.

In this study, coloration and functional finishing of cotton fabric were carried out with combination of titania and green walnut shell dye as a natural dye. Self-cleaning properties, antibacterial and antifungal activities of the cotton samples, and synergism effect of TiO_2 nanoparticles and green walnut shell dye were investigated on these properties.

Experimental

Materials

The bleached plain weave 100 % cotton fabric was prepared from Yazd Baf Co. (Iran). Titanium isopropoxide ($C_{12}H_{28}O_4Ti$) as metal alkoxide reagent for producing nano titanium dioxide and hydrochloric acid (HCl, 37 %) were gained from Merck. Methylene blue (CI 52015) was provided by Uhao Co. (China). The green walnut shell was purchased from Iranian traditional natural dyers.

Apparatus

Surface morphology and energy dispersive X-ray spectroscopy (EDS) studies were performed using field

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emission scanning electron microscopy (FE-SEM, MIRA3 TESCAN, Czech). The X-ray diffraction (XRD) analysis was accomplished using a STOE (model STADI MP) X-ray Diffractometer, Germany. Patterns were recorded in diffraction range of 2θ from angle of 10 ° to 110 ° with a scanning speed of 2 °/min at 2θ step of 0.040 °. Cu Kα radiation (λ=1.540 Å) was used with detector scan mode operating at 40 kV and 30 mA to investigate changes in crystalline. UV radiation source was HPA 400 W lamp (Philips, Belgium). An ultrasonic bath Euronda Eurosonic® 4D, 350 W, 50/60 Hz (Italy) was used for synthesis processing.

Synthesis and Treatment Procedures

Natural dye aqueous solution was prepared by soaking 50 g of dried powder in 1000 m*l* of distilled water and kept for 24 h with intermittent shaking at 25 °C. The mixture was filtered to obtain brown solution for synthesis. To synthesize modified titanium dioxide nanoparticles, diverse amount of titanium isopropoxide were used. Hydrolysis was carried out at 60-65 °C by controlled drop-wise addition of titanium isopropoxide in natural dye solution under ultrasonic irradiation for 1 h. pH was held at 5-6 by hydrochloric acid. Finally, the bleached cotton fabrics were immersed in the aqueous suspension of nano-TiO_2 with various concentrations and heated for 40 min at 70 °C. Then, treated fabric was kept in an oven at 80 °C for 30 min to fix coatings. For comparison, cotton fabrics were treated with titanium dioxide nanoparticles under same conditions without green walnut shell dye. The exact formation and tests results for each sample examined in this study are summarized in Table 1.

Test Methods

Photocatalytic activities of treated fabrics were estimated by decolorization of methylene blue solution under sunlight irradiation [17]. The concentration of dye in the solution was calculated by Varian Cary 300 UV-Vis spectrophotometer using calibration curve. Treated cotton fabrics (4×6 cm^2) were added into 100 m*l* of dye solution (10 mg/*l*). Firstly, solution mixture was stirred for 15 min without irradiation in order to get equilibrium of dye adsorption. Then the solution was irradiated with sunlight (Yazd, Iran) for 3 consecutive days under continuous stirring (100 rpm). Degradation degree of methylene blue was calculated according to equation (1).

$$\text{Degradation (\%)} = (C_0 - C_e) / C_0 \tag{1}$$

Here, C_0 and C_e correspond to initial and final concentration of dye before and after sunlight irradiation.

Colorfastness of treated cotton fabrics to light was also evaluated after 72 hours UV lamp irradiation using a reflectance spectrophotometer (BYKGardner, India, with CIELAB 1976 color space and D65-light source). CIE Lab color coordinate values (L^*, a^*, and b^*) were measured for each specimen before and after UV irradiation. L^* represents lightness/darkness, a^* value represents red or green chroma, and b^* represents chromaticity coordinate for yellow/blue. The total color difference (ΔE^*) was calculated according to equation (2).

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{2}$$

AATCC 100-2004 test method was selected as a quantitative technique for measuring antibacterial properties of treated samples against *Escherichia coli* (*E. coli*, ATCC 25922) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923) as ordinary pathogenic bacteria. This method is specially designed for specimens treated with nonreleasing antibacterial agents under dynamic contact conditions. To carry out antifungal experiment, the diploid fungi *Candida albicans*

Table 1. Experimental conditions and tests results

Walnut shell dye	Titanium isopropoxide (m*l*)	Color coordinates			Fastness against photoactivity (ΔE^*)±SD	Water absorption (s)±SD	Bending length (cm)±SD	Bending rigidity (mg cm)
		L^*	a^*	b^*				
-	0	81.55	-0.21	-0.13	-	11±1	1.25±0.1	20.48
	1	83.71	0.11	0.45	-	74±1	1.30±0.1	23.04
	2	84.78	0.12	0.32	-	90±1	1.40±0.1	28.78
	3	86.11	0.13	0.36	-	114±2	1.50±0.2	35.40
	4	86.97	0.12	0.38	-	123±2	1.55±0.1	39.06
	5	87.67	0.12	0.41	-	137±2	1.60±0.2	42.96
With natural dye	0	36.33	9.76	12.01	1.11±0.02	13±1	1.25±0.1	20.54
	1	44.17	9.12	12.35	1.37±0.03	79±1	1.30±0.1	23.11
	2	47.32	8.89	11.34	1.65±0.02	88±1	1.35±0.2	25.88
	3	50.03	8.76	11.84	1.69±0.02	122±2	1.45±0.1	32.16
	4	56.91	9.59	12.55	1.75±0.01	131±1	1.55±0.1	39.36
	5	62.23	8.13	12.45	1.88±0.01	135±1	1.55±0.2	39.43

(NCPF 3153) was used. Antimicrobial activity was expressed in terms of percentage reduction of micro-organisms and calculated as:

$$\text{Percentage reduction of micro-organisms (R)\%} = (A - B)/A \times 100 \qquad (3)$$

where A and B are the number of micro-organisms colonies on untreated and treated fabrics, respectively.

There was 3.4×10^5 colony forming units (cfu) of bacteria in primary inoculum. Saline solution 8.5 g/*l* sodium chloride to 1000 m*l* distilled water was used as neutralizing solution. Serial dilution of 10-10,000 was made for incubation on agar plate. Tryptic soy agar (Merck, Germany) was applied as the agar.

Stiffness of fabric samples was determined according to ASTM D 1388-96 (2002) test method. Bending rigidity of the fabrics was measured using equation (4).

$$G = M \times (C)^3 \qquad (4)$$

where G is bending rigidity (mg cm), M fabric weight (mg/cm^2) and C, average bending length (cm).

Also, hydrophilicity of samples was evaluated according to AATCC 79-2000 standard method.

Results and Discussion

Characterization

Figure 1 demonstrates XRD patterns of raw and nano-TiO_2 treated cotton fabrics with and without natural dye. The diffraction peaks at 2θ values of 13°, 16° and 22.8° are diffraction peaks of cellulose which is a main substrate. There are no obvious differences of diffraction peaks in nano-TiO_2 treated fabrics in the presence of green walnut shell dye in comparison with cotton treated with titania alone. In treated cotton samples, three reflection peaks appeared at 2θ values of 25.3°, 35° and 54° indexed as anatase structure of titanium dioxide which were consistent with the values in the standard card (JCPDS Card No. 21-1272). Diffraction peaks belonging to other polymorphs of titanium dioxide, namely rutile and brookite, are not present. In addition, based on equation (5), the crystal size was calculated at 2θ=25.3° and for titania was 314 Å.

$$\text{Crystal size (Å)} = (K \times \lambda \times 180)/(\text{FWHM} \times \pi \times \cos\theta) \qquad (5)$$

where K=0.9 is the shape factor, λ=1.54 is the wavelength of X-ray of Cu radiation, FWHM is full width at half maximum of peak and θ is diffraction angle.

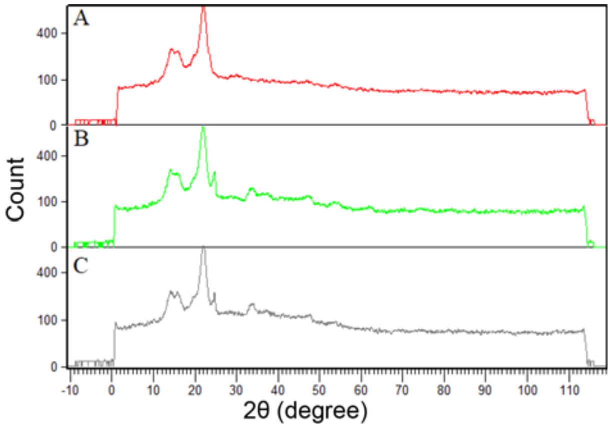

Figure 1. XRD patterns of various cotton fabric samples; (A) raw, (B) treated with 5 m*l* titanium isopropoxide, and (C) treated with 5 m*l* titanium isopropoxide along with green walnut shell dye.

Figure 2 exhibits the surface morphologies of pristine cotton and titania treated fabrics with and without green walnut shell dye. As shown in Figure 2(A) and (B), the surface of raw cotton is neat and smooth and there is no particle existing on its surface. In titania treated cotton (Figure 2(C), (D)) nanoparticles deposited on the surface of cotton fabric. TiO_2 nanoparticles have agglomerated together to form nanoclusters. Cluster formation was reduced in nano-TiO_2 treated fabric in presence of green walnut shell dye (Figure 2(E), (F)). It is obvious that nano-TiO_2 coated on the cotton fabric were uniform and close-packed, which caused complete surface coverage of the fibers. Images at higher magnification indicate the presence of spherical shaped particles; with an average size in the range of 30-37 nm (Figure 2(G), (H)).

Figure 3(A) displays EDS pattern of treated fabric with titania in presence of green walnut shell dye, which indicates the presence of C, O, Ti and Au elements on the surface of fabric. The presence of Au element in EDS pattern is due to coating of gold layer on the fabric before FE-SEM observation. The distribution of C, O and Ti elements in treated cotton is investigated by elemental mapping (Figure 3(B)). It is clearly illustrated that distribution of Ti on the fabric surface is uniform.

Coloring effect of applied treatment on cotton fabrics was obtained using data color spectrophotometer according to CIELAB system. As presented in Table 1, raw cotton fabric had a white color with high L^* value and negligible a^* and b^* values. In comparison with raw fabric, the L^* value of fabrics treated with nano-TiO_2 increased due to lightness of titania nanoparticles immobilized on fabric surface. After treatment with green walnut shell dye, the L^* values of treated fabrics decreased significantly which confirmed the darkness of samples. The a^* and b^* values of titania treated fabrics in presence of natural dye were in the range of 8.13 to 9.76 and 11.34 to 12.55, respectively, which corresponded to brown color of samples. Based on obtained results, the L^* value of treated cotton samples increased from 44.17 to 62.23 by increasing amount of titanium isopropoxide from 1 m*l* to 5 m*l* in the impregnating bath which is a result of aggregation of white TiO_2 nanoparticles on cotton surface.

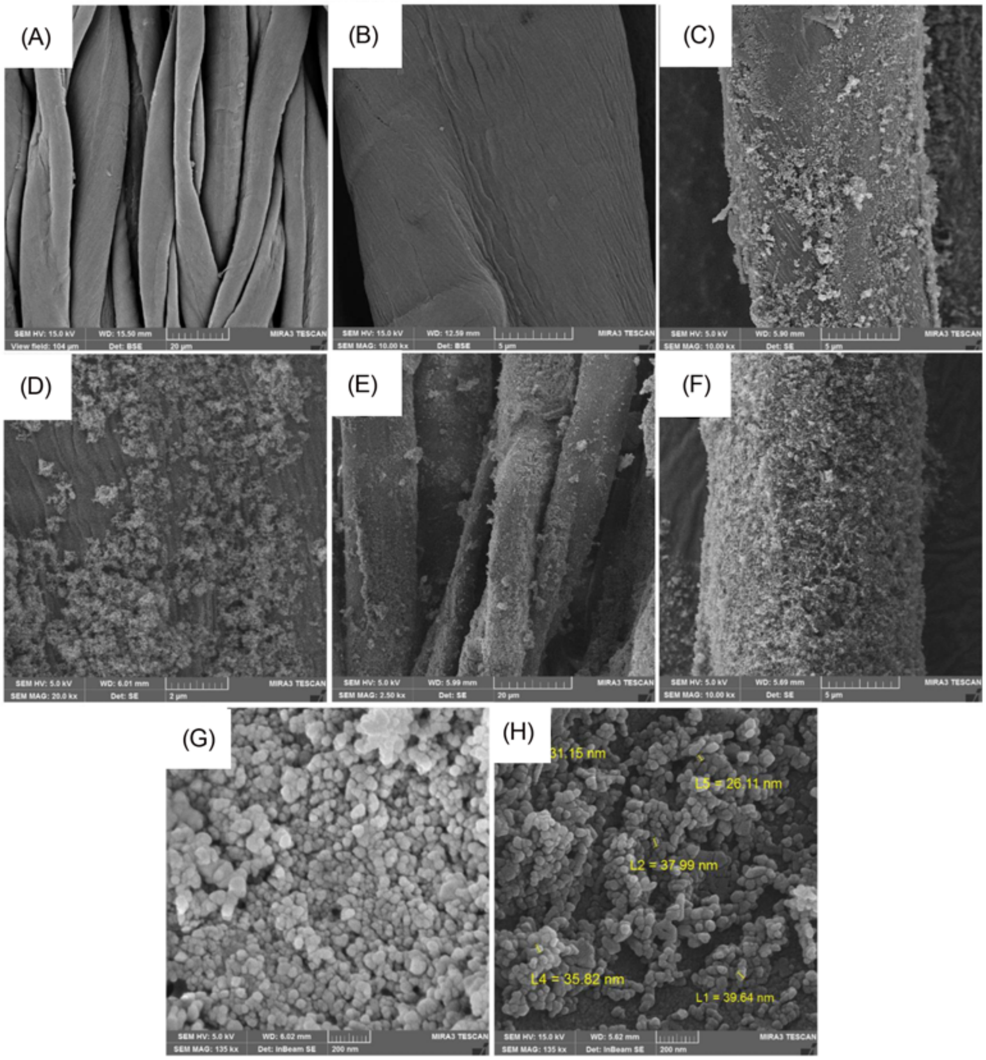

Figure 2. FE-SEM images of various cotton fabric samples; (A) and (B) Raw, (C) and (D) treated with titania (5 m*l* titanium isopropoxide), and (E)-(H) treated with titania (5 m*l* titanium isopropoxide) in presence of green walnut shell dye.

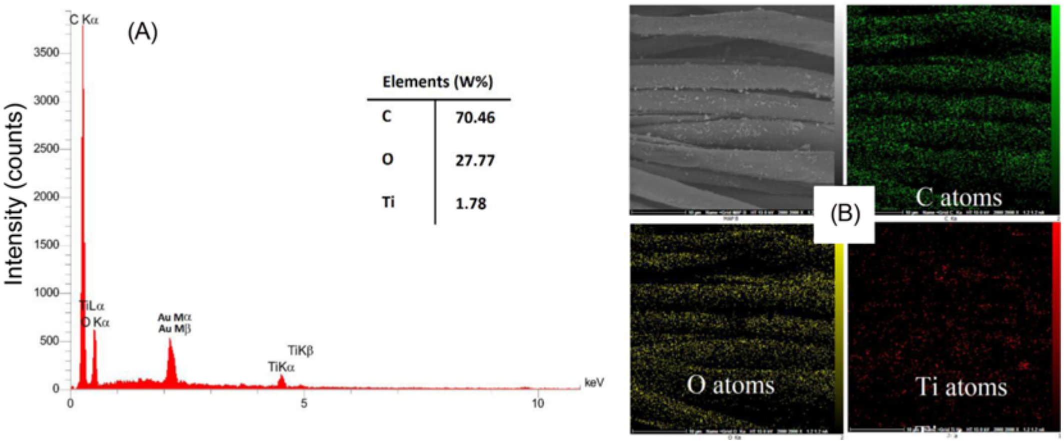

Figure 3. EDS spectrum (A) and X-ray mapping images (B) of treated cotton fabric with titania (5 m*l* titanium isopropoxide) in presence of green walnut shell dye.

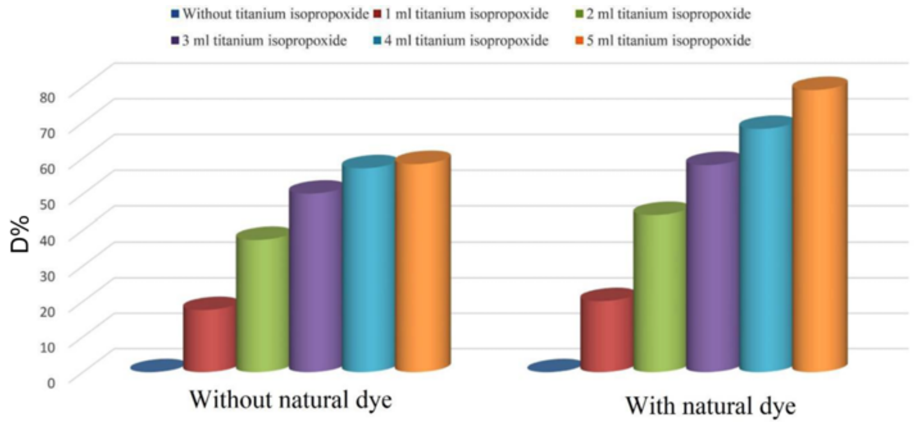

Figure 4. Photocatalytic activity of titania treated cotton samples with and without walnut shell dye.

Photo-activity

Photocatalytic efficiency of raw and treated cotton fabrics was determined utilizing rate of decomposition of dye under sunlight irradiation. As illustrated in Figure 4, methylene blue concentration change was negligible during irradiations in contact with blank cotton. Also, dyed cotton fabrics (without nano-TiO_2) show no photocatalytic activity under sunlight irradiation. Cotton fabrics treated with titanium isopropoxide exhibits higher photocatalytic efficiency. Also, more titanium isopropoxide led to better photocatalytic activity (D%) possibly due to more TiO_2 nanoparticles absorption by fabric. When photocatalyst is illuminated by a light with energy higher than its bandgap energy, electron-hole pairs diffuse out to the surface of photocatalyst. Created negative electrons and oxygen combine into O_2^-, and positive electric holes and water generate hydroxyl radicals. These highly active oxygen species are able to oxidize pollutants [25].

Based on obtained results, adding natural dye to titania had tangible effect on its photocatalytic activity. D% values of nano-TiO_2 treated cotton fabrics in the presence of walnut shell dye were more than titania-treated cotton fabrics alone. This improvement is due to adsorption of dye molecules on titania surface. Natural dye is excited rather than TiO_2 by visible light and excited dye molecule could make an electron transfer into the conduction band of semiconductor, and injected electron in conduction band reacts with oxygen molecule adsorbed on TiO_2 surface to generate active oxygen species [26-28]. Charge injected into conduction band of TiO_2 is affected by type of attraction between sensitizer and its anchoring group with TiO_2 [29]. As shown in Figure 5, dye structure of walnut shell dye possesses C=O and -OH groups which are capable of anchoring to Ti sites on titania surface [30,31].

The photocatalytic activity of titania led to color fading of dyed textiles due to degradation of the chemical structures of dyes [32]. Colorfastness of nano-TiO_2 treated fabrics was assessed in presence of walnut shell dye by examining their color changes after high intensity UV irradiation. As demonstrated in Table 1, the ΔE^* values of treated cotton fabrics after 72 h UV irradiation were not significantly different from the dyed fabric (without nano-TiO_2). Therefore, photocatalytic activity of titanium dioxide did not cause remarkable changes in color of treated samples. Consequently, the colorfastness properties of treated cotton samples were satisfactory.

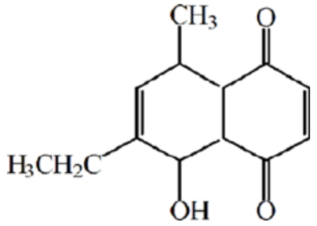

Figure 5. Chemical structure of walnut shell dye.

Antimicrobial

Antimicrobial activities of raw and treated cotton samples were evaluated quantitatively by AATCC agar diffusion test method 100 and results are presented in Figure 6. Raw cotton fabrics provide a suitable media for microorganisms' growth. The reason could be that raw cotton does not have any antimicrobial agent in its surface. The nano-TiO_2-treated cotton sample exhibited 27 % reduction for *S. aureus*, 35 % reduction for *E. coli* and 12 % reduction for *C. albicans*. Nano-TiO_2 treated sample indicated higher antimicrobial activity in presence of natural dye than nano-TiO_2 treated cotton. Adding walnut shell dye to nano titanium dioxide had a remarkable effect on antimicrobial activity of treated cotton fabrics. Observed enhancement in antimicrobial activity of treated samples might be explained on the basis of distinct antimicrobial activity of green walnut shells. The presence of phenolic and naphthoquinone compounds in

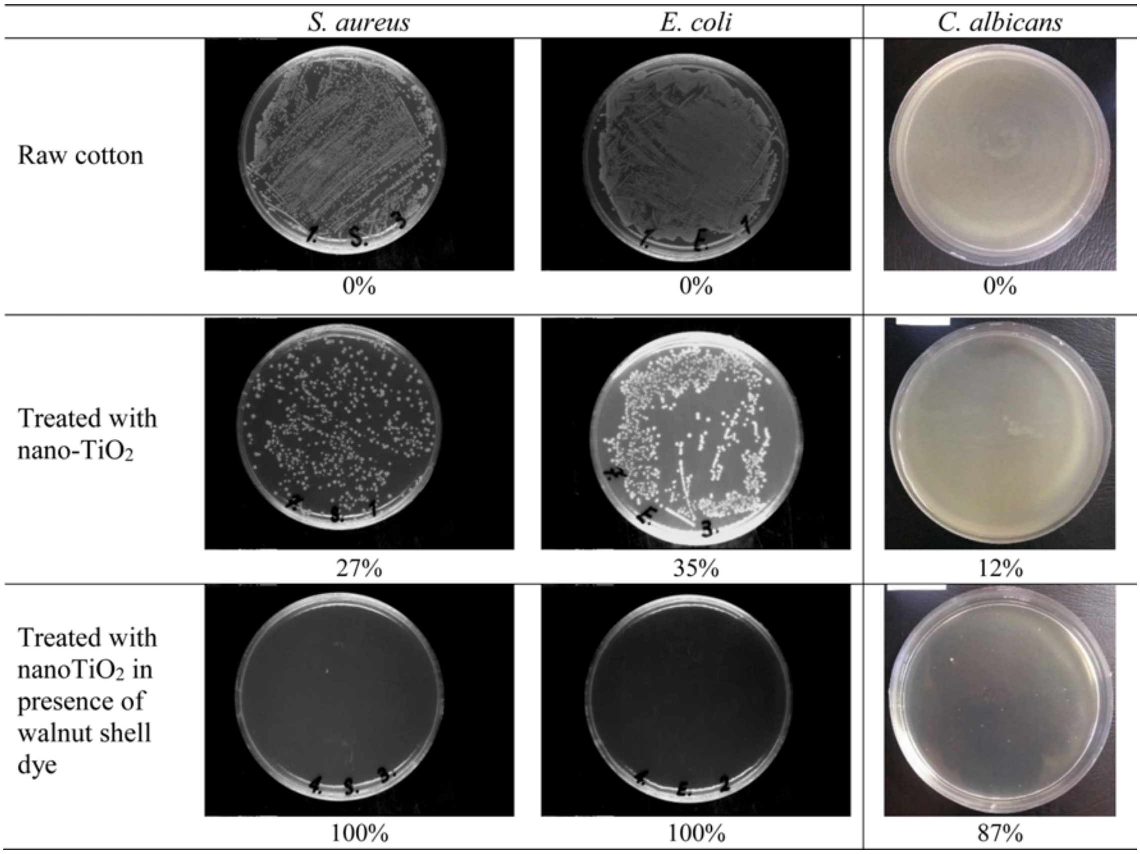

Figure 6. Antimicrobial activity measurement of raw and treated cotton fabrics.

walnut shells led to a considerable improvement in antimicrobial activities [30,33]. Nano-TiO_2 treated sample exhibited 100 % reduction in presence of the walnut shell dye for both *S. aureus* and *E. coli.* However, the antifungal efficiency of sample against *C. albicans* was 87 %. This might be due to thickness of cell wall of different microorganism [34].

Flexibility and Wettability

Bending length, bending rigidity and time of water droplet absorption of different cotton fabrics are presented in Table 1. Loading of titanium dioxide with or without natural dye caused increase in the time of water absorption in cotton fabrics due to blocking of hydrophilic groups of cellulosic substrate by nanomaterials [35]. Also, in comparison with raw cotton fabric, bending lengths values of treated cotton fabrics increased which confirms lower flexibility of samples.

Conclusion

As presented in paper, simultaneous coloration and functional finishing of cotton fabric was developed by modification of nano-TiO_2 with green walnut shell dye. Combination of titania with green walnut shell dye in finishing process led to exploit the properties of either nano-TiO_2 or natural dye on cotton fabrics. Functional characteristics of titania treated cotton in presence of walnut shell dye including self-cleaning, antibacterial, and antifungal properties were superior compared to treated cotton with nano titanium dioxide alone. It is expected that modified nano TiO_2 could be applied to produce high performance fabrics and smart textiles.

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