BLEACHED cotton fabrics were pre-treated with *Moringa oleifera* leaf extract as natural bioactive materials to impart the fabrics dual antibacterial and sun protective properties. The fabrics were the treated with titanium dioxide nanoparticles (TiO$_2$NPs) and zinc oxide nanoparticles (ZnONPs) separately with concentration 2wt.% and 1 wt.% respectively in presence of 1,2,3,4-butane tetracarboxlyic acid (BTCA) as non-formaldehyde crosslinking agent by using pad dry cure method. The treated cotton fabrics were evaluated via monitoring morphological changes of the fibers by using scanning electron microscopy and X-ray diffraction, scanning electron microscopy (SEM&EDX), mechanical properties (tensile strength and elongation at break), roughness, ultra-violet protection factor (UPF). In addition, evaluation of antibacterial activity the treated fabrics by using disk inhibition zone. Research output disclosed that the fabrics treated with moringa extract and then with titanium dioxide nanometal oxide powder show the best results.

**Keywords:** Cotton fabrics, *Moringa oleifera* extract, Titanium dioxide nanoparticles, Zinc oxide nanoparticles.

**Introduction**

Cotton fabric consider one of the most widely used natural fibers in textiles, because of its unique properties such as it is breathable, soft, and degradable nature as wellas its easy mass production. For practical applications, cotton fabric has been endowed with different functions including self-cleaning and superhydrophobicity [1-10], UV blocking [1, 8, 11], flame retardation [12-14]. Cotton fabric can also be made electrically conductive [15-18] and antibacterial [1, 19-25].

Nanotechnology is an emerging technique can be applied in many fields such as textiles, catalysis, electronic and medical fields. Metal nanoparticles are usually defined as particulate materials with at least one dimension less than 100 nanometers (nm), even the particles could be of zero dimension as in the case of quantum dots. Metal nanoparticles have a high specific surface area and a high fraction of surface atoms [26-28].

ZnO nanoparticles are widely used to textile fabrics due to their unique such as photocatalytic, electrical, optical, dermatological and antibacterial properties [29-34]. Moreover, ZnO nanoparticles are actually one of best Eco-friendly absorbers of harmful UV radiation [35]. In order to decrease the health risks coming from overexposure to UV radiation, the World Health Organization (WHO) has also recommended the use of loose-fitting, full-length clothes with a high protection factor [36].

Titanium dioxide nanoparticles (TiO$_2$NPs) impart textile fabrics simultaneously trilateral
properties namely, antibacterial, UV protective and self-cleaning properties. Taking into account ever growing consumer demands, the fact that small amount of TiO$_2$NPs provides desirable effects as well as simple synthesis and application procedures, it becomes clear why such multifunctional textile materials are of interest for textile industry [37-40]. The problematic issues are primarily related to the possible degradation of the fabrics treated with photocatalyst TiO$_2$NPs and exposed to longer UV irradiation.

*Moringa oleifera* (*Moringingaceae*, English: drumstick tree) is native to sub-Himalayan regions of, Pakistan, India, Bangladesh, and Afghanistan as well as tropic areas. *Moringa oleifera* has been used as an ingredient of Indian diet since centuries. It is cultivated almost all over the country and its leaves and fruits are used as vegetables. *Moringa oleifera* is considered as an important source of food in some world regions, as it had easily and cheaply growth and its leaves have ability to retain a lot of minerals and vitamins over dryness[41]. *Moringa oleifera* utilized to treat pockets of infection (abscesses), dandruff, athlete’s foot, snake bites, gum disease (gingivitis), wounds and warts [42]. In addition, The leave of plant has been reported for its antitumor, hypotensive, cardioprotective, wound healing activities and use for eye diseases [42]. Almost all parts of the plant have been utilized in traditional medicine properties. Table 1 shows the components of *Moringa oleifera* leaf[42].

The aim of the present work is to develop cotton fabrics with an improving of its antibacterial and sun protective properties through treatment with Titanium dioxide nanoparticles and zinc oxide nanoparticles together with *Moringa oleifera* extract. The effect of each treatment on the final properties of the fabric is elucidated. Titanium dioxide and zinc oxide nanoparticles on the treated fabric surface is estimated by SEM analysis.

**Materials and Methods**

**Materials**

Mill desized, scoured and bleached cotton fabrics were supplied by El- Nasr Company for spinning weaving and dying El-mahallah El-kubra, Egypt. Zinc oxide nano powder, Titanium dioxide nano powder were supplied from Sigma Aldrich company. 1,2,3,4-butane tetra carboxylic acid, was supplied from el-Gomhoria company, Cairo egypt. Egyptol: nonionic detergent, from starch and Yeast Co.,Alexandria, Egypt.*Moringa oleifera* leaves were obtained from Egyptian Scientific Society of Moringa (ESSM), National Research Centre, Dokki, Cairo, Egypt.

**Preparation of Moringa oleifera Extract:**
10g from *Moringa oleifera* leaves (powder) were inserted in conical flask and 100 ml of distilled water was added. The solution was boiled for 30 min then left to cool at ambient conditions, finally filtered off.

**Preparation of Cotton Fabrics:**
Cotton fabrics were washed in aqueous solution containing, 2 g/l sodium carbonate and nonionic wetting agent at 60°C for 30 min followed by washing with tap water and finally dried at room temperature.

**Treatment of Cotton Fabrics with Moringa oleifera Extract and Nanoparticles**
Cotton fabrics were immersed in the *Moringa oleifera* extract and squeezed to a wet pick-up of ca 100%, then dried at 80°C for 5 min. the moringa treated fabrics were immersed in an aqueous solution containing zinc oxide and titanium dioxide nano powder with concentrations (1%, 2%) respectively in presence of 0.5% 1,2,3,4-butanetetracarboxyclic acid (BTCA) using material to liquor ratio (L.R), 1:20. The fabric were leaved for 15 min then squeezed to wet pickup of 100% using laboratory padding machine. Finally, the treated samples were dried at 80 °C for 5 min then cured at 120°C for 3 min.

**Testing and Analysis:**
Tensile strength and elongation at break were determined by strip method according to ASTM, standard Test method “Breaking load and elongation of Textile fabric” D-1682-94. Surface roughness was monitored according to JIS94 standard, using surface roughness measuring instrument, SE 1700a Made in Japan. Values recorded in (µm)unit and represent the average of 5 readings. Ultraviolet protection factor (UPF) was measured using UV Shimadzu 3101 PC-Spectrophotometer. UPF was determined by measuring the Ultraviolet radiation transmittance value of each fabric across the wavelength range 280 - 400 nm. The UPF of the treated samples were obtained used ‘Ultra Violet Transmittance Fabric Analyzer- Lab sphere- USA. The UPF values are calculated automatically, in accordance with Australia/ Newzeland standard AS/NZS 4399:1996. The antimicrobial activity of the treated fabrics was examined against *Staphylococcus aureus*,

**TABLE 1: Moringa oleifera leaf, raw; Nutritional value per 100g (3.5oz)**

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>64kcal (270 kJ)</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>8.28 g</td>
</tr>
<tr>
<td>Dietary fiber</td>
<td>2.0 g</td>
</tr>
<tr>
<td>Fat</td>
<td>1.40 g</td>
</tr>
<tr>
<td>Protein</td>
<td>9.40 g</td>
</tr>
<tr>
<td>Vitamin A equiv.</td>
<td>47%378 μg</td>
</tr>
<tr>
<td>Thiamine (B1)</td>
<td>22%0.257 mg</td>
</tr>
<tr>
<td>Riboflavin (B2)</td>
<td>55%0.660 mg</td>
</tr>
<tr>
<td>Niacin (B3)</td>
<td>15%2.220 mg</td>
</tr>
<tr>
<td>Pantothenic acid (B5)</td>
<td>3%0.125 mg</td>
</tr>
<tr>
<td>Vitamin B6</td>
<td>92%1.200 mg</td>
</tr>
<tr>
<td>Folate (B9)</td>
<td>10%40 μg</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>62%51.7 mg</td>
</tr>
<tr>
<td>Calcium</td>
<td>19% - 185 mg</td>
</tr>
<tr>
<td>Iron</td>
<td>31% - 4.00 mg</td>
</tr>
<tr>
<td>Magnesium</td>
<td>41% - 147 mg</td>
</tr>
<tr>
<td>Manganese</td>
<td>17% - 0.36 mg</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>16% - 112 mg</td>
</tr>
<tr>
<td>Potassium</td>
<td>7% - 337 mg</td>
</tr>
<tr>
<td>Sodium</td>
<td>1% - 9 mg</td>
</tr>
<tr>
<td>Zinc</td>
<td>6% - 0.6 mg</td>
</tr>
<tr>
<td>Water</td>
<td>78.66 g</td>
</tr>
</tbody>
</table>

and *Escherchia coli*, by antimicrobial agar diffusion test according to reported method [43, 44]. Scanning electron microscopy and electron X-ray diffraction (SEM&EDX) of the treated fabrics was examined using a scanning electron probe micro analyzer (type JXA 840A) Japan. Surface morphologies were imaged at different magnifications, using 30kV accelerating voltage.

**Result and Discussion:**

**Ultraviolet Protection Factor (UPF):**

Recently, UV protection is considering one of the most important functional finishes of textiles. Inorganic UV blockers are more preferable to organic ones, as they are non-toxic and chemically stable under exposure to both high temperatures and UV. Inorganic UV blockers are usually certain semiconductor oxides, such as TiO$_2$, ZnO, SiO$_2$ and Al$_2$O$_3$ [45].

Titanium dioxide nanoparticles (TiO$_2$NPs) has good ultraviolet blocking power and is very attractive in practical applications due to its non-toxicity, chemical stability at high temperature, and permanent stability under UV exposure [46].

Bleached cotton fabrics were pre-treated with moringa leaf extract as natural bioactive materials to impart the fabric dual antimicrobial and sun protective properties. The fabrics were the treated with TiO$_2$NPs and ZnONPs separately as described in the experimental part. The treated fabrics were monitored for UPF analysis. Results obtained are set out in Table 2. UPF of untreated fabrics are set out in the same table for comparison.
Results of Table 2 make it clear that:

1- Treatment of cotton fabric with moringa leaf extract enhances UPF of the fabric from 9 to 50. The latter UPF value represents super protective against UV radiation compared with the untreated fabric, which shows poor protection.

2- Further treatment of the fabrics with TiO₂NPs and ZnONPs separately enhance UPF of the fabric to 59 and 53 respectively. These results indicate that, the effect of both moringa extract and TiO₂NPs and ZnONPs feeding of the UPF properties of each treatment.

3- The ability of moringa leaf extract to enhance UPF of the cotton fabric up to 50 may be attributed to the presence of minerals like Zn, vitamin as well as phenolic compounds in the extract.

Tensile Strength and Surface Properties

Tensile strength and surface properties of the fabrics were monitored before and after treatments. These properties include tensile strength, elongation at break and surface roughness. Results obtained are set out in Table 3: results of Table 3 make it clear that:

1- The tensile strength of the fabrics decreased from 59 kg.f to 52 kg.f after treatment with moringa extract and butantetra carboxylic acid (BTCA). However, the decrement was within the acceptable value and is attributed to the crosslinking effect of BTCA.

2- Results of Table 3 show also that roughness of fabrics treated with moringa extract and TiO₂NPs and ZnONPs was marginally improved which may be attributed to the effect of active component of moringa leaf extract.

Fig. 1. SEM and EDX OF untreated cotton fabrics
Antimicrobial Properties:

In the last two decades, the antimicrobial finishing treatment of cotton fabric gains much attention for customer demand. Imparting antimicrobial properties to the cotton fabrics has dual importance. The first is to protect wearers from harmful microbes whereas the second importance is to protect the fabrics itself from the attack and degradation [47].

The antimicrobial properties of cotton fabrics before and after treatment were examined against gram positive bacteria (\textit{Bacillus subtilis} and \textit{Staphylococcus}) and geram negative bacteria (\textit{E. coli} and \textit{Pseudomonas aeruginosa}). The results were recorded as inhibition zone (mm) and set out in Table 4. The results of Table 4 make it clear that, treatment of bleached cotton fabric with moringa extract impart the fabric higher antibacterial
properties where the inhibition zone increased up to 12 mm. This was observed all kind of bacteria used in the evaluation. Enhancement of antibacterial properties of cotton fabrics after treatment with moringa extract is attributed to the active phenolic compounds and other mineral constitution in the extract[48]. Results of Table 4 clarify also that, further treatment of cotton fabrics with ZnONPs does not greatly affect the antibacterial properties of the fabric whereas treatment with TiO₂NPs reduces the antibacterial properties of the fabrics compared with those fabrics treated with moringa extract.

Surface morphology of cotton fabrics treated with 10%, moringa extract then with 2%, TiO₂ NPs and 1%, ZnO NPs in presence of BTCA as crosslinking agent were examined with SEM and EDX.

Figure 1 shows SEM and EDX analysis of untreated cotton fabrics. Figure 2 shows SEM and EDX analysis of the fabric treated with moringa extract. The moringa extract forms a thin film on the fabric surface showing peaks for calcium and magnesium. Figures 3&4 shows EDX and SEM of the cotton fabrics treaded with moringa extract then with TiO₂NPs and ZnONPs respectively.
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Improving antibacterial and ultraviolet properties of cotton...

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In the initial stage, the cotton fabrics were treated with mango leaf extract as a biologically active material to add antibacterial and UV-blocking properties to the fabric. Two concentrations of 1% and 2% of ZnONP and TiO2NP were used, and the cotton was treated with a four-carboxylic acid using a dry technique. The treated fabrics were evaluated using morphological changes of the fibers under an electron microscope (SEM & EDX), and the physical properties of the fabric, such as tensile strength and softness, were measured. The antibacterial activity of the treated fabrics was also evaluated, in addition to the UV-blocking properties of the treated fabrics.