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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.

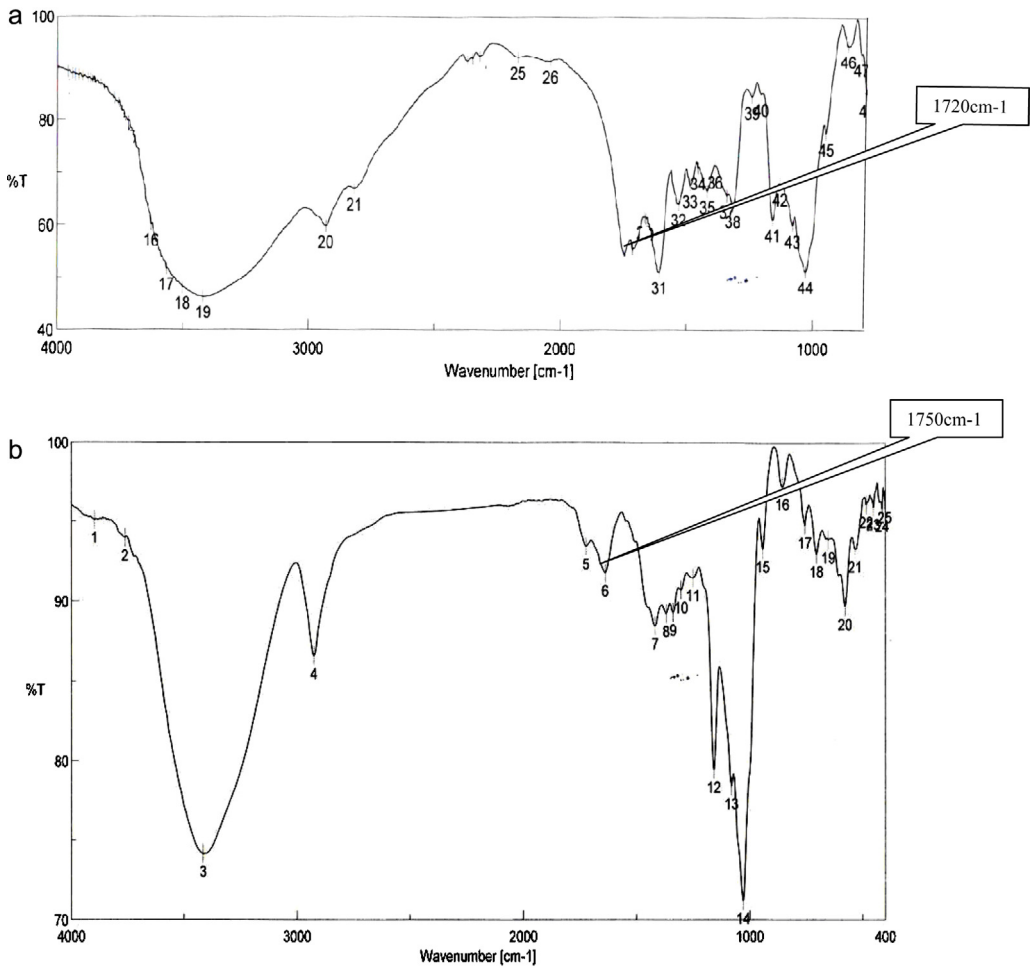


Fig. 1. (a) FTIR spectroscopy of reactive cyclodextrin-polyacrylic acid copolymer (MCT-βCD-g-PAA). (b) FTIR spectroscopy of beta cyclodextrin-polyacrylic acid copolymer (βCD-g-PAA).

Fig. 2a and b show the differences in particle shape of the blank (reactive cyclodextrin) MCT-βCD (Fig. 2a) and reactive copolymer MCT-βCD-g-PAA, in (Fig. 2b) as highlighted by SEM. In these pictures, high particle massing of PAA graft appears as compact particles.

Fig. 3a and b show the scanning electron microscopy of the prepared normal copolymer. These figures show the differences in particle shape of the blank (β-cyclodextrin) β-CD in (Fig. 3a) and normal copolymer βCD-g-PAA in (Fig. 3b) as highlighted by SEM. Here too, high particle massing of PAA graft appears as compact particles.

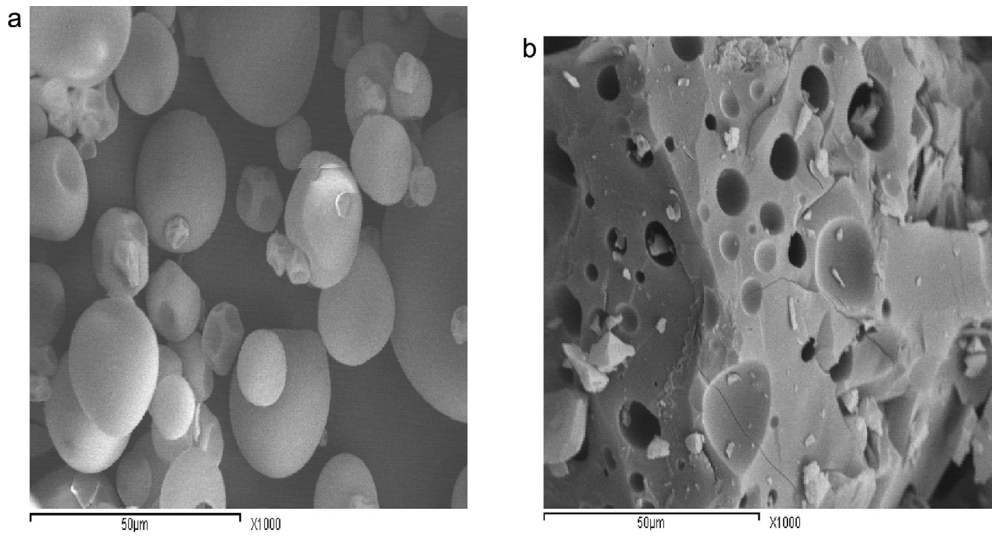


Fig. 2. (a) SEM of MCT-βCD. (b) SEM of MCT-βCD-g-PAA.

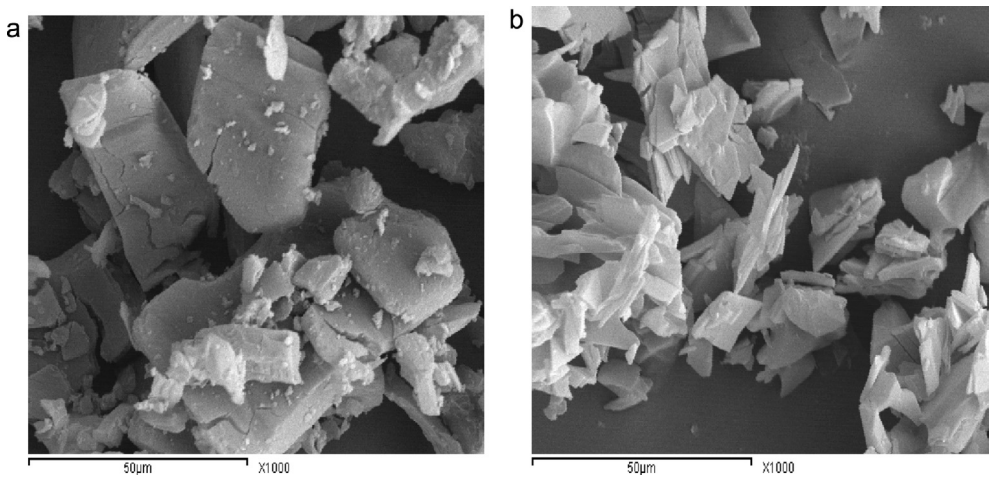


Fig. 3. (a) SEM of β-CD. (b) SEM of βCD-g-PAA.

3.2. Nanosilver-loaded cotton modified using reactive copolymer

Cotton fabric was chemically reacted with (MCT-βCD-g-PAA) to an add-on of 50% in the presence of sodium hydroxide and the resultant chemically modified fabric was treated with solution of silver nitrate. Next the Ag ions present in the fabric were reduced to Ag nanoparticles by making use of normal copolymer (βCD-g-PAA). In a parallel experiment the reduction of silver ions to silver nanoparticles was performed using sodium borohydride for comparison. Scheme 1 illustrates the steps involved in preparation of the chemically modified cotton loaded with silver particles.

Fig. 4 shows the inhibition zone diameter, as a measure of the antibacterial activity of nanosilver-loaded fabric chemically modified using the reactive copolymer (MCT-βCD-g-PAA). Obviously, the use of the normal copolymer or sodium borohydride as a reducing agent succeeded to convert silver ions to silver nanoparticles. However, the normal copolymer is more effective than sodium borohydride as evidenced by the values of the inhibition zone diameter. The advantage of our copolymer speaks not only of its reducing power but also of role as a stabilizing agent which, capping the nanosilver particles prevent or at least decreases the particles agglomeration and aggregation.

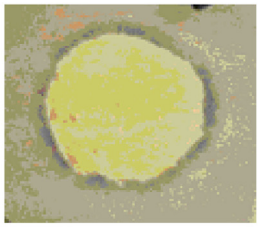
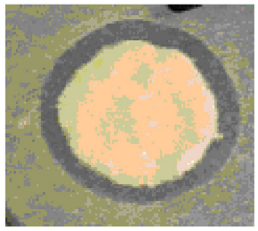
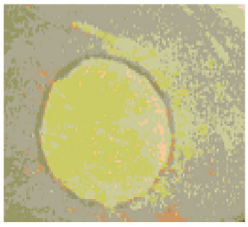
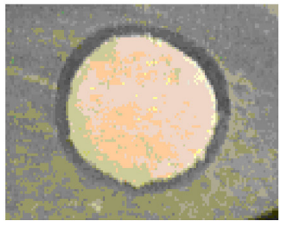
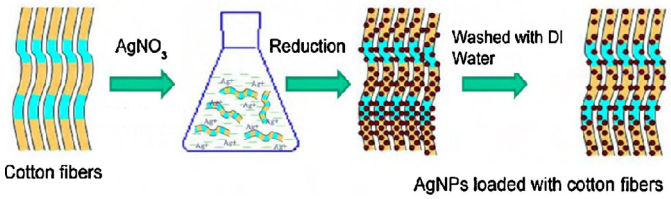
Reducing agent	Inhibition zone diameter (mm/1cm Sample)	
	Escherichia coli (G^-)	Staphylococcus aureus (G^+)
Reduction with (βCD-g-PAA)	18 mm/cm sample 	20 mm/cm sample 
Reduction with sodium borohydride	15 mm/cm sample 	16 mm/cm sample 

Fig. 4. Inhibition action of nanosilver-loaded fabric chemically modified using the reactive copolymer (MCT-βCD-g-PAA).



Scheme 1. Schematic illustration of silver nanoparticles loaded cotton fibers where the preparation method consisting of 3 steps. (1) Cotton fabrics reacted grafted with MCT-βCD-PAA then the obtained modified cotton was immersed in silver nitrate solution. (2) The reduction process of silver nitrate into silver nanoparticles takes place by using either βCD-PAA or sod. borohydride. (3) The formed particles on fibers are stabilized by hydroxyl/carboxyl functional groups of the copolymer solution deposited on nanoparticles.

The antibacterial action of the cotton fabrics in question is unequivocally due to the release of Ag^+ from the Ag nanoparticles present in the fabric. These Ag^+ ions come in contact with bacterial cells and kill them. The bactericidal action of Ag-loaded fabric is manifestation of the nature of the cotton substrates and ability of the latter to adsorb the silver nanoparticles. Introduction of the reactive copolymer molecules would certainly open up the structure of cotton thereby helps establish better adsorption of nanosilver particles. Hydrophilicity of these molecules by virtue of their carboxylic groups enhances the swell-ability of cotton fabric and, therefore, diffusion and adsorption of nanosilver particles. Presence of CD cavities in the chemically attached copolymer would act in favor of agglomeration and accommodation of nanosilver particles. Obviously, then, all these effects taken together may account for superior bactericidal properties of the chemically modified cotton under investigation.

3.2.1. *Characterization of in situ formed nanosilver particles in cotton chemically modified using the reactive copolymer*

Fig. 5 shows SEM image of fabric chemically modified using the reactive copolymer MCT-βCD-g-PAA after being treated with silver nitrate and the latter was reduced to silver nanoparticles using the normal copolymer (βCD-g-PAA). Fig. 6 shows similar SEM but when the reduction of silver nitrate was effected under the action of sodium borohydride. Obviously, the using of the copolymer as a reducing agent results in much smoother surfaces along with much more uniform distribution of the silver nanoparticles as compared

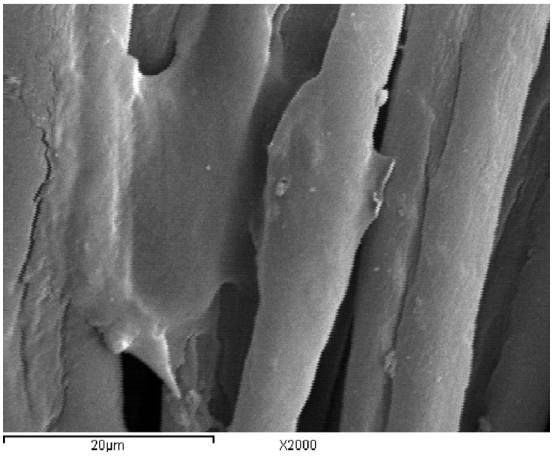


Fig. 5. SEM image of modified cotton fabric prepared by padding in 3% reactive copolymer in the presence of NaOH at 30 g/l concentration then drying at 85 °C for 15 min followed by treatment in 1 g/l silver nitrate solution and drying at 85 °C for 15 min and then reduction with (βCD-g-PAA) at 1.0% concentration in Na_2CO_3 solution of 1% concentration.

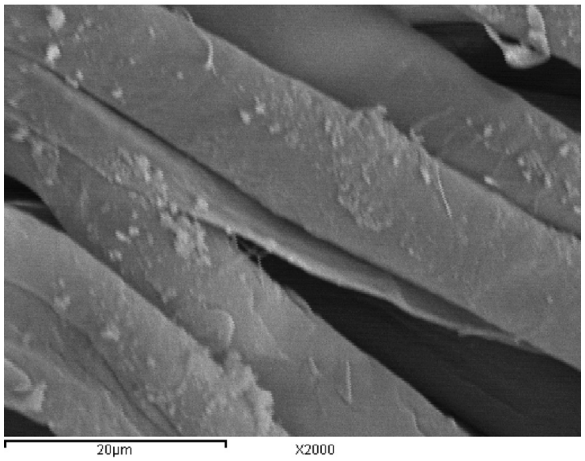


Fig. 6. SEM image of modified cotton fabric prepared through padding in 3% reactive copolymer in the presence of NaOH at 30 g/l concentration then drying at 85 °C for 15 min followed by treatment in 1 g/l silver nitrate solution and drying at 85 °C for 15 min and then padding in sodium borohydride solution at 0.66 mole/l concentration.

with sodium borohydride. In combination with this is eco-friendly behavior of the copolymer *vis-à-vis* sodium borohydride.

Thus the high effectiveness of the copolymer and its eco-friendly dimension would make it superior to the conventional reducing agent used. The *in situ* formation of silver nanoparticles in fabric chemically modified using the reactive copolymer (MCT-βCD-g-PAA) was proved by XRD. The latter confirms the formation of the cubic face silver characteristics. The pattern was slightly broader than the micron size of silver powder. This suggest that the particle diameter is actually much smaller peaks of silver nanoparticles network in the cotton fabric when the reduction of Ag ions present in the fabrics to Ag nanoparticles it was effected using the copolymer (βCD-g-PAA) at 3% concentration. This is clearly shown in Fig. 7.

3.2.2. *Resilience*

Table 1 shows the dry and wet crease recovery angles of cotton fabric prepared using the reactive cyclodextrin copolymer 3% (MCT-βCD-g-PAA), followed by treatment with silver nitrate then reduction of the latter using either the β-cyclodextrin copolymer (βCD-g-PAA) or sodium borohydride. It is seen that there is significant improvement of the dry and wet crease recovery angles after the cotton fabric were subjected to the said treatments. However,

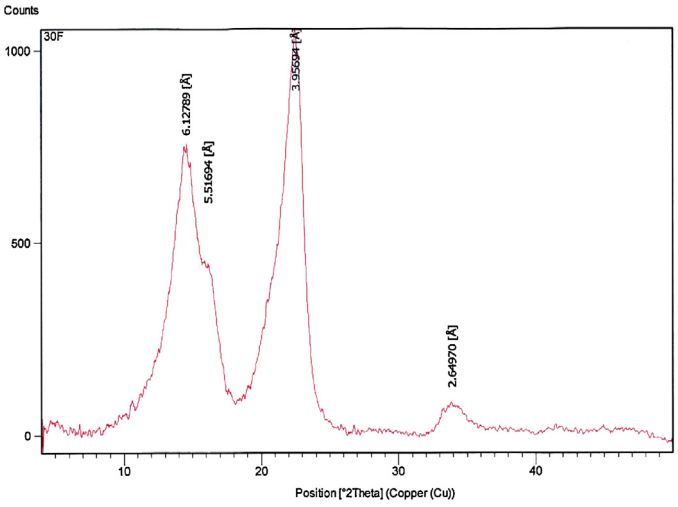


Fig. 7. XRD of *in situ* prepared silver nanoparticles in cotton fabric.

Table 1
Dry and wet crease recovery angles of cotton fabric using the reactive cyclodextrin copolymer, treated with silver nitrate then reducing the latter with either the β-cyclodextrin copolymer or sodium borohydride.

Resilience	Blank	*In situ* reduction of silver ions	
	Untreated cotton fabric	Sod. borohydride	β-Cyclodextrin copolymer (βCD-g-PAA)
D CRA° (W + F	126	189	194
W CRA° (W + F)	107	212	219

the improvement in wet crease recovery angles tends to be higher than those of dry crease recovery.

Higher improvement in the wet than the dry crease recovery angles could associated with: (a) occurrence of crosslinking when the modified cotton was in the wet state and (b) the length of the crosslinks were too long as compared with these formed during conventional crosslinking using, for example, polycarboxylic acids or reactant resins (i.e. N-methylol compounds). In current situation self-crosslinking occurs; the crosslinks are most probably brought about through reaction of carboxylic groups of MCT-βCD-g-PAA with hydroxyl groups of cotton cellulose of the modified fabric.

A close examination of dry and wet crease recovery values would reveal that these values are higher when the βCD-g-PAA was used to reduce silver ions to nanosilver particles than upon using sodium borohydride for such reduction. This suggests that the copolymer (βCD-g-PAA) interacts with the modified cotton and as a result, partial association of the copolymer with the later takes place. This seems to contribute in fabric stabilization, a point which accompanied for higher crease recovery in case of the copolymer than in case of borohydride.

4. Conclusions

Research was designed to impart antibacterial activity to cotton fabrics. Accordingly the fabrics were reacted with cyclodextrin polyacrylic acid copolymer which was newly synthesized. Specially this copolymer was prepared thought 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. As the situation dictates with each of these candidates FTIR, SEM, and X-ray diffraction were harnessed to elucidate microstructural features and provides evidences for anticipated structures. Conclusion arrived at from such investigations is that the finished cotton fabric exhibits superior antibacterial activity for G−ve, and G+ve bacterial along with appreciable resilience properties. It is certain, however, that the use of the copolymer βCD-g-PAA for reduction of silver ions to silver nanoparticles is a better selection than sodium borohydride which represents the conventional reducing agents.

References

Cheung, H. Y., Ho, M. P., Lau, K. T., Cardona, F., & Hui, D. (2009). Natural fibre-reinforced composites for bioengineering and environmental engineering applications. *Composites: Part B*, *40*, 655–663.

Dastjerdi, R., Mojtahedi, M., & Shoshtari, A. M. (2009). Comparing the effect of three processing methods for modification of filament yarns with inorganic nanocomposite filler and their bioactivity against *Staphylococcus aureus*. *Macromolecular Research*, *17*(6), 378–387.

Dastjerdi, R., & Montazer, M. (2010). A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties. *Colloids and Surfaces B: Biointerfaces*, *79*, 5–18.

Hebeish, A., El-Shafei, A., Sharaf, S., & Zaghloul, S. (2011). Novel precursors for green synthesis and application of silver nanoparticles in the realm of cotton finishing. *Carbohydrate Polymers*, *84*, 605–613.

Hyung, W. K., Bo, R. K., & Young, H. R. (2010). Imparting durable antimicrobial properties to cotton fabrics using alginate – Quaternary ammonium complex nanoparticles. *Carbohydrate Polymers*, *79*, 1057–1062.

Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Tapia, J., & Yacaman, M. J. (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology*, *16*, 2346–2353.

Pollini, M., Russo, M., Licciulli, A., Sannino, A., & Maffezzoli, A. (2009). Characterization of antibacterial silver coated yarns. *Journal of Materials Science – Materials in Medicine*, *20*, 2361–2366.

Ravindra, S., Murali Mohan, Y., Narayana Reddy, N., & Mohana Raju, K. (2010). Fabrication of antibacterial cotton fibres loaded with silver nanoparticles via "Green Approach". *Colloids and Surfaces A – Physicochemical and Engineering Aspects*, *367*, 31–40.

Russell, A. D., & Hugo, W. B. (1994). Antimicrobial activity and action of silver. *Progress in Medicinal Chemistry*, *31*, 351–370.