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Development of improved nanosilver-based antibacterial textiles via synthesis of versatile chemically modified cotton fabrics

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ABSTRACT

Cationization of cotton fabric form was effected by reacting the cellulose with 3-chloro-2 hydroxypropyl trimethyl ammonium chloride in presence of sodium hydroxide as per the pad dry cure method. Thus obtained cationized cotton cellulose was reacted with a reactive copolymer, namely, reactive β-cyclodextrin grafted with polyacrylic acid (MCT-βCD-g-PAA).Bridging of another copolymer, namely, β-cyclodextrin grafted with polyacrylic acid (βCD-g-PAA) to the cationized fabric using epichlorohydrin crosslinker was also performed. Inclusion of Ag nanoparticles in these three cotton substrates via treatment of the latter with colloid of Ag nanoparticles or through in situ formation of the former was exercised. Characterization of cotton fabric before and after being chemically modified was carried out using FTIR, XRD and SEM. Bacterial examination of the cationized cotton containing either (MCT-βCD-g-PAA) or (βCD-g-PAA) incorporated with Ag nanoparticles showed these substrates function against G+ve and G−ve bacteria. Ability of (MCT-βCD-g-PAA) modified cotton to include hydrophobic molecules was examined.

1. Introduction

Nanotechnology is an newly developed technology which is expected to have a great impact on medical technology. Nowadays new silver-based antimicrobial polymers represents a great challenge for industrial application. Silver is a nontoxic inorganic metal (Raffi, Hussain, Bhatti, & Akhter, 2008). It is well known that silver has a broad antibacterial activity while exhibiting low toxicity toward mammalian cells (Fong, Wood, & Fowler, 2005; Heggers, Goodheart, & Washington, 2005; Poon & Burd, 2004). Thus, silver has the ability to be an excellent antibacterial agent. Silver nanoparticles AgNPs have been reported to exhibit antimicrobial properties (Egorova, 2011; Navarro, Piccapietra, Wagner, & Marconi, 2008; Okafor, Janen, Kukhtareva, & Edwards, 2013). Using AgNPs leads to increasing the number of particles per unit area thereby maximizing the antibacterial effects can be maximized (Kim, Kim, Park, & Shin, 2012). It is believed that this effect arises from strong affinity of silver toward sulfur or phosphorus. AgNPs can react with sulfur-containing proteins inside or outside the bacterial cell membrane, which in turn affects bacterial cell viability (Matsumura, Yoshikata, Kunisaki, & Tsuchido, 2003). It was also reported that the released silver ions (particularly Ag^+) from AgNPs (Ag°) can interact with phosphorus moieties in DNA, leading to inactivation of DNA replication, or react with sulfur containing proteins, resulting in the inhibition of enzyme functions (Selvam, Gandhi, Suresh, & Gowri, 2012). These properties facilitate the diffusion of AgNPs into various matrices such as textiles and wound dressing materials (Abdelgawad & Samuel, 2014; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Hebeish, El-Shafei, Sharaf, & Zaghloul, 2011; Konwarh, 2011). However,the incorporation processes occurs through using commercial AgNPs or require to prepare Ag-coated matrices via multiple steps and complex reagents (El Shafei, Shaarawy, & Hebeish, 2010).

In addition to research in developing and synthesizing new fiber-forming polymers with specialized properties,surface modification of fiber is considered as one of the main areas of research in the expansion of functional fibers.

Cotton is considered as the purest source of fibers of cellulose that normally occurs in nature (Hebeish, Higazy, El-Shafei, & Sharaf, 2010). Cationization process has been discussed via various studies as a method for cellulose modification (Hashem, El-Bisi, Sharaf, & Refaie, 2010; Hebeish, Sharaf, Refaie, & El Shafei, 2012). Cationization is a method used to change the surface charge of cellulosic fibers.

Cyclodextrins have been prototyped for novel host compounds and catalysts. Cyclodextrins can be obtained by the enzymatic

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degradation of starch. Depending on the nature of the enzyme employed and how the reaction is being controlled, the main product is α, β, or γ-cyclodextrin (6, 7, and 8 glycopyranose units, respectively). They have an endolipophilic cavity, which is made water-soluble by the outward pointing OH group. A fascinating property of the cyclodextrins is their ability to incorporate other organic compounds into their cavity, both in the solid state and in solution. The complexation is based, depending on the solvent and the type of host and guest, on a combination of several intermolecular interactions (Abdelgawad & Samuel, 2014; Hashem, El-Aref, & Refaie, 2008), steric fit, Van der Waals· interactions, dispersive forces, dipole–dipole interactions, charge–transfer interactions, electrostatic interactions, and hydrogen bonding.

This work is targeted toward development of versatile cotton substrate, a green reductant and a good application technique that – all together – guarantee production of cotton fabrics with reliable antibacterial activity and perfumed release. To achieve the goal cotton fabrics are chemically modified through introduction of cationic and cyclodextrin as well as acrylic moieties in the molecular structure of cotton cellulose. Synthesis and characterization of beta cyclodextrin copolymerized with polyacrylic acid will be conducted using the most-up-to-date facilities. Silver nanoparticles are included in the synthesized chemically modified cotton fabrics by preparation of the nanoparticles as well as by in situ formation.

2. Experimental

2.1. Materials

3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (65%), a technical grade chemical, was kindly supplied by Dow Chemical Company, USA, which sells the chemical under the commercial name (Quat-188). 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, sodium hydroxide, acetic acid, hydrochloric acid, sodium carbonate, were of laboratory grade.

2.1.1. Cationization of the cotton fabric

Cationic modification of the cotton fabric was applied by using the pad-dry-cure method. The experimental procedures were carried out as follows: Quat-188 was mixed with sodium hydroxide solution at a NaOH/Quat-188 molar ratio of 2:1. The fabrics were padded in this mixture in two dips and nips, and then squeezed to a wet pick-up of about 100%. The cotton fabric was dried at 40 °C for 10 min and then cured at 120 °C for 3 min. The fabric was washed with cold water and 1% acetic acid, followed by several washing cycles and finally dried under the normal laboratory conditions.

2.1.2. In situ preparation of nanosilver loaded fabrics

A solution of silver nitrate obtained by dissolving 15 mg in definite amount of distilled water. In this solution, dry preweighed piece of cationized cotton fabric was immersed for 1 h, followed by padding (squeezing). The so padded fabric was impregnated in a solution containing either normal polymer βCD-g-PAA or reactive polymer MCT-βCD-g-PAA at 30 °C for 1 h; this is done to reduce silver ions to silver nanoparticles. The fabric was then squeezed and dried at 40 °C. The fabric acquired dark brown color indicating formation of silver nanoparticles within the molecular structure of cotton cellulose of the fabric.

2.1.3. Treatment of cotton bearing cationic and cyclodextrin moieties with nanosilver colloids

Cationized cotton fabrics were prepared as described above using different concentrations of Quat-188 ranging from 25 to 100%. The cationized fabrics so obtained were padded in aqueous solutions containing the reactive copolymer (MCT-βCD-g-PAA) or the normal copolymer (βCD-g-PAA) at concentrations of 2–5%. Fabrics were padded to a wet pick up of 100% then dried at 80 °C. At this end these fabrics were immersed for 5 min in a freshly prepared nanosilver bath at ambient temperature, the fabrics were then dried at 80 °C for 5 min and cured at 140 °C for 5 min; finally the fabrics were rinsed with water and dried in absence of light at room temperature.

2.1.4. Treatment of finished fabrics with perfumes

Fabric samples processed as described above were treated via impregnation in water/alcohol solutions of Jasmine oil perfume. The treatment was carried out as per the exhaustion technique at room temperature for 2 h. The samples were then dried at ambient conditions for at least 3 h followed by conditioning at standard conditions for 24 h before testing.

2.2. Testing and analysis

2.2.1. 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}

2.2.2. X-ray diffraction

The X-ray diffraction method was used to identify Ag nanoparticles loaded in the polymer matrix by monitoring the diffraction angle from 5 to 65 (2 h)

2.2.3. Scanning electron microscopy measurements

Surface morphology of treated fabric samples was examined on a JEAOL JXA-840 scanning electron microscope (SEM). The prepared samples were coated with a thin layer of palladium gold alloy after mounting on a double sided carbon tape.

2.2.4. Antibacterial tests

The antibacterial activity of fabric samples was evaluated against *Escherichia coli* and *staphylococcus aureus*, (ATCC 1533) bacteria using disk diffusion method.

- Crease recovery angles (CRA) of the treated samples were determined in warp and weft direction; ($w+f$) according to the AATCC standard method [66-1966].
- The ability of the fabric to keep fragrance upon storing under ambient conditions in stagnant air for 1 week, 2 weeks, 1 month and 3 months was monitored by evaluating the percent loss in weight after the desired time. Another sensorial evaluation of the results was also performed by a group of 5-well trained persons-in insulated booths where the fabric were kept on an open desk at room temperature, and smelled every 5 days in order to sense the scents (Geranio, Heuberger, & Nowack, 2009)

3. Result and discussion

To start with, cotton fabric was subjected to cationization with a view to make the fabric more amenable to adsorption, deposition and/or sedimentation of silver nanoparticles. Further chemical modification of the cationized cotton was performed by reacting it with a reactive copolymer (MCT-βCD-g-PAA) synthesized purposely for enhancing hydrophilicity, swellability and opening up the cotton structure thereby guaranteeing uniform distribution of the nanosilver particles therein. Bridging of another copolymer (βCD-g-PAA) to the cationized fabric using epichlorohydrin crosslinker was also done. Inclusion of silver nanoparticles in these

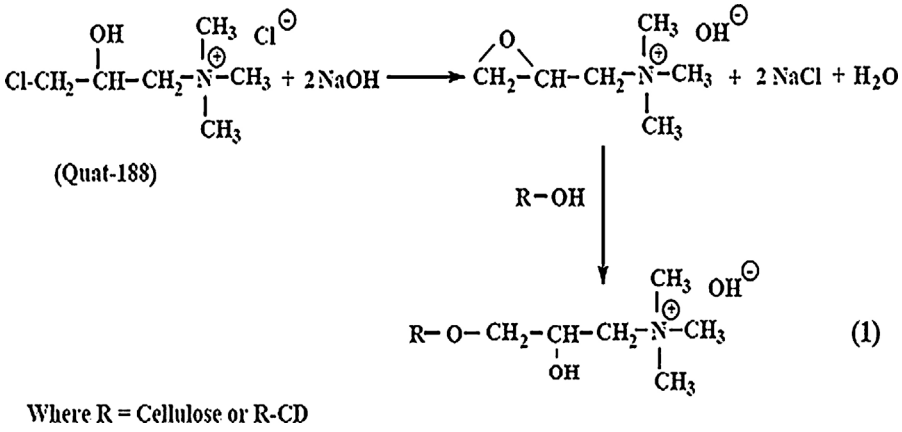

Fig. 1. reaction of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Quatt-188) with cotton cellulose in presence of sodium hydroxide.

substrate via in situ formation was exercised. Characterization and functionalization of the obtained chemically modified cotton fabrics against G+ve and G−ve bacteria were investigated. Results of these studies and their discussion were given below

3.1. Cationization of cotton fabrics

Cationized cotton was prepared by reacting 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat-188) with cotton cellulose in presence of sodium hydroxide. The reaction involved may be represented as follows:

Fourier-transform infrared (FTIR) spectra were used to identify the presence of functional groups, namely, cationic groups on the solid surface of the cationized cotton. Fig. 1a and b shows the FT-IR spectra of (a) bleached cotton, (b), cationized cotton, respectively. FT-IR spectra of both samples showed characteristic cellulose peaks around 1000–1200 cm^{-1}. Other characteristic bands related to the chemical structure of cellulose were the hydrogen-bonded OH stretching at ca. 3550–3100 cm^{-1}, the CH stretching at 2917 cm^{-1}, and the CH wagging at 1316 cm^{-1}. Compared with the bleached cotton, cationized cotton has an obvious new peak at 1491 cm^{-1} (CN), which should be attributed to the quaternary ammonium groups. These results prove the successful conversion of cotton into cationized cotton Analysis based on the determination of absorptions at 1431 cm^{-1} (characteristic band of cationizing agent attached to the fibers) vis-à-vis absorption at 1648 cm^{-1} (absorption band related to the cellulose fibers) reveals that about 23% of the fibers have been cationized during the cationization process.

As seen In Fourier-transform infrared spectra (FTIR) (Fig. 2a and b) no new peaks appear in the silver colloids treated samples, and there is a similarilty in (FTIR) of cotton and cationized cotton samples before and after treatment with silver colloids These results indicating that no chemical reactions occurred between silver nanoparticles and cellulose fibers during the treatment of the uncationized and the cationized cottons with the said colloids. Therefore, silver adsorption on the surface of fibers cannot be related to the formation of chemical bonds between silver nano particles and the functional groups on the surface of the fibers. It follows from this that inclusion of silver nanoparticles in the substrates under investigation occurs via physical adsorption and sedimentation. However the magnitude of latter two physical processes was much greater with cationized cotton than the uncationized cotton fabric.

The appearance of silver nanoparticles only on the cationized cotton fabrics may be explained as follows. The physical and chemical strcucture of the fibers. control The maximum amount of nanoparticles adsorbed on the fibers When cotton fibers are immersed in a nanosilver colloid solution, there will be a repulsion force between negatively charges resulting from dissociation of the functional groups of cellulose and the anions on the surface of the silver nanoparticles. Thereby inhibiting the deposition of silver nanoparticles on the surface of the fibers. Consequently, adsorption of silver nanoparticle is much higher on cationized cotton fibers containing (MCT-βCD-g-PAA) or (βCD-g-PAA) than on bleached uncationized cotton. These highly positive charges on cationic fabric surface lowering the zeta potential of its surface, cause increase in the deposition of silver particles due to attractive forces generated between the cationized modified fabric and the nanosilver (Buchbauer, 1996).

3.2. Antibacterial activity

Antibacterial activity of fabric samples will be detected by inhibition zone test. The control samples, namely, bleached uncationized cotton and cationized cotton fabrics without treatment with silver colloidal solutions, did not display any antibacterial activity. Results of antibacterial activity tests are shown in Table 1. These results signify that increase the concentration of nanosilver in the bath, more silver adsorbed on the fibers cause increase in inhibition zone diameter. The results clarify further that antibacterial efficiency against *E. coli* (Fig. 3a) and *staphylococcus aureus* (Fig. 3b) bacteria is dependent on the content of silver nanoparticles in the fabric samples; samples with greater silver content exhibit stronger antibacterial activity.

3.3. in situ formation of silver nanoparticles within cotton containing cationic, cyclodextrin and acrylic acid moieties

We have disclosed that introduction of cationic groups and moieties of β-cyclodextrin copolymerized with polyacrylic acid in the

Table 1
Antibacterial activity of cationized cotton fabrics containing β-cyclodextrin or reactive cyclodextrin copolymerized with polyacrylic acid together with silver nanoparticles.

Sample	Inhibition zone diameter (mm/1 cm sample)	
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)
Cationized cotton	0.00	0.00
Cationized cotton containing MCT-βCD-g-PAA and incorporated with silver nanoparticles	14.00	15.00
Cationized cotton containing βCD-g-PAA incorporated with silver nanoparticles	15.00	16.00

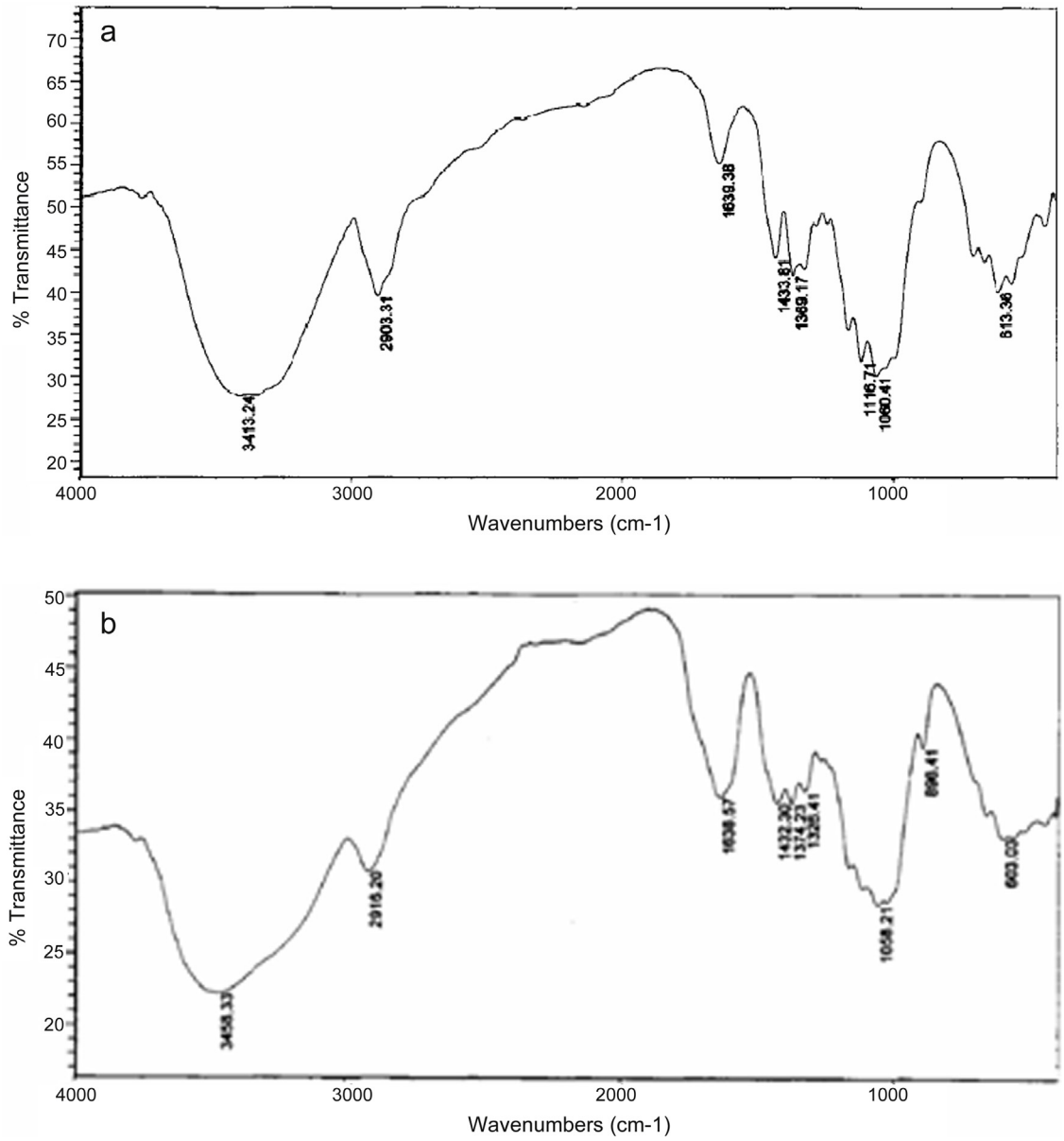

Fig. 2. (a) FT-IR spectra of bleached cotton fabric (identical spectra were obtained after treatment with colloids of silver nanoparticles). (b) FT-IR spectra of cationized cotton fabric (identical spectra were obtained after treatment of this cationized cotton with colloids of silver nanoparticles).

molecular structure of cotton cellulose favors deposition of nanosilver particles therein and, as a result, fabrics with antibacterial properties could be achieved.

In this section, we make use of the functionality of the modifying agents under investigations in effecting both chemical modification of cotton and reduction of silver nitrate to silver nanoparticles as per two approaches. The first approach involves treatment of cationized cotton fabric with silver nitrate. Reduction of the latter is effected by βCD-g-PAA or MCT-βCD-g-PAA. The second approach, on the other hand, entails treatment of cationized cotton grafted with MCT-βCD-g-PAA and silver nitrate followed by reduction of the latter with either βCD-g-PAA or sodium borohydride. Needless to say that in both approaches reduction of the silver ions gives rise to silver nanoparticles formed in situ where the silver ions are distributed within the molecules structure of cotton.

Table 2 shows the antibacterial activity of nanosilver-loaded fabric for fabrics that have been cationized, treated with silver nitrate then reduced using either βCD-g-PAA or MCT-βCD-g-PAA. Results of the inhibition zone diameter are 17 and 18 mm/cm sample for gram −ve and gram +ve bacteria respectively only when the nonreactive copolymer (βCD-g-PAA) was used. In contrast the inhibition zone diameter values are zero upon using the reactive copolymer (MCT-βCD-g-PAA).

Table 3 shows the antibacterial activity of nanosilver-loaded fabric for the cationized cotton grafted with MCT-βCD-g-PAA and

Table 2
The inhibition zone for cationized cotton in situ prepared silver nanoparticles reduced either by βCD-g-PAA, or MCT-βCD-g-PAA.

Silver-loaded fabrics	Inhibition zone diameter (mm/1 cm sample)	
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)
Cationized cotton treated with $AgNO_3$ then reduced with βCD-g-PAA	17	18
Cationized cotton treated with $AgNO_3$ then reduced with MCT-βCD-g-PAA	0.00	0.00

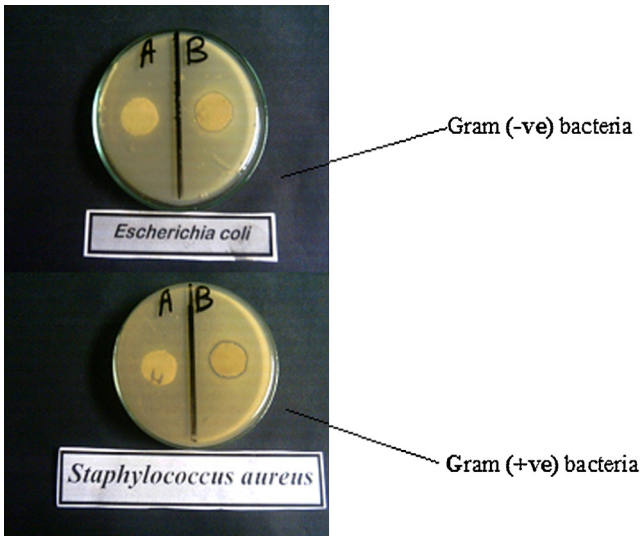

Fig. 3. (a) Gram (−ve) bacteria. (b) Gram (+ve) bacteria.

Table 3
The inhibition zone for cationized cotton grafted with MCT-βCD-g-PAA and in situ prepared silver nanoparticles reduced either by βCD-g-PAA, or sod. borohydride.

Silver-loaded fabrics	Inhibition zone diameter (mm/1 cm sample)	
	Escherichia coli (G^-)	*Staphylococcus aureus* (G^+)
Cationized cotton grafted with MCT-βCD-g-PAA and silver nitrate followed by reduction with βCD-g-PAA	19	21
Cationized cotton grafted with MCT-βCD-g-PAA and silver nitrate followed by reduction with sod. borohydride	15	16

silver nitrate followed by reduction of the latter with either βCD-g-PAA or sodium borohydride. Results of the inhibition zone for the silver nitrate reduced to nanosilver by using βCD-g-PAA more effective than that reduced with sodium borohydride

Fig. 4 shows the SEM image of cationized cotton treated with silver nitrate solution then subjected to reduction using βCD-g-PAA. The image presents a photograph at 500 times magnification. The presence of silver nanoparticles confirmed by the presence

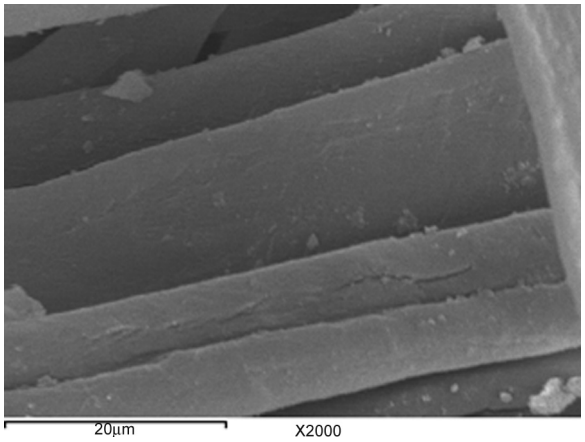

Fig. 4. SEM of cationized cotton (50 g/l) after padding in 1 g/l silver nitrate solution and drying at 85 °C for 15 min, then treated cotton in βCD-g-PAA with 3% concentrations followed by drying at 85 °C for 5 min and thermo fixation for 3 min at 140 °C.

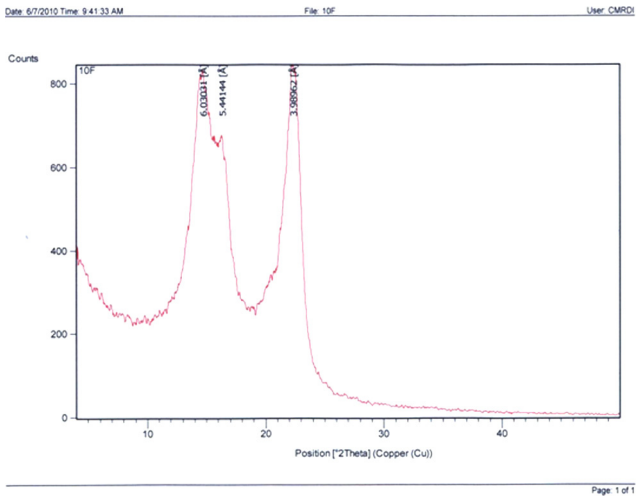

Fig. 5. XRD of *in situ* prepared silver nanoparticles in cotton fabric.

of dark texture on the ultrafine fibers. Furthermore, the observed uniformity of the dark texture make us conclude the uniform distribution of silver nanoparticles within the grafted-copolymer network of the fabric which is the major advantage of our developing method to prepare silver-loaded grafted fabric

When fabric containing [(MCT-βCD-g-PAA) or (βCD-g-PAA) is put in distilled water, the hydrophilic character of the constituents of the modified cotton as well as the presence of carboxylic groups result from the ionization of AA moieties along the macromolecular chains in the network causes the swelling of attached copolymer network .Hydrophilicity, chain-relaxation, and osmotic swelling pressure facilitate the swelling of the network. When the swollen fabric is placed in an aqueous solution of $AgNO_3$, Ag ions penetrate the swollen copolymer network due to following factors: (a) Ag+/H+ ionic exchange between Ag^+ ions of silver nitrate solution and H^+ ions of swollen network, and (b) the ability of Ag^+ ions to bind with the electron-rich N and O atoms of amide and carboxylate groups. In this way, Ag^+ ions become strongly embedded in the polymeric network. Finally, when swollen fabric containing Ag^+ ions is put in an aqueous βCD-g-PAA solution as a reducing agent, the Ag^+ ions converted to Ag nanoparticles. This in situ formation of silver nanoparticles in the fabric was proved by the XRD which assures the formation of the peaks of silver nanoparticles network in the cotton fabric as shown in Fig. 5.

3.4. Resilience properties

Resilience properties expressed as dry and wet crease recovery angles of cationized cotton at different cationizing agent concentration are shown in Fig. 6. As is evident, there is a tendency that the crease recovery angles increase by increasing the cationizing agent concentration. This is the case with the wet and dry crease recovery but with the certainly that the cationized fabrics exhibit higher wet than dry crease recovery angles for reason associated with the state of cotton during cationization. The condition of the latter did not allow cotton to attain a dry collapsed state during introduction of the cationized groups which are likely responsible for the observed improvement in fiber–fabric resilience. In short, stabilization of the cotton fabrics occurs while the cotton fabric is in a relatively swollen state during cationization and, as a result, resilience is more significant in the wet than the dry state of the cationized fabrics.

Fig. 7 shows the relationship between wet and dry crease recovery angles of cationized cotton samples and the concentrations of the reactive copolymer used for treatment of these samples. It is

Table 4
Evaluation of the perfume by weight.

Reactive copolymer conc.	Blank	Cationized cotton prepared using 50 g/L Quat-188				Cationized cotton prepared using 75 g/L Quat-188			
	0%	2%	3%	4%	5%	2%	3%	4%	5%
1 day storing	0.93	3.54	3.47	3.28	3.21	3.67	2.69	2.53	2.55
1 week storing	0.07	3.43	2.87	3.12	2.85	2.54	2.49	2.41	2.50
2 weeks storing	0.00	2.85	2.18	1.88	1.95	1.67	2.35	2.04	2.28
3 weeks storing	0.00	2.56	1.39	1.11	0.95	0.68	2.05	1.18	1.44
4 weeks storing	0.00	1.90	1.17	0.88	0.34	0.36	1.70	0.45	0.91
5 weeks storing	0.00	0.65	0.83	0.35	0.00	0.00	0.77	0.24	0.28
6 weeks storing	0.00	0.00	0.27	0.00	0.00	0.00	0.28	0.00	0.00
7 weeks storing	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00	0.00
8 weeks storing	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

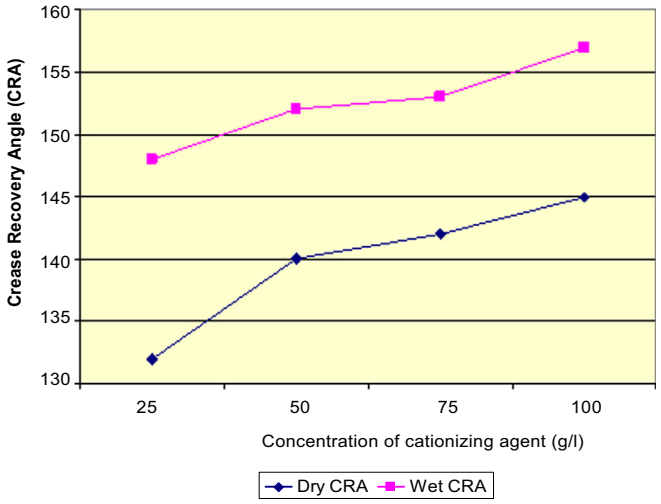

Fig. 6. Effect of using cationized cotton with different concentration on Crease Recovery Angle.

clear that treatment of cationized cotton with the reactive copolymer (MCT-βCD-PAA) at a concentration of 75% is accompanied by significant enhancement in both wet and dry crease recovery angles. Here too treatment of the cationized cotton with the reactive copolymer was performed under conditions which favors greater stabilization and, therefore, higher resistance in the wet than the dry state of the fabric.

Fig. 8 shows the wet and dry crease recovery of cationized cotton fabrics versus concentration of the copolymer (βCD-g-PAA). The result produces trends which are similar to those of Fig. 6 and could be described on similar lines. At any event, however, the enhancement in crease recovery angles is logically due to ionic crosslinking.

Ionic crosslinking is created in the molecular structure of cotton because of the cationic characteristic induced therein by cationization and the anionic characteristics induced by the carboxylate anions of polyacrylic acid in each of the copolymers used. In addition to ionic crosslinking, the copolymers under investigation seem to confer on cotton fabric a sort of fiber stabilization which help establish high fiber–fabric resilience.

3.5. Treatments of cotton fabrics with perfumes

It has been disclosed that cyclodextrins form complexes with perfumes or fragrances which can be stored over a long period without loss of these substances (Ristić & Ristić, 2012). The complexes of organic substances are only set free when they are in contact with moisture. In current work, the fabrics were finished through cationization followed by treatment of the cationized cotton with MCT-βCD-PAA as described in the experimental section. The so finished fabrics were then treated with jasmine perfume oil. These fabrics together with blank (untreated) fabric were monitored for loss in fabric weight was calculated after storing for different periods of time.

It is observed (Table 4) that treatment of the control (unfinished) fabric with the perfume oil then storing for 2 weeks and calculating the loss in fabric weight results in zero loss in fabric weight, indicating complete evaporation of the perfume. After storing duration as short as 1 day and 1 week, the loss in fabric weight attains values that are as low as 0.93% and 0.07%, respectively. This reflects the inability of the cotton fabric to retain the perfume for longer durations. On the contrary, application of our novel MCT-βCD-PAA finishes on the cationized cotton fabric brings about

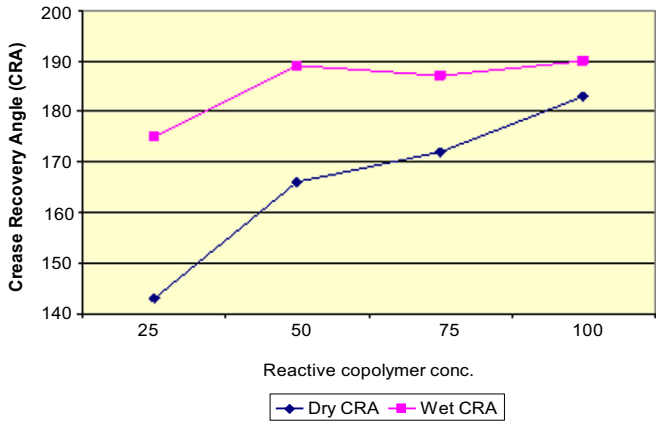

Fig. 7. Effect of different concentrations of the reactive copolymer (MCT-βCD-g-PAA) on the crease recovery (wet and dry) of cationized cotton.

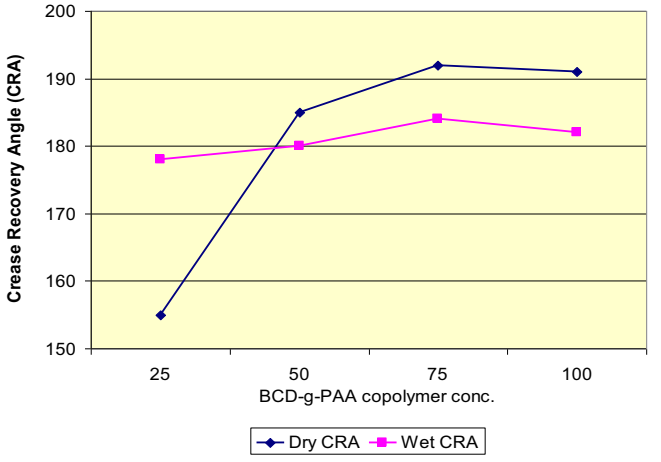

Fig. 8. Effect of different concentrations of the copolymer (βCD-g-PAA) on the wet and dry crease recovery of cationized cotton.

Table 5
Evaluation of the perfume by smell.

Reactive copolymer conc.	Blank	Cationized cotton prepared using 50 g/L Quat-188				Cationized cotton prepared using 75 g/L Quat-188			
	0%	2%	3%	4%	5%	2%	3%	4%	5%
1 day-storing	–	+++++	+++++	+++++	++++	++++	+++++	+++++	+++++
1 week storing	–	+++++	+++++	+++++	++++	++++	+++++	+++++	+++++
2 weeks storing	–	++++	+++++	++++	++++	++++	+++++	++++	++++
3 weeks storing	–	++++	++++	++++	+++	+++	++++	++++	++++
4 weeks storing	–	+++	++++	+++	+++	+++	++++	+++	+++
5 weeks storing	–	++	+++	+++	++	++	+++	++	++
6 weeks storing	–	–	+	++	+	–	+	–	–
7 weeks storing	–	–	–	+	–	–	–	–	–
8 weeks storing	–	–	–	–	–	–	–	–	–

+++++ very high smell.
++++ high smell.
+++ medium smell.
++ poor smell.

finished products which retain measurable loss in fabric weight even after a duration as long as 7 weeks. This is unequivocally due to inclusion of the perfume in cyclodextrin (CD) cavities of the finish. It is understandable that inclusion occurs via complexation of the hydrophobic perfume molecule with hydrophobic cavity of CD together with Vander Waals forces.

Results of Table 4 reveal also that the loss in fabric weight due to perfume release relies on the concentration of MCT-βCD-PAA finish used in the finishing treatment when the two different concentrations of cationized agent, viz. 50 and 75% were employed. The loss in fabric weight decreases from 3.55 to 3.21% by increasing the concentration of the finish in the treating bath from 2 to 5%, respectively, after one day storing. These decrements range from 0.65 to 0% for the same finish range, i.e. from 2 to 5% but after 5 weeks storing. Such adverse effect of the high concentration of the finish could be interpreted in terms of increased viscosity of the finishing bath at high concentrations of the finish. This impedes diffusion of the finish molecules into the molecular structure of cotton cellulose and their distribution therein and, in turn, lower opportunity for the finish to react with the cotton fabric. That is, the extents of grafting of MCT-βCD-PAA finishing onto the cationized cotton fabric are lower at higher (i.e. 4 and 5%) than at lower concentrations (i.e. 2 and 3%) of the finish due to the high viscosity of the finishing bath at high concentrations of the finish.

Results of smell-based assessment imply the absence of perfume smell after 7 weeks storing. Apart of this, all the results of Table 5 are in full agreement with those of Table 2 indicating the validity of the two methods used for evaluation of the perfume release. It is, therefore, concluded that reactive cyclodextrin copolymerized with acrylic acid (MCT-βCD-PAA) may be regarded as a novel finish for production of perfume-containing cationized cotton textiles. Encapsulation of the perfume in the CD cavities prevents evaporation of the perfume and, instead, allows slow and regular release of the perfume through absorption of small amounts of water. By and large, the latter originates from atmospheric humidity or from human skin or baths in certain cases.

4. Conclusion

Cotton cellulose in the fabric form was subjected to the following successive sequences of treatments: (1) treatment involving reaction of cotton cellulose with 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (known commercially as Quat-188) to synthesize cationized cotton, (2) treatment of this cationized cotton with reactive cyclodextrin graft copolymerized with polyacrylic acid (MCT-βCD-g-PAA) to obtain cotton bearing cationic and cyclodextrin moieties, (3) treatment of the so modified cotton with nanosilver colloids. The three treatments were carried out using different concentrations of Quat-188, reactive copolymer and silver nanoparticles. FTIR, antibacterial activity test and crease recovery were used to characterize and evaluate the said modified cotton before and after treatment with nanosilver colloids. Results obtained conclude that: (a) silver nanoparticles adsorption was much greater on cotton bearing both cationic and cyclodextrin moieties than on cationized cotton only, (b) antibacterial activity (gram +ve and gram −ve) were realized and depends on the content of silver nanoparticles in the cotton sample, (c) cationization was accompanied by improvement in crease recovery and further improvement was observed by further modification of cationized cotton using the reactive cyclodextrin copolymer and, cationized cotton fabric was treated with silver nitrate followed by reduction of the latter by βCD-g-PAA or MCT-βCD-g-PAA In this approaches reduction of the silver ions gave rise to silver nanoparticles formed in situ. Conclusions arrived at from these studies are: (1) MCT-βCD-g-PAA failed to induce reduction of silver ions to silver nanoparticles (2) βCD-g-PAA, on the other hand, succeeded to induce such reduction (3) in situ formation of silver nanoparticles were uniformly distributed within the grafted copolymer network of the fabric and, therefore the latter exhibited stronger antibacterial activity, (4) the in situ formation of the silver nanoparticles in the fabric was proved by XRD whereas SEM image verified surface characteristics and the uniform distribution of the nanoscale silver particles, and (5) the treatments involved in the in situ formation of nanosilver particles brought about improvement in fiber–fabric resilience.

References

Abdelgawad, A., & Samuel, M. (2014). Antimicrobial wound dressing nanofiber mats from multicomponent (chitosan/silver-NPs/polyvinyl alcohol) systems. *Carbohydrate Polymers*, *100*, 166–178.

Buchbauer, G. (1996). Methods in aromatherapy research. *Perfume & Flavorist*, *21*, 31–36.

Egorova, E. M. (2011). Interaction of silver nanoparticles with biological objects: Antimicrobial properties and toxicity for the other living organisms. *Journal of Physics*, *291* http://dx.doi.org/10.1088/1742-6596/291/1/012050

El Shafei, A., Shaarawy, S., & Hebeish, A. (2010). Application of reactive cyclodextrin poly butyl acrylate preformed polymers containing nano-ZnO to cotton fabrics and their impact on fabric performance. *Carbohydrate Polymers*, *79*(4), 852–857.

Fong, J., Wood, F., & Fowler, B. (2005). A silver coated dressing reduces the incidence of early burn wound cellulitis and associated costs of inpatient treatment: Comparative patient care audits. *Burns*, *31*, 562–567.

Geranio, L., Heuberger, M., & Nowack, B. (2009). Behavior of silver nanotextiles during washing. *Environmental Science and Technology*, *43*, 8113–8118.

Hashem, M., El-Aref, A. T., & Refaie, R. (2008). Cotton fabric bearing cationic and β-cyclodextrin moieties: A study of the reaction parameters. *Research Journal of Textile and Apparel*, *8*(2), 76–94.

Hashem, M., El-Bisi, M., Sharaf, S., & Refaie, R. (2010). Pre-cationization of cotton fabrics: An effective alternative tool for activation of hydrogen peroxide bleaching process. *Carbohydrate Polymers*, *79*, 533–540.

Hebeish, A. A., El-Rafie, M. H., Abdel-Mohdy, F. A., Abdel-Halim, E. S., & Emam, H. E. (2010). Carboxymethyl cellulose for green synthesis and stabilization of silver nanoparticles. *Carbohydrate Polymers*, *82*, 933–941.

Hebeish, A. 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.

Hebeish, A. A., Higazy, A., El-Shafei, A., & Sharaf, S. (2010). Synthesis of carboxymethyl cellulose (CMC) and starch-based hybrids and their applications in flocculation and sizing. *Carbohydrate Polymers*, *79*(1), 60–69.

Hebeish, A. A., Sharaf, S., Refaie, R., & El Shafei, A. (2012, May 16). Multifinishing of cotton fabrics using microwave techniques. *Research Journal of Textile & Apparel*, *2*, 68.

Heggers, J., Goodheart, R., Washington, J., McCoy, L., Carino, E., Dang, T., et al. (2005). Therapeutic efficacy of three silver dressings in an infected animal model. *Journal of Burn Care and Rehabilitation*, *26*, 53–56.

Kim, T.-H., Kim, M., Park, H.-S., Shin, U. S., Gong, M. S., & Kim, H. W. (2012). Size-dependent cellular toxicity of silver nanoparticles. *Journal of Biomedical Materials Research: Part A*, *100*, 1033–1043.

Konwarh, R. K. (2011). Effect of sonication and aging on the templating attribute of starch for green silver nanoparticles and their interactions at bio-interface. *Carbohydrate Polymers*, *83*, 1245–1252.

Matsumura, Y., Yoshikata, K., Kunisaki, S., & Tsuchido, T. (2003). Mode of bactericidal action of silver zeolite and its comparison with that of silver nitrate. *Applied and Environmental Microbiology*, *69*, 4278–4281.

Navarro, E., Piccapietra, F., Wagner, B., Marconi, F., Kaegi, R., Odzak, N., et al. (2008). Toxicity of silver nanoparticles to *Chlamydomonas reinhardtii*. *Environmental Science & Technology*, *42*, 8959–8964.

Okafor, Janen, A., Kukhtareva, T., Edwards, V., & Curley, M. (2013). Green synthesis of silver nanoparticles, their characterization, application and antibacterial activity. *International Journal of Environmental Research and Public Health*, *10*, 5221–5238. http://dx.doi.org/10.3390/ijerph10105221

Poon, V., & Burd, A. (2004). In vitro cytotoxicity of silver: Implication for clinical wound care. *Burns*, *30*, 140–147.

Raffi, M., Hussain, F., Bhatti, T., Akhter, J., Hameed, A., & Hasan, M. M. (2008). Antibacterial characterization of silver nanoparticles against *E. Coli* ATCC-15224. *Journal of Materials Science and Technology*, *24*(2), 192–196.

Ristić, N., & Ristić, I. (2012). Cationic modification of cotton fabrics and reactive dyeing characteristics. *Journal of Engineered Fibers and Fabrics*, *7*, 4–12.

Selvam, S., Gandhi, R., Suresh, J., Gowri, S., Ravikumar, S., & Sundrarajan, M. (2012). Antibacterial effect of novel synthesized sulfated β-cyclodextrin crosslinked cotton fabric and its improved antibacterial activities with ZnO, TiO_2 and Ag nanoparticles coating. *International Journal of Pharmaceutics*, *434*(1–2), 366–374.