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In situ formation of silver nanoparticles for multifunctional cotton containing cyclodextrin

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ABSTRACT

This research presents new approach for functionalization of cotton fabrics against antibacterial. It comprises: (a) synthesis and characterization of two polymeric products that can referred to as reactive copolymer (monochlorotriazinyl-β-cyclodextrin grafted with acrylic acid AA, MCT-βCD-g-PAA) and normal copolymer (β-cyclodextrin grafted with acrylic acid AA, βCD-g-PAA), (b) reacting cotton with the reactive copolymer (c) treatment of the chemically modified cotton so-obtained with silver nitrate, (d) *in situ* reduction of silver ions using either the copolymer (βCD-g-PAA) or a conventional reducing agent, namely, sodium borohydride, and (e) monitoring the antibacterial activity and resilience properties of the modified cotton fabrics. FTIR, SEM, and X-ray diffraction were employed to prove the structure of the synthesized polymeric products as well as micro structural changes in cotton cellulose as a result of the aforementioned treatments. The finished fabrics displayed superior antibacterial activity along with good fabric stabilization as indeed by fabric resilience.

1. Introduction

The growing demand for comfortable, clean, and hygienic textile goods has provoked an urgent need for production of antimicrobial textile goods. Nowadays significant development in new technologies can meet the increased needs of consumers in terms of health and hygiene without compromising issues related to safety, human health, and the environment (Dastjerdi & Montazer, 2010).

Bacteria, both pathogenic and odor-causing, interact with fibers in several phases including the initial adherence, subsequent growth, damage to the fibers, and dissemination from them. The attachment of bacteria to fabrics is dependent upon the type of bacteria and the physicochemical characteristics of the fabric substrate. Microbial adherence is also affected by the substrate and bacterial cell wall hydrophobicity (Morones et al., 2005; Russell & Hugo, 1994). The retention has been shown to depend on the duration of contact between the fabric and microbe. By and large, the rougher the surfaces, the greater the retention (Dastjerdi, Mojtahedi, & Shoshtar, 2009). Cotton, wool, jute, and flax are reported to be most susceptible to microbial attack (Cheung, Ho, Lau, Cardona, & Hui, 2009).

Antimicrobial agents act in various ways. The main modes of action are (Cheung et al., 2009): (i) protein coagulation; (ii) disruption of cell membranes resulting in exposure, damage, or loss of the contents; (iii) removal of free sulphydryl groups essential for the functioning of enzymes; and (iv) substrate competition. A compound resembling the essential substrate of the enzyme diverts or misleads the enzymes necessary for the metabolism of the cell and causes cell death.

Silver kills bacteria by strangling them in a warm and moist environment (Ravindra, Murali Mohan, Narayana Reddy, & Mohana Raju, 2010). Highly bioactive silver ions bind with proteins inside and outside bacterial cell membranes, thus inhibiting cell respiration and reproduction. Silver is 3–4 times more active at pH 8 than at pH 6. Silver products are effective against bacteria but not as effective against other organisms like fungi, mold, and mildew; they can be used with polyester where many other products cannot. Alginate and chitosan have also been used to make novel antimicrobial materials in combination with silver (Ravindra et al., 2010).

Silver, both as a metal and in ionic form, exhibits strong cytotoxicity toward a broad range of microorganisms, and its use as an antibacterial agent is well known (Pollini, Russo, Licciulli, Sannino, & Maffezzoli, 2009). It has been reported that the mode of antibacterial action of silver nanoparticles is similar to that of silver ion. However, the effective biocidal concentration of silver nanoparticles is at a nanomolar level in contrast to a micromolar level of silver ions (Hyung, Bo, & Young, 2010; Hebeish, El-Shafei, Sharaf, & Zaghloul, 2011). Nano-silver particles have an extremely large specific surface area, thus increasing their contact with bacteria or fungi and vastly improving their bactericidal and fungicidal effectiveness.

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The present research is undertaken with a view to functionalize cotton fabrics against bacteria. To achieve the goal, the fabrics were reacted cyclodextrin–polyacrylic acid copolymer which newly synthesized. Specifically the copolymer was prepared through grafting of monochlorotriazinyl-β-cyclodextrin with polyacrylic acid MCT-βCD-g-PAA using $K_2S_2O_8$ as initiator. The so-obtained chemically modified cotton was immersed in silver nitrate solution followed by reduction of the silver ions to silver nanoparticles. Reduction was effected either another newly prepared copolymer named β-cyclodextrin grafted with acrylic acid βCD-g-PAA or conventional reducing agent, namely, sodium borohydride. Finished fabrics were monitored for antibacterial activity, and resilience properties.

2. Experimental

2.1. Materials

Monochlorotriazinyl-β-cyclodextrin, referred to here as reactive β-cyclodextrin (MCT-βCD), and β-cyclodextrin (βCD) were provided by Waker Chemie GmbH, Germany. The chemicals acrylic acids (AA), potassium persulphate ($K_2S_2O_8$) sodium borohydride, sodium hydroxide, acetic acid, hydrochloric acid, sodium carbonate, were of laboratory grade.

2.2. Methods

2.2.1. Synthesis of β-cyclodextrin grafted with acrylic acid (βCD-g-PAA)

Graft polymerization of βCD with AA was carried out in 100 ml stopper flask 5 g of βCD was firstly dissolved in 25 ml of water as desired, then 2.5 ml AA monomer was added and the flask placed in thermostatic water bath adjusted at 65 °C. The initiator 0.025 mole/l $K_2S_2O_8$ was introduced in the flask containing βCD and AA. At this end the polymerization reaction was allowed to proceed for 60 min at 65 °C. After the desired time, the contents of the flask (polymerization mixture) were poured in a large amount of ethyl alcohol where a precipitate was formed. The precipitate was filtered, washed thoroughly with acetone, and dried at 50 °CC.

2.2.2. Synthesis of monochlorotriazinyl-β-cyclodextrin with polyacrylic acid (MCT-βCD-g-PAA)

Similar to the above synthesis, 5 g MCT-βCD was firstly dissolved in a 25 ml of water as desired then 2.5 ml of AA monomer was added and the flask placed in thermostatic water bath adjusted at 65 °C. The initiator 0.025 mole/l $K_2S_2O_8$ was introduced in the flask containing MCT-βCD and AA. At this end the polymerization reaction was allowed to proceed for 60 min at 65 °C. After the desired time, the contents of the flask (polymerization mixture) were poured in a large amount of ethyl alcohol where a precipitate was formed. The precipitate was filtered, washed thoroughly with acetone, and dried at 50 °C.

2.2.3. In situ formation of silver nanoparticles within cotton fabric containing MCT-βCD-g-PAA

An aqueous solution of silver nitrate was prepared by dissolving 15 mg in 30 ml distilled water. In this solution, dry pre-weighed piece of cotton fabric containing 3% MCT-βCD-g-PAA was immersed for 1 h, followed by padding (squeezing), then subjected to reduction by using either βCD-g-PAA or sodium borohydride during fixation at 130 °C for 5 min. The fabric acquired dark brown color indicating formation of silver nanoparticles within the molecular structure of cotton cellulose of the fabric.

It is not out of place that the dark brown color of the fabric might be a limiting factor for use as decorative clothing materials; this preparation of Ag-loaded fabric can be used as universal antiseptic substrate for clinical application. In addition, this process can be used for the fabrication of antibacterial surgical gloves and pads face masks.

2.3. Testing and analysis

2.3.1. Infrared spectroscopy (IR)

FTIR spectroscopy was measured using FT-IR–FT-Raman, model: Nexus 670 (Nicollet-Madison-WI-USA). Cotton fabric was cut into very small pieces; these pieces were mixed with KBr. The spectral range was 400–4000 cm^{-1}.

2.3.2. X-ray diffraction

X-ray diffraction patterns of samples were recorded on a STOE STADI P transmission X-ray powder diffractometer system by monitoring the diffraction angle from 5 to 65 (2 h) using monochromatized Cu Ka (k = 1.54051 Å) radiation.

2.3.3. Scanning electron microscopy measurements

Microscopic investigations on fabric samples were carried out using a Philips XL30 scanning electron microscope (SEM) equipped with a LaB6 electron gun and a Philips-EDAX/DX4 energy-dispersive spectroscope (EDS). Images were taken at different magnifications (from 1500 to 30,000), using secondary electrons (SE) in accordance with the clarity of the images. Fabric samples were fixed with carbon glue and metalized by gold vapor deposition to record images.

2.3.4. Antibacterial tests

All antibacterial activity tests were done in triplicate to ensure reproducibility. The antibacterial activity of fabric samples was evaluated against *Escherichia coli* and *Staphylococcus aureus*, (ATCC 1533) bacteria using disk diffusion method. A mixture of nutrient broth and nutrient agar in 1 L distilled water at pH 7.2 as well as the empty Petri plates were autoclaved. The agar medium was then cast into the Petri plates and cooled in laminar airflow. Approximately 105 colony-forming units of *E. coli* bacteria were inoculated on plates, and then 292 cm^2 of each fabric samples was planted onto the agar plates. All the plates were incubated at 37 °C for 24 h and examined if a zone of inhibition was produced around samples.

3. Result and discussions

In this work, a new approach is undertaken to impart antibacterial to cotton fabrics. The approach comprises: (a) synthesis and characterization of two polymeric products which can referred to as reactive copolymer (MCT-βCD-g-PAA), and normal copolymer (βCD-g-PAA), (b) reacting cotton with the reactive copolymer (c) treatment of the chemically modified cotton so-obtained with silver nitrate, and (d) *in situ* reduction of silver ions using the normal copolymer *vis-à-vis* a conventional reducing agent, namely, sodium borohydride. Beside enhancing the opening up and swell-ability of the cotton fabric, which are essential for diffusion and adsorption of silver nanoparticles, the chemically attached copolymer bears cyclodextrin (CD) thereby providing additional centers for agglomeration and accommodation of silver nanoparticles. Results of these studies along with appropriate discussion are given hereunder.

3.1. Characterization of MCT-βCD-g-PAA and βCD-g-PAA

The characterization of the graft copolymer in question was made using FTIR spectroscopy and the spectra obtained therefrom are shown in Fig. 1a and b. It is seen that new peaks at 1720 cm^{-1} and 1750 cm^{-1} appear in spectra indicating the presence of —COOH in the backbone of either MCT-βCD-g-PAA or β-CD-PAA, respectively.