TiO$_2$/Cu Composite NPs Coated Polyester Fabric for the Enhancement of Antibacterial Durability

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Abstract. Copper nanoparticles (Cu NPs) were synthesized on a plasma treated polyester fabric having a coating of TiO$_2$ NPs. The fabric was treated with cold O$_2$ plasma first to enhance the surface affinity for TiO$_2$ NPs, then coated with TiO$_2$ NPs via a heat pressing, and finally synthesize Cu NPs on the complex surface using a dip-coating process. The resulting fabric shows an excellent antibacterial effect and outstanding laundering durability, as it has satisfactory bacterial reduction performance against $S$. aureus and $E$. coli higher than 98% and behaves stable even after 50 washing cycles. This methodology for preparing antibacterial polyester fabric maybe of high potential applications in cosmetic and medical textiles.

1. Introduction

Polyester (PET) fiber is the second most widely used fiber after cotton fiber for textiles due to its excellent wearing and comfort properties. However, PET textile products frequently need further upgrades to meet uncommon antimicrobial problems because they are easily influenced and affected by microorganisms. The growth and reproduction of these species even have detrimental impacts on human health. In reality, the particular requirements may be reached out to blinds, floor coverings, bed sheets, socks, and therapeutic materials those made of PET fibers. Actually, there are many antibiotic chemicals, for example, N-halamines, triclosan and inorganic nanoparticles, have been tried to prepare antimicrobial PET textile products. Among them, inorganic nanoparticles with effective antibacterial function are profound required [1-4]. It was well known that metal nanoparticles on the textile fabrics can effectively inhibit the growth of bacteria [5]. Especially, nanoparticles of Cu, Fe, TiO$_2$, Zn, and Ag have been demonstrated to be outstanding on antibacterial performance [6-9]. However, the use of these nanoparticles is complex on the finishing procedures due to their low adhesion force on the PET fiber surface that have to be overcome. Although a number of methodologies have been reported, antimicrobial PET fabrics with satisfying washing durability and enough stability on the fiber surface still a challenge in the textile engineering [10].

Among these metal-based antibacterial compounds, use of TiO$_2$ and Cu NPs is most efficient and easily processable. Furthermore, the TiO$_2$ and Cu NPs have low toxicity against the human body, which makes it suitable for antibacterial material on textile substrates such as cotton, PET, and silk fabrics, as reported in previous studies [11]. To improve the adhesion force on fiber surface, a variety of binders have been synthesized by using graft-polymerization for the immobilization of TiO$_2$ and Cu NPs on the polyester fabrics. Although these modified fabrics showed improved antibacterial performance able to withstand 20-30 washing cycles, higher stability and improved antibacterial efficiency are further required. Some chemical treatment and surface modification have also been reported in previous studies,
such as dopamine, Bovine serum albumin (BSA), Cetyltrimethylammonium bromide (CTAB), (3-Aminopropyl) triethoxysilane (APTES) and 3-aminopropyltrimethoxysilane (APTMS) also used as the binders to improve the stability, durability of antibacterial performance of the cotton and polyester fabrics with Cu NPs, TiO$_2$ NPs and Ag NPs [12-14]. Another concern for these metal-based particles is oxidation. To avoid the oxidation-reduction several capping agents, and binding polymers such as Polyamide (PA), poly (methyl acrylic acid) (PMA), Polyvinyl alcohol (PVA), poly-di-methyl-siloxane (PDMs), Polyurethane (PU) and Polystyrene (PS) have been tried for the immobilization of in previous studies during last few decades [15, 16].

For industrial-scale fabrication and functional finishing of textiles, several techniques established showed feasible, economical, and commercially available features. These approaches are including, pad-dry-cure, dip coating, spin coating, spray coating, screen printing, and microwave-assisted, ultrasonication and ultraviolet radiation reduction. Both the organic and inorganic compounds can be secure processing and easy handling steps for several functional finishes [17-22].

Synthetic fibers are mostly used in the textile industry, but among them, polyester is highly popular because it is very durable, extremely strong, wrinkle and abrasion resistance and resistance to most chemicals, easily process able and recyclable. This remarkable property of Polyester makes it a good candidate to variety application not only limited but also technical textiles, domestic textiles, the automotive industry and medical textiles. Most of the textile industry are preferred to use PET and it is still dramatically increasing and also it grabbing the market from cotton. The reason behind this, PET material is available, cheap and very much possible to recycle, so opens a path of a sustainable product. PET is one of the popular among all synthetic fiber because of its variety of application and property. But their main disadvantage is it is hydrophobic in nature which causes many problems is a different stage of textile processing. To aid textile processing make easy, it is important to modify the PET fabric. Conventionally, surface modification of PET fabric to improve hydrophilic character using NaOH or KOH is possible, but such chemical treatment requires lots of chemical uses, high energy consumption and can damage the fiber and the wastewater can be harmful to the environment. The wastewater also harmful to the environment. Plasma as dry and said the environmentally friendly process can be carried out on PET fabric to developed required properties which can aid the textile processing in the different process. Plasma can introduce oxygen-containing polar group on the surface of PET which gives a PET a hydrophilic property [23-24]. The study shows that the fabric coated with TiO$_2$ and Cu NPs has improved performance in terms of antibacterial as well as improved stability against several washes. But only TiO$_2$ treated fabrics have not shown good result against E. coli and S. aureus. In order to get good results, we mixed TiO$_2$ with CuSO$_4$. As during the addition of the Copper nanoparticles significantly influenced the antibacterial performance and higher stability against washing, which may contribute to the higher interconnection between the nanoparticles as well as amongst the fiber through bonding and cross-linking effect as compared to the pristine TiO$_2$ coated polyester fabric used in microwave-assisted reduction.

Therefore, in this research work, we demonstrated a binder-free one bath fabrication and stabilization of TiO$_2$-Cu NPs as highly active material on polyester fabric for antibacterial performance. To prevent the mobilization and oxidation of the NPs, sodium borohydride was used as reducing and stabilizing agent respectively followed by heat pressing at different temperature range for better fixation of the NPs on the textile substrate [25]. The resultant plasma functionalized textile substrate showed improved adhesion and higher stability of NPs and excellent bactericidal performance against S. aureus and E. coli without compromising the stability more than 50 cycles of home and laundering cycles with a few dip coatings, drying and fixation steps.

2. Experimental

2.1. Material

PET fabrics were obtained from Hangzhou Textile Co., Ltd. (China) and the specifications of the fabric was the warp and weft 100x100 cm$^{-1}$, thickness 0.3 mm and 80 grams per square meter (GSM). Before
plasma surface modification, the samples were cut into 30 mm × 30 mm size, ultrasonically cleaned in ethanol (50 mL, 30-60 minutes) and washed three times in deionized water (50 mL) for 30 mins. Yeast extract powder was from Nanjing Mao Jie Microbial Technology Co., Ltd. The metal salts (TiO₂ and CuSO₄), Nutrient Agar, Sodium Dodecyl Sulphate (SDS), NaCl other reagents were purchased from Shanghai Aladdin Co., Ltd. (China) and used without further purification.

2.2. Methods

2.2.1. Surface Functionalization of Polyester Fabric. At first, the pre-washed and cleaned polyester fabric was cut into 30 × 30 cm and placed in a plasma chamber (HD-1A, Changzhou Chagatai Plasma Technology Development Ltd, China) to pass O₂ plasma with a pressure of 85-130 KPa at an intensity of 60 W for 3-5 minutes.

2.2.2. NPs Fabrication on Functionalized Polyester Fabric. PET samples with plasma treatment were washed to remove the additives and impurities with a solution of SDS (1% w/w). The cleaned fabric sample was then successively dip dry and heat pressed to obtain the final product. Briefly, the fabric sample was first emerged in the TiO₂ (1%) solution for 30 min with uniform stirring followed by heat pressing at variable temperature of 120-180 °C for 3 min. Then the fabric sample was dipped in the solution containing CuSO₄ (100 mL, 0.04 mol L⁻¹) and citric acid (4.76 mmol) subsequently magnetic agitation for 30 min. Then NaBH₄ (10 ml, 0.13 mol/l) was added in the mixture to reduce the Cu NPs while the temperature was kept constant and the process was continued for 1 h. The resultant fabric was then washed thrice with distilled water and dried in the open air for 5h to obtain the TiO₂-Cu NPs loaded polyester fabric. Then the fabric samples were stored in a dried and moisture resistance desiccator for subsequent characterization and antibacterial test.

2.2.3. Characterization. The surface morphology of the fabric samples was studied using FESEM (Zeiss ultra-scanning electron microscope, (Ultra-55, Zeiss, Germany). The X-Ray diffraction (XRD) study was carried out on the Thermo-Fisher scientific (ARL XTRA, Switzerland). All the XRD data were recorded for 0-90° angle at a scanning rate of 5 °/min. The functionalized polyester fabric samples were characterized using ATR-FTIR 370 Spectrometer (Nicolet Company, Madison, USA). TGA was performed using a TGA/DSC 1/1600, Mettler Toledo, Switzerland with a heating rate of 10 °C min⁻¹ in an inert (N₂) gas flow at 20 mL min⁻¹.

2.2.4. Antimicrobial Test. The microorganisms Escherichia coli (E. coli, ATCC 1555) and Staphylococcus aureus (S. aureus, ATCC 547) were used as the model according to the modified method (AATCC 100-1999). At first, it was utilized with the agar dispersion plate strategy and was performed by the ISO-20645:2004 (E) standard. Rapidly, the bacteria were incubated in Lathen Broth fluid nutrient agar medium (containing 0.5 g/100 ml yeast extract, 1.0 g/l B.R, 1.0 g/l NaCl and adjust pH to 7.4) at 36.5-37.0 °C for 24-48 h before the antibacterial test.

For the antibacterial performance of the samples was carried out with fabric specimens of an average weight of (0.02-0.05 g). Each specimen was cut into 5x5 mm size, sterilized under UV light for 1hr and 30 minutes and placed in 20.0 μl activated E. coli and S. aureus (100 CFU/ml) fluid nutrient medium. The samples were added into sterile tubes for the activation of the bacteria at 25 °C for 24 h with 130 rpm. The specified proportions of the supernatant were diluted and dispersed in the nutrient agar plates and incubate at 37 °C at pH 7.4 for 24 h. The growth and survival of the microorganisms was calculated by manually counting the colonies forming unit (CFU/mL), and the bacteriostatic reduction rate was calculated by using the equation (1):

\[
BR = \frac{B-A}{B} \times 100\% \quad (1)
\]

where A and B are the (CFU/ml) microorganisms surviving in the agar plate after 24 h for the modified and control sample, respectively [26].
2.2.5. Laundering Test. Laundering durability was assessed as the antimicrobial efficacy measurement of the functionalized polyester samples after repeated stringent washing cycles. The polyester fabrics (5 cm × 5 cm) were washed by 50 ml of aqueous solution of sodium dodecyl sulfonate (SDS) (1.0 %, w/w) in a glass beaker with a constant magnetic stirring (300 rpm) at 25 °C for 10 min followed by rinsed with distilled water (100 ml) for 3 times and dried at 60 °C. The antibacterial activity of the laundered samples was evaluated using the aforementioned method.

2.2.6. Tensile Properties. The PET fabrics treated with TiO$_2$-CuSO$_4$ were analysed using an electronic tensile tester (YG065, China) [27]. The sample specimen was cut into a rectangle shape (100 × 25 mm) according to the ASTM standard strip test method for woven textile fabrics. The specimen was run at a stretching rate of 20 mm/min warp and weft direction.

3. Results and Discussion

The temperature effect on the loading of the TiO$_2$-CuNPs on fabric can be seen in the optical images presented in figure 1. The colour of the fabric changes from light blueish green to dark brown, can be seen in figures 1a-1d respectively.

![Figure 1. Polyester fabric coated (a) TiO$_2$ and TiO$_2$-CuNP with different temperature, (b)120 °C, (c) 160 °C and (d)180 °C.](image)

During, thermal reduction temperature was varied from 120, 160, and 180 °C, during the heat-pressing of the as-coated samples. The as-coated samples were dipped into NaBH$_4$ as reducing agent and reduced during one step reduction and curing in the above temperature range.

3.1. Surface Analysis

SEM analysis was performed of each of the fabric samples coated with TiO$_2$-CuSO$_4$ at three temperatures: 120 °C, 160 °C and 180 °C. The SEM results showed significant improvements for the decoration of the NPS on the fibre surface with increased temperature. The higher loading of the NPs may attribute to the plasma functionalization and thermal treatment. In figure 2, without Plasma treated SEM results demonstrated in different temperature less Quantity particles are loaded on the fiber surface and particles are not well condensation on the fabric surface.

It is clear by the SEM results that the samples treated at 120 °C have less thermal fixation of the NPs on the fiber surface when compared to the samples obtained as 160 °C and 180 °C [28, 29]. It demonstrated in figure 3 as the heating temperature was increased from 120 °C to 160 °C, the fiber surface becomes rough and more quantity of TiO$_2$ NPs are loaded on the fiber surface. These appearances become more significant as the temperature raised to 180 °C. Whereas, the reduction of TiO$_2$-CuSO$_4$ NPs was significantly influenced the particle size and shape, as well as the fiber surface, was also significantly influenced which can be seen in figures 4a-4e, respectively.
Figure 2. Without Plasma treated polyester fabric coated TiO$_2$-CuNPs with different temperature: (a) 120 °C, (b) 160 °C and (c) 180 °C.

Figure 3. SEM images of the TiO$_2$ heat pressed polyester fabric (with different magnification) at (a, a’, a’’) 120 °C, (b, b’, b’’) 160 °C and (c, c’, c’’) 180 °C.
Figure 4. SEM images of the TiO$_2$/Cu NPs coated polyester fabric (with different magnification) at (a, a’, a’’) 120 °C, (b, b’, b’’) 160 °C and (c, c’, c’’) 180 °C.

Some of the NPs have changed their agglomeration into Micro cubes, and the overall surface of the fiber was coated entirely with TiO$_2$-CuNPs at lower to higher temperature range. Whereas, the fixation and stability of the NPs may improve which may be introduced due to the heat setting and fixation of NPs inside the polymer as compared to low temperature treated samples, which shows a more significant number of NPs remained on the surface of the fiber. Therefore, the SEM images demonstrate that fiber surface becomes rougher at higher temperature above the glass transition (Tg) temperature, which may introduce some cracks in the fiber surface. The resultant fabric showed improved tensile strength at lower temperature range for heat setting, which is decreased at higher temperature range as shown in tensile strength analysis in figure 4, and with an agreement to SEM images.

3.2. Chemical Analysis
The XRD spectra with diffraction peaks show that the TiO$_2$-CuSO$_4$ was successfully loaded on the surface of the fiber. The shape and size of the typical crystal structures are presented in the results as shown in figure 5a, with 2θ = 20-22, and 25° presents the diffraction peaks of Anatase, rutile, and brutilite. The highest and sharper peak positioned at 20 is allocated to Anatase for TiO$_2$, with a smaller peak positioned at 22 attributed to rutile. The rutile peaks for TiO$_2$ are further extended up to 35 positions and mentioned as P2, P3, P4 and P5, and P6 respectively, which can be seen in XRD diffraction of pure Titanium dioxide. The crystal growth of the TiO$_2$ NPs appeared up to 35°. The diffraction other sharper peaks denoted as 20 values of 45.4°, 50.5° and 60.5° for the indices of crystal planes (111), (200) and (220) of Cu nanoparticles, respectively. These crystal planes are grown due to the heat treatment at 120,
160, and 180 °C, respectively. These results are in complete agreement with SEM results, the formation of different morphological, structural shape with tetrahedral, octahedral, and octahedrons. These rutile octahedrons vortexed with different crystal planes are up to eight octahedrons, adjustment with each other showing linear chain crystal formation of TiO$_2$.

On the other hand, the XRD peaks of Cu NPs on the surface of the polyester fabric are presented with new peaks seemed at different positions for 2θ values of 43.5, 50.8° and 64.5° and 75.3° respectively with index (111), (200) and (220) and (222) planes of the Cu nanoparticles respectively. The XRD results demonstrated that the TiO$_2$ and Cu NPs were successfully coated and immobilized on the surface of the polyester fabric with different crystal growth which may occur due to the change in temperature during thermal reduction and heat setting. The crystal size growth and shapes were analysing for the XRD crystal planes patterns using the Debye-Scherrer equation [30]. The XRD analysis results shown in figure 5 demonstrates the formation of different nanoparticle, nanocubes, as well as the TiO$_2$-CuSO$_4$ Nanoparticles using hydrothermal reduction reaction on the fiber surface [31]. The XRD results were found in agreement with previously reported results and the findings of this research work, as presented in SEM, FTIR analysis respectively for better understanding of the Nanoparticle’s and their successful fabrication.

![Figure 5](image)

**Figure 5.** (a) XRD pattern and (b) ATR-FTIR of the pristine polyester and heat pressed TiO$_2$-Cu NPs loaded polyester samples.

Figure 5b shows the FTIR spectra for the polyester fabric; the as-coated fabric showed broader and sharper peaks located at the position of the peak at 3335 cm$^{-1}$ could be assigned to the -OH group [32]. Compared with the original, untreated samples, the TiO$_2$-CuSO$_4$-polyester fabric showed a sharp peak located at 1750 cm$^{-1}$, which may attribute to the C=O (an ester group) group. The FTIR Results suggested the confirmation of the esterification reaction occurred between the CuSO$_4$ atoms and TiO$_2$ atoms on the fiber surface. As the TiO$_2$-CuSO$_4$ polyester fabric surface was entirely covered with Cu NPs and TiO$_2$ [33]. The FTIR results indicated that intensity peaks of the CuSO$_4$ are shaper as compared to TiO$_2$, which are highly attached due to hydrophilic nature of the polyester after plasma treatment and fixation using thermal and chemical reduction on the polyester fabric. The broader and broader peaks are allocated with low-intensity peaks as compared with the CuSO$_4$. The FTIR results present the well addressed, and a clear demonstration that, the TiO$_2$ and CuSO$_4$ have been successfully fabricated on the surface of the polyester fabrication using simple one-step thermal heat setting and chemical reduction.

### 3.3. Thermal and Mechanical Analysis

The thermal stability against heat setting and thermal reduction for the polyester was analysed using thermogravimetric analysis [34]. The TGA analysis was performed for the treated samples with TiO$_2$, CuSO$_4$, and TiO$_2$-CuSO$_4$ on polyester fabrics, as mentioned in figure 6. The results, clearly demonstrate, the pristine polyester fabric showed lower thermal stability and higher duration and weight loss about
80% at 460 °C, which is similar in trend, but slightly higher for thermally treated samples at different temperature range during thermal and chemical reduction [35]. The results presented in figure 6 demonstrate the maximum weight loss of the coated fabrics samples was improved from 75.4-73.6 and improved up to 60.5 % for the TiO$_2$-CuSO$_4$ coated samples at 180 °C, respectively. This stability may attribute to the higher loading and content percent of NPs on the surface and inside heat pressed polymer structure, which makes it more stable to thermal reduction as compared to pristine polyester and low-temperature heat setting. The TGA results demonstrate, well that there is a significant contribution of the temperature and heat setting time on the TiO$_2$-CuSO$_4$ coated fabrics as compared to untreated polyester fabric. The results also present, the effect of temperature on the tensile strength of the polyester fabric as compared to untreated samples as presented in SEM and tensile strength performance of the coated polyester fabric.

![Figure 6. TGA analysis of the (a) TiO$_2$ NPs heat pressed polyester fabrics and (b) TiO$_2$/Cu NPs coated fabric.](image)

Figure 6. TGA analysis of the (a) TiO$_2$ NPs heat pressed polyester fabrics and (b) TiO$_2$/Cu NPs coated fabric.

The tensile strength test of the coated samples was performed according to the ASTM standard. The original sample without treated and treated sample was compared to the original samples, as shown in figure 7. The tensile strength of coated fabric was increased in terms of the breaking strength was increased due to the coating the surface of the fabrics. S1, S2, S3 and S4 in figure 7 demonstrate that the tensile strength was increased from 40 MPa-50 MPa at a lower temperature range of 120 °C. The original, untreated samples exhibited better flexibility, as compared with the height of treated one increased up to 70 MPa for 160 °C, which is decreased on the further increased temperature of 180-200 °C due the decomposition and degradation of the sample as shown in SEM results figure 2c). The fabric showed increasing tensile strength and decreased in strain, due to higher loading percentage of TiO$_2$ and CuSO$_4$ and damage on the fibers at a higher temperature.

![Figure 7. Stress-Strain of pristine fabric (Sample 1), heat pressed TiO$_2$ and Cu NPs at 120 °C (Sample 2), 160 °C (Sample 3), and 180 °C (Sample 4).](image)
We next concentrated the covering security utilizing washing test looking like that in clothing applications. Figure 8 looks at the high-amplification SEM picture, S mapping, and TiO$_2$/Cu NPs mapping picture of TiO$_2$/Cu NPs on Polyester fabric in various temperature when 50 washing tests [36]. Analyse figure 8 in various temperature 120, 160 and 180 °C that a great deal of TiO$_2$/Cu NPs still exist on the surface on the plasma treated Polyester fabric considerably after withstand 50 washing cycles. In this figure 8 show the EDS mapping pictures of the TiO$_2$/Cu NPs Polyester in various temperature, it was affirmed again that the TiO$_2$ and Cu NPs were immobilized on the Polyester texture even withstand 50 washing cycles [37]. Agreeing high amplification SEM picture of the TiO$_2$/Cu NPs Polyester texture, we make measurable examination of the brilliant focus on the TiO$_2$/ Cu NPs polyester in various temperature, giving a size circulation outlines appeared in figure 9. It was discovered that normal size of the TiO$_2$/ Cu NPs become littler, this outcome show that the size of the TiO$_2$/Cu NPs diminishes by the temperature [38]. To inspect the decreases in amount of TiO$_2$/Cu component covered on the fabric surface, the covered fabric TiO$_2$/Cu NPs were additionally examined utilizing ICP-MS examination. The loss of TiO$_2$/Cu component brought about by the 50 washing tests is about 9% (table 1), this outcome demonstrating the TiO$_2$/Cu NPs with the Cold plasma treated are solid for the scraped area power happened during the washing Procedure.

![Figure 8](image)

**Figure 8.** SEM images of the TiO$_2$/Cu NPs coated polyester fabric (with High magnification), S mapping image, TiO$_2$/Cu mapping images of the TiO$_2$/Cu NPs Polyester fabric at 120 °C (a, b, c, d), 160 °C (a’, b’, c’, d’) and 180 °C (a’’, b’’, c’’, d’’).
Figure 9. Particle size distribution of TiO$_2$-Cu NPs on polyester fabric at (a) 120 °C, (b) 160 °C and (c) 180 °C.

Table 1. Effect of washing cycles on the antibacterial performance of the E. coli and S. aureus bacterial with TiO$_2$-CuSO$_4$ before and after washing.

| S. No | Washing cycles | TiO$_2$-Cu (mg/g) | E. coli (%) | S. aureus (%) |
|-------|----------------|-------------------|-------------|---------------|
| 1     | 0              | 13.8              | 98          | 99            |
| 2     | 5              | 13.5              | 97.5        | 98            |
| 3     | 10             | 13.1              | 96          | 97            |
| 4     | 20             | 12.9              | 94          | 95            |
| 5     | 30             | 12.6              | 92          | 93            |
| 6     | 50             | 12.5              | 90          | 91            |

3.4. Antibacterial Performance

The antibacterial performance for the TiO$_2$-CuSO$_4$ on the polyester fabric was analyse in the agar plates. The inhibition zone around the fabric does not show any significant influence in figures 10a and 10b, whereas the circular region around the fabric sample placed in the agar plates shows, that antibacterial performance. The bacterial growth on the textile substrate was reduced with stability for 24-48 h, which is a positive effect towards the microbial growth. Which shows, that the resultant TiO$_2$-CuSO$_4$ coated fabric has a higher inhibitory effect on both of the bacteria E. coli and S. aureus, as shown in figures 10 (a, a’, a’’), and 10 (b, b’, b’’) respectively.

Figure 10 (a, b) show higher growth of the bacterial for without treatment of the sample, and figure 10 (a’, b’) show the BR rate for TiO$_2$-CuNP and 10 (a’’, b’’) polyester fabric coated with TiO$_2$-CuSO$_4$ for both of the classes of the bacteria, i.e., E. coli and S. aureus respectively [39]. The BR performance value for TiO$_2$-Cu was nearly 99.0% which near to the 98% for coated polyester fabric sample during the antibacterial analysis using 24-48 h incubation at 37 °C (RT) at pH 7.4. The results are the crystal-
clear evaluation and evidence showing that the polyester fabric coated with TiO$_2$ and Cu showed highly improved antibacterial performance as potential materials.

Figure 10. Optical image of the antibacterial culture medium of TiO$_2$-Cu NPs coated 160 °C polyester fabric for _E. coli_ (a, a’, a’’) and (b, b’, b’’) _S. aureus_.

Figures 11 and 12 further demonstrates, the overall antibacterial performance both of the bacteria _E. coli_ and _S. aureus_. These results showed, that coating of the TiO$_2$ and Cu NPs the polyester fabric at a different temperature range of 120, 160 and 180 °C during the heat pressing, enhance the stability and significantly improved the antimicrobial against both _E. coli_ and _S. aureus_.

Figure 11. _E Coli_. antibacterial effect on polyester fabric (a) main sample, (b) Cu/TiO$_2$-120 °C, (c) Cu/TiO$_2$-160 °C, (d) Cu/TiO$_2$-180 °C.
Figure 12. S. aureus antibacterial effect on polyester fabric (a) main sample, (b) Cu/TiO$_2$-120 °C, (c) Cu/TiO$_2$-160 °C, (d) Cu/TiO$_2$-180 °C.

We considered the practical end use of the TiO$_2$ and CuSO$_4$, which is required and needs necessary modifications to monitor the laundering durability of the polyester fabric. The results show in figure 13, that the reduction percentage was increased from 85-99 and 98 % for E. coli and 82-97 to 89 % at different temperature range for both of the bacteria.

Figure 13. Antibacterial performance of the polyester fabric coated with TiO$_2$/Cu NPs heat press coted sample antimicrobial activity.

3.5. Washing Durability against Laundry Cycles

The washing durability of the TiO$_2$-CuSO$_4$ coated polyester fabric was performed and analysed using common Laundry. The washing was performed using regular detergent, alkali, and Surfactant Sodium Dodecyl Sulphate (SDS) up to five to 50 cycles. The antibacterial performance of the resultant fabrics was analysed after several washing cycles [40, 41]. The bacteriostatic reduction (BR) was changed from 97% and 98% for both the E. coli and S. aureus not significantly influenced. The results are presented in figure 14.

The polyester fabric coated with TiO$_2$-CuSO$_4$ was cut into (2.5 x 2.5 cm) and washed with an aqueous solution of the sodium dodecyl sulfonate (2.5% w/w) in 50 mL with continuous stirring at 250 rpm on a magnetic stirrer at room temperature (RT) for 5-10 minutes. The samples were finally rinsed with DI water (25.0 mL) five times and dried at 60 °C. Later on, after repeated washing cycles were performed for 50 cycles, and antibacterial performance was analysed using antibacterial tests as presented above.

The washing performance of the as-coated TiO$_2$-CuSO$_4$ samples polyester sample for (160 °C) showed higher antibacterial performance, as an optimized sample with an efficiency of 99.0 % was used.
The results presented in figure 13 and table 1 demonstrate that there was no significant difference observed for several washes up to 50 cycles on the antibacterial performance. Table 1 shows that the TiO$_2$-CuSO$_4$ NPs were highly immobilized on the surface of the fiber and showed more excellent stability against 50 washing cycles.

![Figure 13](image-url)  
**Figure 13.** Effect of different washing cycles on the antibacterial performance of TiO$_2$-Cu coated polyester fabric for *S. aureus* and *E. coli*.

In a comparison of washed and unwashed samples, the SEM results showed that the sample becomes more cleaned and clear particle-free fiber surface after several washes. The trapped particles inside the polymer fiber retained their higher stability against long-term antibacterial use as compared to other techniques used in previous studies. The results showed favourable findings which are much better than previously reported studies against washing stability and durability towards the antibacterial performance of the washable wearable textiles. The removal percentage of the TiO$_2$ and Cu particles after the 50 washing tests was found to be 5.9 as which is 33.0-3.5% higher than the result indicated in the literature for the Cu NPs with the stability against the 50 washing cycles.

### 4. Conclusions

We conclude the high potential of TiO$_2$-Cu NPs towards a binder-free approach with tightly adhered NPs for improved washing, antibacterial and more extended time stability performance for two different types of bacteria, i.e., *E. coli* (gram-positive) and *S. aureus* (gram negative) bacteria respectively. The preliminary finding and data analysis determined with the deficient percentage of weight loss 8.5%, of the loaded NPs on the polyester fabric and washing stability up to ~50 washing cycles. It may also be addressed as the resultant moieties retained its performance with enhanced adhesion of the NPs with several washing cycles. This approach may also be used for other metal particles on textile materials using heat pressing technique for potential end users in bio-medical textiles in the future.

### Competing interests

The authors declare that they have no financial or ethical competing interests either.

### Authors’ Contributions

SS conceived the study, carried out the data analysis, and drafted the manuscript. MR carried out the sample preparation and the experimental measure. NA participated in the study of material structures and the data analysis. DPP and QX coordinated the research. XD revised and finalized the manuscript. All authors read and approved the final version of the manuscript.

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