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Preparation and Characterization of Zinc Oxide Nanoparticles and a Study of the Anti-microbial Property of Cotton Fabric Treated with the Particles

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ABSTRACT

Nanotechnology is an emerging interdisciplinary technology that has been booming in many areas during the recent decade. Nanostructures are capable of enhancing the physical properties of conventional textiles, in areas such as antimicrobial properties, water repellence, soil resistance, antistatic, anti-infrared and flame retardant properties, dyeability, color fastness and strength of textile materials. Studies have been carried out in the present work to fine-tune the properties of zinc oxide nanoparticles for special applications. Soluble starch (stabilizing agent), zinc nitrate and sodium hydroxide (precursors) were used for the preparation of zinc oxide nanoparticles by the wet chemical method. Cotton fabric (honeycomb-weave) was coated with the synthesized nanoparticles and the antibacterial property of the coated fabric was determined. Techniques such as scanning electron microscopy (SEM) and physical and chemical characterization were employed to determine the phase and morphology of the final nanoparticles coated fabric. The results indicate that coated fabric with 2% zinc oxide nanoparticles have high antibacterial efficiency (up to 99.9%). The nanoparticles synthesized in this work have an average size of 50 nm and the physical and chemical properties of the treated fabric are markedly different from those of the untreated fabric.

Keywords: Nanotechnology, nanoparticles, coated fabric, zinc oxide

1. Introduction

Increasing awareness of general sanitation, contact disease transmission and personal protection in general has led to the development of fibers with antimicrobial property. The fibers are engineered to protect wearers against the spread of bacteria and diseases rather than to protect the quality and durability of the textiles they may be converted into. Most of the processes to create antibacterial fibers invariably require the attachment of biocidal or bacteriostatic agents to the fabric surface (Gupta *et al* 2008).

Nanotechnology is an emerging, highly interdisciplinary field, based on the ability to manipulate structural materials on the level of individual atoms and molecules. Research interest in the use of nanotechnology in the textile industry has increased rapidly in recent times. This is mainly due to the fact that textile fabrics constitute one of the best substrates for the application of nanotechnology**.** Nanotechnology is understood as **"**research and technology development at the atomic, molecular or macromolecular levels using a length scale of approximately 1-100 nm in any dimension", including the ability to "control or manipulate matter on an atomic scale" (Kathirvelu *et al* 2008).

Textile goods, especially those consisting of cotton fiber, are normally known to possess large surface area and therefore to provide a conducive environment for bacterial growth. The effect of prolonged bacterial action is to give rise to objectionable odor, dermal infection, product deterioration, allergic responses and other related diseases (Saengkiettiyut *et al* 2008). Textiles made from natural fibers such as cotton are also well known to be more susceptible to microorganisms than the synthetic fibers because they are predominantly hydrophilic in nature. As a result, they are capable of easily holding water, oxygen and nutrients and therefore provide a favorable environment for bacterial growth. The major benefits of antimicrobial finishing of textile materials are (1) to control the onset and spread of disease and (2) to prevent or control the development of odor from perspiration (Rattanawaleedirojn *et al* 2008).

The application of antimicrobial agents to textiles was started a very long time ago. Historical evidence shows that Egyptians used spices and herbs to preserve mummy wraps. German soldiers' uniforms were treated with quaternary ammonium compounds to prevent infection and odour during World War II (Smith and Block 1982). Research initiatives to cause improvement in human life in the context of environmental pollution have led to renewed interest in antibacterial finishing of textiles during the last few decades. Preventive and control measures to combat microbes have permeated into functional textile applications such as hospital and household clothing (Rattanawaleedirojn *et al* 2008). Nanotechnology has attracted global attention because nanoparticles have properties that are unique when compared with their bulk equivalents. Nanoparticles of Ag, CuO and ZnO are being used industrially for several purposes including modifications to textiles, cosmetics, sprays, plastics and paints. A common feature of these three types of nanoparticles is their antimicrobial activity. The antimicrobial activity of nanoparticles has been studied largely with human pathogenic bacteria, mainly *Escherichia coli* and *Staphylococcus aureus* as standard test strains (Gajjar *et al* 2009).

Zn is an essential element for cells; levels of Zn above the essential threshold level inhibit bacterial enzymes including dehydrogenase and certain protective enzymes, such as thiol peroxidase, and glutathione reductase. It has been suggested that the respiratory chain of *E. coli* is impeded by the Zn inhibition of NADH oxidase. Additionally, it has been reported that loss of membrane potential is associated with inhibition by Zn ions at cytochrome c oxidase in *Rhodobacter sphaeroides* (Gajjar *et al* 2009). ZnO is a bio-safe and biocompatible material and can be directly used for biomedical applications without coating. Due to the novel and exceptional properties of ZnO, much effort has been directed to the fabrication of ZnO with interesting morphologies and assemblies (Hussain *et al* 2006). The purpose of this study is firstly to examine the antibacterial activity of cotton fabric coated with zinc oxide nanoparticles against *Staphylococcus aureus* and *Escherichia coli*, which are the microbes commonly occurring in household and hospital environments and next to physically and chemically characterize the nanoparticles containing cotton fabric.

2. Materials and Methods

2.1 Synthesis of zinc oxide nanoparticles

Chemicals have been obtained from Himedia Laboratories, Mumbai, India and these are of the highest purity available. A typical procedure for making nano-zinc oxide particles is as follows. The zinc oxide nanoparticles were prepared by wet chemical method as discussed by Yadav *et al.*, (2006) using zinc nitrate and sodium hydroxide as precursors and soluble starch as stabilizing agent. 0.1% starch solution was prepared using a microwave oven. 0.1 mol of zinc nitrate was added to the above solution. The resulting solution was then kept under constant stirring using a magnetic stirrer to completely dissolve the zinc nitrate. After complete dissolution of zinc nitrate, 0.2 mol of sodium hydroxide solution was added carefully drop-wise along the side walls of the solution vessel with the solution under continuously stirring. The reaction was allowed to proceed for 2 hr after complete addition of sodium hydroxide. After completion of reaction, the solution was allowed to settle overnight. The supernatant liquid was then carefully decanted and the remaining solution was centrifuged at 10,000 x g for 10 minutes. The nanoparticles that resulted were then washed three times using distilled water. Washing was carried out to remove the by-products and any starch bound to the nanoparticles. The washed nanoparticles were dried overnight at 80 ˚C. Drying causes the complete conversion of $Zn(OH)_2$ to ZnO.

2.2. Coating of cotton fabrics with zinc oxide nanoparticles

A fine-medium weight 100% cotton fabric (Honeycomb weave, Ends/inch: 46, Picks/inch: 43) was used for the purpose. Zinc oxide nanoparticles were applied to the fabric by the pad-dry-cure method. The cotton fabric, cut to a size of 30 x 30 cm, was immersed in a solution of 2% zinc oxide nanoparticles for 5 min and then passed through a padding mangle run at a speed of 15 m/min and a mangle pressure of 15 kgf/cm^2. The padded fabric was air-dried and then cured for 3 min at 140 ˚C. The coated fabric was then immersed for 5 min in 2 g/l of sodium lauryl sulphate to remove any unbound nanoparticles. The fabric was next rinsed 10 times to completely remove any traces of soap. The fabric was finally dried in ambient air.

2.3. Evaluation of antibacterial activity

The antimicrobial activity was quantitatively evaluated against *Staphylococcus aureus* (ATCC 6538), a Gram-positive organism and *Escherichia coli* (ATCC 8739), a Gram-negative organism in accordance with AATCC 100 test method. Fabric samples of 4.8±0.1 cm diameter were placed in a 50-ml conical flask with 0.5 ml of bacterial inoculums. After incubation over contact periods of 24 hr, the solution was serially diluted. The diluted solution was placed on a nutrient agar and incubated for 24 hr at 37±2°C. Colonies of bacteria recovered on the agar plate were counted and the percent reduction of bacteria (R) was calculated using the following equation:

$$R(\%) = (B - A) \times 100 / B$$

where A is the number of bacteria colonies from treated specimen after inoculation over 24 hr contact period and B is the number of bacteria colonies from untreated control specimen after inoculation at 0 contact time.

2.4. Characterization of zinc oxide nanoparticles finished fabric

The surface topography of zinc oxide nanoparticles finished fabric was observed with a scanning electron microscope (SEM). The physical properties of the finished fabric were determined and the values compared with those of the unfinished fabric which served as the control fabric.

3. Results and discussion

Zinc oxide nanomaterials have some excellent properties like exceptional mechanical strength and good antistatic, antibacterial and UV absorption properties (Yadav *et al.*, 2006). The antimicrobial activity of the fabric containing zinc oxide nanoparticles against the stated microorganisms are shown in Table 1 and the related photographs are included in Figure 1. The treated fabric displays very high activity with >99.99% reduction of bacteria. As per AATCC standards, the fabric showing maximum activity either against gram-positive organism or gram negative organism can be validated to have excellent antibacterial property though the activity against the other tested organism is little less than the maximum.

Table 1: Antimicrobial activities of cotton fabric containing zinc oxide nanoparticles against microorganisms (AATCC 100 test method)

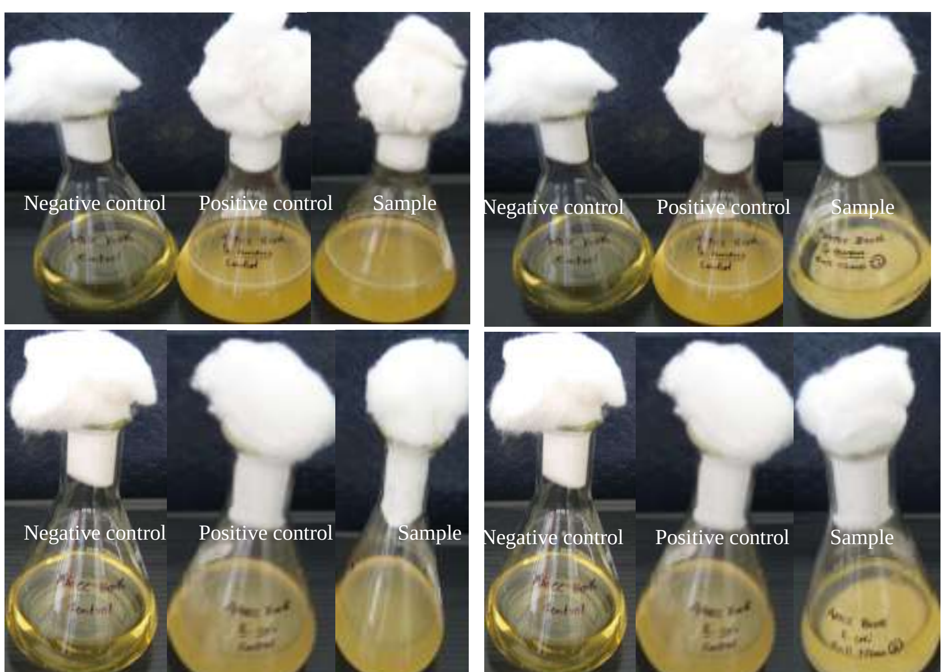
Test organism	**A. Bacterial count (cfu/ml) after 24 hours**		**% Reduction**
	Control sample	**Treated sample**	
Staphylococcus aureus	**10×10^7**	**30×10^2**	**> 99.99**
Escherichia coli	**11×10^7**	**22×10^6**	**80.00**

Figure 1: Photos of Antimicrobial activity (% Bacterial reduction) of cotton fabric finished with zinc oxide nanoparticles (AATCC 100 test method)

Control sample **Treated sample**

Staphylococcus aureus

Escherichia coli

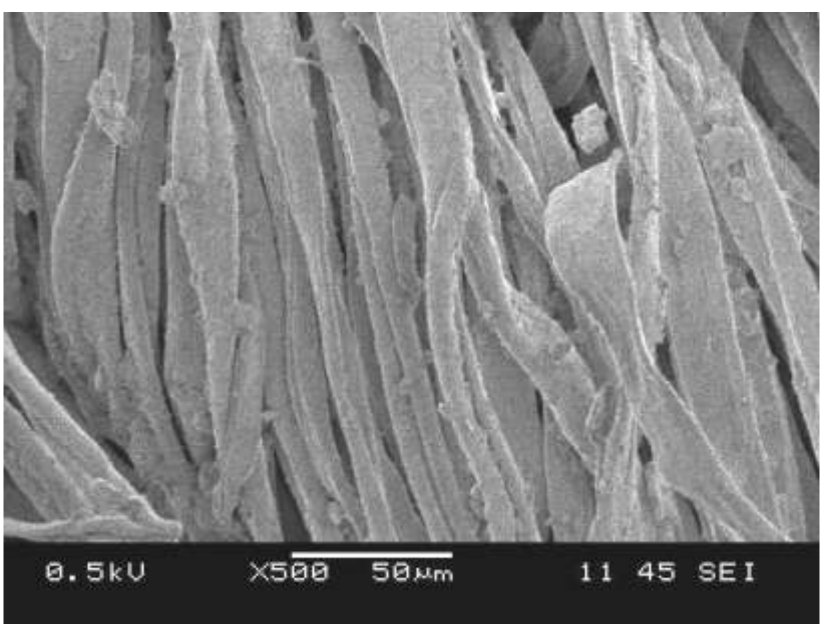


The dominant mechanisms of such antibacterial behavior are found to be either or both of chemical interactions between hydrogen peroxide and membrane proteins, and the chemical interactions between other unknown chemical species generated due to the presence of zinc oxide nanoparticles with the lipid bilayer (Zhang *et al* 2009).

The antibacterial activity of the zinc oxide is mainly by the generation of highly reactive species. The generation of highly reactive species such as OH^-, H_2O_2 and O_2^{2-} is explained as follows. Since both UV and visible light can activate ZnO with defects, electron-hole pairs ($e-h^+$) can be created. The holes split H_2O molecules (from the suspension of ZnO) into OH^- and H^+. Dissolved oxygen molecules are transformed to superoxide radical anions ($\bullet O^-_2$), which in turn react with H+ to generate ($HO_2\bullet$) radicals, which upon subsequent collision with electrons produce hydrogen peroxide anions (HO_2-). They then react with hydrogen ions to produce molecules of H_2O_2. The generated H_2O_2 can penetrate the cell membrane and kill the bacteria. Since, the hydroxyl radicals and superoxides are negatively charged particles, they cannot penetrate into the cell membrane and must remain in direct contact with the outer surface of the bacteria; however, H_2O_2 can penetrate into the cell. Considering the size of the bacteria, it is evident that a single isolated colony of *E. coli* of 2 μm diameter can accommodate a large number of ZnO. Once ZnO kills/captures the cell membrane, the ZnO nanoparticles presumably remain tightly adsorbed on the surface of the leftover/dead bacteria preventing further bacterial action. However, ZnO nanoparticles continue to release peroxides into the medium even after the surface of the dead bacteria are completely covered by ZnO nanoparticles, thereby showing high bactericidal efficacy (Padmavathy and Vijayaraghavan 2008).

The surface appearance of zinc oxide nanoparticles finished fabric is shown in Figure 2 depicting a scanning electron micrograph. The micrograph shows that the zinc oxide nanoparticles are well distributed on the cotton fiber surface. Further observations revealed that the size of the zinc oxide nanoparticles coated on the fabric was in the nanoscale range. From the figure 2, it is clear that the size of the cotton fibers is in the range of 50 μm, but the size of the nanoparticles coated on the fabric is much smaller i.e., nanoscale level, in the range of 50 nm.

Figure 2: SEM of zinc oxide nanoparticles coated cotton fabric



The physical properties of the nanoparticles coated fabric were compared with those of the uncoated fabric (Table 2). The results indicate that the coated fabric has only 80% and 85% respectively of its original warp-way and weft-way tensile strength. The fabric also suffers a drop in tear strength, but the loss is much lower, the corresponding fall being 7% and 6% respectively. The abrasion resistance is also comparatively less. There is a marginal increase in the dimensional stability ranging about 7.2% in the warp and 4% in the weft directions respectively. There was only a minimal change in the pilling resistance. Thus the general mechanical behavior of the coated fabric appears to be reduced.

Table 2: Physical characteristics of the uncoated and zinc oxide nanoparticles coated fabric

S. No.	Physical properties		Uncoated fabric	Fabric coated with zinc oxide nanoparticles
1.	Tensile strength		Warp: 20.1 kgf (197 N) Weft: 22.7 kgf (222 N)	Warp: 15.7 kgf (154 N) -21.9 Weft: 19.3 kgf (189 N) -15
2.	Tear strength		Warp: 3584 g (35.1 N) Weft : 6003 g (58.8 N)	Warp: 3326 g (32.6 N) -7% Weft : 5632 g (55.2 N) -6%
3.	Resistance to abrasion		No breakdown of the specimen up to 15000 cycles	End point reached at 5000 rubs
4	Resistance to pilling	**No. of cycles**	**B. Rating**	**Rating**
		125	4-5 (slight surface fuzzing to no change)	4 (slight pilling)
		500	4 (slight surface fuzzing)	4 (slight pilling)
		1000	4 (slight surface fuzzing)	4 (slight pilling)
		2000	4 (slight surface fuzzing)	3-4 (Moderate to partially formed pills)
5.	Dimensional stability		Single wash (-) Shrinkage Warp: (-) 14.0% Weft : (-) 8.4 %	Single wash (-) Shrinkage Warp: (-) 6.8% Weft : (-) 4.4 %

The ZnO nanoparticles used in this work have been found to be about 50 μm in size and cotton fibers are known to be about 10 to 25 μm in width. It is likely that the nanoparticles reduce the free movement of the cotton fibers in the fabric during the mechanical action resulting from the tensile or tearing tests. This would cause a reduction in the load-bearing elements at any given time during the tests. The overall effect is to reduce mechanical performance.

Considering that the ZnO-nanoparticle coated fabric is intended for use mainly for its functional property of anti-microbial resistance, its lower resistance to mechanical forces may not really be a disadvantage. Hospital-wear for example, for which this coated fabric would be ideally suited, will normally be passed through a much lower life-cycle compared with that for a regular garment meant for everyday use. The big advantage of the coated fabric is the fact that it displays excellent resistance to bacteria, a factor of prime importance for hospital-wear.

4. Conclusion

In conclusion, it may be stated that the application of nano zinc oxide particles to cotton fabric imparts to it the functional property of antibacterial resistance. About 99.99% antibacterial activity was observed against *Staphylococcus aureus* and 80% against *Escherichia coli*. The SEM analysis reveals that the size of the nanoparticles is about 50 µm. The resistance of the fabric to mechanical forces is visibly reduced, but not to the extent that the fabric is rendered useless for the intended functions.

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