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# Producing a New Acid Dye and Multifunctional Wool and Nylon Fabrics Using Hydroxyapatite, Titanium dioxide, Zinc oxide and Magnesium oxide nanoparticles

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**Abstract**

This study focuses on the synthesis of new acid dye, imparting multifunctional properties, i.e., ultraviolet (UV) blocking as well as antimicrobial properties onto nylon and wool fabrics dyed with a new acid dye (1), through using the properties and applications of inorganic nanostructured materials with good antimicrobial activity, potential self-cleaning, and ultraviolet protection. Hydroxyapatite nanoparticles ($Ca_{10}PO_4OH$) and three other nano metal oxides (titanium dioxide, magnesium oxide, and zinc oxide) were synthesized, prepared and used to treat both wool and nylon fibers with different concentrations using three methods: pre, post treatment, and one bath process. The synthesized new acid dye was characterized by IR, and 1H-NMR. Also, Nanoparticles were examined through transmission electron microscopy (TEM). The effect of the applied metal that subsequently improves the dyeability of the treated fabrics was evaluated. The results demonstrated that the applied nanoparticles exhibited excellent colorfastness properties for wool and nylon fabrics as well as good antibacterial activity, self-cleaning, and high ultraviolet protection.

Keywords: Metal nanoparticle, Nano-dihydroxyapatite, Wool treatment, Nylon treatment, Antimicrobial, Anti UV, self-cleaning.

## 1. Introduction

Textile fibres, both natural and synthetic, are the primary structural components of textiles, each with its own set of strength and physical properties. The repeating units of monomers in polymeric structures of these fibres, such as amino acids in wool and silk, cellulose in cotton, and caprolactam in nylon, are responsible for these characteristics. [1-2].Extensive researches have focused on nanoparticle (NPs) applications on both natural and synthetic textile materials to convert them into a technical textile with distinct functional performance. Since nanoparticles have a wide surface area and high surface energy, they provide good durability for treated fabrics, resulting in a stronger affinity for fabrics and an improvement in the durability of the desirable textile function.Furthermore, a nanoparticle coating on fabrics has no little effect on their breathability or tactile feel. It is feasible to consider that the larger particle agglomerates will be quickly removed from the fiber surface, while the smaller particles will penetrate deeper and bind closely to the fabric matrix [3]. Consequently, the decreasing of particles size to nano-scale dimensional significantly alters the properties of the material and indeed the entire substance. The nanoparticles utilization permits textiles to become multifunctional and create fabrics with unique functions, including UV-protection, easy-clean, antibacterial, water- and stain repellent, anti-odour and many more [4]. The research that focuses on using inorganic nanoparticles to create multifunctional substrates has increased because of its capacity to develop materials with diverse functional properties, processing stability, lower energy consumption with an environmental focus [5,6]. Considering these inorganic nanoparticles, metal oxides-based nanoparticles, such as magnesium oxide (MgO), zinc oxide (ZnO), and titanium dioxide (TiO₂) NPs are popular for various technologies application due to their multifunctional properties, excellent physiochemical properties, and cheapness [7-10]. Recently, the utilization of metal nanoparticles in textile antibacterial finishing is widely recognized in the literature. Whereas, scientists have discovered that the ions generated by metallic nanoparticles interact with sulfur-containing proteins in bacterial cells, affecting the vitality of the bacterial cells [11].

UV-protective nanoparticle finishes have recently been produced using a variety of processes

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and approaches. Nano sized semiconductor oxides like TiO$_2$, MgO, and ZnO are increasingly being used as UV blockers in significant potential areas of nano finishing [2].

On the other hand, hydroxyapatite is another inorganic material that can be produced at the nanoscale and has high biocompatibility of different morphologies [12]. Polyethylene, polyamide, and poly-hydroxy-ethyl methacrylate have recently been reinforced with nano-hydroxyapatite to improve bioactivity and mechanical strength [13, 14].

This paper provides an overview onsynthesisof a new acid dye 1, also ZnO, TiO$_2$, MgO and hydroxyapatite NPs weresynthesized and prepared to be applied on nylon and wool fabrics. The aim of these treatments is producing fabrics able to afford photo catalytic, self-cleaning technology that are often used in daily life, and antimicrobial activity and ultraviolet (UV) protection properties.

## 2. Experimental

### 2.1. Materials and Substrates

Wool and nylon fabrics were provided from El Shorpagy Co., Cairo, Egypt.  A new synthesized acid dye 1, which was synthesized according to the published methods [15]and its structure, is as shown in Figure1, all materials and solvents were obtained from Fluka and Aldrich and were used without further purification.
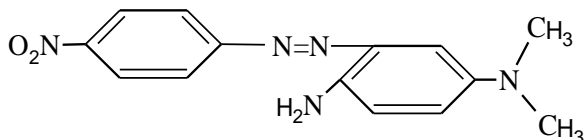


**Figure 1(Acid dye 1)**

### 2.2. Synthesis of Acid Dye 1

p. NO$_2$ aniline (1.38g, 0.01 mol) was dissolved in concentrated HCl (37%, 3ml) and poured over ice (50g) at 0°C, NaNO$_2$ (0.72 g) was added dropwise over 30 min. the reaction mixture was stirred at 0°C for 40 min and the excess nitrous acid was removed by adding a small amount of sulfamic acid. The resultant solution was added to N,N-dimethyl,p-phenylendiamine (1.362   gm, 0.01mol) ,which dissolves in an appropriate amount of water at 5-6°C over 30 ‑ 45 min at pH 4-5. The coupling was stirred until pH was stabilized. The precipitate was collected by filtration. The filter cake was washed with 50 parts 1% hydrochloric acid, and then washed with water until the filter cake was free of acid [15].

**IR (KBr) υmax/cm$^{-1}$**: 3346.85(NH$_2$), 1482(N=N).
**$^1$HNMR (DMSO) ppm:**δ16.7 (s, 1 H, NH$_2$,which disappear in D$_2$O), 8.5 - 6.1 ppm (d, 7 H, aromatic H), 3.398 (s,6 H,-N (CH$_3$)$_2$)As shown in Figures 2 and 3.
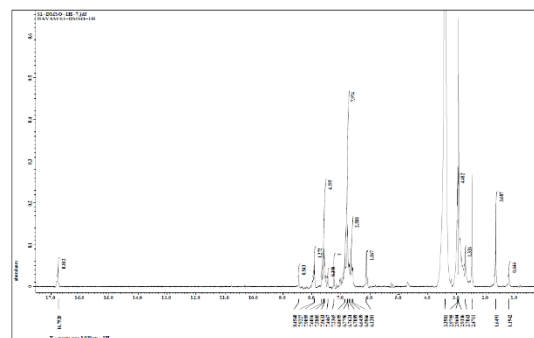


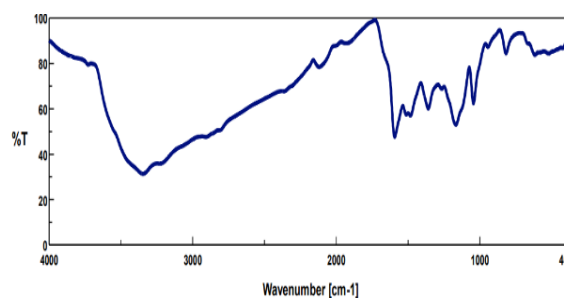Figure 2 1HNMR of powder prepared for acid dye 1



Figure 3  IR spectra of powder prepared for acid dye 1

### 2.3. Preparation of Nanoparticles

#### 2.3.1. Synthesis of Hydroxyapatite Nanoparticles

24.89 g anhydrous calcium carbonate (CaCO3, Iso Chem, 99 percent purity) was precisely weighed and calcined at 900°C for around 3 hours, until constant weight was achieved, to form calcium oxide, which was then added to distilled water and diluted to 500 ml to produce slaked lime solution. Similarly, distilled water was used to dilute 10.25 ml of orthophosphoric acid solution (H$_3$PO$_4$, Iso Chem, 85 percent) to 500 ml. For the manufacture of hydroxyapatite, two stock solutions, slaked lime and phosphoric acid, were utilized as calcium and phosphorous precursors. The calcium hydroxide solution was placed into a separating funnel with the phosphoric acid solution. The stoichiometric proportions of each calcium hydroxide and phosphoric acid were carefully determined to have a Ca/ P ratio of 1.67 when thoroughly mixed. The mixture was kept at a constant temperature of 70°C 2 K. To adjust the pH to 10, ammonia solution (NH$_4$OH) was added. When phosphoric acid was added to the solution, it produced a white precipitate (ppt) that was mostly hydroxyapatite. The precipitate was decanted, Buchner filtered using grade 42 ashless filter paper, rinsed with distilled water multiple times, and then dried overnight at 100°C. [16].

#### 2.3.2. Synthesis of ZnO, TiO2 and MgO Nanoparticles

Zinc oxide, titanium dioxide and magnesium oxide nanoparticles were prepared according to a procedure previously reported in the literature.

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### 2.4. Finishing (Nano Materials Treatment)

Wool and nylon fabrics treatment using $TiO_2$, MgO, ZnO and hydroxyapatite NPs was carried out by three methods. The first method involved the treatment of Wool and nylon fabrics with $TiO_2$, MgO, ZnO and hydroxyapatite NPs and then dyeing by a new synthesized acid dye, so, it is called the pre - treatment method. In the second method the $TiO_2$, MgO, ZnO NPs and hydroxyapatite NPs are incorporated in the dyeing bath in one step. The third method entailed dyeing first by a new synthesized acid dye then $TiO_2$, MgO, ZnO and hydroxyapatite NPs treatment. This method is post-treatment method. More details about the three methods are given below.

### 2.4.1. Pretreatment Method

The fabrics were subjected to an impregnation process in aqueous baths of ZnO, $TiO_2$, MgO and hydroxyapatite NPs at six concentration values (0.5%, 1.0%, 1.5%, and 2.0%,2.5% and 3% o.w.f; on-weight-fabric). The baths were then heated at $80°C$ for 20 min. The applied liquor ratio was at 1:30 and the impregnation process was performed in presence of a dispersing agent to facilitate a homogenous suspension of the metal oxide NPs in water. The fabrics were then subjected to be padded and squeezed to 80% pick-up followed by drying at $60°C$. The padded samples which treated with ZnO, $TiO_2$ and hydroxyapatite NPs were cured at $140°C$ for 10 min, while the fabrics treated with MgO NPs were cured at $120°C$ for 3 min. Finally, the samples were exposed to be washed at $60°C$ for 20 min followed by air-drying.

### 2.4.2. One- Bath Process

In this method ZnO, $TiO_2$, MgO and hydroxyapatitetreatments were performed first followed by dyeing with a new synthesized acid dye 1 using the same bath. Where, the nanoZnO, $TiO_2$, MgO and hydroxyapatite were allowed to interact with wool and nylon fabrics and thus treated fabrics were dyed using a new synthesized acid dye during the dyeing and its auxiliaries in the same bath.

### 2.4.3. Post- Treatment Method

In this method, wool and nylon fabrics were dyed with a newly synthesized acid dye 1, then treated with ZnO, $TiO_2$, or MgO and hydroxyapatite NPs. Finally, the fabrics were washed and dried as described above.

### 2.5. Dyeing

A common procedure was used to dye treated and untreated wool and nylon fabrics with newly synthesized acid dyes 1. The dyeing process was carried out at pH 4.4-5 by adding acetic acid, liquor ratio at 1:40. The dye bath contained 2% dye, dyeing process started at $45°C$, the temperature was raised to $100°C$ for 60 min. After that, dyed samples were then washed by warm water followed by cooled water and dried at room temperature.

## 3. Analysis and Measurements

### 3.1. Evaluation of Color Strength and Lab Values

The colour yield of dyed samples was evaluated by the light reflectance technique using the Perkin-Elmer, UV/V Spectrophotometer (Model, Lambda 3B). The colour strength (K/S value) was assessed using Kubelka-Munk equation.

$$K/S = \frac{(1-R)^2}{2R} \qquad (1)$$

Where, R = decimal fraction of the reflection of the dyed fabric,K = absorption coefficient, and S = scattering coefficient

### 3.2. Antimicrobial Activity

The antibacterial activity was qualitatively evaluated both pre- and post- treated wool and nylon fabrics against *Escherichia coli* (G-) and *Staphylococcus aureus* (G+). The number of bacteria colonies on the agar plate pre-and post- treatment was counted for all samples and the results reported as percentages of bacteria reduction according to the following Equation:

Relative [OD Reduction (%)] = (B- A /B) × 100 Where B: the (OD) of control flask contains pathogenic strains only without any treatment. A: the (OD) of tested flasks after applying a textile disc treated [17-20].

### 3.3. Self-Cleaning Activity

The self -cleaning action of $TiO_2$ treated wool and nylon fabrics were investigated by exposing samples with adsorbed coffee stain to visible radiation. Measured quantity of 6% coffee solution was introduced on the wool and nylon fabrics and was allowed to spread. One half of each stain on the fabrics was exposed to sun light for 12-48 h, while the other half was covered with a black paper to prevent radiation from sunlight. The exposed part of the stain was compared with that of the covered part for self-cleaning action.

### 3.4. Ultraviolet Protection

The ultraviolet protection factor (UPF) was determined according to AS/NZS 4399:1996 standard procedure. The ultraviolet transmission through the fabric was determined by a Cary Varian 300 UV-Vis spectrophotometer under AATCC 83:2010 UVA Transmittance [21-23].

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### 3.5. High-Resolution Transmission Electron Microscope (TEM)

The particle sizes of wool and nylon samples treated with ZnO, TiO$_2$, MgO and hydroxyapatite NPs

were examined under a high-resolution transmission electron microscope [(JEM-1230) JEOL].

### 3.6. Fastness Testing

The dyed samples were subjected to rubbing, washing, perspiration and light according to standard ISO methods, ISO 105-X12 (1987), ISO 105-co4 (1989), ISO105-EO4 (1989), ISO 105-BO2 (1988), respectively.

## 4. Results and Discussion

### 4.1. Transmission electron microscopy

The fabrics treated with produced metal oxides NPs at optimum concentration 1.0 % o.w.f, it was under the range of ≤ 100 nm, which was validated by transmission electron microscopy as in (Fig.4). The nanoparticle size of ZnO, TiO$_2$, MgO and hydroxyapatite created a larger surface area, increased the active sites, and allowed faster contact between the dye molecules and binding sites.

### 4.2. Color strength

Because of their nanoscale structure, nanomaterials have improved chemical, physical, and biological properties. Both wool and nylon fabrics were treated with ZnO, MgO, TiO$_2$, and hydroxyapatite NPs before, after, and during dyeing to compare and investigate their functional properties. To find the best concentration for each nanoparticle, six different concentrations (0.5, 1, 1.5, 2, 2.5 and 3 %o.w.f.) were used. The colour strengths of treated wool and nylon fabrics were shown to be dependent on the type and concentration of nanoparticles used, as well as the treatment method used (pre-, post-, or one bath).

In the case of pretreatment, as shown in Tables (1,2), the colour strength values declined dramatically with TiO$_2$ and ZnO, but increased moderately with MgO and hydroxyapatite nanoparticles as the concentration of nanoparticles increased.

In a single-step treatment process, Tables (3, 4) showed that increasing the concentrations of TiO$_2$ and MgO NPs increased the K/S value up to 1% and after that the K/S values decreased. This could be because nanoparticle molecules compete with dye molecules, causing dye precipitation and causing the wool and nylon fabrics to absorb dye unevenly, while increasing the concentration of ZnO and hydroxylapatite NPs increased the K/S values.

In the case of post-treatment, as shown in Tables (5,6), the colour strength values were found to moderately decrease significantly with TiO$_2$ and MgO, and significantly increase with ZnO and

hydroxyapatite nanoparticles as the concentration of nanoparticles increased. This proved that treating the wool fabric with the lowest concentration of titanium dioxide (0.5 percent) was adequate.
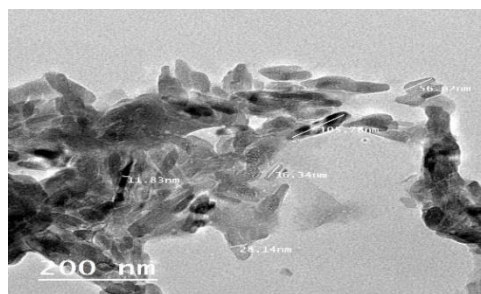

TEM images of treated wool with hydroxyapatite
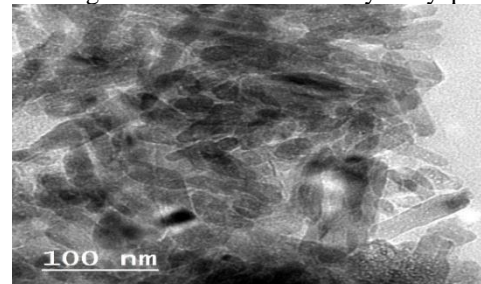

TEM images of treated nylon with hydroxyapatite
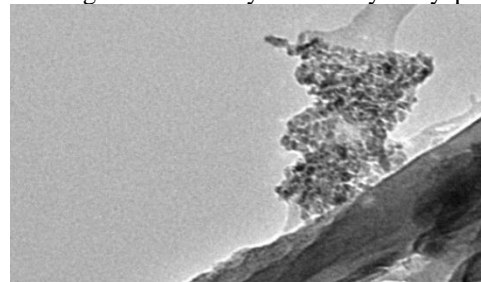

TEM images of treated nylon with MgO
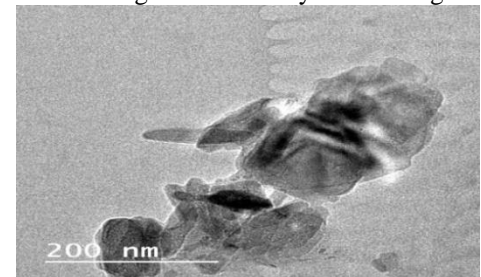

TEM images of treated nylon with ZnO
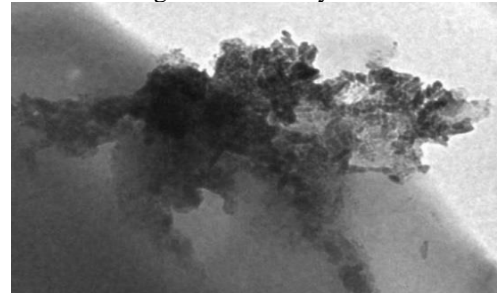

TEM images of treated nylon with TiO$_2$
Figure 4. TEM images of treated wool and nylon with ZnO, MgO, TiO$_2$, and hydroxyapatite NPs

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The higher colour strength observed at the lowest titanium dioxide concentrations could be ascribed to Ti+4 ions, which resulted in more positive charges, producing more ionic attraction to acid anionic dyes and accelerating the dye-to-fabric bonding process. However, increasing the concentration of titanium dioxide nanoparticles above 0.5 percent (from 1% to 3% o.w.f.) resulted in a slight decrease in colour strength, which could be attributed to a large increase in positive charges with high repulsion forces with each other, reducing the bonding process between dyes and fabric [24-26]. As a result, the optimal conditions for the application of TiO$_2$ nanoparticles for the pretreatment process were discovered to be at the lowest content (0.5 percent o.w.f.).

The colour strengthvalues of most treated wool and nylon materials were slightly higher than the colour strength values of the control fabrics, which were dyed without nanoparticle treatment. The pretreatment approach had a higher colour strength than the post- and single-treatment processes, according to the findings. Metal cations, which accelerated the bonding process between dyes and the pretreated fabric, were responsible for this. Metal cations were not present in the post- and single-treated fabrics to promote the bonding process between dyes and cloth during the dyeing process [27-29].

In addition, all tables included the colour difference (E) values (1-6). These tables showed that when the quantity of nanoparticles increased, there was no discernible colour difference (E) between the samples.

The colour strength valueswere raised in the pretreatment process in the order TiO$_2$> MgO> ZnO > hydroxyapatite nanoparticles, as shown.

### 4.3. Self-Cleaning Activity

One of the most essential qualities of fabrics treated with metal oxide nanoparticles is the ability to convert absorbed light into self-cleaning molecules that breakdown the stain. After 12 hours of exposing sunlight to the prepared coloured fabrics which pretreated with metal oxide NPs were shown in Table (7). Metal oxide nanoparticles were used to pretreat wool and nylon samples, resulting in a thin film of nanoparticles that increased the hydrophobic characteristics of the fabric surface. The Lotus effect was used to inspire the idea of creating hydrophobic surfaces. Water can clean the treated fabric surface from any surface dirt as a result of the hydrophobic effect caused by the metal oxide nanoparticles on the fabric surface [30– 32].

### 4.4. Ultraviolet Protection Activity

The ultraviolet shielding effect of all dyed fabrics treated with ZnO, MgO, TiO$_2$ and hydroxyapatite nanoparticles was improved. The UPF values of fabrics treated with ZnO, MgO, TiO$_2$ and hydroxyapatite NPs increased with the order of pretreated > post-treated > one bath procedure, as shown in Tables 8 and 9. The UPF values for the post-treated and one bath processes coloured samples were increased with an increase in the concentration of metal oxide NPs. From tables 8, 9 we could see that the UPF values increased as the concentrations of metal oxide NPs were also increased in the dyed/pretreated wool/MgO, dyed/pretreated nylon/TiO$_2$, and nylon /ZnO samples. Also, the UPF values decreased by increasing the concentration of metal oxide nanoparticles in the dyed/pretreated wool/TiO$_2$, wool/ZnO, wool/ hydroxyapatite, nylon/ hydroxyapatite and nylon/MgO samples.

Table 1: Effect of different concentrations of MgO and TiO$_2$ NPs on both K/S, L, a, b, and ΔE values of wool and nylon fabrics dyed with new synthesized acid dyes using a pretreatment process.

| Conc. of NPs % | K/S | | L | | a | | b | | ΔE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ |
| Nylon fabric | | | | | | | | | | |
| 0 | 13.52 | | 25.67 | | 13.87 | | -5.45 | | 53.22 | |
| 0.5 | 15.62 | 19.66 | 24.04 | 21.36 | 16.52 | 16.57 | -6.47 | -5.49 | 55.78 | 58.41 |
| 1 | 15.91 | 19.34 | 23.82 | 20.89 | 17.61 | 14.31 | -7.82 | -4.92 | 56.27 | 58.38 |
| 1.5 | 16.85 | 19.16 | 20.80 | 20.41 | 14.50 | 14.02 | -5.62 | -5.04 | 58.48 | 58.78 |
| 2 | 18.89 | 18.34 | 21.07 | 21.55 | 16.20 | 15.89 | -6.42 | -6.03 | 58.57 | 58.78 |
| 2.5 | 19.14 | 17.91 | 21.42 | 21.70 | 14.93 | 14.57 | -5.67 | -5.71 | 57.96 | 57.62 |
| 3 | 19.47 | 16.01 | 23.30 | 23.51 | 17.75 | 15.95 | -6.25 | -4.39 | 56.82 | 56.20 |
| Wool fabric | | | | | | | | | | |
| 0 | 19.83 | | 17.21 | | 11.98 | | -6.35 | | 62.11 | |
| 0.5 | 22.26 | 26.01 | 19.41 | 17.66 | 13.73 | 12.48 | -7.61 | -6.50 | 64.96 | 66.09 |
| 1 | 22.95 | 25.44 | 17.43 | 17.52 | 12.83 | 12.44 | -7.18 | -6.59 | 66.54 | 66.23 |
| 1.5 | 23.13 | 24.95 | 17.83 | 17.65 | 13.32 | 12.52 | -7.43 | -6.21 | 66.32 | 66.04 |
| 2 | 24.51 | 24.88 | 17.85 | 18.06 | 12.89 | 12.62 | -7.14 | -6.69 | 66.14 | 65.78 |
| 2.5 | 25.30 | 23.98 | 19.21 | 18.55 | 14.51 | 12.83 | -6.65 | -6.98 | 65.09 | 65.43 |
| 3 | 27.15 | 23.95 | 19.08 | 18.29 | 13.44 | 12.30 | -6.70 | -6.51 | 64.99 | 65.46 |

Different concentrations (0.5- 3 %) of MgO and TiO$_2$ NPs,liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60$^{\circ}$C, cured at 140$^{\circ}$C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120$^{\circ}$C for 3 min. Washed at 60$^{\circ}$C for 20 min followed by air-drying.

Table 2: Effect of different concentrations of ZnO and hydroxyapatite NPs on both K/S, L, a, b, and ΔE values of wool and nylon fabrics dyed with new synthesized acid dyes using a pretreatment process.

| Conc. of NPs % | K/S | | L | | a | | b | | ΔE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite |
| | Nylon fabric | | | | | | | | | |
| 0 | 13.52 | | 25.67 | | 13.87 | | -5.45 | | 53.22 | |
| 0.5 | 18.42 | 12.13 | 22.56 | 25.66 | 17.70 | 19.79 | -6.45 | -3.16 | 57.52 | 55.32 |
| 1 | 18.29 | 12.95 | 20.35 | 24.51 | 13.63 | 20.52 | -4.92 | -7.96 | 58.77 | 56.48 |
| 1.5 | 18.15 | 14.89 | 21.38 | 23.88 | 16.38 | 20.84 | -6.25 | -8.36 | 58.33 | 57.18 |
| 2 | 18.00 | 15.20 | 21.99 | 26.14 | 17.06 | 21.75 | -6.87 | -9.49 | 57.89 | 55.40 |
| 2.5 | 14.24 | 16.40 | 22.14 | 27.69 | 16.57 | 21.89 | -6.27 | -11.22 | 57.63 | 54.09 |
| 3 | 13.87 | 17.50 | 22.14 | 28.37 | 15.88 | 21.52 | -5.82 | -10.90 | 57.47 | 53.31 |
| | Wool fabric | | | | | | | | | |
| 0 | 19.83 | | 17.21 | | 11.98 | | -6.35 | | 62.11 | |
| 0.5 | 20.16 | 17.12 | 21.40 | 21.47 | 16.13 | 15.61 | -8.91 | -9.02 | 64.03 | 63.86 |
| 1 | 20.11 | 17.77 | 21.15 | 21.64 | 15.75 | 15.64 | -8.91 | -8.61 | 64.16 | 63.60 |
| 1.5 | 19.43 | 17.92 | 21.67 | 22.01 | 15.78 | 15.42 | -8.95 | -9.04 | 63.70 | 63.32 |
| 2 | 19.00 | 18.22 | 21.94 | 22.09 | 16.32 | 15.79 | -9.57 | -8.84 | 63.77 | 63.28 |
| 2.5 | 18.62 | 19.03 | 22.01 | 22.07 | 16.06 | 15.68 | -8.85 | -8.85 | 63.43 | 63.28 |
| 3 | 18.08 | 19.23 | 22.23 | 22.50 | 15.64 | 15.45 | -9.00 | -9.03 | 63.16 | 62.87 |

Different concentrations (0.5- 3 %) of MgO and TiO$_2$ NPs, liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60$^{\circ}$C, cured at 140$^{\circ}$C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120$^{\circ}$C for 3 min. Washed at 60$^{\circ}$C for 20 min followed by air-drying.

Table 3: Effect of different concentrations of MgO and TiO2 NPs on both K/S, L, a, b, and ΔE values of wool and nylon fabrics dyed with new synthesized acid dyes using a one- bath process.

| Conc. of NPs % | K/S | | L | | a | | b | | ΔE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ |
| | Nylon fabric | | | | | | | | | |
| 0 | 13.52 | | 25.67 | | 13.87 | | -5.45 | | 53.22 | |
| 0.5 | 12.12 | 15.40 | 34.49 | 28.02 | 22.55 | 21.53 | -13.26 | -10.18 | 48.32 | 53.59 |
| 1 | 13.33 | 16.40 | 30.62 | 26.77 | 21.45 | 20.87 | -11.39 | -9.26 | 51.23 | 54.49 |
| 1.5 | 12.21 | 13.85 | 29.87 | 26.91 | 22.10 | 20.52 | -12.16 | -8.04 | 52.23 | 54.25 |
| 2 | 11.03 | 13.73 | 28.27 | 25.11 | 21.21 | 19.74 | -11.08 | -8.39 | 53.30 | 55.67 |
| 2.5 | 10.28 | 12.72 | 28.05 | 24.60 | 20.61 | 19.98 | -11.05 | -7.62 | 53.29 | 56.22 |
| 3 | 9.76 | 12.27 | 28.39 | 29.04 | 21.18 | 25.12 | -9.08 | -7.92 | 53.08 | 52.08 |
| | Wool fabric | | | | | | | | | |
| | 19.83 | | 17.21 | | 11.98 | | -6.35 | | 62.11 | |
| 0.5 | 22.06 | 23.72 | 18.50 | 17.45 | 13.57 | 12.26 | -6.27 | -6.02 | 65.46 | 66.14 |
| 1 | 24.49 | 24.87 | 17.79 | 16.86 | 12.65 | 12.37 | -6.25 | -5.83 | 65.94 | 66.68 |
| 1.5 | 23.17 | 24.81 | 17.74 | 13.57 | 12.76 | 11.60 | -6.38 | -5.68 | 66.04 | 69.66 |
| 2 | 23.02 | 24.42 | 17.39 | 15.47 | 12.78 | 11.92 | -5.75 | -6.01 | 66.23 | 67.96 |
| 2.5 | 21.96 | 24.06 | 17.62 | 16.31 | 13.69 | 11.63 | -7.01 | -5.73 | 66.50 | 67.05 |
| 3 | 22.16 | 23.49 | 18.20 | 17.06 | 12.93 | 12.83 | 06.35 | -6.74 | 65.63 | 66.79 |

Different concentrations (0.5- 3 %) of MgO and TiO$_2$ NPs, liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60$^{\circ}$C, cured at 140$^{\circ}$C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120$^{\circ}$C for 3 min. Washed at 60$^{\circ}$C for 20 min followed by air-drying.

Table 4: Effect of different concentrations of ZnO andHydroxyapatite NPs on both K/S, L, a, b, and ΔE values of wool and nylon fabrics dyed with new synthesized acid dyes using a one- bath process.

| Conc. of NPs % | K/S | | L | | a | | b | | ΔE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite |
| Nylon fabric | | | | | | | | | | |
| 0 | 13.52 | | 25.67 | | 13.87 | | -5.45 | | 53.22 | |
| 0.5 | 11.27 | 12.11 | 28.98 | 27.99 | 20.92 | 19.95 | -11.19 | -9.47 | 52.55 | 53.05 |
| 1 | 13.29 | 12.74 | 26.92 | 26.95 | 18.63 | 19.94 | -9.29 | -10.56 | 53.63 | 54.07 |
| 1.5 | 14.09 | 13.77 | 26.75 | 26.47 | 21.20 | 19.92 | -9.59 | -10.08 | 54.64 | 54.49 |
| 2 | 14.72 | 14.54 | 25.29 | 25.18 | 19.39 | 19.90 | -9.30 | -9.42 | 55.41 | 55.68 |
| 2.5 | 15.36 | 14.77 | 25.06 | 24.22 | 19.22 | 19.60 | -8.53 | -7.20 | 55.56 | 56.47 |
| 3 | 15.77 | 15.55 | 25.42 | 23.56 | 20.44 | 20.94 | -8.51 | -11.01 | 55.60 | 57.63 |
| Wool fabric | | | | | | | | | | |
| 0 | 19.83 | | 17.21 | | 11.98 | | -6.35 | | 62.11 | |
| 0.5 | 21.02 | 19.17 | 19.75 | 19.57 | 13.98 | 14.00 | -6.99 | -7.16 | 64.85 | 64.76 |
| 1 | 21.06 | 19.45 | 18.91 | 19.39 | 13.42 | 14.02 | -6.62 | -7.42 | 64.54 | 65.00 |
| 1.5 | 21.54 | 19.67 | 18.76 | 19.20 | 13.35 | 14.26 | -6.45 | -7.89 | 65.13 | 65.35 |
| 2 | 22.24 | 20.02 | 18.17 | 19.87 | 13.78 | 14.40 | -7.65 | -7.86 | 65.21 | 64.75 |
| 2.5 | 22.74 | 21.68 | 19.33 | 19.83 | 14.13 | 14.51 | -7.20 | -8.22 | 65.21 | 64.85 |
| 3 | 22.98 | 22.02 | 19.46 | 19.57 | 14.62 | 14.12 | -8.00 | -8.03 | 65.02 | 64.67 |

Different concentrations (0.5- 3 %) of MgO and TiO$_2$ NPs, liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

Table 5: Effect of different concentrations of MgO and TiO2 NPs on both K/S, L, a, b, and ΔE values of wool and nylon fabrics dyed with new synthesized acid dyes using a post – treatment method process.

| Conc. of NPs % | K/S | | L | | a | | b | | ΔE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ | MgO | TiO$_2$ |
| Nylon fabric | | | | | | | | | | |
| 0 | 13.52 | | 25.67 | | 13.87 | | -5.45 | | 53.22 | |
| 0.5 | 12.20 | 15.87 | 30.18 | 28.19 | 18.58 | 18.59 | -8.56 | -7.29 | 50.50 | 55.43 |
| 1 | 11.77 | 15.19 | 29.22 | 29.20 | 21.59 | 21.27 | -10.67 | -9.26 | 52.52 | 52.37 |
| 1.5 | 11.35 | 13.42 | 28.88 | 28.74 | 21.77 | 21.78 | -10.50 | -9.58 | 52.90 | 52.36 |
| 2 | 9.98 | 12.12 | 28.72 | 20.89 | 22.08 | 20.99 | -11.48 | -8.32 | 53.23 | 58.38 |
| 2.5 | 9.37 | 11.60 | 31.62 | 25.52 | 20.65 | 21.26 | -10.45 | -9.29 | 49.94 | 55.69 |
| 3 | 8.34 | 11.44 | 31.97 | 27.24 | 18.01 | 21.12 | -10.15 | -9.55 | 50.12 | 54.15 |
| Wool fabric | | | | | | | | | | |
| 0 | 19.83 | | 17.21 | | 11.98 | | -6.35 | | 62.11 | |
| 0.5 | 26.98 | 27.08 | 18.21 | 17.57 | 13.32 | 11.92 | -6.95 | -6.39 | 65.84 | 66.04 |
| 1 | 26.05 | 27.07 | 17.56 | 17.57 | 12.37 | 12.42 | -6.76 | -5.85 | 66.22 | 66.02 |
| 1.5 | 26.01 | 26.36 | 17.29 | 16.63 | 12.46 | 10.86 | -6.21 | -5.66 | 66.37 | 66.59 |
| 2 | 25.72 | 25.38 | 16.76 | 17.29 | 11.37 | 11.69 | -5.91 | -6.17 | 66.61 | 66.22 |
| 2.5 | 24.31 | 25.20 | 17.55 | 17.69 | 12.11 | 11.51 | -6.66 | -6.00 | 66.16 | 65.77 |
| 3 | 23.34 | 25.00 | 18.08 | 18.42 | 12.38 | 13.13 | -6.10 | -7.18 | 65.58 | 65.66 |

Different concentrations (0.5- 3 %) of MgO and TiO$_2$ NPs, liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

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Table 6: Effect of different concentrations of ZnO andHydroxyapatite NPs on both K/S, L, a, b, and ΔE values of wool and nylon fabrics dyed with new synthesized acid dyes using a post – treatment method process.

| Conc. of NPs % | K/S | | L | | a | | b | | ΔE | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite | ZnO | Hydroxy apatite |
| Nylon  fabric | | | | | | | | | | |
| 0 | 13.52 | | 25.67 | | 13.87 | | -5.45 | | 53.22 | |
| 0.5 | 13.77 | 12.27 | 27.02 | 27.69 | 20.95 | 21.89 | -8.68 | -11.22 | 54.27 | 45.09 |
| 1 | 14.24 | 12.72 | 26.73 | 28.37 | 21.58 | 21.52 | -9.44 | -10.90 | 54.78 | 53.59 |
| 1.5 | 15.10 | 13.02 | 23.91 | 25.66 | 20.40 | 19.79 | -8.03 | -3.16 | 57.01 | 55.32 |
| 2 | 16.60 | 13.73 | 25.37 | 24.51 | 20.86 | 20.52 | -9.10 | -7.96 | 55.80 | 56.48 |
| 2.5 | 16.87 | 15.07 | 25.05 | 23.88 | 22.58 | 20.84 | -9.46 | -8.36 | 56.70 | 57.18 |
| 3 | 17.61 | 17.76 | 26.95 | 26.14 | 21.11 | 21.75 | -8.73 | -9.49 | 54.39 | 55.40 |
| Wool  fabric | | | | | | | | | | |
| 0 | 19.83 | | 17.21 | | 11.98 | | -6.35 | | 62.11 | |
| 0.5 | 26.09 | 22.40 | 17.42 | 17.25 | 11.46 | 12.82 | -5.03 | -6.43 | 65.80 | 66.53 |
| 1 | 26.51 | 23.72 | 16.82 | 16.74 | 11.45 | 12.21 | -5.67 | -5.90 | 66.51 | 66.78 |
| 1.5 | 26.83 | 23.79 | 16.67 | 16.25 | 12.66 | 11.49 | -6.35 | -5.19 | 67.04 | 66.96 |
| 2 | 27.07 | 24.58 | 16.66 | 16.77 | 11.69 | 11.49 | -5.47 | -6.24 | 66.66 | 66.68 |
| 2.5 | 27.55 | 24.71 | 16.59 | 16.82 | 12.27 | 11.51 | -5.99 | -5.99 | 66.96 | 66.60 |
| 3 | 28.52 | 24.85 | 17.25 | 17.40 | 12.00 | 11.81 | -5.77 | -6.00 | 64.96 | 66.09 |

Different concentrations (0.5– 3 %) of MgO and $TiO_2$ NPs, liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and $TiO_2$ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

Table 7: Self-cleaning activity of wool and nylon samples dyed with acid dye 1 and pre -treated with metal oxide NPs at the optimum conditions.

| sample | Dye Removal % |
|---|---|
| Wool/$TiO_2$ | 85 |
| Wool/MgO | 85 |
| Wool/ZnO | 90 |
| Wool/hydroxapatite | 85 |
| Nylon/$TiO_2$ | 85 |
| Nylon/MgO | 85 |
| Nylon/ZnO | 90 |
| Nylon/hydroxapatite | 85 |

Pretreated wool and nylon fabrics with ZnO, MgO, TiO2, and hydroxyapatite NPs (1.0% o.w.f; on-weight-fabric), liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO2 NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

### 4.5. Antibacterial Performance of Treated and Untreated wool and nylon Fabrics

The antibacterial efficacy of wool and nylon fabrics varied based on the type of nanoparticle, as shown in Table 10. It also showed that the antibacterial efficiency of the pretreatment procedure was higher than the antibacterial efficiency of the post-treatment process. In most cases, the antibacterial activity of nanoparticle-treated fabrics against gram-positive bacteria was higher than that against gram-negative bacteria.$TiO_2$ nanoparticles had the highest antibacterial effectiveness when compared to hydroxyapatite, ZnO, and MgO nanoparticles. It was also worth noting that the untreated/blank wool and nylon materials had no antibacterial action, as shown in Table 10. Due to the excellent photocatalytic influence of $TiO_2$ NPs, wool fabric prepared with $TiO_2$ nanoparticles demonstrated the largest reduction in bacterial count percent. The antimicrobial mechanism of action of NPs, is

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generally described as adhering to one of three models: oxidative stress induction, metal ion release, or non-oxidative mechanisms. These three types of mechanisms can occur simultaneously. The major processes underlying the antibacterial effects of NPs are; disruption of the bacterial cell membrane, generation of ROS, penetration of the bacterial cell membrane and induction of intracellular antibacterial effects, including interactions with DNA and proteins [33]. The antibacterial action of $TiO_2$ NPs or nanometal oxides, is due to the generation of numerous active oxygen species, such as superoxide anions, hydrogen peroxide, singlet oxygen, and hydroxyl radicals, which are responsible for the destruction of bacteria. When photons with energy greater than the bond-gap of $TiO_2$ nanoparticles are exposed to light, electrons are stimulated to go up to the conduction band. The excited electrons in the crystal structure system interact with oxygen in the air, forming free radical oxygen atoms with the ability to oxidize and break down the bacterial cell wall through an oxidation/reduction process. The antibacterial action of ZnO nanoparticles, on the other hand, arises from the development of oxidative stress due to the generation of active oxygen species capable of degrading the bacterial cell membrane.

### 4.5. Fastness properties

The fastness properties of nanoparticle-treated wool and nylon fabrics before dyeing were more resistant to rubbing, washing, and perspiration than those treated after dyeing and one bath treatments, as shown in Table 11. The increased dye penetration and interaction with fabrics might explain the enhanced colour resistance of the pretreated dyed samples by nanoparticles. In addition, we could see that the light fastness varied from fair to exceptional in each situation.

Table 8: Ultraviolet (UV) blocking of nanoparticles (pre, post-treated and one bath processes) of wool fabric dyed with new synthesized (acid dye).

| sample | | UPF | | |
|---|---|---|---|---|
| | | Pre-Treated | Post-Treated | one bath process |
| Wool/TiO₂ | 0.5% | 2804.2 | 1355.8 | 1113.5 |
| | 1% | 2179.5 | 1428.2 | 1156 |
| | 1.5% | 1825.2 | 1466.5 | 1177 |
| | 2% | 1819.6 | 1511 | 1365.1 |
| | 2.5% | 1069.9 | 1881.4 | 1496.8 |
| Wool/MgO | 0.5% | 1027.8 | 206.9 | 199.6 |
| | 1% | 1281.8 | 1243 | 232.6 |
| | 1.5% | 1437.9 | 1291 | 376.5 |
| | 2% | 1497.1 | 1362.8 | 418.5 |
| | 2.5% | 1586 | 1399.6 | 434.4 |
| Wool/ZnO | 0.5% | 1992.5 | 1045 | 466.4 |
| | 1% | 1809.1 | 1158.2 | 525.3 |
| | 1.5% | 1783.5 | 1277 | 564 |
| | 2% | 1494.8 | 1312.3 | 584.9 |
| | 2.5% | 1325.7 | 1456 | 600.4 |
| Wool/hydroxyapatite | 0.5% | 5010.5 | 193.6 | 183.2 |
| | 1% | 10701.1 | 387.9 | 243.9 |
| | 1.5% | 9052.9 | 575.2 | 249 |
| | 2% | 4558.4 | 717.3 | 254.4 |
| | 2.5% | 3838.8 | 1035.6 | 327.7 |

Treated wool and nylon fabrics with ZnO, MgO, TiO₂, and hydroxyapatite NPs (0.5- 2.5 % o.w.f; on-weight-fabric), liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO₂ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

Table 9: Ultraviolet (UV) blocking of nanoparticles (pre, post-treated and one bath processes) of nylon fabric dyed with new synthesized (acid dye).

| sample | | UPF | | |
|---|---|---|---|---|
| | | Pre-Treated | Post-Treated | one bath process |
| Nylon/TiO$_2$ | 0.5% | 51.7 | 37.7 | 34.7 |
| | 1% | 52.6 | 39.1 | 39.4 |
| | 1.5% | 52.9 | 42.2 | 40.4 |
| | 2% | 54.2 | 43.3 | 40.9 |
| | 2.5% | 59.2 | 45.8 | 42.5 |
| Nylon/MgO | 0.5% | 33.0 | 27.7 | 18.4 |
| | 1% | 31.8 | 28.0 | 19.0 |
| | 1.5% | 31.4 | 28.8 | 19.8 |
| | 2% | 30.1 | 32.2 | 20.2 |
| | 2.5% | 28.8 | 34.4 | 21.6 |
| Nylon/ZnO | 0.5% | 29.3 | 28.2 | 24.2 |
| | 1% | 31.5 | 29.6 | 25.0 |
| | 1.5% | 33.1 | 30.7 | 27.1 |
| | 2% | 33.6 | 31.3 | 31.6 |
| | 2.5% | 34.7 | 32.8 | 32.2 |
| Nylon/hydroxyapatite | 0.5% | 55.7 | 39.7 | 31.5 |
| | 1% | 54.8 | 41.6 | 33.2 |
| | 1.5% | 53.5 | 43.4 | 35.5 |
| | 2% | 53.1 | 45.1 | 35.4 |
| | 2.5% | 52.0 | 46.6 | 36.1 |

Treated wool and nylon fabrics with ZnO, MgO, TiO$_2$, and hydroxyapatite NPs (0.5- 2.5 % o.w.f; on-weight-fabric), liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

Table 10: Antibacterial activity for thetreatedwool and nylon fabrics dyed with new synthesized acid dye with ( pre, post-treated and one bath processes)

| Sample | Pre-Treatment | | Post-Treatment | |
|---|---|---|---|---|
| | S. aureus (G+) % | E. coli (G -) % | S. aureus (G+) % | E. coli (G -) % |
| Control | 0 | 0 | 0 | 0 |
| Wool/TiO$_2$ | 97.22 | 86.74 | 80.3 | 79.6 |
| Wool/MgO | 77.85 | 44.81 | 36.6 | 24.9 |
| Wool/ZnO | 86.63 | 86.26 | 65.7 | 45.4 |
| Wool/hydroxyapatite | 95.47 | 92.11 | 84.65 | 74.14 |
| Nylon/TiO$_2$ | 83.6 | 32.5 | 48.3 | 28.3 |
| Nylon/MgO | 70.9 | 66.2 | 54.4 | 42.1 |
| Nylon/ZnO | 79.7 | 68.8 | 77.2 | 46.7 |
| Nylon/hydroxyapatite | 83.2 | 24.5 | 69.7 | 73.9 |

Treated wool and nylon fabrics with ZnO, MgO, TiO$_2$, and hydroxyapatite NPs (1.0% o.w.f; on-weight-fabric), liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO$_2$ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

Table 11: Colourfastness properties of nanoparticles treated wool and nylon fabrics for pre, post treatment and one bath processes dyed with new synthesized acid dyes.

| conditions | Metal Oxides NPs | Rubbing | | Washing | | | | Perspiration | | | | | | | | Light |
| | | Wet | Dry | St. C | St. N | St. W | Alt. | Acidic | | | | Alkaline | | | | |
| | | | | | | | | St. C | St. N | St. W | Alt. | St. C | St. N | St. W | Alt. | |
| Wool pre-treatment | Control | 4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | ZnO | 4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | MgO | 4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 7 |
| | TiO₂ | 3–4 | 3 | 4 | 4 | 4 | 4 | 3-4 | 4 | 3-4 | 3-4 | 4 | 4 | 4 | 4 | 6-7 |
| | hydroxyapatite | 3–4 | 3 | 4 | 4 | 4 | 4 | 3-4 | 4 | 3-4 | 3-4 | 4 | 4 | 4 | 4 | 6-7 |
| Wool post-treatment | ZnO | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| | MgO | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 7 |
| | TiO₂ | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| | hydroxyapatite | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| Wool one path treatment | ZnO | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| | MgO | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 7 |
| | TiO₂ | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| | hydroxyapatite | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| Nylon pre-treatment | Control | 4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | ZnO | 4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| | MgO | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6-7 |
| | TiO₂ | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6 |
| | hydroxyapatite | 3–4 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 6 |
| Nylon post-treatment | ZnO | 3–4 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | MgO | 3–4 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | TiO₂ | 3 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6 |
| | hydroxyapatite | 3 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6 |
| Nylon one path treatment | ZnO | 3–4 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | MgO | 3–4 | 3 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6-7 |
| | TiO₂ | 3 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6 |
| | hydroxyapatite | 3 | 3–4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4-5 | 4 | 4 | 4 | 4 | 6 |

Where: Alt. = alteration, St.W = staining on wool, St. C = staining on cotton and St. N= staining on nylon
Treated wool and nylon fabrics with ZnO, MgO, TiO₂, and hydroxyapatite NPs (1.0% o.w.f; on-weight-fabric), liquor ratio 1:30, padded and squeezed to 80% pick-up followed by drying at 60°C, cured at 140°C for 10 min and after treated with MgO and TiO₂ NPs were cured at 120°C for 3 min. Washed at 60°C for 20 min followed by air-drying.

## 5. Conclusion

This research explores new synthesized acid dye for dyeing wool and nylon fabrics. Both transmission electron microscopy (TEM) of the dyed textile substrates and IR, H-NMR of prepared new acid dye were described. In this work, the treatment with ZnO, TiO₂, MgO and hydroxyapatite NPs using the methods (pre-, post-, or one bath) of wool and nylon fabrics is to produce fabrics with special functions including self-cleaning, antibacterial, and ultraviolet (UV) blocking, also enhancing the colour strength as well as colour fastness properties of coloured wool and nylon fabrics especially the pretreated process. The antibacterial efficiency of the pretreatment was higher than the antibacterial efficiency of the post-treatment process and TiO₂ NPs had the highest antibacterial effectiveness when compared to hydroxyapatite, ZnO, and MgO NPs. The UPF ratings of fabrics treated with ZnO, MgO, TiO₂ and hydroxyapatite NPs increased according to the sequence: pretreated > post-treated > one bath process.

## 6. Conflicts of interest

The authors declare they have no financial interests.

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