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# Fabrication of ZnO Nano Particles Using Sonochemical Method and Applying on Cotton Fabric Using In Situ and Pad-dry-cure Methods

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**Abstract:** ZnO nanoparticles (ZnO-NPs) were prepared by sonochemical method at room temperature and were applied on to the 100 % cotton woven fabric using in situ and pad-dry cure methods. The results show that nanoparticles with average sizes of 20-100 nm with different morphologies have been created on the surface of samples. Synthesis of ZnO-NPs was varied in the morphological transformation by changes in zinc acetate dehydrate concentration. Characterizations were carried out using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Spectrophotometery. The antibacterial activities of the fabrics were assessed semi-quantitatively by the colonies count method. The results show that the finished fabric demonstrated significant antibacterial activity against S.aureus in antibacterial test.

**Keywords:** ZnO nanoparticles, In situ, Antibacterial, Fabric, Pad-dry-cure

## Introduction

In the recent years, much attention has been paid towards creating more comfortable living conditions, especially in reference with health and hygiene matters. For example, fabrics treated with antimicrobial agents are used to suppress bacteria, molds, algae and microorganisms that cause some problems such as corruption, spots, and odor [1-3]. Antimicrobial agents are natural or synthetic compounds that inhibit microbial growth. Various classes of antimicrobial agents are used in the textile industry, most of which are biocides. The use of inorganic material has advanced rapidly due to the amount of work done towards the synthesis and modification of particles for biomedical applications. Many heavy metals and metal oxides either in their free state, or in compounds at very low concentrations, are toxic to microbes. These inorganic materials kill bacteria through various mechanisms, such as by binding to intracellular proteins and inactivating them, generation of reactive oxygen species and via direct damage to cell walls [4-7].

Recently, synthesis of inorganic materials with specific size and morphology have attracted significant attention due to their possible use in different fields [8,9]. Of the inorganic materials, metal oxides such as $TiO_2$, ZnO, MgO and CaO are of particular interest as they are not only stable under harsh process conditions but also are generally regarded as safe materials to human beings and animals [10-12]. The application of nanoparticles to textile materials has been the object of several studies aimed at producing finished fabrics with different performances [13-18]. The use of nanoparticles of silver and zinc oxide has been seen as a viable solution to stop infectious diseases due to the antimicrobial properties of these nanoparticles [10,13,14]. In this nanosized range, they are expected to possess interesting physical properties and pronounced coupling quite different from their bulk counterpart [9]. Zinc Oxide (ZnO) exhibits several unique properties, such as semiconducting and piezoelectric behavior, and it is consequently used in a wide variety of sensors and actuators, ZnO nanostructures have been explored for a wide range of applications in nanoscale and microscale devices, such as generators, sensors, field-emission transistors, ultraviolet photo detectors and in biomedical systems, such as ultrasensitive DNA sequence detectors [19] and dermatological and antibacterial properties [5,6]. Antibacterial effect of ZnO-NPs on textiles has already been shown by various researchers [19-24]. Recently, it is aimed to reduce the number of production steps, energy and costs required for production. It should also be possible to recycle the majority of the chemicals for reuse in the process rather than disposal. There are currently three kinds of nano-ZnO synthesis approaches namely: the Solid, the Solution and the Vapor Phase Methods [5,23]. The Sonochemical Method is a green and feasible technique [19-22], which has been proven to be a useful technique in obtaining novel materials with interesting properties. It is based on acoustic cavitations resulting from the continuous formation, growth and implosive collapse of bubbles in a liquid. This method has so far been used for synthesizing many kinds of nanomaterials [25-28]. In this study, the simple method was used to in situ grow ZnO nanoparticles on the cellulose fiber.

An advantage offered by this method is the mentioned materials are readily available and that their reaction conditions make it possible to accomplish mass production. This method also provides other advantages such as large deposition area, uniform deposits on the objects, desired shapes, and short processing time [20].

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## Experimental

### Material

Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), ethanol and sodium hydroxide have been purchased from Merck Co. The samples used in this investigation are plain woven 100 % cotton fabrics supplied by the Baft Azadi Co. (Tehran, Iran).

### Synthesis of ZnO Nanoparticles

In order to prepare the ZnO nanoparticles, 100 m*l* of NaOH solution with a concentration of 0.1 M was added to 25 m*l* of the 0.05, 0.1, 0.2, 0.4 M solutions of $Zn(CH_3COO)_2 \cdot 2H_2O$ in ethanol solutions at room temperature. This was followed by stirring for 5 minutes.

The mixtures were sonicated for 1hour with 60 W ultrasound power. The generator frequency was 20 Khz. All these process were carried out at room temperature without any specific conditions. Whole of sonochemical process was along with stirring. After one hour ultrasonic treatment, the solutions were heated at a temperature of 75 °C for 1 h until ethanol was evaporated and powders of ZnO-NPs were obtained (Figure 1).

### Characterization of ZnO Nanoparticles

The morphology and size of the prepared ZnO nanoparticles was observed using a Scanning Electron Microscope (SEM) (KYKY, 3200 EM). All of the samples were gold coated before conducting the SEM examination. The X-ray diffraction (XRD) patterns of the product were collected utilizing Cu K$\alpha$ X-ray radiation with a voltage of 40 kV and a current of 30 mA by X'pert pro diffractometer (Philips, Holland). The size of the ZnO nanoparticles estimated from Debye-Scherer formula [29].

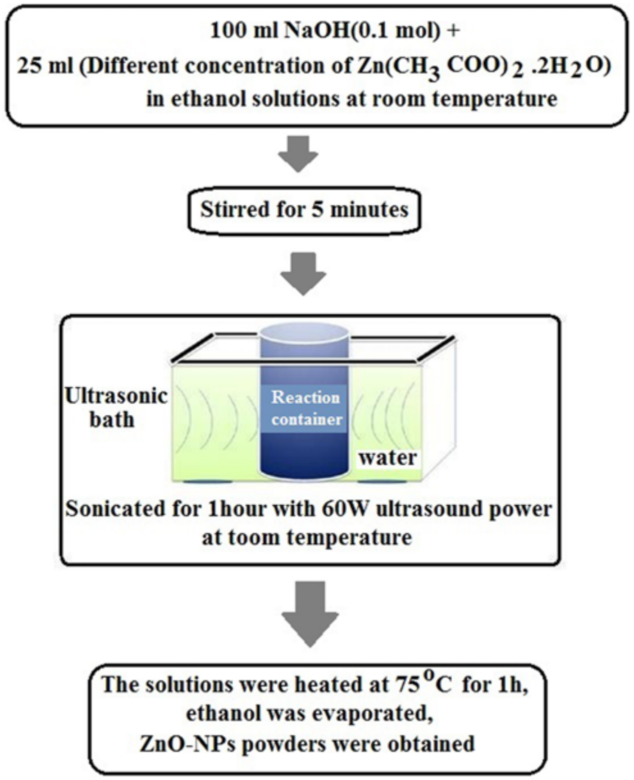


**Figure 1.** Method of preparation of ZnO-NPs using sono chemistry.

### In situ Growth of ZnO Nanoparticles on Cotton Fabrics

All samples of fabrics (10×10 cm$^2$) before treatment were scoured at 80 °C for 30 min by nonionic detergent solution (0.5 g/*l*) in order to remove wax, grease and other impurities. Then these samples were rinsed five times by water and cured in a curing oven (Memmert ULE800 Universal Oven, Germany) at 80 °C for 5 min.

Four pieces of prepared fabrics were added to the mentioned solution of ethanol and zinc acetate dehydrate with different concentrations of 0.05, 0.1, 0.2 and 0.4 M. Then 100 m*l* of sodium hydroxide with a concentration of 0.1 M was added to the solutions at room temperature followed by stirring for 5 min. The mixtures were sonicated for 1 h with 60 W ultrasound power. Whole of sonochemical process was along with stirring.

The cotton fabric was then taken out from the solution, washed three times with DD water (Distilled-Deionized water). The fabric was then dried in the curing oven at 80 °C for 10 min (Figure 2). The specimen was then conditioned for 24 h under a standard condition (humidity: 65±2 %, temperature: 21±1 °C).

### Treatment of ZnO Nanoparticles on Cotton Fabrics Using Pad Dry Cure Method

Immediately after synthesis, ZnO nanoparticles were applied to cotton fabric by a pad-dry-cure method.

Under the Padding Method, aqueous solutions containing 2.0 wt% of synthesized ZnO nanoparticles from different concentration of Zinc acetate (0.05, 0.1, 0.2 and 0.4 M) have been employed. The bath ratio was 1:20 (1 g of fabric in 20 m*l* of ZnO nanoparticle solution). A schematic diagram of a pad-dry-cure process is shown in Figure 3 [30,31].

Cotton fabric was padded with the mentioned solution of ZnO nanoparticles at 70 % wet pickup, dried at 100 °C for

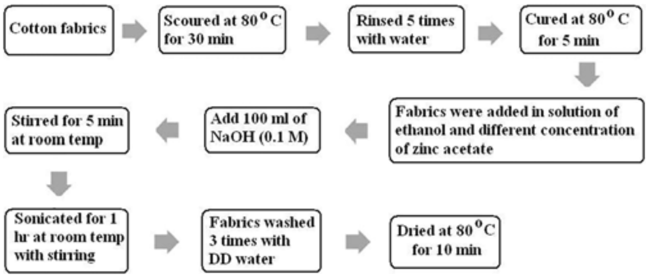


**Figure 2.** In situ coating of cotton fabrics with ZnO-NPs.

5 min, and cured at 140 °C for 3 min. The padded fabrics were washed three times with DD water. The fabric was then dried in the curing oven at 80 °C for 10 min.

### Characterization of ZnO Nano Particle Treated Cotton

The morphology of the fabrics was observed using a SEM (KYKY, 3200 EM). All of the samples were gold coated before conducting the SEM examination. To investigate the optical properties of the samples, optical reflectance measurements were performed using a UV-VIS-NIR spectrophotometer (Varian, Cary 500) in a range of 100 nm to 800 nm. The blank reference was air. The UV profiles of the untreated samples were compared with the spectra collected from the same fabrics treated with ZnO-NPs.

For Bacteria counting test, according to standard AATCC 100-2004, Luria Bertani media (LB) broth was used as growing medium for *Staphylococcus aureus* (gram positive) bacteria. Bacteria were dripped in 10 m*l* of LB broth to reach a cell concentration of $1\times10^8$ (CFU)/m*l*. Then it was diluted to a cell concentration of $1\times10^5$ (CFU)/m*l*. $1\times1$ cm$^2$ fabric sample was cut and put into 1ml bacteria suspension. All samples were incubated for 24 h at 37 °C. From each incubated sample, 100 *μl* of solution was taken and distributed onto an agar plate. All plates were incubated for 24 h and colonies formed were counted. The percentage reduction was determined as follows:

$$\text{Reduction (\%)} = (C-A)/C \tag{1}$$

where $C$ and $A$ are the colonies counted from the plate of the control and treated sample, respectively.

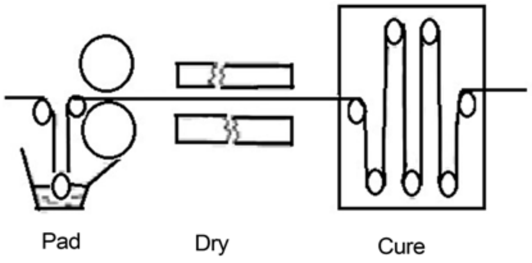


**Figure 3.** The schematic of pad-dry-cure method.

## Results and Discussion

In the present work, ZnO nanoparticles were prepared by sonochemical method at room temperature and were applied on to the 100 % cotton woven fabric using In situ and pad-dry-cure methods.

XRD analysis revealed the presence of the crystalline ZnO nanoparticles on the cotton samples. The XRD pattern of the as-prepared ZnO nanoparticles of 0.05 M showed the presence of broad peaks (Figure 4), the diffraction peaks corresponding to the (010), (002), (012), (110), (013), (112) and (011) planes of sphalerite-type ZnO. The broad peaks indicate that the crystal size is small.

The size of the ZnO nanoparticles estimated from Debye-Scherer formula is 20 nm. The reaction between zinc acetate and sodium hydroxide to form zinc oxide has been shown in Scheme 1.

The morphology, structure and size of prepared nanoparticles were observed using a scanning electron microscope. The SEM images of prepared ZnO-NPs with different concentration of zinc acetate are shown in Figure 5.

Figure 5 indicates that the original morphology of the particles is almost spherical with the diameter varying in sizes ranging from 20 nm to 100 nm. The achieved results are in good agreement with the particle size observed by XRD.

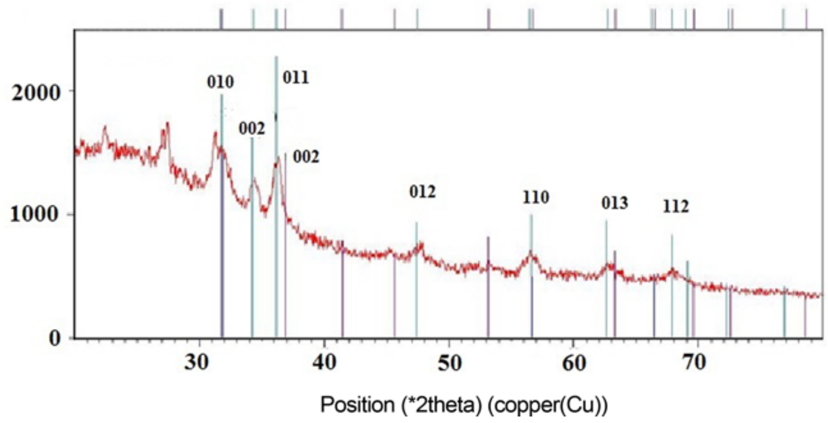


**Figure 4.** XRD patterns of the ZnO nanoparticles in case of using 0.05 M of zinc acetate.

$$\mathrm{Zn(CH_3COO)_2 \,.\, 3H_2O + NaOH} \xrightarrow{\text{Solvent}} \mathrm{Zn(OH)_4^{2-}} \xrightarrow{\text{Under ultrasound power}} \text{Nanoparticles of ZnO}$$

**Scheme 1.** The mechanism of ZnO formation.

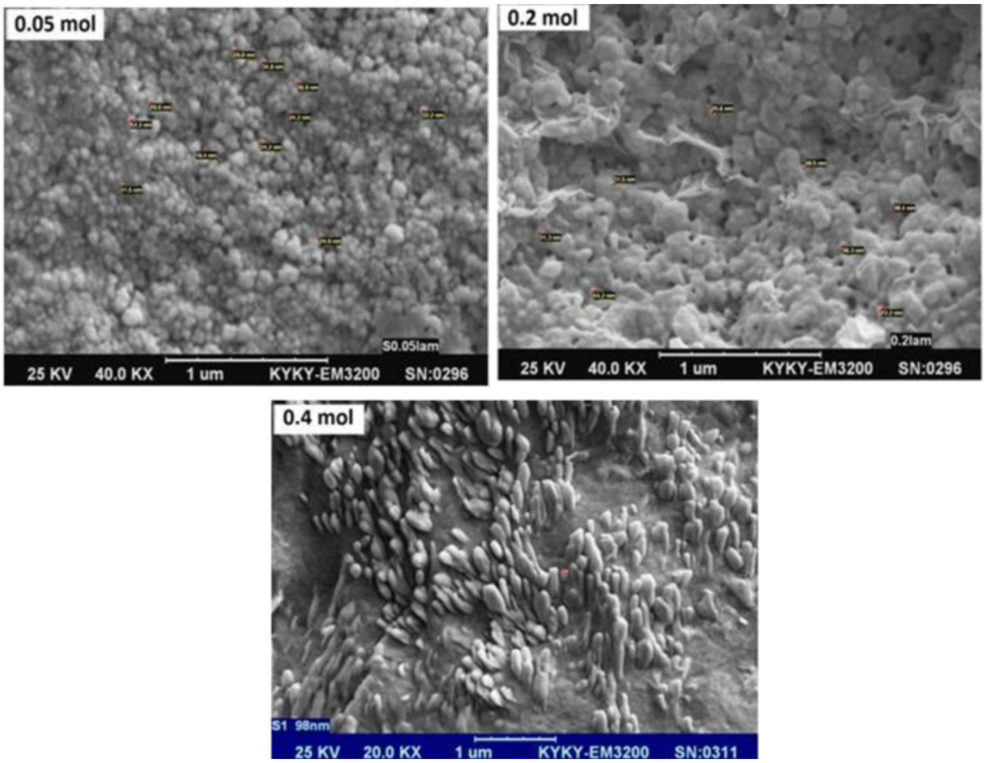
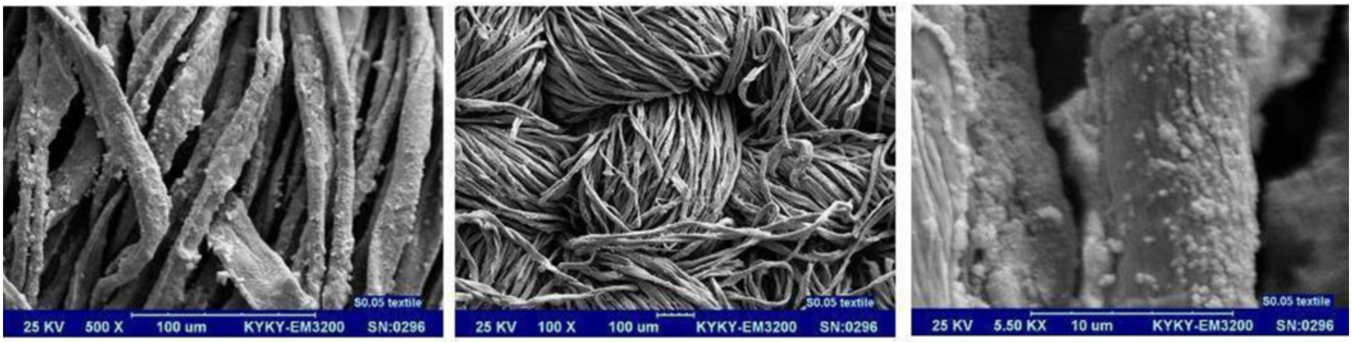
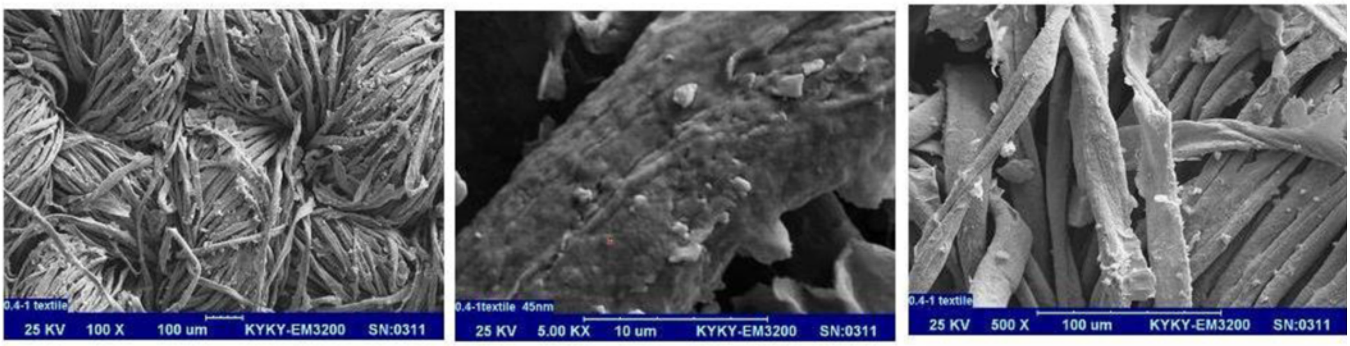


**Figure 5.** SEM images of prepared ZnO nanoparticles.



In situ treated cotton with ZnO-NPs (0.5 M)



In situ treated cotton with ZnO-NPs (0.4 M)

**Figure 6.** SEM images of in situ coated cotton with ZnO-NPs using different concentration of zinc acetate.

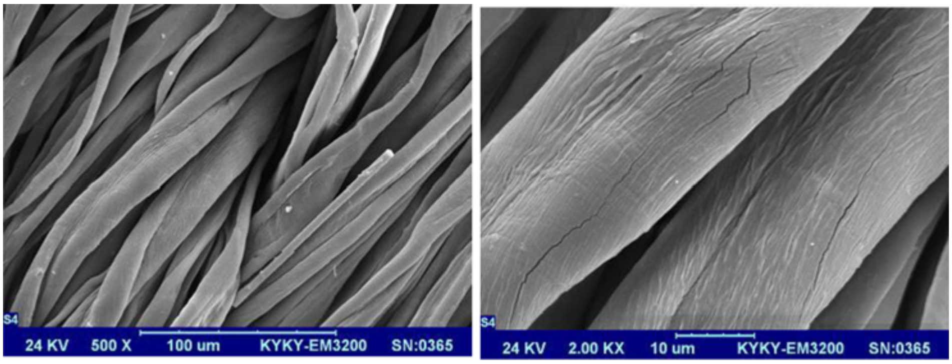
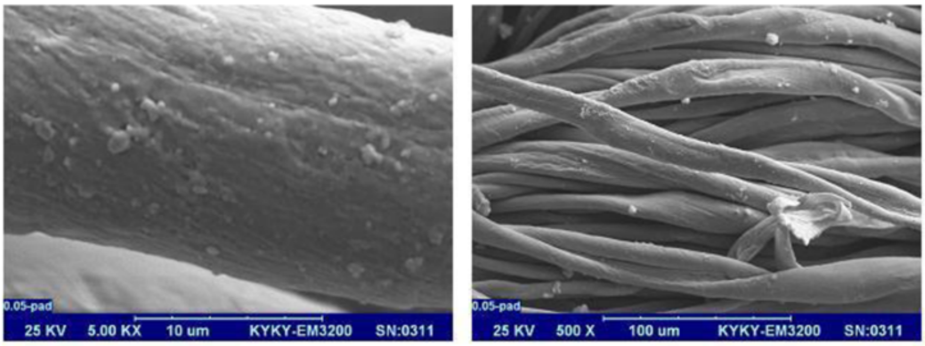
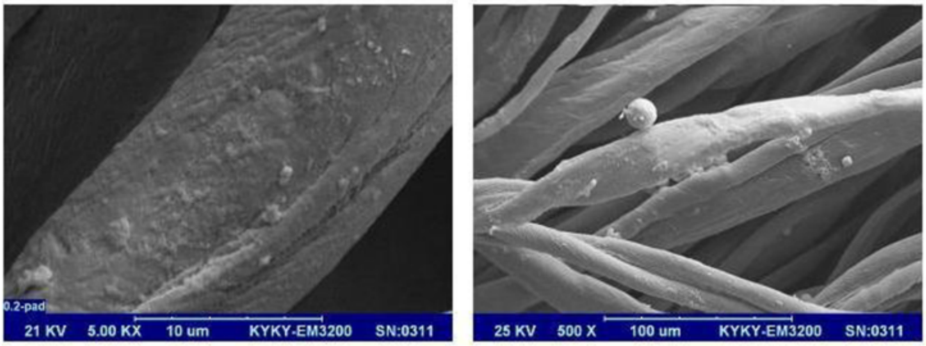


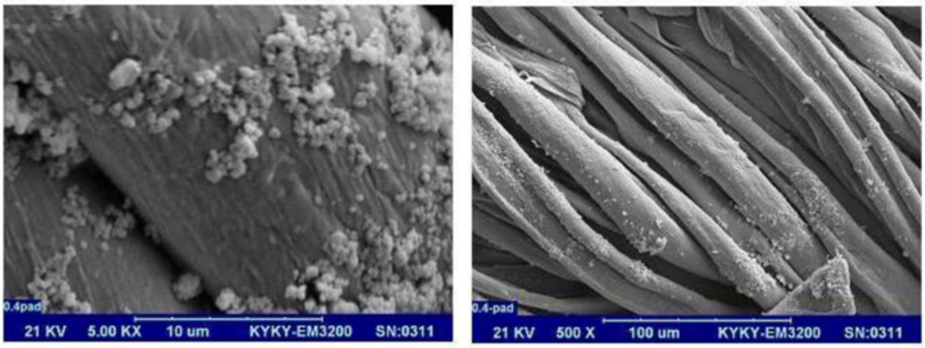
**Figure 7.** SEM images of untreated cotton.



Padded cotton with ZnO-NPs (0.05 M)



Padded cotton with ZnO-NPs (0.2 M)



Padded cotton with ZnO-NPs (0.4 M)

**Figure 8.** SEM images of padded cotton with ZnO-NPs using different concentration of zinc acetate.

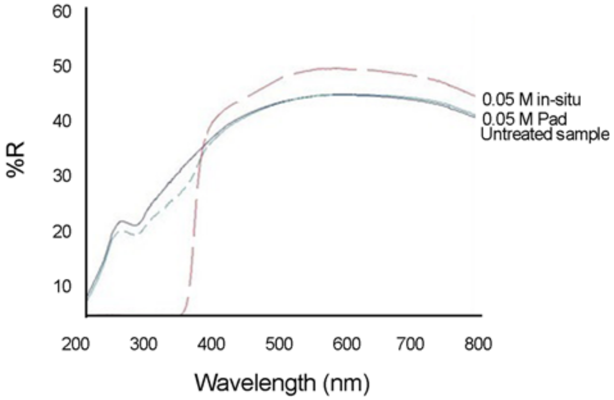


**Figure 9.** Reflection spectrophotometer of the fabric's samples, 0.05 molar.

As it is observed, the size of the particles has become larger due to increasing concentration. The average particle size in case of using 0.05 M of zinc acetate is about 24 nm. By increasing the concentration of zinc acetate to 0.2 M and 0.4M, the average particle size increase to 45 nm and 98 nm, respectively. The SEM images of in situ ZnO-NPs treated cotton with different concentration of zinc acetate are shown in Figure 6. As can be observed, by increasing the concentration of zinc acetate, additional amounts of ZnO-NPs are deposited on the surface of cotton fabric. For comparison, the SEM images of untreated cotton with two different magnifications are shown in Figure 7. The results show that, ZnO-NPs cover the surface of cotton fibers completely. In case of padded fibers with ZnO-NPs, it is seen that, the amounts of nanoparticles are significantly less on the surface of fibers than in situ treated cotton (Figure 8). Increasing the concentration of zinc acetate to 0.4 M, leads to a boost in the number of nanoparticles on the surface of the fabric.

As mentioned in the experimental part, the reflection factor of both untreated and treated fabrics was investigated using reflectance spectrophotometery. The results are shown in Figure 9. As it is seen, the reflection factor for in situ treated cotton in wavelength range of 200 nm to 360 nm is about zero. Apart from transmission and reflection, radiation absorption is one of the ability for textile material. A portion of the UV radiation can be absorbed by the atoms and molecules of fibre and converted into various forms of energy [32]. It demonstrates maximum UV absorption in this area of In situ treated cotton. It should be mentioned that, the reflection factor for prepared ZnO-NPs with zinc acetate concentration of 0.05 M have been studied. The results for padded sample as compared with untreated cotton show that, the reflection factor for padded sample is less than untreated one. It can be concluded that, by applying the ZnO-NPs on cotton fabric, the Ultra Violet Protection Factor improves significantly. It should be mentioned that, In situ treatment is more effective in improving UPF factor of cotton fabric in comparison with the pad-dry-cure method.

UV absorbers refer to the ZnO-NPs which are capable of absorbing the UV in the wavelength range of 290 nm to 360 nm [32].

In fact, very small particles have a higher blocking efficiency. This supports Rayleigh's scattering theory; the intensity of the scattered light varies as the sixth power of the particle size and varies inversely with the fourth power of wavelength [33].

For testing the antibacterial activity of the samples,

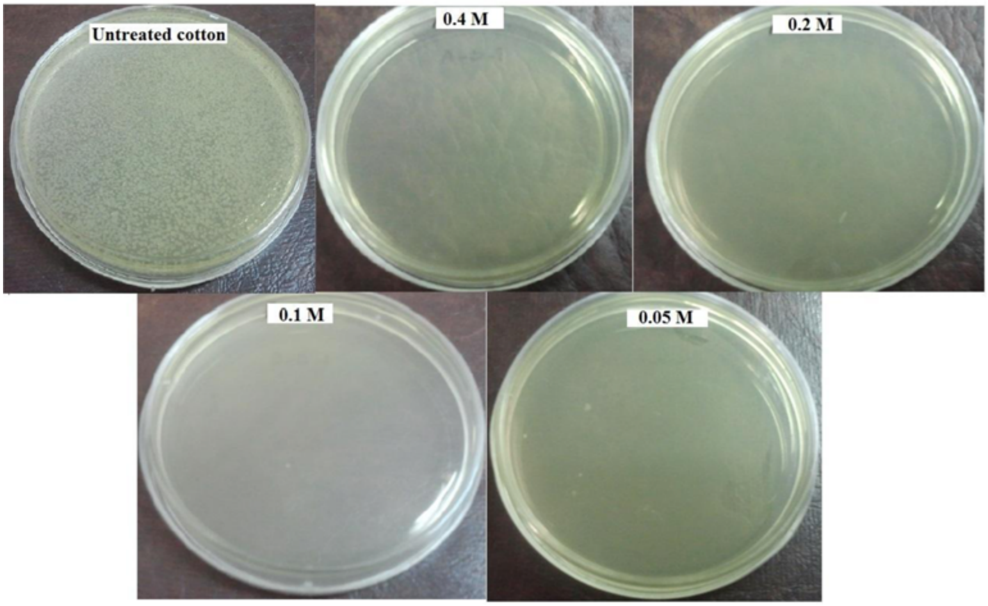


**Figure 10.** Antibacterial activity results for in situ coated fabric with ZnO-NPs.

**Table 1.** Results of bacterial counting test

| Sample | Bacterial reduction (%) |
|---|---|
| Untreated cotton | 6 |
| In situ (0.05 M) | 95 |
| In situ (0.1 M) | 100 |
| In situ (0.2 M) | 100 |
| In situ (0.4 M) | 100 |
| Pad-dry-cure (0.05 M) | 93 |
| Pad-dry-cure (0.1 M) | 100 |
| Pad-dry-cure (0.2 M) | 100 |
| Pad-dry-cure (0.4 M) | 100 |

bacterial counting test has been used. Figure 10 illustrate the test results for the untreated and in situ treated fabric. This control test shows that the untreated fabric does not have any antibacterial properties (Figure 10 (untreated)); On the other hand, the ZnO-NPs treated samples demonstrated strong antibacterial activity. The results in Table 1, show that, by increasing the concentration of zinc acetate more than 0.05 M, 100 % reduction of bacteria can be achieved and both in situ and padded fabrics have very good antibacterial properties.

A study by Yamamoto *et al*. [32], stated that the presence of reactive oxygen species (ROS) generated by ZnO nanoparticles is responsible for their bactericidal activity. Zhang *et al*. further showed that the antibacterial behavior of ZnO nanoparticles could be due to chemical interactions between hydrogen peroxide and membrane proteins, or between other chemical species produced in the presence of ZnO nanoparticles and the outer lipid bilayer of bacteria. The hydrogen peroxide produced enters the cell membrane of bacteria and kills them. It was shown in the study that nano sized ZnO particles are responsible for inhibiting bacterial growth [33-35]. Padmavathy and Vijayaraghavan, further elucidated the bactericidal activity of ZnO nanoparticles. According to them, once hydrogen peroxide is generated by ZnO nanoparticles, the nanoparticles remains in contact with the dead bacteria to prevent further bacterial action and continue to generate and discharge hydrogen peroxide to the medium [36-39]. Our results correspond with the results of the authors above, showing that ZnO nanoparticles applied on to fabrics have an excellent antimicrobial activity. The same results were achieved for padded samples with ZnO-NPs.

## Conclusion

In the present work, ZnO nanoparticles were prepared by the sonochemical method at room temperature and were applied on to the 100 % cotton woven fabric using In-situ and pad-dry-cure methods. The SEM images show that particles have spherical shape with the diameter varying between 20-100 nm. The antibacterial activity of untreated and treated samples was investigated by bacterial counting test method. The results show very strong antibacterial activity for ZnO-NPs on coated sample. However, the effectiveness of antibacterial activity in 0.05 M of coated samples was reduced slightly. The results shows that ZnO-NPs applied on to fabrics are followed by excellent antimicrobial activity. The results related to reflective spectrophotometery show that, the reflection factor of in-situ treated cotton in range of 290-360 nm decrease noticeably. Therefore, it may be concluded that, In-situ treatment is more effective in improving UPF factor of cotton fabric by using ZnO-NPs as compared with the pad-dry-cure method.

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