Functionalized Cotton Fabrics with Nano-TiO_2-Cellulose Coatings

Bandu Madhukar Kale[1,*], Zehra Yildiz[2], Jakub Wiener[1], Hana Krizova[1], Abdul Jabbar[1], Irena Lovetinska Slamborova[1], Samson Rwawiire[1], Nilkanth Kisan Kale[3] and Jiri Militky[1]

[1]*Department of Material Engineering, Technical University of Liberec, Studenska 2, 461 17 Liberec, Czech Republic*

[2]*Department of Textile Engineering, Marmara University, 34722, Istanbul, Turkey*

[3]*Sir Parshuram College, Tilak road, Sadashiv Peth, Pune-411030, Maharashtra, India*

Abstract: Functional cotton fabrics having self-cleaning, antibacterial, and antifungal properties were developed with the help of nano-titanium dioxide (TiO_2)-cellulose coatings. Coating formulations were prepared by dispersing the TiO_2 nanoparticles in cellulose solution in sulfuric acid. Cellulose layer helped to bind the TiO_2 nanoparticles to the cotton fabric surface. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) patterns proved the attachment of nano-TiO_2-cellulose layer to the cotton fabric surfaces. Self-cleaning ability of coated cotton fabrics were evaluated by using red wine stain degradation under UV light. Samples with 3, 5, and 10% nano-TiO_2 loadings showed almost complete degradation of red wine stain after 15 minutes of irradiation under UV light. The bacteria reduction performance of nano-TiO_2-cellulose coated cotton fabrics against Staphylococcus aureus (SA), and methicillin-resistant Staphylococcus aureus (MRSA) bacteria were recorded as 98.2% and 81.6%, respectively. 5 and 10% nano-TiO_2-cellulose coated samples showed significant disinfection of cotton fabric from fungal colonization.

Keywords: TiO_2 Nanoparticles, Antibacterial, Antifungal, Cellulose Coating, Self-Cleaning, Cotton Fabric.

INTRODUCTION

Nanoparticles like TiO_2, ZnO, CuO, Ag, carbon nanoparticles/nanotubes (SWCNTs and MWCNTs) etc. show excellent antibacterial activity. TiO_2 is the most environment-friendly among all other nanoparticles [1]. The TiO_2, in contact with water and oxygen molecules adsorbs some radiation with an intensity of energy that is larger than the characteristic band-gap. Electrons promoted from valence to conduction band create free electrons and electron holes' pairs. These pairs produce reactive oxygen species like superoxide anions, hydroxyl radicals, and hydrogen peroxide molecules, which can oxidize organic compounds. These radicals can also inactivate bacteria, viruses, fungi, and algae [2-6]. It is believed that the main reason of the biocidal effect of TiO_2 is a damage of the cell membrane [7] and its polyunsaturated phospholipids [8]. TiO_2 can be applied on various substrates like glass, stainless steel, textile materials, composites, activated carbon etc. There are different methods to incorporate TiO_2 such as facile synthesis of casein-based TiO_2 nanocomposite [9], platinum (IV) chloride modified TiO_2 and N-TiO_2 coatings for self-cleaning cotton fabrics [10], TiO_2 doped with SnO_2 thin films preparation by sol-gel method [11], slightly carboxymethylated cellulose supported TiO_2 nanoparticles [12], finishing self-cleaning material on cotton fabric [13], coating of TiO_2 on cementitious materials [14], and so on.

Cellulose is very important biomaterial and most abundant in nature. Antibacterial, antifungal, and self-cleaning properties of cellulose based textile materials are desired in the market [15-18]. Cellulose molecule is very stable in nature due to its strong inter and intra molecular hydrogen bonding. Solvents such as ionic liquids [19], 60% sulfuric acid [20], sodium hydroxide-carbon disulfide solvent system, can disturb hydrogen bonding and dissolve cellulose. In this study, 60% sulfuric acid was chosen to prepare the cellulose solution. TiO_2 nanoparticles were dispersed in the cellulose solution by stirring in order to coat the cotton fabrics. In recent years researchers have been trying to make cotton fabric antibacterial, antifungal, and self-cleaning in different ways such as: antibacterial finishing of cotton by microencapsulation [15], by synthesizing photo-bactericidal porphyrin-cellulose nanocrystals [21], treating cotton fabric by SBA-15-NH_2/polysiloxane hybrid containing tetracycline [22], plasma treatment and ZnO/carboxymethyl chitosan composite finishing [23], antifungal cotton fabric via molecular encapsulation of terbinafine [24], antifungal textiles by silver deposition in supercritical carbon dioxide [25], antimicrobial efficacy by finishing extracts of the Syzygium aromaticum buds [26], multifunctional cotton fabric by ultrasound mediation for one-pot sono-synthesis and deposition of magnetite nanoparticles on cotton/polyester fabric [27], self-cleaning by

*Address correspondence to this author at the Department of Material Engineering, Technical University of Liberec, Studenska 2, 461 17 Liberec, Czech Republic; E-mail: bmkale41@gmail.com

copper(II)porphyrin/TiO_2 visible-light photocatalytic system [28], coating with nano-TiO_2-acrylate copolymer [29], nano-TiO_2 coating after treatment of cotton fabric with carboxylic acids such as oxalic, succinic, and adipic acid [30], functionalizing cotton fabric with p-BiOI/n-TiO_2 heterojunction [31], bleaching and cationized cotton using nano-TiO_2 [16] etc. But the biggest problem of the designed systems in all these cases is the durability of coating layer on fabric surface. In order to overcome this problem, a novel route is needed by coating the TiO_2 nanoparticles along with cellulose prior to coating on fabric. In our previous study, we tried to coat TiO_2 nanoparticles-cellulose on the cotton fabric for durable self-cleaning and stiffness characteristics [32]. In this report, we described antibacterial, antifungal, and photocatalytic self-cleaning properties of nano-TiO_2-cellulose coated cotton fabric. Wine, tea, coffee stains are very common stains which are hard to remove and that is why red wine stain was chosen to evaluate the self-cleaning ability here in this report.

EXPERIMENTAL

Materials

Viscose fiber and cotton fabric were both obtained from Tepna Nachod, Czech Republic. Viscose was used as a source of cellulose for coating whereas cotton fabric was used as a base layer for coating. TiO_2 nanoparticles with the average size of 50nm and red wine for staining were obtained from Merck. Sulfuric acid and sodium carbonate were purchased from Lachner, Czech Republic. All microorganisms originated from the pure culture collection of the Czech Collection of Microorganisms (Masaryk University, Brno, Czech Republic).

Cellulose-TiO_2 Coating on Cotton Fabric

Cellulose (viscose fibers) was dissolved in 60% H_2SO_4 in order to prepare 10% cellulose solution at 20°C. Nano-TiO_2-cellulose dispersions with different concentrations (1, 3, 5, and 10%) of TiO_2 nanoparticles were prepared by mechanical stirring at 20°C and 150rpm for 5min. Nano-TiO_2-cellulose dispersions were coated on cotton fabric surfaces by using a roller padding at 20°C quickly in 20 sec. After padding, fabrics were washed with 100mg/L aq.(aqueous) sodium carbonate solution and water for neutralization. The washed fabrics were dried in an oven at 70°C for 25 min.

Characterization

The mechanical characterization of the pure fabric and coated fabrics was performed by Testometric M250-2.5 machine according to the ISO 1924-2 standard. The morphology of nano-TiO_2-cellulose coated cotton fabrics was observed by scanning electron microscopy (SEM). The coated cotton fabrics were cut and placed on SEM stubs by two sided tape and then morphology was observed using TS5130 Vega-Tescan at voltage of 30 kV acceleration. The X-ray diffraction (XRD) scan of the coated cotton fabrics was performed on X'Pert³ X-ray powder diffractometer (PANalytical, USA) by using CuKα radiation. The fabric samples were scanned over the range of angle 8° to 70° in steps of 0.017. In order to investigate the photocatalytic self-cleaning performance, the red wine stain was used on the nano-TiO_2-cellulose coated fabrics. Fabrics were stained with red wine with a constant quantity of 50 µL. After staining with red wine, the fabrics were irradiated under UV light. For irradiation of red wine stain, Philips TL 6W/05 CE UV tube (400-320nm) was employed. Irradiated samples were scanned with 300dpi resolution, afterwards images were analyzed by 'Image J' software [33]. The quantitative and qualitative evaluation of anti-bacterial activity of the coated fabrics was performed according to the AATCC–100 [34] and AATCC-147 [35] standards, respectively. The names of the bacteria that were used in antibacterial testing are as follows; Escherichia coli (EC), Klebsiella pneumoniae (KP), Staphylococcus aureus (SA), and methicillin-resistant Staphylococcus aureus (MRSA). The sample was wetted in distilled water with the dimension of 18x18mm then was placed on a wet filter paper and was put together in a covered petri dish. The sample was placed into a sterile container and exposed to UV radiations for 15 minutes. Thereafter 50µL of bacterial stain (inoculums) was applied on the sample and allowed to wick through the sample stack. The inoculated swatches incubated for 24 hours at 37°C. Thereafter a neutralizing broth composed of 50mL of saline was added and container was shaken so as to release the inoculums from the test swatches through the neutralizing broth. The bacteria present in this liquid was obtained as the percentage reduction. Anti-bacterial activity of the fabric samples was quantitatively analyzed using the AATCC 100 method [34, 36]. The reduction percentage in the number of bacteria was calculated according to the Equation 1:

$$R(\%) = (B - A)\frac{100}{B} \quad (1)$$

Where R is the reduction percentage; A and B are the numbers of bacteria recovered from the inoculated treated and untreated fabrics, respectively. The antifungal properties of the coated cotton fabrics were measured using the following fungi mixture in aqueous suspension at a concentration of 10^6 CFU/ml: Penicillium digitatum (CCM F-382), Rhizopus stolonifer (CCM F-445), Cladosporium sphaerospermum (CCM F-351), Chaetomium globosum (CCM 8156). Three samples of cotton fabrics with $4cm^2$ area were coated with nano-TiO_2 in different TiO_2 concentrations (0, 1, 3, 5 and 10%) then samples were placed on agar medium (Malt agar, Cadersky-Envitek, Ltd, Brno, Czech Rep.) and were inoculated with a suspension of testing moulds. Incubation of the tested samples was conducted for two weeks at a temperature of 22 ± 3 °C, under daylight (near a window). After testing, the evaluation of the antifungal activity was done on the basis of visual assessment according to the BS EN 14119:2003 standard [37] by determining the degree of mould growth on the surface of fabric samples. The rating system for mold growth was as follows: 0 – no visible growth evaluated microscopically, 1 – no visible growth evaluated with the naked eye but clearly visible microscopically, 2 – growth visible with naked eye, covering up to 25% of tested surface, 3 – growth visible with naked eye, covering up to 50% of tested surface, 4 – considerable growth, covering more than 50% of tested surface, 5 – very intense growth, covering all tested surface.

RESULTS AND DISCUSSION

Tensile Testing

The mechanical characterization of pure cotton, cellulose coated, and nano-TiO_2-cellulose coated cotton fabrics was performed by tensile testing. The tensile strength values of the fabric samples were given in Table **1**. Accordingly, due to the interchain linkages between cotton fabric and cellulose coating layer via hydrogen bondings, the tensile strength was increased after the cellulose coating process. When the nano-TiO_2 particles were also applied on cotton fabrics, a slightly decrease (3 N) in tensile strength value was observed. This result can be explained by the reduction of the amount of hydrogen bondings due to the presence of solid nano-TiO_2 particles which were interact with both cotton surface and cellulose coating layer. The nano-TiO_2 particles cause irregularities on the cellulose coating layer thus lead to decline in tensile strength value.

Table 1: Tensile Strength Values of the Cotton Fabrics before/after Coating Processes

Cotton Fabric Samples	Tensile Strength (N)
Pure	497
Cellulose Coated	582
Nano-TiO_2-Cellulose Coated	579

SEM Analysis

The morphological characterization of nano-TiO_2-cellulose coated cotton fabrics was performed by using SEM analysis (Figure **1**). In order to investigate the effects of TiO_2 nanoparticles, cotton fabric was also coated by only cellulose without TiO_2 inclusion (Figure **1b**). Figure **1a** belongs to the pure cotton fabric without any coating layer. Figure **1b** shows that the cellulose coating layer is smoothly attached to the fabric surface. According to the Figure **1c**, the white particles on the fabric surface prove the existence of TiO_2 particles in the coating layer. There is no agglomeration was observed in Figure **1c**, supporting that a uniform TiO_2 dispersion was succeeded. In our previous study, [32] it was proved that the cellulose coating layer stays with the cotton fabric permanently. The coated cellulose does not get washed away unlike starch because it forms an interchain linkage by intermolecular hydrogen bonding with cotton cellulose during coating. Since solvent is strong the solvent molecules try to interact with the surface of the cotton fabric and during interaction coated cellulose forms hydrogen bonding with cotton cellulose. It is not easy to prove hydrogen bonding by spectroscopic method because both are the same molecule. In order to observe the attachment of nano-TiO_2 particles on cotton fabric surface, the SEM image of Figure **1d** was captured with higher magnification (x1k).

XRD Analysis

In order to detect the TiO_2 particles on nano-TiO_2-cellulose coated cotton fabric surfaces, XRD technique was employed. Figure **2** shows the XRD patterns of control (pure cotton fabric), cellulose coated and nano-TiO_2-cellulose coated cotton fabrics, respectively. Both cellulose and nano-TiO_2-cellulose coated cotton fabrics show the characteristic diffraction peaks of cellulose I at 22.3°, 16.4°, and 14.6°. All three samples had the diffraction peaks of cellulose II at 12. 4° and this shows that there was no significant effect of solvent on cotton fabric during coating process. The nano-TiO_2-cellulose

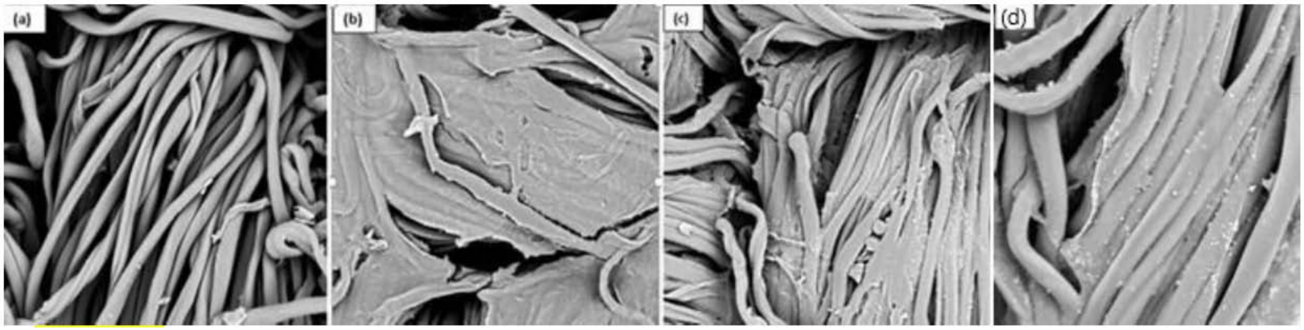

Figure 1: SEM micrographs of cotton fabrics in x500 magnification; (**a**) pure cotton (**b**) only cellulose coated, (**c**) nano-TiO_2-cellulose coated, (**d**) nano-TiO_2-cellulose coated, in x1k magnification.

coated sample shows the characteristic peak of TiO_2 at 25.4°. This peak confirms that TiO_2 particles are existing on cotton fabric surface. From these results, it can be concluded that TiO_2 particles were successfully attached to the cotton fabric surface with the help of cellulose layer.

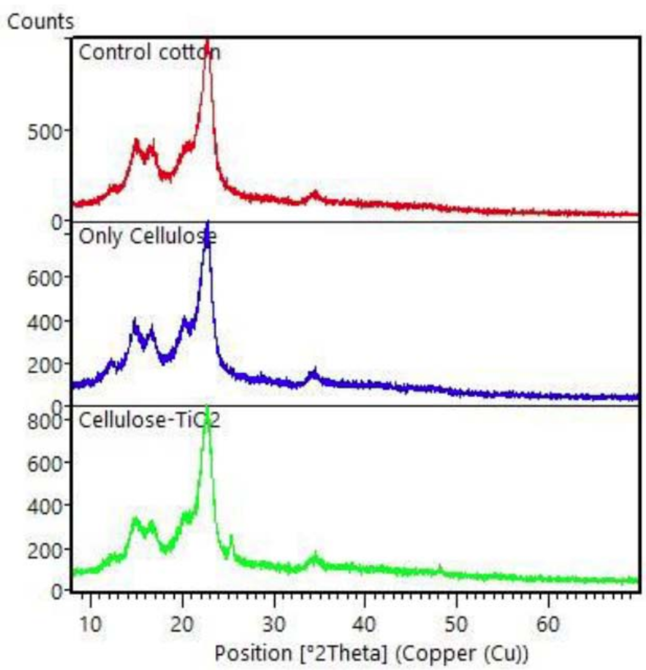

Figure 2: X-ray diffraction pattern of control, only cellulose coated and nano-TiO_2-cellulose coated cotton fabric.

Photocatalytic Self-Cleaning Performance

The photocatalytic self-cleaning ability of nano-TiO_2-cellulose coated cotton fabrics with red wine stain was observed under UV light. UV light irradiated cotton fabrics were scanned on the scanner and then evaluated by using ImageJ software. Figure **3** shows the scanned images of control (pure cotton fabric), only cellulose coated and 1, 3, 5, and 10% nano-TiO_2 included cellulose coated cotton fabrics with red wine stain after 15 minutes of irradiation by UV light. According to the Figure **3**, the red wine stain in 3, 5, and 10% nano-TiO_2-cellulose coated samples were degraded whereas control, only cellulose coated samples remained unaffected. Due to low concentration of TiO_2 in 1% loading, less degradation of red wine stain was obtained.

The effect of TiO_2 concentration on red wine stain degradation was observed by using ImageJ software. This software measures the color intensity by using the color histogram tool. Accordingly, when the color of the sample turns whiter, the color intensity value (counts) increases. As can be seen in Figure **4**, the degradation of stain increases with increasing irradiation time and concentration of TiO_2. The 3, 5, and 10% TiO_2 loadings show significant discoloration of stain after irradiation under UV light for 15 minutes. Figure **4** shows that the degradation of stain increases with increasing amount of TiO_2 in coating layer.

Antibacterial Activity

The effect of TiO_2 coating on the growth of bacteria's such as EC G- CCM 2024, KP G- CCM 2318, SA G+ CCM 226 and MRSA G+ CCM 4223 were all investigated in nano-TiO_2-cellulose coated cotton fabrics. Figure **5** shows the pictures of bacterial growth on coated and uncoated cotton fabrics against SA (Figure **5a**) and MRSA (Figure **5b**) bacteria, respectively. According to the images, the area of bacterial growth decreases with increasing TiO_2 amount in coating. Table **2** reflects the observation of bacterial reduction by AATCC-100 standard and it shows that compact bacteria were obtained in case of Gram negative (G-ve) EC and KP bacteria.

A quantitative evaluation of bacterial reduction cannot be performed in the samples with EC and KP bacteria since only a compact bacteria occurrence was recorded in these samples. Table **3** gives the

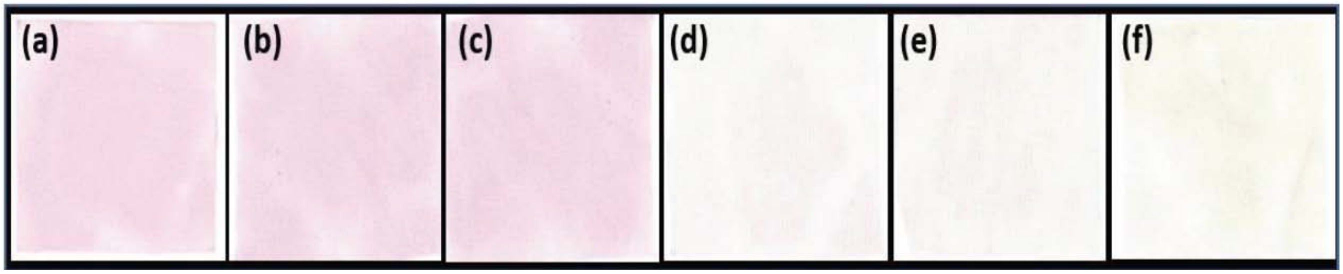

Figure 3: Scanned pictures of stained cotton fabrics after irradiation of red wine stain under UV light; (**a**) control sample, (**b**) only cellulose coated cotton fabric, (**c**, **d**, **e**, **f**) nano-TiO_2-cellulose coated cotton fabrics with 1, 3, 5, 10% TiO_2 loadings.

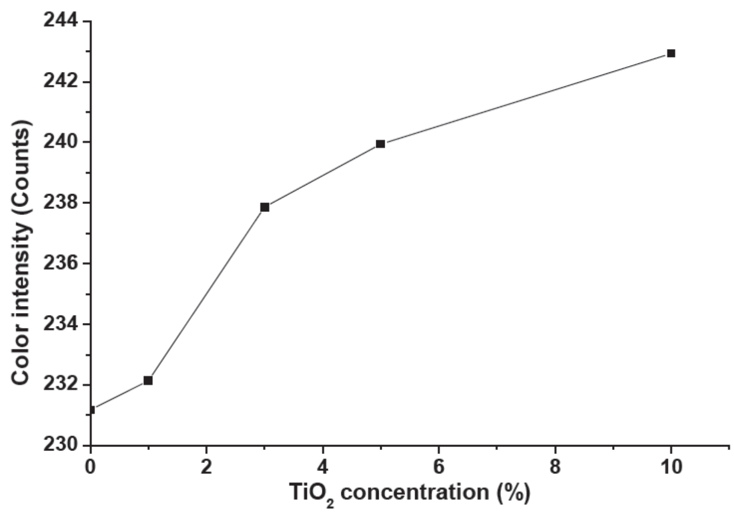

Figure 4: Effect of TiO_2 concentration on wine stain degradation.

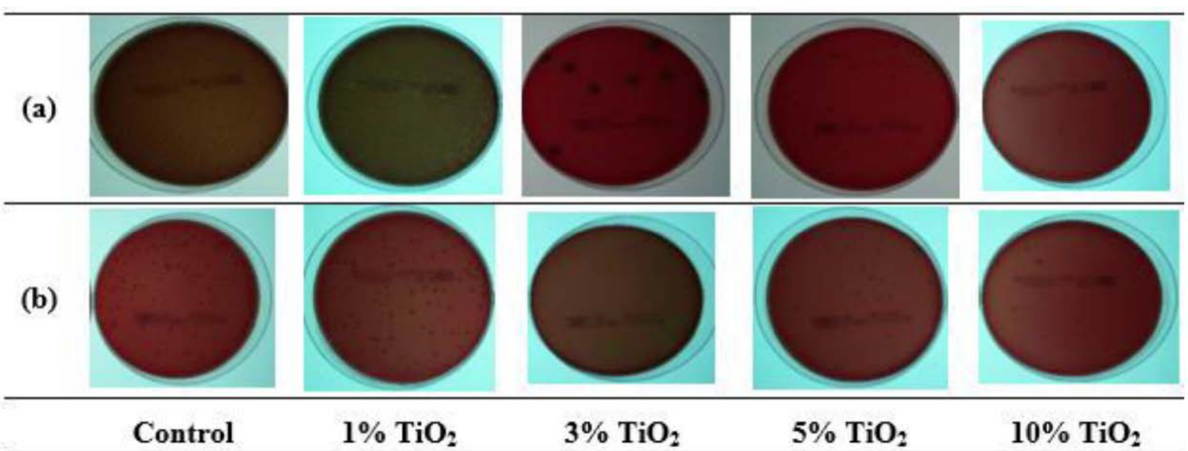

Figure 5: Antibacterial activity against (**a**) Staphylococcus aureus bacteria (SA), (**b**) Methicillin-resistant Staphylococcus aureus (MRSA).

reduction/multiplication percentage of the Gram positive (G+) bacteria SA and MRSA. It is observed that the coating of fabrics with nano-TiO_2-cellulose had a positive reduction of SA bacteria and MRSA bacteria. The effectiveness of the antimicrobial activity increased with increasing nano-TiO_2 loading in coating layer. Fabrics treated with 1% TiO_2 had the lowest SA bacterial reduction. However, with an increase in the concentration of TiO_2, there was a high jump from 6.3% to 96.7% reduction of SA bacteria on 3% nano-TiO_2 included sample. These results confirm that sample coated with 3, 5 and 10% nano-TiO_2-cellulose show strongest inhibition efficiency against bacteria. The effectiveness of the antimicrobial activity increased with increasing nano-TiO_2 amount in coatings.

Table 2: Observation of Bacterial Reduction by AATCC-100

Method AATCC-100	Control	Cellulose coated	1% TiO_2	3% TiO_2	5% TiO_2	10% TiO_2
EC 10^5 CFU/ml	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence
KP 10^5 CFU/ml	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence	Compact bacteria occurrence
SA 10^5 CFU/ml	960	900	68	32	22	17
MRSA 10^5 CFU/ml	104	120	98	42	34	22

Table 3: Quantitative Evaluation of Bacterial Reduction

Test Sample	Bacterial Reduction/Multiplication (%)	
	Staphylococcus aureus (SA)	Methicillin-resistant Staphylococcus aureus (MRSA)
Control Sample	-	-
1% TiO_2	6.3	13.3
3% TiO_2	96.7	65.0
5% TiO_2	97.7	68.3
10% TiO_2	98.2	81.6

Same samples were also analyzed according to the AATCC-147 standard in order to investigate the antibacterial activity qualitatively. Unlike AATCC-100, the results from AATCC-147 (Table **4**) shows no effect of nano-TiO_2-cellulose coating on G- bacteria such as EC and KP. Also there is no effect of coating on G+ SA and MRSA.

Antifungal Properties

Antifungal activity of nano-TiO_2-cellulose coated cotton fabrics was evaluated with the fungi mixture of Penicillium digitatum (CCM F-382), Rhizopus stolonifer (CCM F-445), Cladosporium sphaerospermum (CCM F-351), Chaetomium globosum (CCM 8156) in aqueous suspension at a concentration of 10^6 CFU/mL. Figure **6** (**a**, **b**, **c**, **d** and **e**) shows the results of antifungal test. The surface of agar in the Petri dishes was completely covered with fungi (filamentous hyphae forming the mycelium) in the first 4 days. However, the filamentous hyphae (mycelium) started to lose from the surface over the second week. Finally, the samples containing the 5 and 10% TiO_2 were most cleared. The reason of this antifungal activity is the photocatalytic effect of TiO_2, but this effect occurred slowly and later

Table 4: Evaluation of Antibacterial Testing by AATCC-147

Method AATCC-147	Control Cotton fabric	Cellulose coated cotton fabric	1 % TiO_2	3 % TiO_2	5 % TiO_2	10 % TiO_2
EC 10^5 CFU/mL	No effect	No effect	No effect	No effect	No effect	No effect
KP 10^5 CFU/mL	Halo zone not clear ∅ 1,74 mm	No effect	No effect	No effect	No effect	No effect
SA 10^5 CFU/mL	Halo zone not clear ∅ 4,93 mm	No effect	No effect	No effect	No effect	No effect
MRSA 10^5 CFU/mL	No effect	No effect	No effect	No effect	No effect	No effect

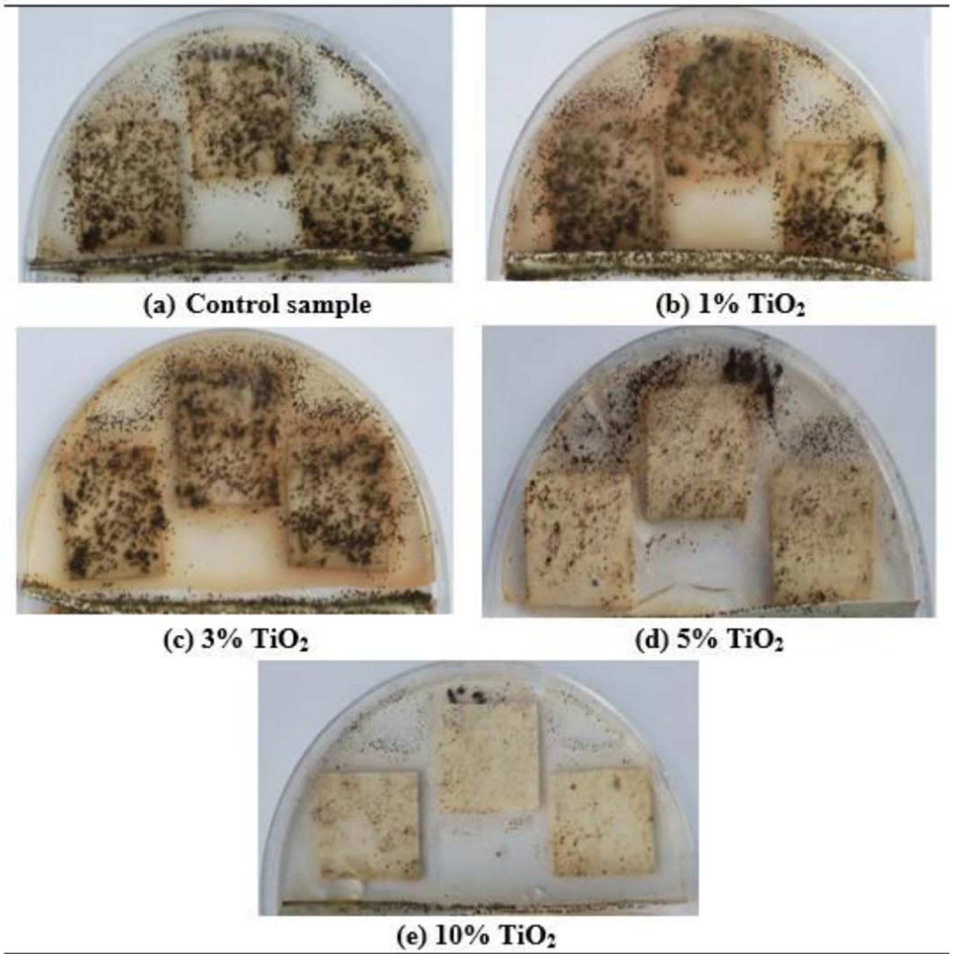

Figure 6: Antifungal activity of (**a**) Control sample, (**b**) 1% TiO_2, (**c**) 3% TiO_2 (**d**) 5% TiO_2 and (**e**) 10 % nano-TiO_2-cellulose coated cotton fabric.

(during the second week of cultivation). The amount of fungi was decreased with increasing concentration of TiO_2 from the beginning. Thus, long-term antifungal effect was observed on the samples of cotton fabrics coated with TiO_2 at concentration of 5% or higher. According to the BS EN 14119:2003 standard [37] the growth of fungi is in the ranges of between degree 2 (high concentration of TiO_2) and 4 (low concentration of TiO_2) on the samples.

CONCLUSIONS

Cellulose solution was prepared by dissolving the viscose fibers in 60% H_2SO_4 solution. Then nano-TiO_2-cellulose dispersions were prepared with 1, 3, 5, and 10% nano-TiO_2 loadings. Cotton fabrics were coated with nano-TiO_2-cellulose formulations by using a roller padding for antibacterial, antifungal, and self-cleaning properties. Tensile strength was increased with the cellulose coating layer due to the interchain linkages between the cotton fabric and cellulose coating layer. XRD patterns and SEM micrographs confirmed that TiO_2 was successfully attached on cotton fabrics via cellulose coating layer. Samples coated with nano-TiO_2-cellulose showed significant reduction in growth of SA and MRSA bacteria under UV light. Samples containing more than 3% nano-TiO_2 showed strongest inhibition efficiency against these bacteria. Antifungal testing results showed that the photo-catalytic activity of TiO_2 nanoparticles allows a disinfection of cotton fabric from fungal colonization. The evaluation of red wine stain degradation proved that cotton fabrics coated with nano-TiO_2-cellulose layer are capable of self-cleaning activity. The antibacterial, self-cleaning, and antifungal properties of coated samples were increased with increasing amount of TiO_2. In summary, it is possible to attach the nanoparticles along with cellulose layer on cotton fabrics. The nano-TiO_2-cellulose coating gives cotton fabrics a self-cleaning, antibacterial, and antifungal properties. Furthermore, the other nanoparticles such as carbon, zinc, copper etc. can also be tried and investigated in place of nano-TiO_2 as future work.

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