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Development of UV Protective, Superhydrophobic and Antibacterial Textiles Using ZnO and TiO_2 Nanoparticles

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Abstract: In this research work, multifunctional cotton fabric comprising of UV protection, superhydrophobicity and antibacterial activity has been developed using facile pad-dry-cure method. In the first step, the concentration of repellent chemical has been optimized. Then, formulations containing nanoparticles of ZnO or TiO_2 along with optimized concentration of repellent chemical and organic-inorganic binder have been applied to cotton fabric followed by the evaluation of functional properties. The surface morphology and elemental composition of treated fabric has been characterized through SEM and EDX, respectively. The treated samples have shown promising UV protection, superhydrophobicity and antibacterial properties durable upto 20 washing cycles.

Keywords: Functional textiles, UV protection, Superhydrophobicity, Antibacterial textiles, Nanoparticles

Introduction

Functional textiles are those which in addition to performing their routine job provide additional functions such as UV protection, self-cleaning, lotus effect, superhydrophilicity, fire retardancy, moisture management, antibacterial activity etc. Due to growing market demand, the researchers have focused their attention on development of multifunctional textiles using non-conventional techniques. These techniques include the use of nanotechnology or nanomaterials either to deposit nanoparticles on textiles to functionalize them or to develop nanofibers which are used for manufacturing of fabrics with functional characteristics. The development of multifunctional fabrics having trifunctional characteristics durable to washing are interesting for broad spectrum applications and need to be studied comprehensively.

The use of nanoparticles, nanofinishes and nanostructures is very useful for enhancing and developing superior performance characteristics of conventional textiles including antimicrobial activity, water repellency, self-cleaning, soil-resistance, anti-static, anti-infrared and flame-retardancy. The dyeability and color fastness of textile materials can also be enhanced by creating nanostructure surfaces [1]. UV protection property of a textile fabric can be achieved by dye, pigment, delustrant (TiO_2) or UV absorber finish. These materials can provide protection against UV radiation by absorbing and blocking its penetration through a fabric. In recent years, lot of research has been done to develop functional textiles using nanoparticles of ZnO, SiO_2, and TiO_2 etc. Excellent UV protection was achieved by deposition of TiO_2 on polyester fabric [2]. TiO_2 and ZnO nanoparticles are also used for this purpose as they have good UV protection properties. They give protection by reflecting, scattering or absorbing harmful UV radiations of sun. They are more stable when compared to organic UV-blocking agents. Nanoparticles of ZnO can be prepared by wet chemical technique followed by application on fabrics for enhanced UV protection [3-6].

For antimicrobial finishing, several materials are used including nano-sized Ag, TiO_2 and ZnO particles. Metallic ions and metallic compounds also show some degree of sterilizing effect. It is considered that oxygen in the air or water is turned into active oxygen species by means of catalysis with the metallic ions so dissolving the organic substances to create a sterilizing effect. Antibacterial effects on textile fabric can be maximized using nanoparticles because of the increased surface area [7-10].

Nano-rough super-hydrophobic surfaces can be prepared by controlling surface topography by many processing methods which include sol-gel technique, organic/inorganic hybrid method, CVD, electrochemical deposition, embossing, plasma processing and phase separation technique. The incorporation of TiO_2 nanoparticles by titania sol-gel coating can cause surface roughness for enhancing the superhydrophobicity of the fabric [11]. Carbon fabric was coated with silica nanoparticles to make it superhydrophobic [12].

In some recent studies, multifunctional properties have been imparted to textiles. For instance, self-cleaning, antibacterial and UV protective properties have been studied using ZnO nanoparticles [13]. In another study, self-cleaning, lotus effect and antibacterial properties have been developed on polyester fabric by growing ZnO nanorods [14]. The present study is focused on development of durable multifunctional cotton fabric which retains its functional properties up to at least 20 washes. The functional properties developed include UV protection, superhy-

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drophobicity and antibacterial activity. For this, TiO_2 and ZnO nanoparticles along with fluorocarbon and organic-inorganic binder have been used to optimize the multi-functional properties.

Experimental

Materials

Nano particles dispersions of ZnO and TiO_2 were purchased from Bochemie and Inotex, respectively. Organic-inorganic binder was purchased from CHT Bezema. Commercial fluorocarbon based water repellent was purchased from Rudolf. The finish has been applied on 100 % cotton plain weave fabric with 120 GSM.

Preparation of Formulation

Two types of formulations were prepared. First formulation was prepared to optimize the concentration of repellent chemical for superhydrophobicity. To achieve this, solutions with different concentrations of repellent chemicals were prepared and applied on fabric (Table 1). After determining the optimum concentration of water repellent chemical, formulations with nanoparticles, repellent chemical and organic-inorganic binder (15 g/*l* organic-inorganic binder as recommended by the supplier) were prepared according to design of experiment shown in Table 2. Each formulation was sonicated with Ultrasonic probe disperser for 5 min.

Application on Fabric

The formulations were applied on fabric by pad-dry-cure method. The cotton fabric was immersed in the chemical solution containing nanoparticles, repellent chemicals and binder. Then it was passed through a padding mangle to attain 80 % wet pick-up. After padding, the fabric was dried at 120 °C for 5 min and then cured for 2 min at 160 °C.

Table 1. Optimization of concentration of repellent chemical

Sample #	Water repellent (g/*l*)
Pristine cotton	0
1	20
2	40
3	60
4	80

Table 2. Design of experiment

Sample #	ZnO dispersion (g/*l*)	TiO_2 dispersion (g/*l*)	Water repellent chemical (g/*l*)	Binder MTX (g/*l*)
5	30		40	15
6	20	-	40	15
7	10	-	40	15
8	-	30	40	15
9	-	20	40	15
10	-	10	40	15

Characterizations

Surface Morphology and Elemental Analysis

The morphological changes on the surface of cotton fabric after application of formulations were observed by UHR-SEM Zeiss Ultra Plus with an accelerating voltage 2 kV equipped with an Energy Dispersive X-ray spectrometer Oxford X-max 20. EDX analysis of the coated fabric was carried out at 10 kV accelerating voltage to determine the elemental configuration of the deposited materials on the surface of the cotton fabric.

Contact Angle Measurement

Contact angle was measured by using Surface Energy Evaluation (SEE) System. SEE System is a computer-aided instrument for contact angle measurement and surface energy evaluation. The volumes of probing liquids in the measurements were approximately 5 μ*l*. All water contact angle was measured five times, and an average value was used. The contact angle measurement could be easily performed by establishing the tangent angle of a liquid drop with a solid surface. The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions solid/vapor, solid/liquid and liquid/vapor.

UV Protection Properties

The ultraviolet radiation blocked or transmitted by textile fabric was determined by using the standard test method of AATCC 183-2000. Mean UPF, UVA and UVB blocking percentage of samples were calculated using UV Spectrophotometer (M550 SPF).

The cotton samples were conditioned for 4 hours at 21±1 °C temperature and 65±2 % relative humidity by laying each test specimen separately. After that each sample was cut into size 5×5 cm^2. Sample was placed on the flush against the sample transmission port opening in the sphere. Then first UV transmission was measured with the sample oriented in one direction and second measurement was at 0.79 radian or 45 ° to the first and third at 0.79 radian or 45 ° to the second. For each sample, four measurements were performed and the average of all four scans was taken as a final UPF value.

Antibacterial Test

The antibacterial properties of the samples were evaluated against Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria by using the agar diffusion technique (AATCC 147). The zone of inhibition around samples was evaluated after 24 h of incubation in dark at 37 °C.

Washing Durability

Washing durability of functionalized cotton fabrics for superhydrophobicity, UV-protection and antibacterial properties against repeated washing were evaluated according to ISO

105 C06 (B1M). According to this standard, each washing cycle completed with 4 g l^{-1} detergent at 50 °C for 45 min time interval which is equal to five home launderings. After washing samples were then rinsed and dried in oven at 80 °C for 5 min. Moreover, samples were again analyzed against superhydrophobicity, UV-protection and antibacterial properties.

Results and Discussion

Functionalization of Fabric

Figure 1 shows the surface morphology of cotton fibers treated with formulations containing fluorocarbon, organic-inorganic binder, ZnO and TiO_2 nanoparticles. The fibers are almost uniformly covered with nanoparticles as shown in Figure 1(B), (C) and (D). The high resolution micrographs (Figure 1(C) and (D)) of samples treated with 30 g/*l* ZnO and TiO_2 show roughness generated on fiber surface. EDX analysis of treated samples shows elemental composition of cotton fiber surface after application of formulations of nanoparticles (Table 3). Both the samples contain almost similar atomic percentage of elements (C, O, F, Zn or Ti etc).

Figure 2 shows the surface morphology of sample before washing and after 5, 10 and 20 washing cycles. It can be seen that there is no significant change in morphologies of fibers. The nanoparticles uniformly cover the surface of fibers before and even after 20 washing cycles, some bigger particles appear after washing on the surface of fibers and their concentration increases with the increase in washing cycles. This can be attributed to weakly attached particles within the structure of fabric which appear in the form of aggregates on the surface of fabric.

Table 3. Elemental composition of surface of treated cotton fabric

Element	Sample treated with formulation containing 30 g/*l* ZnO (Atomic %age)	Sample treated with formulation containing 30 g/*l* TiO_2 (Atomic %age)
C	58.59	58.06
O	38.89	39.50
F	1.06	1.03
Mg	0.02	0.03
Si	0.14	0.13
Zn	1.3	0
Ti	00	1.34

Ultraviolet Protection

Solar light is composed of UV, visible and infrared radiations. The UV radiations comprise of UVA (400-315 nm), UV-B (315-290 nm) and UV-C (290-200 nm). Due to filtering activity of the upper atmosphere, UV-C and most of UV-B are absorbed by the ozone layer. The sunlight

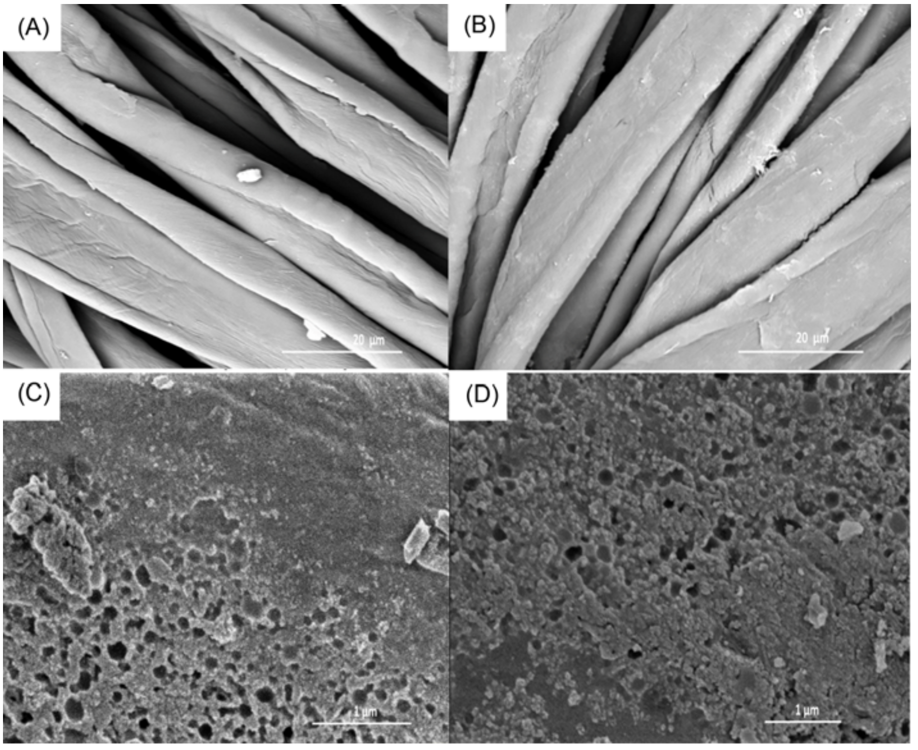

Figure 1. SEM micrographs of (A) untreated cotton fabric, (B) cotton fabric treated with 30 g/*l* ZnO (low resolution), (C) high resolution of same sample, and (D) cotton fabric treated with 30 g/*l* TiO_2.

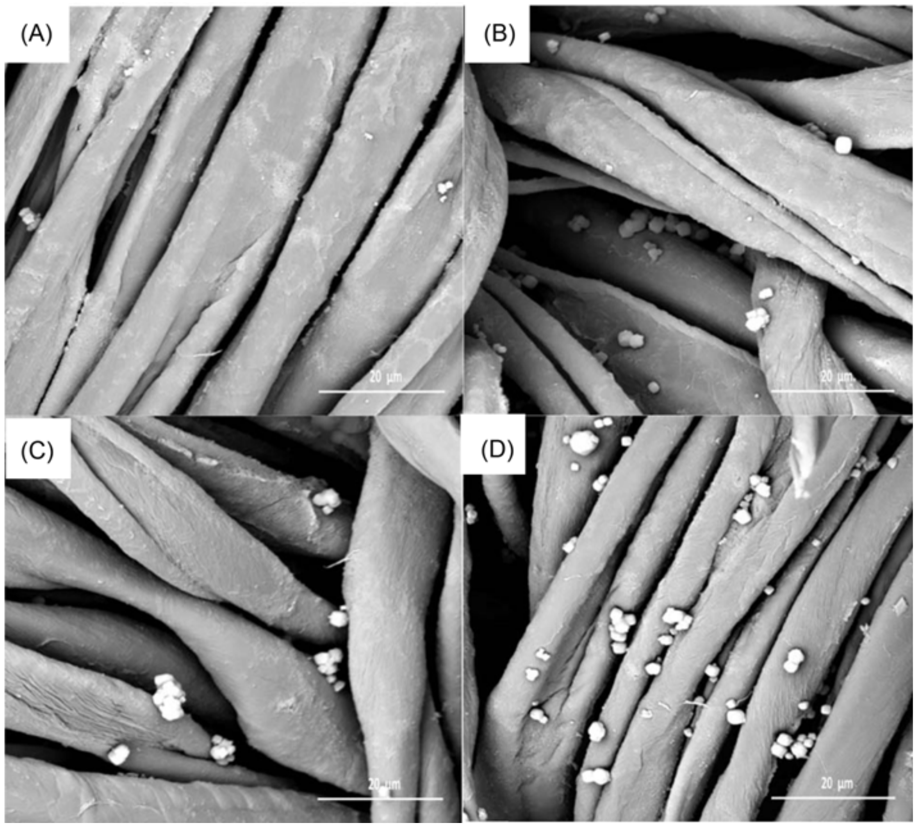

Figure 2. SEM micrographs of sample treated with formulation containing 30 g/*l* of ZnO; (A) before washing, (B) after 5 washing cycles, (C) after 10 washing cycles, and (D) after 20 washing cycles.

reaching the earth contains 5.6 % UV-A and 1 % UV-B. As these radiations have very high energy, therefore, they are highly damaging to humans and are source of many skin diseases including cancers [15]. It is very important to measure UV protection of apparels.

Table 4 presents UPF and %age blocking of UV-A and UV-B by fabrics. The pristine fabric and the one treated with 40 g/*l* fluorocarbon have UPF around 10 which is very low compared to required one. The fabric treated with nanoparticles of ZnO and TiO_2 have significantly higher UPF and it increases with the increase in nanoparticles concentration. With ZnO nanoparticles, the highest UPF is obtained when NPs concentration is 30 g/*l*. At this concentration, UPF, UV-A and UV-B blocking of fabric are 35.7, 91.5 % and 97.8 %, respectively. However, it is still lower than the minimum UPF (40) required for protection. Contrary to this, UPF, UV-A and UV-B blocking of fabric treated with formulation containing 10 g/*l* TiO_2 nanoparticles are 44.8, 89 % and 98.7 %, respectively. It means that UV protection provided by TiO_2 at 10 g/*l* is higher than 30 g/*l* of ZnO. It further increases with the increase in TiO_2 concentration and reaches at UPF of 147.7 and 94 % and 99.8 % blockage of UV-A and UB-B, respectively.

The UV protection imparted by nanoparticles is due to absorbance, reflection and scattering of UV when they strike with them [6]. According to Rayleigh's scattering theory the optimum nanoparticle size should be between 20 and 40 nm for scattering the UV radiation between 200 and 400 nm [16]. As the fabric has been treated with nanoparticles having size less than 40 nm, therefore they cause scattering of UV light along with its absorbance and reflection.

Table 4. UPF and percent UV blocking of different samples for UV-A (315-400 nm) and UV-B (295-315 nm) radiation

Sample #	ZnO disersion (g/*l*)	TiO_2 dispersion (g/*l*)	Mean UPF	UVA Blocking %	UVB Blocking %
Pristine cotton	-	-	5.7	75.4	83.9
2	-	-	10.0	77.6	93.5
5	30	0	35.7	91.5	97.8
6	20	0	20.9	88.4	96.0
7	10	0	15.7	86.1	94.8
8	0	30	147.7	94.0	99.8
9	0	20	72.9	91.2	99.4
10	0	10	44.8	89.0	98.7

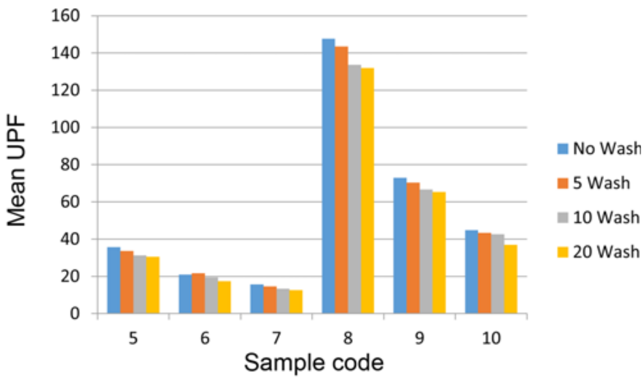

Figure 3. UPF of the washed samples after 5, 10 and 20 cycles of domestic washing.

Similar UPF has been achieved in previous studies using nanoparticles of TiO_2 and ZnO nanoparticles, however, the focus of those studies was to develop single functional property or the process to impart functional properties was not cost effective. For instance, Şule *et al*. obtained self-cleaning and UV protection using layer by layer deposition technique. They deposited 10 to 16 layer of TiO_2 which made process very lengthy [17]. In another study, UPF of cotton fabric treated with ZnO nanoparticles having diameter ranging between 12 nm to 38 nm was 34 which is less than the recommended UPF [6].

The higher UV protection of TiO_2 than ZnO is attributed to its absorbance spectrum which covers more UV region as compared to ZnO [17]. The absorbance of TiO_2 nanoparticles is also significantly higher than nanoparticle of ZnO having same size [18]. TiO_2 (rutile) has a refractive index of 2.7 and ZnO has a refractive index of only 2.0. The scattering intensity of ZnO is significantly smaller than that of TiO_2, provided that the particle size is the same, and hence, gives higher transparency than TiO_2.

The washing durability of UPF of fabric has also been evaluated. For this, the treated fabric has been subject to 5, 10 and 20 washing cycles. It has been observed that there is no significant change in UPF after washings (Figure 3) which shows that organic-inorganic binder is very effective in binding nanoparticles on fabric surface. However, in previous studies where binder has not been used, the particles are removed during washing and UPF decreases after every washing cycles [18]. It shows that the use of binder is necessary to attach nanoparticles on fabric surface.

Superhydrophobicity

The hydrophobicity of treated fabric was optimized in two steps. In the first step, the concentration of fluorocarbon was optimized. Table 5 shows the results of WCA on fluorocarbon treated fabrics. It can be seen that WCA is 132 ^{o} when fluorocarbon concentration is 20 g/*l* and it increases to 144 ^{o} (shown in Figure 4) when fluorocarbon concentration is increased to 40 g/*l*. On further increase in concentration, there is no change in WCA. Therefore, the optimum concentration is 40 g/*l*. At this concentration, the fiber surface is completely covered with fluorocarbons. Therefore, they have the lowest surface free energy.

Once the quantity of repellent chemical has been optimized, the nanoparticles and organic-inorganic binder were added in formulation and applied to textiles to generate nano-roughness so that WCA can be increased [19,20]. Table 6 presents the results of WCA. It shows that WCA increases with increase in concentration of nanoparticles on fabric surface. For instance, the WCA increases from 146 ^{o} to 157 ^{o} when concentration of ZnO nanoparticles increases from 10 g/*l* to 30 g/*l*. The nanoroughness generated due to deposition of nanoparticles reduces the contact area between water droplet and textile surface [21]. According to Cassie and Baxter, lower is the contact area between droplet, higher

Table 5. WCA of samples treated with only fluorocarbon

Sample #	Water repellent (g/*l*)	Contact angle (degree)
1	20	132±3
2	40	143±1.8
3	60	145±2
4	80	144±1

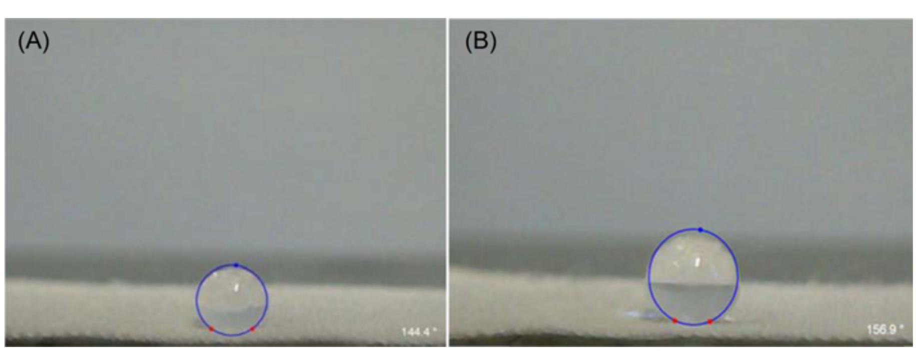

Figure 4. WCA images of (A) cotton fabric treated with 40 g/*l* fluorocarbon, (B) cotton fabric treated with formulation containing 40 g/*l* Fluorocarbon and 30 g/*l* ZnO.

Table 6. WCA of treated samples treated before and after washes

Sample #	ZnO Dispersion (g/*l*)	TiO_2 Dispersion (g/*l*)	WCA on treated fabric (degree)	WCA after 5 washes (degree)	WCA after 10 washes (degree)	WCA after 20 washes (degree)
5	30	0	157±2	145±1.5	140±1.8	132±1.5
6	20	0	152±3	144±2	135±3.2	129±1.5
7	10	0	146±1.8	141±2	135±1.5	133±2.5
8	0	30	160±3	144±1.5	136±2	130±1.8
9	0	20	152±4	143±3	135±2	129±1.5
10	0	10	145±3	140±2	134±1.2	132±3

is the contact angle [22].

Although, the WCA of functionalized fabrics decreases with the increase in washing cycles, but they still retain very good hydrophobicity. It has been demonstrated in the previous section that UPF does not change much with washing cycles which is mainly due to the presence of nanoparticles. Therefore, we can assume that the decrease in WCA after repetitive laundering is due to removal of fluorocarbon from fabric surface and not because of peeling of nanoparticles as shown in Figure 2. A rough estimation was made by measuring atomic percentage of fluorine before and after 20 washing cycles to substantiate our argument. For this, same area was selected for both samples and EDX analysis was carried out. The atomic percentage of fluorine before washing was 1.06 % and after 20 washes, it was reduced to 0.85 %.

The WCA exhibited by treated textiles vary between 150 °C and 160 °C as reported in literature. However, the methods employed cannot be used for bulk production of hydrophobic textiles by conventional textile processing methods. For instance, deposition of nanostructures of TiO_2, SiO_2 and ZnO to generate nanoroughness and hydrophobic chemicals have been done separately [11,19,23,24] which make it cost ineffective. In addition to this, washing durability has been rarely reported. In the present work, all the chemicals and nanoparticles have been applied in the form of single formulation by using conventional textile finishing process which makes it cost effective without compromising the hydrophobicity of textile fabrics.

Antibacterial Activity

The antibacterial activity of the samples was evaluated against Gram-negative *E. coli* and Gram-positive *S. aureus* bacteria by using the agar diffusion method. The zone of inhibition around samples was seen after 24 h of incubation in dark at 37 °C. Pristine cotton sample and water repellent treated cotton sample demonstrated inability to inhibit the growth of bacteria. However, clear zones of inhibition can be seen around samples treated with formulations containing ZnO nanoparticles (Figure 5). It shows that the treated samples before washing have very small zones of inhibition which increases for washed samples. Similar behaviour can

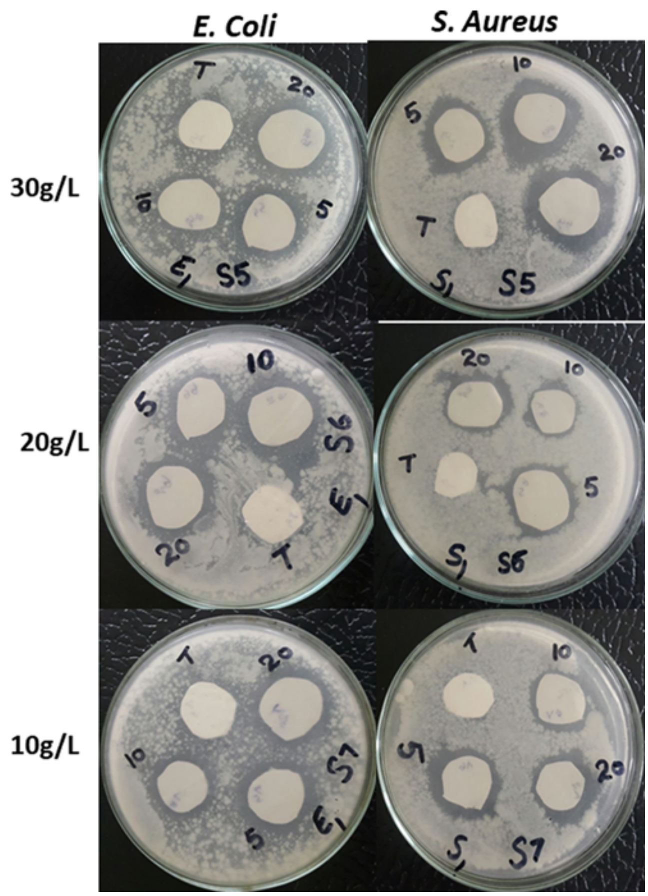

Figure 5. Antibacterial activity of samples treated with formulations containing 30 g/*l*, 20 g/*l* and 10 g/*l* ZnO nanoparticles. T: treated sample without washing, 5. Sample after 5 washes, 10. Sample after 10 washes, 20. Sample after 20 washes.

be seen for the samples treated with formulations containing TiO_2 as shown in Figure 6.

The samples before washing have either no zone of inhibition or very small one. It is because of the deposition of fluorocarbon layer which completely blocks the surface of nanoparticles preventing them to generate reactive oxygen species or Zn^{++} required for antibacterial activity. In our previous study, it has been established that the

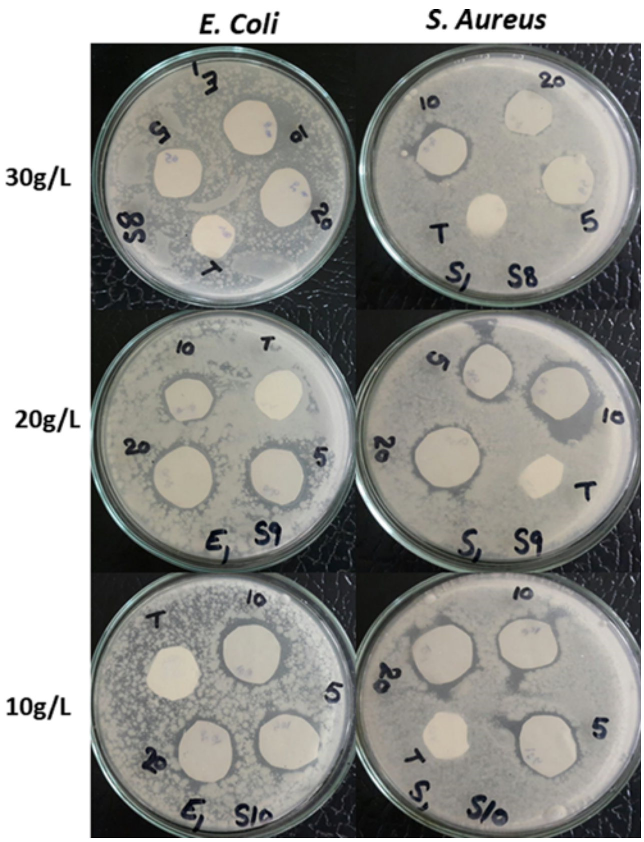

Figure 6. Antibacterial activity of samples treated with formulations containing 30 g/*l*, 20 g/*l* and 10 g/*l* TiO_2 nanoparticles. T: treated sample without washing, 5. Sample after 5 washes, 10. Sample after 10 washes, 20. Sample after 20 washes.

hydrophobic film deposited on nanostructures hinders the antibacterial activity [14]. However, the samples after 5, 10 and 20 washing cycles show clear zone of inhibition for both TiO_2 and ZnO nanoparticles. It has been demonstrated in previous sections, the UV protection remains constant whereas, hydrophobicity decreases with the increase in washing cycles. With the decrease in fluorocarbon concentration on fabric, the reactive oxygen species and Zn^{++} release from nanoparticles surface which inhibit the growth of bacteria near samples.

The antibacterial mechanism of TiO_2 is mainly due to generation of reactive oxygen species such as O_2^{2-} and OH^-/$OH^\bullet$. These species are generated due to redox reaction at the surface of TiO_2 between positive hole, electron, water molecules and oxygen. Due to very high oxidative nature of reactive oxygen species, the membrane of bacteria get oxidized which cause their death. Being photocatalyst, ZnO also have similar mechanism of antibacterial. However, it has been reported in previous studies that the release of Zn^{++} also plays a significant role in inhibiting the growth of bacteria [14,25].

Due to deposited hydrophobic fluorocarbon layer, the water molecules cannot get adsorbed on nanoparticles required for generation of OH^-/$OH^\bullet$ and Zn^{++}, therefore, the samples showed very little or no zone of inhibition before washing. The hydrophobicity decreases due to removal of fluorocarbon with the increase in washing cycles which increases the generation of ^-OH/$^\bullet OH$ and Zn^{++} to inhibit the growth of bacteria. It is worth mentioning that the samples retain antibacterial activity even after 20 washing cycles. Study on washing durability has rarely been reported. If it is reported, then the treated samples do not retain antibacterial activity after 20 washing cycles [26].

Conclusion

A multifunctional cotton fabric has been developed using formulations containing ZnO and TiO_2 nanoparticles, and fluorocarbon based repellent finish. UV protection, highly durable to washing, increases with the increase in nanoparticles concentrations. UV protection exhibited by TiO_2 is better as compared to ZnO. WCA increases with the increase in concentration of nanoparticles in the formulations. Both ZnO and TiO_2 nanoparticles show the similar WCA when applied in same concentrations. WCA decreases with the increase in washing cycles due to removal of fluorocarbon. The treated fabrics showed excellent antibacterial activity against *E. coli* and *S. aureus* which increases with the increase in washing cycles.

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