The present work aims of harnessing nanotechnology as one of the most important frontier sciences to develop the printing of natural cotton fabrics using cationic natural dyes, namely berberine dye to confirm the sustainability of the environment for upcoming generations, decrease pollution resultant from textile printing. In this work, Zinc oxide nanoparticles (ZnO NPs) was applied onto cotton fabric by exhaustion method. Natural dye (berberine dye) and natural thickener (tamarind thickener) are used to produce a natural printing paste for printing cotton fabrics by the flat silk screen printing. In this work, three different methods of treating fabrics were used, which are pre-treatment, simultaneous treatment, and post-treatment with ZnO nanoparticles at varying concentrations. The prepared nanoparticles were analyzed using Scanning electronic microscope(SEM), and transmission, electronic microscope(TEM), tensile strength and elongation, bacterial protection, Color strength K/S values, fastness properties, and Ultraviolet protection factor (UPF) were measured on fabric samples.

The results showed that the K/S values of treated samples were higher than that of the original samples. All treated fabrics have high fastness values for washing, perspiration, rubbing, and light fastness. The antibacterial of all the treated printed fabric samples were higher than those of the blank ones.

**Keywords:** Antibacterial, ZnO nanoparticles, Cotton Fabrics, Berberine Dye, Environmental Materials.

**Introduction**

Textile printing is one of the textile manufacturing processes that causes high water pollution due to unstable color, thickening agent, and other components of printing paste that are released into wastewater needed in developing countries, for irrigation\(^1\). The use of wastewater contaminated with negative health effects on microbial communities in the soil useful\(^2\), and on the germination and growth of plants \(^1\).

Recently, a new trend of natural dyes has emerged mainly due to their environmentally friendly properties, as natural dyes and pigments are found in some plants, animals, insects, bacteria, fungi, and minerals\(^3\).

Cotton is a natural cellulose fibre. The cotton polymer chain consists of several hundred to several thousand units of \(\beta\) (1-4) D-glucose linked together. Cotton is usually dyed with direct and reactive dyes, both of which have anionic properties. Since the fibers assume a negative charge on their surface in an aqueous solution, a large amount of salt is usually required to reduce electrostatic repulsion and promote dye depletion. These salts are not depleted or destroyed but remain in the emptied dye liquid creating a massive environmental problem\(^4\).

Natural cationic dyes can be used to dye jute, acrylic, wool fibers, etc. are easily but there are many problems in using them on cotton fibres,
especially the low affinity and fastness properties of natural dyes towards cotton fibres. To overcome this drawback, anionic active compounds, cross-linking agents, ultrasound energy, metal oxide nanoparticles and enzymes have been used to improve the printability of cotton using natural dyes.

Zinc oxide nanoparticles (ZnO NPs) have been used in an increasing number of industrial products. ZnO NPs have become one of the most widely used metal oxide particles in biological applications since it can provide unique multifunctional properties, such as photocatalytic, self-cleaning, antimicrobial activity, UV protection, flame retardancy, thermal insulation and moisture management, hydrophobicity, and electrical conductivity. In addition to their excellent biocompatibility, bioeconomy, and low toxicity. ZnO NPs have emerged as a promising potential in biomedicine, particularly in the fields of antibacterials, which are involved in their powerful ability to stimulate excess reactive oxygen species (ROS) production, release zinc ions, and induce cell death.

In this study, the roots of Berberis Vulgaris, has been used as a source of a natural colorant named Berberine for printing cotton fabrics. Because of low affinity of the cationic dye to cotton Fiber, the fabric was treatment by 3 different methods with ZnO nanoparticles.

Comparative studies have been conducted for K/S, overall fastness properties, tensile strength, antibacterial activity, etc.

**Experimental**

**Materials**

*Fabrics*: Cotton fabric 100% was supplied from Opera Textiles Co., Cairo, Egypt. Washed with a solution containing 2g/liter non-ionic detergent (TERGITOLTM NP-9 Surfactant), at 60°C and 30 min, then rinsed thoroughly with water and dried with air at room temperature.

*Dye*: natural dye substance Berberine which is only bright yellow natural pigment known in Pyridine based dye category, which is extracted from the roots of Berberies aristata. It was purchased from local market Harraz natural market, Cairo, Egypt.

*Thickeners*: Natural Gum ST 80 is an anionic thickener from (ADGUMS private limited, an exporter of thickener for textile printing). The viscosity 8%, and pH was adjusted to 9-11.

*Other Chemicals*: Urea, Diammonium hydrogen orthophosphate, and all chemicals used in this study were of laboratory grade, and were purchased from El Gamhoria Company, Cairo, Egypt.

**Methods**

**Fabrics treatment methods**

Natural cotton fabrics were treated in three different methods: pretreatment, concurrent treatment and post-treatment with different materials.

**Pretreatment method**

Samples of natural cotton fabrics were treated with different concentrations (0.5%, 1%, 1.5%, and 2% W.O.F) of ZnO nanoparticles, squeezed, and were dried at room temperature then were printed with the natural dyes mentioned above.

**Simultaneous treatment method (single stage)**

In this method of printing and treatment, the materials were made in one step by adding them to the printing paste.

**Post- treatment method**

In this method, the specimens of natural fabric

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**Fig. 1. Benzylisoquinoline Structure in Berberine**

were first printed with natural dyes, and then the printed fabrics obtained were treated with ZnO nanoparticles.

**Treatment of the natural fabrics with ZnO nanoparticles**

**Synthesis of ZnO Nano Particles**

1- Dissolving (5.5 g/l) ZnCl2 (98%) in 200 ml of water at 90 °C in an oil bath.

2- Add 16 ml of 5M NaOH (granules with a minimum of 99%) aqueous solution was added drop wise to the zinc chloride solution with gentle stirring over a period of 10 minutes at 90 °C.

3- Separation of particles from supernatant dispersion by sedimentation.

4- Disposal of the supernatant solution and wash the remaining suspension five times with distilled water to reduce the NaCl concentration to less than 6-10M. Each time, the dilution ratio between the concentrated suspension and the washing solution was approximately 110.

5- Check for complete removal of NaCl from the suspension using AgNO3 solution.

6- the purified particles were then peptized with 2-propanol (98%) in an ultrasound bath for 10 minutes at room temperature as the peptalization process is necessary to inactivate microscopic agglomerations and release nanoparticles of zinc oxide.

7- Particles are collected by centrifugation at 6000 rpm for 15 minutes.

8- Heat treatment of particles at 250 °C for 5 hours leads to formation of zinc oxide.

**Treatment Method by ZnO Nano Particles**

Cotton fabrics were treated with ZnO nanoparticles by exhaustion method with 4 different percentages of ZnO nanoparticles (0.5% - 2% W.O.F) at 80°C for 20 minutes in the presence of a wetting agent in the beaker. The liquor ratio of the bath was 120. After 20 minutes. The treated fabrics were fixed at 140 °C for 10 minutes. Finally, the treated fabrics were washed at 60 °C for 20 minutes, followed by drying.

**Dye Extraction**

Add 100 grams Berberine to 1,000 ml. H2O. Water was boiled for 30 minutes. The solution was cooled and filtered it.

**Preparation of the printing pastes**

The printing paste was prepared according to the following recipe:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural dye (Berberine)</td>
<td>100 g</td>
</tr>
<tr>
<td>Thickener (Tamarind)</td>
<td>67.8 g</td>
</tr>
<tr>
<td>Di-ammonium phosphate</td>
<td>12.5 g</td>
</tr>
<tr>
<td>Urea</td>
<td>40 g</td>
</tr>
<tr>
<td>Water</td>
<td>X g</td>
</tr>
</tbody>
</table>

Total | 1000 g |

Printing technique
The cotton fabrics were printed by flat screen printing. Following printing and drying, the printed fabrics were steamed to 120°C for 20 min. After fixation, all printed samples were washed to remove excess material from the surface of the fabric and to provide stability to the printed material.

The washing process was done as follows:
1. The samples were rinsed in cold water.
2. The samples were washed with warm water.
3. The samples were soaped with a solution containing 2 g/L (TERGITOLTM NP-9 Surfactant) (non-ionic detergent) for 15 min at 60°C.
4. The samples were washed using hot and cold water.
5. The washed samples were allowed to dry at room temperature.

Finally, fabrics were evaluated to measure color strength (K/S), and all fastness properties, antimicrobial properties and tensile strength.

Measurements

Morphological study of ZnO Nanoparticles:
Scanning electron microscope (SEM):
An electron microscope (SEM) was used to scan the surface morphology of printed fabrics treated with ZnO nanoparticles using a scanning electron microscope (SEM), with a JSMT-20, JEOL-Japan.

Transmission Electron microscope (TEM)
TEM was based on the same premise as SEM. Transmission electron microscopy (TEM) was used to analyze the size, morphology, crystalline structure, and chemical composition of a wide range of nanometers (NM). JEOL (TEM-1230, Japan) was used in the transmitter electron microscope.

Measurement of tensile strength and elongation
Tensile strength and elongation tests were carried out on a Tinius Olsen machine (H5KT/130-500) in the context of the ASTM D5035 (Strip Method).

Determination of antibacterial activity of colony forming unit
Antibacterial activities of cotton fabrics treated with ZnO nanoparticles at a concentration of (0.5%, 1%, 1.5%, and 2% W.O.F) were investigated using the colony-forming technique (CFU) for Staphylococcus aureus, and Escherichia coli. The number of viable bacterial colonies on the agar plate for both treated and untreated products was counted and the results of bacterial reduction were reported as per the equation.

\[ R(\%) = \frac{B - A}{B} \times 100 \]

When A corresponds to CFU/ml of the treated sample after 16 hours of incubation and B corresponds to CFU/ml of the non-treated sample after the same incubation period^{10}.

Measurements of color strength (K/S)
The color strength (K/S) of the specimens was evaluated by the light reflectance technique using the Shimadzu UV/Visible spectrophotometer^{11}. K/S in which K and S correspond respectively to the absorption and diffusion coefficients.

Measurements of Fastness properties

UV-protecting properties of printed tissues treated with ZnO nanoparticles
The trial was conducted in accordance with AATCC TM 183-2010.

Results and Discussion

Morphological study of ZnO Nanoparticles
Scanning electron microscopy (SEM) analysis for sample treatment.

The SEM images of untreated fabrics are shown in Fig. 3 (a). Images of fabrics treated with ZnO nanoparticles at the concentration 2% W.O.F (b) in Fig. 3. These images showed that ZnO nanoparticles have been distributed on the surface of the fiber and that the smoothness of the surface has improved. The SEM confirms that ZnO nanoparticles binds well to fibers and not only adheres to the surface, but also penetrates textile deficiencies.

Transmitting electron microscopy (TEM) for ZnO nanoparticles
Transmission Electron Microscopy (TEM) analysis of ZnO nanoparticles revealed that the size of the nanoparticles ranged between 10, and 42nm.
Tensile Strength and Elongation Measurement

The tensile strength test is one of the major sustainability tests of the fabric. The test was carried out on all fabrics treated with ZnO nanoparticles at 2% W.O.F and compared with untreated fabrics. Table 1 gives a summary of the results of the tensile strength and elongation tests for untreated and treated fabrics. The results showed that the tensile strength, and elongation of cotton fabrics treated with ZnO nanoparticles were slight decreases compared to untreated fabrics. That is can be attributed to that increasing in the crosslinking agent concentration induce reduction and crystalline and strength of treated cotton fabrics. The reduction in crystalline contributes greatly to the reduction in interfacial binding strength between the crystalline and the amorphous regions\(^1\).

Determination of antibacterial activity by colony-forming unit

The antibacterial activities of ZnO nanoparticles-treated fabrics at 2% W.O.F were studied using a colony-forming technique (CFU) against Staphylococcus aureus, and Escherichia coli. The results revealed that treated cotton fabrics have excellent antibacterial activity for Staphylococcus aureus, and Escherichia coli.

The activity may be related to the antibacterial mechanism of ZnO nanoparticles is done by direct interaction between ZnO nanoparticles and cell surfaces, which affects the permeability of the membrane as the nanoparticles enter and induce oxidative stress in the bacterial cells, which subsequently inhibition of cell growth and cell death\(^1\).

Effect of biotreatment on Color strength (K/S value) of fabrics

Samples treated with ZnO nanoparticles were subjected to printing using berberine dye was detailed in the experimental dried, steamed and finally were subjected to K/S measurement and all data were embedded in Tables (3, 4, 5) respectively.

It is clear from the data of Tables (3, 4, and 5) that often samples have K/S values higher than that of the untreated blank sample. It is evident from
### TABLE 1. Tensile strength and Elongation of cotton fabrics treated with 2% W.O.F ZnO nanoparticles

<table>
<thead>
<tr>
<th>Treatment material</th>
<th>Type of fabric</th>
<th>Tensile strength @ break kg</th>
<th>Elongation @ break %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Blank</td>
<td>Treated</td>
</tr>
<tr>
<td>ZnO nanoparticles</td>
<td>Cotton 100%</td>
<td>43</td>
<td>40</td>
</tr>
</tbody>
</table>

### TABLE 2. The antibacterial activity of cotton fabrics treated by ZnO nanoparticles

<table>
<thead>
<tr>
<th>Treatment material</th>
<th>Type of fabrics</th>
<th>Sample test</th>
<th>Gram + ve bacteria</th>
<th>Gram – ve bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanoparticles</td>
<td>Cotton</td>
<td>Control</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Treated</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

### TABLE 3. Effect of pretreatment by ZnO nanoparticles on k/s of cotton fabrics printed with beberine dye

<table>
<thead>
<tr>
<th>Type of fabric</th>
<th>Conc.%</th>
<th>K/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton 100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Without</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>0.5%</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>1.5%</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>1.88</td>
</tr>
</tbody>
</table>

### TABLE 4. Effect of simultaneous treatment by ZnO nanoparticles on k/s of cotton fabrics printed with beberine dye

<table>
<thead>
<tr>
<th>Type of fabric</th>
<th>Conc.%</th>
<th>K/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton 100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Without</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>0.5%</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>1.5%</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>2.67</td>
</tr>
</tbody>
</table>

*Fig. 5. Antibacterial activity of cotton fabrics by ZnO nanoparticles*
TABLE 5. Effect of post treatment by ZnO nanoparticles on k/s of cotton fabrics printed with berberine dye

<table>
<thead>
<tr>
<th>Type of fabric</th>
<th>Conc.%</th>
<th>K/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without</td>
<td>2.05</td>
</tr>
<tr>
<td>Cotton 100%</td>
<td>0.5%</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>1.5%</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>1.98</td>
</tr>
</tbody>
</table>

the data that the color strength of simultaneous treatment on cotton fibers with ZnO nanoparticles has high value of color strength than pre and post treatment at concentration 2 % W.O.F. The K/S values were found to have the order of treatment with ZnO nanoparticles simultaneous treatment > posttreatment > pretreatment on cotton fibers.

Effect of biotreatment on Colorfastness of fabrics

The printed samples treated with ZnO nanoparticles by berberine dyes for all treatment method which acquire the highest K/S were chosen and subjected to overall color fastness measurements.

Color Fastness to Washing

Table 6 shows the various fastness categories (washing, rubbing, alkali perspiration, acid perspiration, and lightfastness) of cotton treated printing fabrics using ZnO nanoparticles with berberine natural dye. It is observed that the printed cotton fabrics show good washing fastness with ZnO nanoparticles, where the color change was increase from 4 to 4-5, and staining on cotton was 4-5, and staining on wool showed 4-5.

Color Fastness to Perspiration

The colorfastness to Perspiration of printed samples treated with ZnO nanoparticles showed excellent stability of acidic perspiration and alkaline in discoloration of printed fabrics, also showed excellent stability against staining on cotton and wool fabrics.

Color Fastness to Rubbing

Results of color fastness with rubbing were reported in table 6 as the results indicated high color fastness of rubbing for all printed cotton fabrics treated with ZnO Nano particles. This shows that the majority of the dye molecules are well anchored to the fibers and that the remaining surface dye molecules are minimal. The result may also be that the dye molecules formed bonds between the molecules with the treated material and fabrics as mentioned before.

Color Lightfastness

According to Table 6, the light stability of samples printed with pyrene, and treated with ZnO NPs showed a high light stability, the ROS generated by ZnO NPs causes the degradation of the organic dye in the case of anionic dyes but ZnO NPs is cationic in nature and berberine dye is cationic in nature which makes the interaction between ZnO NPs and dye. Hence, the ROS generator had no degradation of the dye when exposed to light14.

Measurement of UPF Printed Fabrics

The UPF values of all the treated printed fabric samples are higher than those of the blank ones referring to more UV protection. Table 7 showed that Treated printed cotton fabrics showed a slightly increase in UV protection with ZnO Nano particles.

Conclusion

The color strength of simultaneous treatment on cotton fibers with ZnO nanoparticles has high value of color strength than pre and post treatment at concentration 2 % W.O.F. All treated fabrics have high durability values for washing, perspiration and rubbing, as well as excellent resistance to light. The UPF values of all the treated fabrics, printed with berberine dye showed a slightly increase in UV protection with ZnO Nano particles. The results showed that the tensile strength, and elongation of cotton fabrics treated with ZnO nanoparticles were slight decreases compared to untreated fabrics. Berberine dyes were suitable as an antibacterial agent for E. Coli and S. Aureus microorganisms. It is reported that the antimicrobial activities of berberine dye strong which affects the permeability of the membrane as the nanoparticles enter and induce oxidative stress in the bacterial cells, which subsequently inhibition of cell growth and cell death.

TABLE 6. Effect of ZnO nanoparticles on color fastness values of cotton fabrics printed with berberine dye

<table>
<thead>
<tr>
<th>Treatment material</th>
<th>Type of fabric</th>
<th>Treatment method</th>
<th>Con.</th>
<th>Washing fastness</th>
<th>Perspiration fastness</th>
<th>Rubbing fastness</th>
<th>Light fastness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>AL. St. (c)</td>
<td>St. (w)</td>
<td>AL. St. (c)</td>
<td>St. (w)</td>
</tr>
<tr>
<td>ZnO nanoparticles</td>
<td>Cotton 100%</td>
<td>without</td>
<td>0</td>
<td>4</td>
<td>4-5</td>
<td>4</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pretreatment</td>
<td>1.5%</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Simultaneous Treatment</td>
<td>2%</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Post treatment</td>
<td>1%</td>
<td>4</td>
<td>4</td>
<td>3-4</td>
<td>4</td>
</tr>
</tbody>
</table>

Key:
Alt: Color Alteration          St (C): Staining of Cotton           St (W): Staining of Wool

TABLE 7. Effect of ZnO Nano particles on UPF of cotton fabrics printed with berberine dye

<table>
<thead>
<tr>
<th>Treatment material</th>
<th>Type of fabric</th>
<th>Sample test</th>
<th>UPF</th>
<th>As/ nz s4399:1996</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO Nano particles</td>
<td>Cotton 100%</td>
<td>Control</td>
<td>5.1</td>
<td>5.1</td>
<td>138:2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Simultaneous treated</td>
<td>6.6</td>
<td>6.7</td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgements
The authors are grateful to the anonymous reviewers for providing constructive comments.

Conflicts of interest
There are no conflicts to declare and suggestions to improve this article.

Funding Statements
None

References


تحضير جسيمات أكسيد الزنك النانوية وتطبيقاتها في طباعة الأقمشة القطنية بالأصباغ الكاتيونية الطبيعية

منة الله اسامة سعد
قسم طباعة المنسوجات والصباغة والتجهيز - المعهد العالي للفنون التطبيقية - التجمع الخامس - القاهرة - مصر.

يهدف العمل الحالي إلى تسخير تقنية النانو كواحدة من أهم العلوم لتطوير طباعة الأقمشة القطنية الطبيعية باستخدام الأصباغ الطبيعية الكاتيونية، وهي صبغة البربرين تتألف من الأصباغ الطبيعية القطنية، وقابل التلوث النهائي عن طباعة المنسوجات. في هذا العمل، تم تطبيق جزيئات أكسيد الزنك النانوية (ZnO NPs) على نسيج قطني بطريقة الاستنفاذ.

تستخدم الصبغة الطبيعية (صبغة البربرين) والمكثف الطبيعي (مذخو النمر الهندي) لإنتاج معجون طباعة طبيعي لطباعة الأقمشة القطنية عن طريق طباعة الشاشة الحريرية المنحني. في هذا العمل، تم استخدام ثلاث طرق مختلفة لمعالجة الأقمشة، وهي المعالجة السريعة والمعالجة المتزامنة والمعالجة المزدوجة بجزيئات ZnO النانوية بتركيزات مختلفة. تم تحليل الجسيمات النانوية المحضرة باستخدام مجهزات المسح الإلكتروني (SEM) والمجهر الإلكتروني (TEM)، وقياس قوة الشد والمقاومة، والحماية البكتيرية، وقوة اللون، وخصائص اللثبات، وعامل الحماية من الأشعة فوق البنفسجية (UPF) للعينات النسيج.

أظهرت النتائج أن قيم K / S للعينات المعالجة كانت أعلى من العينات الأصلية. جميع الأقمشة المعالجة لها قيم ثبات عالية للغسل والعرق والفرك وثبات الضوء. كانت مضادات البكتيريا لجميع عينات النسيج المطبوعة المعالجة أعلى من تلك الموجودة في العينات الغير معالجة.