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An Experimental Study on the Multi-functional Efficacy of Nano TiO_2 Treated Denim Fabrics

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ABSTRACT

In this research work, an attempt has been made to impart multi-functional finish on denim fabric for value addition using titanium-di-oxide. The denim fabrics were treated with synthesized nano-TiO_2 particle using three methods like direct exhaust, microencapsulation and nano encapsulation. The efficacies of the functional effects like UV resistant property, antibacterial and stain release ability of the treated denim fabrics were analyzed. The denim fabrics were also tested for their physical properties to analyze any change in the properties before and after finishing. It was noted that the TiO_2 proved best results in inhibiting the growth of bacteria with agar diffusion test method. The UV radiation protection results reveal that the treatment has improved the UPF R to 97% in all the three methods. The blocking of UV-A, B radiation is also more than 82%, irrespective of the treatment. It has poor stain repellency against stains like pickle and oil but shows good result in case of vegetable, soil and saffron stains. The result also proved that, the treated material remains unaltered in most of the basic physical property. From the research work, it is evident that the nano TiO_2 treated fabric shows good stain release property and also gives protection to the human body against UV radiation and better microbial protection as well; thus the single entity serves as a multi –functional property to the denim world.

Keywords: Denim fabric, Nano-TiO_2, UV Resistance, Antimicrobial effect, Stain repellency

1. INTRODUCTION

Denim is one of the world's oldest fabrics, yet it remains eternally young. The word denim is an Americanization of the French name "serge de Nimes," a fabric which originated in Nimes, France during The Middle Ages. In 1864, Webster's dictionary listed the shortened English version: denim. The warp yarn is traditionally dyed with the blue pigment obtained from indigo dye. Indigo was the most significant natural dye known to mankind until the introduction of synthetic dyes, at the end of the 19th century[1].

Denim is evergreen classic in the fashion cycle. It has been proved by many fashion designers and the following statements support the same. "Denim is popular because it is comfortable, it looks good and it is versatile" (Keith M Hull, CEO, UCO Raymond Denim Holding), "Denim is a cradle-to-grave product. It is the best and most versatile global fabric. It can take on so many different looks through yarns, construction and laundering" (John Heldrich, President and CEO, Swift Denim).

Denim's popularity to casual dress has also been appreciated in the workplace. "Denim is both fashion and performance driven"[2]. Hence in this research, an effort has been taken to impart some functional effect in denim material using synthesized TiO_2 Nanoparticles.

Nanotechnology is concerned with materials whose structure exhibit significantly novel and improved physical, chemical, and biological properties, phenomena and functionality due to their nano scaled size[3]. The impact of nanotechnology in the textile finishing area has brought up innovative finishes as well as new application technique. The finishes obtained using nanotechnology are claimed to be more durable than conventional ones. These advanced finishes setup an unprecedented level of textile performances of stain-resistant, hydrophilic, antistatic and wrinkle resistant and shrink proof abilities[4].

Nano-size particles have larger surface area and hence higher efficiency than larger size particles[5]. Nano-size particles are transparent; hence it does not blur color and brightness of the textile substrate. Some of the textile products based on nanotechnology have just begun to hit the market and it is only a matter of time before one can see a large scale application of nanotechnology not only in textiles, but in applications affecting our day today life.

Growing awareness of health and hygiene has increased the demand for bioactive textiles[6]. With the advent of nano science and technology, a new area has developed in the realm of textile finishing[7]. The UV blocking property of a fabric is enhanced when a dye, pigment, delustrant or UV absorber finish is present in the fabric that absorbs UV radiation and blocks its transmission through the fabric to the skin[8]. The conventional methods used to impart different properties to fabrics often do not lead to permanent effects and it will lose their functions subsequently after laundering or wearing. Nanotechnology can provide high durability for fabrics, because nano-particles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function[9]. In addition, a coating of nano-particles on fabrics will not affect the breathability or hand feel of the fabric[10.] The field of nano finishing in textile technology is very promising due to various end uses like protective textiles for soldiers, medical textiles and smart textiles. With the advancements in synthesis and characterization of various types of nano materials, standardization of application protocol is a must to impart functional finishing to textile materials[11]. In this work an attempt has made to convert the TiO_2 particle in to nano TiO_2. The synthesized nano TiO_2 were applied on the denim fabric and thereby to produce multi-functional effects. The treated material has been studied for their UV protection ability, antimicrobial ability and stain repellent properties and few essential physical properties, to find the effect of treatment on the fabric.

2. METHODOLOGY

2.1 Fabric development

Light weight denim fabric was developed using 100% indigo dyed cotton yarns. The structure of the fabric developed was 2/1 Right hand twill with warp count (Ne) 26's and weft count (Ne) 30's. The warp and weft density were 125 and 72 respectively. The weight of the fabric/square yard was 5.5 oz., which is suitable for shirting or tops. The fabric was desized and enzyme washed before the application of titanium dioxide.

2.2 Synthesis of Titanium Dioxide Nanoparticles

The Titanium Dioxide Nanoparticles were prepared by the hydrolysis of titanium tetraethoxide using a Semi batch-batch two stage mixed method. The nano particles were prepared using the two-stage reactor (semi batch - batch) process. A micro feed pump with the starting solution A (tetraethylortotitanat, HPC- Hydroxypropyl cellulose and ethanol) is taken in a reactor and solution B (water and ethanol) is added to the same reactor. Thereafter, the mixture prepared by the semi batch reaction was agitated for 60 minutes under an N_2 atmosphere. After the first stage reaction (semi batch) was finished, a batch reaction was initiated as the second stage. Solutions A and B were again added into the reactor along with the solution prepared by the first reaction. The reaction mixture was vigorously stirred for 60 min. The TiO_2 aerosols were transferred out of the reactor and the powders washed with ethanol by repeated centrifugation (at 3000 rpm for 5 min) and dried at 70ºC for 12 hrs.[12]

2.3 Characterization of Titanium Dioxide Nanoparticles

In order to determine the size of the nanoparticles, the synthesized nanoparticles were characterized. The Titanium dioxide nanoparticles prepared by the above method were characterized using Scanning Electron Microscopy (SEM). The surface topography of nanoparticles finished fabric was observed with a scanning electron microscope (SEM) to prove the presence of nano particles in the fabric.

2.4 Finishing of Titanium Dioxide Nanoparticles onto the Denim Fabric

2.4.1 Direct Method

The fabric sample was treated with the prepared nanoparticles of Titanium dioxide directly using exhaustion method. The fabric was immersed for 30 minutes in the prepared solution as given in the Table 1. After 30 minutes, the fabric was removed, rinsed (single time), squeezed and dried at 80 – 85 ºC in the oven for 5 minutes and cured at 150 ºC for 2 minutes.

Table 1. Recipe for finishing the fabric by direct exhaustion

Nanoparticles solution	10 ml
Citric acid	8.0%
Temperature of bath	50 ºC
M: L ratio	1:20
Time	30 minutes

2.4.2 Microencapsulation method

The nano TiO_2 was microencapsulated using sodium alginate. Microcapsules containing nanoparticles were prepared employing sodium alginate, 3% sodium alginate was prepared and 2% nano TiO_2 was added. This was sprayed into calcium chloride solution by means of a sprayer. The droplets were retained in calcium chloride for 15 minutes. The microcapsules were obtained by decantation and repeated washing with Isopropyl alcohol followed by drying at 45 °C for 12 hours. The microcapsules were then used for finishing on the selected fabrics by the same exhaustion method.[13]

2.4.3 Nanoencapsulation method

The TiO_2 nanoparticles were nano encapsulated using bovine albumin fraction as the wall material and the TiO_2 nanoparticles as the core material. The TiO_2 nanoparticle enclosed bovine serum albumin protein nanoparticle was prepared by coacervation process followed by cross-linking with glutaraldehyde. The nanoparticle was incubated with the required protein solution (2% W/V) for an hour at room temperature. The pH of the solution was adjusted to 5 .5 by 1M HCl using digital pH meter. Then ethanol was added to the solution in the ratio of 2:1 (V/V). The rate of ethanol addition was carefully controlled at 1 ml per minute. The coacervate so formed was hardened with 25% glutaraldehyde for 2 hours to allow cross-linking of protein. Organic solvents were then removed under reduced pressure by rotary vacuum evaporator and the resulting nanocapsules were purified by centrifugation at (10,000 rpm) at 4 ºC. Pellets of nano capsules thus obtained were then suspended in phosphate buffer (pH -7.4; 0.1 M) and each sample finally was lyophilized with mannitol (2% W/V) [14]. The prepared microcapsules and nanocapsules were finished onto the fabrics using the exhaustion method.

2.5 Functional Analysis

2.5.1 Antibacterial test (AATCC 147 – qualitative test)

The treated fabric samples with the diameter of 2cm ± 0.1cm were taken for the analysis. Both the sides of samples were pre-sterilized under ultra violet radiation for 15minutes. Sterile bacteriostasis agar was dispensed in sterile petri dishes. Broth cultures (24 hours) of the test organisms were used as inoculum. Using sterile cotton swab the test organisms (Escherichia coli & Staphylococcus aureus) were swabbed over the surface of the agar plate. Pre-sterilized samples were placed over the pre-swabbed agar surface by using sterile spatula. After placing the samples all the plates were incubated at 37ºC for 18 to 24 hours. After incubation the plates were examined for the zone of bacterial inhibition around the fabric sample. The size of the clear zone was used to evaluate the inhibitory effect of Titanium di oxide nano particles[15].

2.5.2 Analysis of Ultraviolet Protection Factor

The ability of a fabric to block UV light is assessed based on the ultraviolet protection factor (UPF) values. The UPF values are calculated according to AATCC test method 183-2004: transmittance or blocking of erythemally weighted ultraviolet radiation through fabrics. Erythema refers to the abnormal redness of the skin (sun burn) due to capillary congestion (as in inflammation)[16].

Measurements were performed in a UV–visible spectrophotometer using an integrating sphere loaded with conditioned sample (21 ± 1 ◦C, 65 ± 2% RH, for 4 h) from 280 nm at an interval of 1 nm. The percentage blockings of UV-A (315–400 nm) and UVB (280–315 nm) were calculated from the transmittance data. The ultraviolet protection factor (UPF) was calculated using the following equation 1:

$$UPF_i = \frac{\sum_{\lambda=280}^{400} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{\lambda=280}^{400} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda} \quad \text{-------- (1)}$$

Where Eλ is the relative erythermal spectral effectiveness, Sλ is the solar spectral irradiance, Tλ is the average spectral transmission of the specimen, and Δλ is the measured wavelength interval (nm). The UPF equation weighs the UV-B radiation more heavily than UV-A.

The average A-range ultraviolet (UV-A) transmittance:

$$T(\mathrm{UVA})_{AV} = \frac{\sum_{315\,nm}^{400\,nm} T_\lambda \times \Delta\lambda}{\sum_{315\,nm}^{400\,nm} \Delta\lambda} \quad \text{--------- } \mathbf{(2)}$$

The average B-range ultraviolet (UV-B) transmittance:

$$T(\mathrm{UVB})_{AV} = \frac{\sum_{280\,nm}^{315\,nm} T_\lambda \times \Delta\lambda}{\sum_{280\,nm}^{315\,nm} \Delta\lambda} \quad \text{----------- } \mathbf{(3)}$$

The percent blocking for UV-A and for UV-B using

= 100%-*T*(UV-A)
= 100%-*T*(UV-B)
Where:
T(UV-A) or *T*(UV-B) is expressed as a percentage.

2.6 Physical Testing

The following physical tests were done before and after the nano-ZnO treatment.

- Fabric Tear strength (ASTM D-1424-96)
- Fabric Shirley Stiffness test (BS 3356-90)
- Fabric drape measurement (BS 5058:1973)
- Fabric Air permeability (ASTM D 737-2004)
- Stain release property (AATCC 130-2000)
- Abrasion resistance (BS 5690)

3. RESULTS AND DISCUSSIONS

3.1 Characterization of Nanoparticles

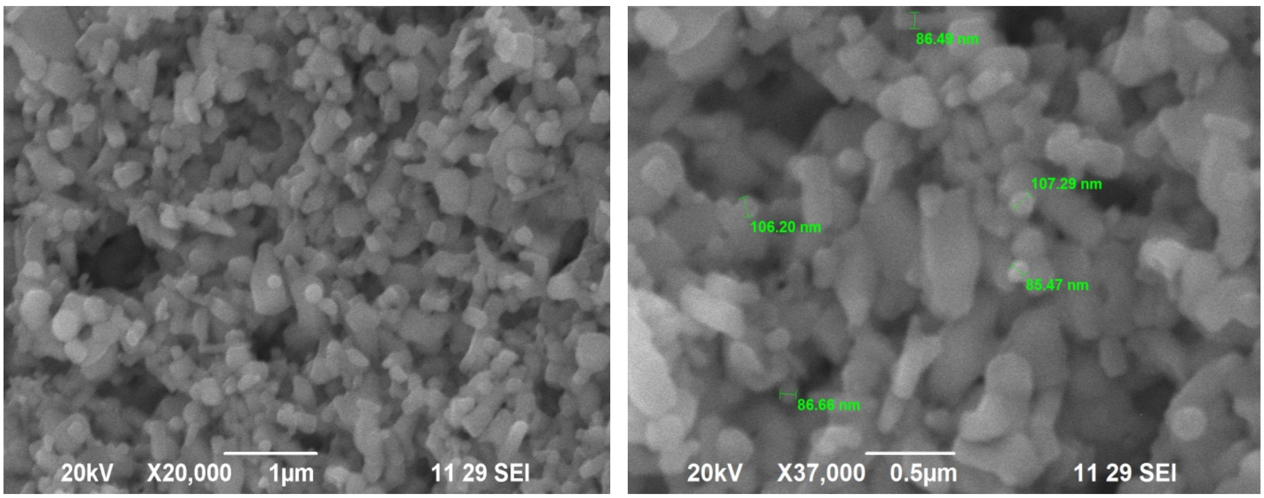


Figure 1. Nano Particles at 20,000 x magnification, 37,000 x magnifications

The nano particles were analyzed using a Scanning Electron Microscope at a magnification of 20,000 and 37,000. Figure 1 shows that the synthesized TiO_2 particles are of nano size. The size of the particle is approximately about 100nm.

3.2 Characterization of the Finished Fabric:

3.2.1 SEM image of the fabric finished by Exhaustion method:

The Figure 2 shows the SEM image of the fabric finished by exhaustion, micro encapsulate coated and nano encapsulate coated fabrics respectively. The fabric was analyzed at a magnification of 5000X. The presence of nanoparticles in the fabric is proved from the above figures. The uptake of nano particles is more uniform in nano encapsulation than the other two techniques. In both the techniques SEM images shows the presence of the nano particle on the fiber surface. This confirms the deposits in the fabric after the finishing process.

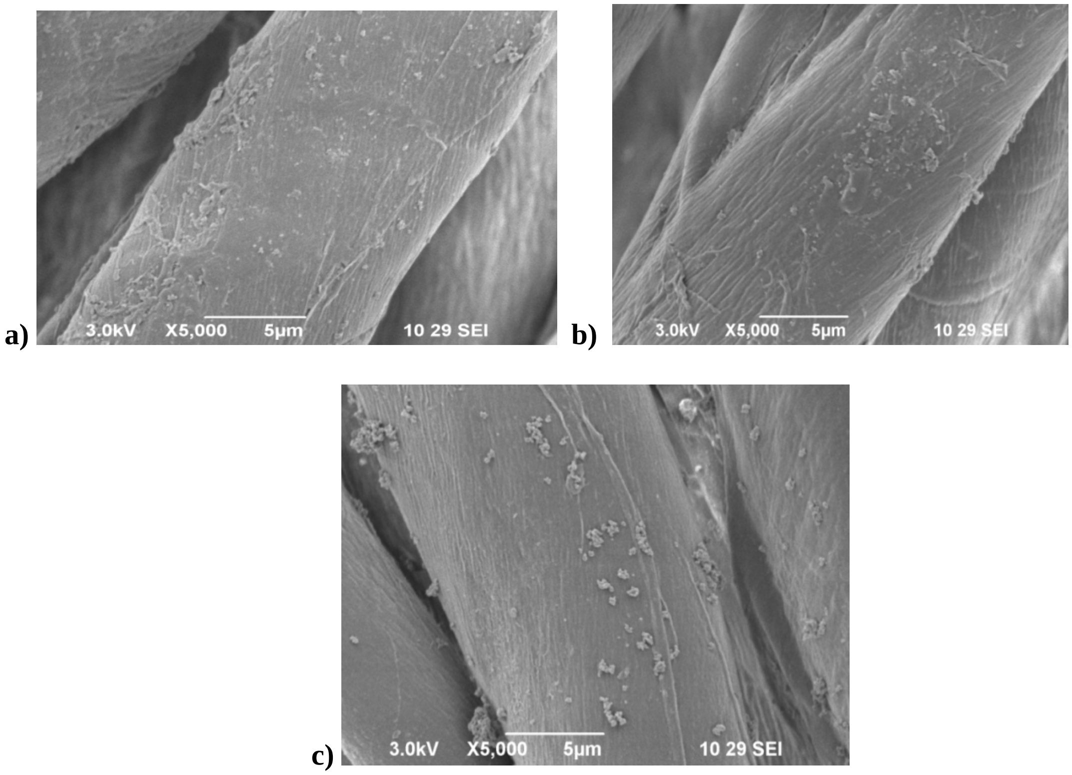


Figure 2. SEM image of the fabric finished by a) Exhaust Method b) Micro encapsulation method c) Nano capsulation method

3.2.2 Antibacterial screening for fabric (AATCC 147- qualitative test)

The TiO_2 finished denim fabric has very good bacterial resistance against both gram negative and positive organisms. Figure 3a depicts the control denim fabric and the denim fabric treated with nano TiO_2 by direct exhaustion method. This shows the maximum amount of bacterial resistance against Staphylococcus aureus. In Figure 3 b the fabric treated by microencapsulation and nano encapsulation method against Staphylococcus aureus is depicted. The Microencapsulation and nano encapsulation process holds the TiO2 nano particle inside the wall material. Hence the potential of microbial resistance is less compared to direct method. But the subsequent wash will improve the leach ability of the nanoparticles[17].

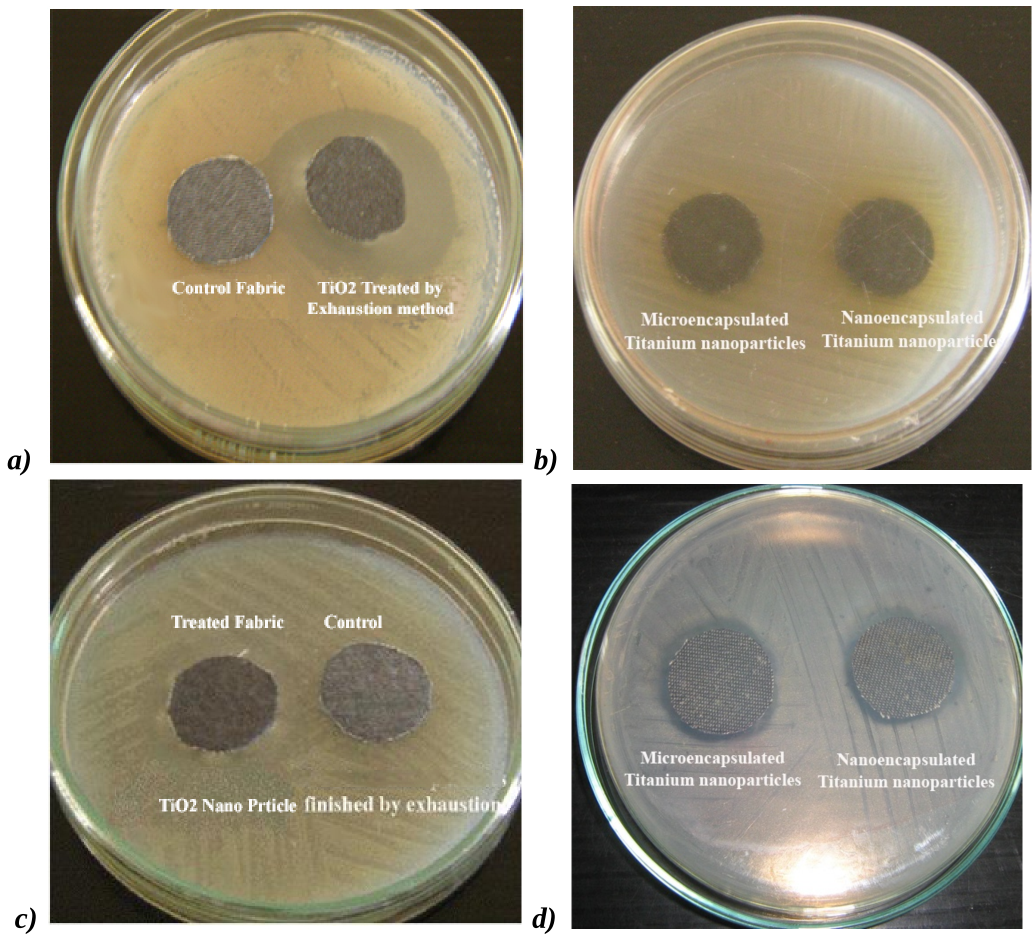


Figure 3. Anti-bacterial activity (a & b) against *Staphylococcus aureus (c & d*) against *Escherichia Coli*

Figure 3 **c** and **d** are the inhibition zone of treated fabric against E. Coli. Table 2 shows the zone of inhibition of fabric. The results indicate that, the zone of inhibition was less against E. Coli. The E. Coli has multi cellular wall structure in the outer structure; hence, the inhibition of E. coli is more complicated than S. Aureus. It has the potential to survive in mild antibodies. The maximum of 40 mm is noted in direct exhaust method against and 32 mm in case of E. Coli.

Table 2. Antibacterial activities of finished fabric (AATCC 147- Qualitative Test)

S.No	Fabric Samples	Antibacterial activity (mm)	
		E. coli	***S. aureus***
1	Control Fabric	0	0
2	Exhaustion method using synthesized Nanoparticles	32	40
3	Exhaustion using Microencapsulated nano particles	24	27
4	Exhaustion using Nanoencapsulated nano particles	23	27

3.2.3 Analysis of UV Transmission according To AATCC 183-2004

Ultraviolet protective factor measures the effectiveness of textile fabrics in protecting the human skin from ultraviolet radiations. It is expressed as the ratio of extent of time required for the skin to show redness (erythema) with & without protection, under continuous exposure to solar radiation[18].

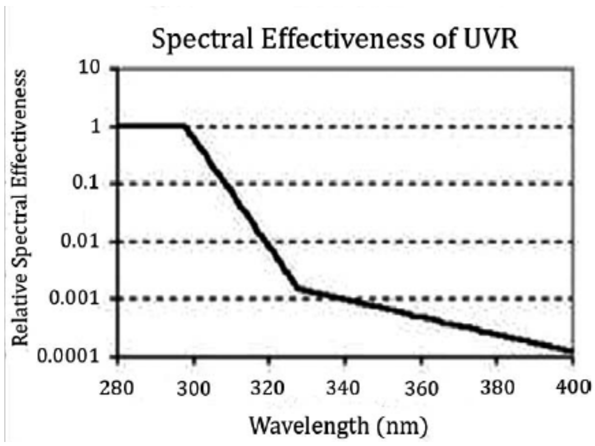


Figure 4. Relationship between wavelength and relative spectral effectiveness

Erythemal effectiveness of light is thus proportional to harmfulness. The erythemal effectiveness of ultraviolet light is shown in Figure 4. It is clear from the figure that, wavelength of 280 nm -300 nm is 1000 times more harmful than wavelength 340 nm[19].

Table 3. UV rays Transmission Values

S.No	Wave length (nm)	Average % of UV Transmission		
		Exhaustion	Micro encapsulation	Nano Encapsulation
1	326	13.620	13.687	14.387
2	344	14.439	14.308	15.213
3	346	14.359	14.139	15.215
4	354	17	16.548	17.692
5	568	22.549	21.83	24.357
6	606	21.407	20.799	23.089
7	660	20.798	20.293	22.339
8	788	60.961	57.868	65.931

The table 3 shows the Transmission percentage of TiO_2 treated fabric by different method. The values of the ultraviolet protection factor (UPF) for UV-A and UV-B ranges were calculated according to Equations (1, 2 and 3) are listed in Table 4. The data reflects the higher protection against UV radiation provided by the TiO_2-treated fabrics. For the calculation of UPF R, The calculated UPF value (or the lowest measured value) is rounded down to the nearest multiple of five to give the reported UPF rating. One effect of this is that materials actually need to achieve a calculated UPF value of 55 or higher in order to be classified as UPF 50+. Table 5 mentions the effectiveness UPF R value as per *AS/NZS 4399, Sun protective clothing - Evaluation and classification* (1996)[20].

Table 4. Ultraviolet Protection factor

Test type	Direct method	Micro encapsulation	Nano encapsulated
UPF R	31	32	29
% of Blocking UV A	82.22	82.91	81.08
% of Blocking UV B	87.27	87.22	86.55

Table 5. UPF Standard Grades and classification of UPF (in accordance with AATCC 183)

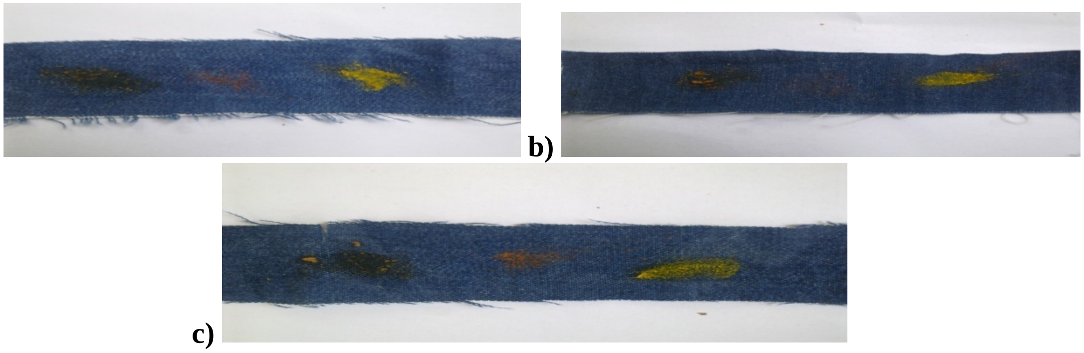
UPF Rating	% of UVB	UV Protection category
15 -24	93 – 96%	Good
25 - 39	96 – 97%	Very good
40 - 50+	97 – 99+%	Excellent

The results confirm that the nanoTiO_2 treated cotton fabric has 96 to 97.4% of UV rays blocked. Irrespective of the treatment method, the treated fabric blocks the radiation in very good level. So, it is evident from the results that there is a great prospective for application of nano TiO_2 as a UV protective material in denim materials.

3.2.4 Analysis of Stain Release (AATCC 130-2000)

The stained samples were washed and dried as mentioned in the AATCC (130-2000) standard. The treated fabric samples are stained with five selected stains like vegetable, soil, pickle, saffron and oil. Figure 5 depicts the stained denim fabrics and figure 6 depicts the washed denim fabric after staining. were independently compared with the residual stain on the test specimen with the stains on the stain release replica and each test specimen was rated to the nearest 0.5 grade according to AATCC 130:2000 standard[21]. Table 6 shows the different grading offered by judges for various stains. Irrespective of the treatment method, all the three methods showed more or less the same repellency towards the stains. Among all the selected five stains, pickle and oil stains were given with poor rating.

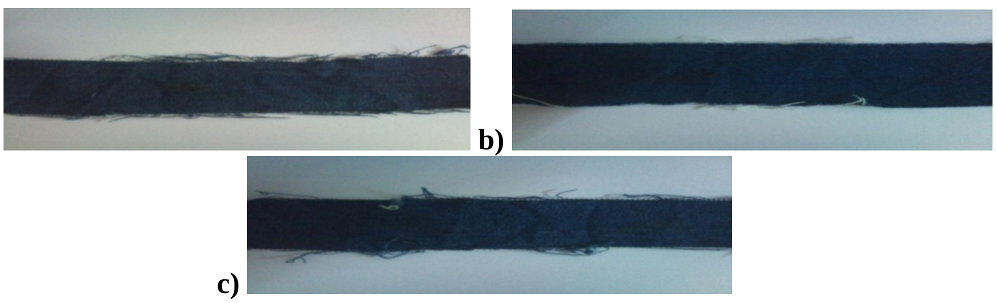
Samples prior to staining



a) b) c)

Figure 5. a) Exhaustion Sample stained, b) Micro encapsulation Sample stained, c) Nano encapsulation Sample stained

Samples after washing



a) b) c)

Figure 6. a) Exhaustion sample after washing, b) Micro encapsulation sample after washing, c) Nano encapsulation samples after washing

Table 6. Subjective analysis of stain release

S. No	Fabric sample	Veg. stain	Soil stain	Pickle	Saffron	Vegetable oil
1	Nanoparticles coated fabric	5	5	1	4	1
2	Microencapsulated coated fabric	5	5	1	4	1
3	Nanoencapsulated coated fabric	5	5	1	4	1

3.2.5 Analysis of Physical Properties of Treated and Untreated Fabrics

From the Table 7 it can be noted that, the nano-TiO_2 treatment has very minimum influence on the basic physical properties. The result shows that there is very negligible reduction in the air permeability of the finished fabric. This is because of the finishing treatment, the coating of the TiO_2 on the surface blocks the inter fiber and intra fiber pores. The tearing strength values also have been reduced insignificantly.

The stiffness of the fabric is also affected considerably in warp direction. The drape coefficient value shows that the nano-TiO_2 treatment increases the drapeability of the fabric in a considerable amount. There is a slight variation in abrasion resistance observed in both warp (increase) and weft (Reduction) direction. However, this study suggests that the treatment of nano TiO_2 in various methods has very few amount of the influence on the physical property of the denim fabric. Hence, this study proves that the Multifunctional effect can be given to the denim fabric with the help of TiO_2 without affecting the physical properties of the textile material.

Table 7. Analysis of physical properties of treated and untreated fabrics

Particulars	Untreated	Treated
Fabric Tear Warp gf Weft gf	 2713.6 1984.0	 2419.2 1996.8
Air- Permeability in c.c/cm.sq./sec	16.7	12.3
Fabric- Shirley Stiffness Test. Bending length in cm: Warp Weft	 3.00 1.63	 1.73 1.52
Fabric – Drape Measurement Mean drape coefficient%	83.38	72.38
Fabric - Abrasion Resistance (Flex) Warp Weft	 149 296	 149 250

4. CONCLUSIONS

The synthesis of Titanium dioxide nano-particles were done using reversible reaction in semi batch-batch mixed method and the nanoparticles appeared to be nearly spherical and with a quite narrow size range. Nano-particles were analysed through Scanned Electron Microscopy (SEM). The denim fabric was treated with the synthesised Nanoparticles of TiO_2 by three methods, direct exhaustion of the TiO_2 Nanoparticles; microencapsulation of TiO_2 nanoparticles and nano encapsulation of TiO_2 nanoparticles. The efficacy of TiO_2 was tested for its multi-functional properties like anti-bacterial, UV Protection and Stain repellency. From the research work, it is evident that there was significant increase in stain release property of the nano TiO_2 treated fabrics and it also gives protection to the body against solar radiation and microbes. The result reveals that the multifunctional effect can be imparted to the 100% cotton denim fabric treated with nano TiO_2 without affecting their basic textile characteristic. Washing using enzymes and various chemicals gives different effects to denim garments like fading, vintage, streaks etc.; this study will create great potential and pave a new way to the denim industry in imparting value addition to the denim products.

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