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Effect of cationization on adsorption of silver nanoparticles on cotton surfaces and its antibacterial activity

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Abstract Cotton was cationized by exhaustion method using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) as a cation-generating agent. Adsorption of silver nanoparticles on normal and cationized cotton was studied by exhaustion method at temperatures of 80°C and 100°C. Two exhaustion baths were used, containing nanosilver colloidal solutions stabilized by two different stabilizers and various concentrations of silver nanoparticles. Fourier-transform infrared (FT-IR) spectra of normal and cationized samples confirmed the existence of quaternary ammonium groups on cationized cellulose fibers. X-ray diffraction (XRD) patterns showed that crystallinity of the modified cellulose fibers was decreased. Scanning electron microscope (SEM) images revealed that the surface of the modified cotton was rougher than that of normal cotton. In addition, SEM images showed the presence of silver nanoparticles on the surface of treated fabric samples. The amount of silver particles adsorbed on the fabric samples was determined using inductively coupled plasma-optical emission spectrometer. Antibacterial tests were performed against *Escherichia coli* bacteria as an indication of antibacterial effect of samples. Cationized cotton samples adsorbed more silver nanoparticles and then had greater ability to inhibit bacteria.

Keywords Antibacterial · Cationization · Cotton · Exhaustion · Modification · Silver nanoparticles

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Introduction

Nanotechnology is an extremely powerful emerging technology which is expected to have a substantial impact on medical technology now and in the future. Nowadays the introduction of new silver-based antimicrobial polymers represents a great challenge for both academia and industry (Kumar and Munstedt 2005). Silver is a nontoxic inorganic metal that is a strong agent capable of killing ca. 650 disease-causing organisms in the body (Jeong et al. 2005). It is well known that silver has a broad antibacterial activity while exhibiting low toxicity towards mammalian cells (Yuranova et al. 2003; Lee et al. 2007; Wang et al. 2007; Sambhy et al. 2006). Thus, silver has the potential to be an excellent antibacterial agent.

Modification of fiber surfaces has been one of the main areas of research in the development of functional fibers. In addition to research in developing

and synthesizing new fiber-forming polymers with specialized properties, surface modification offers many new opportunities. Various techniques are available for surface modification of different fibers. Balu et al. (2008) have employed oxygen plasma processing technique to give superhydrophobicity to cellulose fabrics. To improve dyeability, air and argon atmospheric plasma has been used for surface activation of cotton fabrics (Karahan et al. 2008). Better and faster dye uptake on textiles was achieved using surface modification of wool and cotton fabrics after environmentally safe enzyme pretreatment (Kantouch et al. 2006; Vankar and Shanker 2008). Modification of silk with aminated polyepichlorohydrin to improve dyeability with reactive dyes was carried out by Weibin et al. The effects of various pretreatments and dyeing conditions were studied. The quality of the dyed silks obtained after pretreatment was shown to be satisfactory and the dyeing effluent was less polluted (Weibin et al. 2007). Biomimetic procedure as a surface modification process has been used to prepare superhydrophobic cotton textiles (Hoefnagels et al. 2007). By in situ introduction of silica particles to cotton fibers to generate a dual-size surface roughness, followed by hydrophobization with polydimethylsiloxane (PDMS), normally hydrophilic cotton can easily be converted to superhydrophobic fabric.

Cotton is the most significant and also the purest source of fibers of cellulose that normally occurs in nature (Gordon and Hsieh 2007). Various studies have been performed on cellulose modification via cationization process in order to investigate the effect of cationic agents on the dyeing properties of cellulosic fibers. The effects of various compounds containing cationic and anionic groups as fixing agents on the dyeing properties of cotton fabrics have been evaluated (Sharif et al. 2008, 2007; Xie et al. 2008; Mughal et al. 2007; Zhang et al. 2007, 2005; Montazer et al. 2007; Fang et al. 2005). The results indicated that pretreatment of cotton fabrics with cationic agents enhanced the color strength and fastness properties of dyeings over untreated dyeings without using high electrolyte concentrations. Cationic modification is a method that has been employed in order to change the surface charge of cellulosic fibers (Chen et al. 2004; Kim and Sun 2002; Wu and Kuga 2006; Rong and Feng 2006). In these studies, a variety of cationic agents with amino, ammonium, sulfonium, phosphonium, and other groups have been employed to modify cellulose fabrics. However, disadvantages such as high cost, inadequate reactivity, fabric yellowing, excessive fabric tendering, and toxicity were observed in the case of these substances, which prevented their industrial applications. CHPTAC is a relatively cheap, reactive, and low toxic chemical which is potentially a good cationic agent for the modification of cellulosic fibers (Liu et al. 2007; Montazer et al. 2007; Kanik and Hauser 2004; Hashem et al. 2003). Dyeing and printing properties of the chemically modified cellulosic fibers using this agent are greatly improved. However, no previous attempts appear to have been made to study the effect of the cationization process on the adsorption of silver nanoparticles on the cellulose fibers. The aim of the present work is to study surface modification of cellulose fibers by CHPTAC and its effect on adsorption of silver nanoparticles on the surface of cotton fibers.

Experimental

Materials

Desized, scoured, and bleached plain woven cotton fabric (Yazd Baf Co., Ltd., Iran) was used in this work. Two commercial water-based nanosilver colloids with two different stabilizers and concentration of 2,000 mg L^{-1} (L) and 4,000 mg L^{-1} (LS) were supplied by Pars Nano Nasb Co., Ltd., Iran. The cationic agent CHPTAC is commercially available as a 65% aqueous solution and was purchased from Fluka. Reagent-grade NaOH crystals, nitric acid, and acetic acid were purchased from Merck (Germany). Double-distilled water was used throughout the experiments.

Methods

Cationization of the cotton fabric

Cationized cotton was prepared by using CHPTAC to insert cationic groups on the surface of cotton fibers. The reaction of cationic agent with cotton in the presence of alkaline catalyst yields cationic cotton (Montazer et al. 2007; Hyde et al. 2007). In the exhaustion method, at 30:1 liquor ratio, cationic

agent solution was mixed with water to prepare a bath containing cationic agent with 20% w/w fiber samples. The samples were introduced into the bath and, after 5 min dwell time, the temperature was increased from ambient to 60°C at 2–2.5°C/min and then held constant during the cationization process. The bath was well agitated during the process. After that, 15% on weight of fabric, sodium hydroxide (40 g/L) was added in three steps every 5 min, and after the last addition the mixture was agitated for 10 min. At the end of the reaction the samples were removed from the bath, rinsed several times with water, and acidified with 1% acetic acid. They were then again rinsed with water and dried at ambient temperature.

Adsorption of nanosilver colloids

Fabric samples were treated with nanosilver colloids by conventional exhaustion method, at 30:1 liquor ratio. The silver concentration was varied as 10, 25, 50, 100, and 150 mg L^{-1} of nanosized silver particles in the exhaustion bath. Samples were immersed in a fresh colloidal bath for 5 min at ambient temperature and then the temperature of the bath was increased to 80°C and 100°C during 20 min and held at final temperature for 30 min. Finally, the samples were taken out of the bath, rinsed with water, and dried in the dark at room temperature.

Measurements

UV–visible spectrophotometry

Solutions of two different nanosilver colloids (L and LS) were characterized by a Varian-Cary 100 scan ultraviolet (UV)–visible spectrophotometer.

Dynamic light scattering

The particle size distribution of silver colloidal solutions was determined by dynamic light scattering (DLS) using a SEM-633 goniometer (SEMATech) with a He–Ne laser ($\lambda = 632.8$ nm) at room temperature.

Fourier-transform infrared spectroscopy

Infrared spectra of the cotton samples were obtained by KBr pellet technique. Samples were ground and well mixed with the KBr and pressed in an evacuated die under suitable pressure. Fourier-transform infrared (FT-IR) spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer, which operated from 400 to 4,000 cm^{-1} with resolution of 4 cm^{-1} at room temperature.

X-ray diffractometry

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° (2θ) using monochromatized Cu K_α ($\lambda = 1.54051$ Å) radiation.

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 150× to 3,000×), 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.

Inductively coupled plasma optical emission spectrometry

Inductively coupled plasma-optical emission spectrometry (ICP-OES) CCD Dimultaneous was used on Varian Vista Pro (argon plasma, Ag 328.068-nm excitation, Ag sensitivity 0.004 mg L^{-1}), Australia to measure the quantity of silver concentration on fabric samples. Fabric samples (0.5 g) were incinerated in a digitally controlled furnace. Temperature was gradually increased to 600°C and then maintained for 60 min. Remaining ashes were dissolved in concentrated nitric acid in a 50-mL volumetric flask, which was then filled with double-distilled water to the indication line. All solutions were stored in plastic containers at room temperatures unless otherwise mentioned. Measurements for each sample were performed in triplicate and average results are reported.

Antibacterial tests

All antibacterial activity tests were done in triplicate to ensure reproducibility. The antibacterial activity of fabric samples was evaluated against *Escherichia Coli* (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 10^5 colony-forming units of *E. coli* bacteria were inoculated on plates, and then 2×2 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.

Results and discussion

Characterization of nanosilver colloids

The silver nanoparticles were characterized by UV–vis spectroscopy; this technique has proved useful for the analysis of colloid nanoparticles (Shahverdi et al. 2007). We used two commercial nanosilver colloids (L and LS) with two different stabilizers in this study. L and LS nanosilver colloid solutions have a dark brown and bright yellow color, respectively. Figure 1a, b illustrates UV–vis spectra of L (50 mg L^{-1}) and LS (4,000 mg L^{-1}) colloid solutions. Surface plasmon resonance bands observed in the UV–vis spectra at 404 and 416 nm are the characteristics of the silver metallic nanoparticles (Shervani et al. 2008), because surface plasmon absorbance occurs in particles having a particle size smaller than a 100 nm (Dubas et al. 2006). These two peaks at 404 and 416 nm confirm that the size of the silver nanoparticles in the solutions are approximately between 4 and 20 nm, being smaller in the LS colloid than in the L colloid solution. However, for further verification particle size measurements were carried out on L and LS solutions. The size distribution of silver particles in L and LS solutions was in the range 3–20 and 2–12 nm, respectively (Fig. 2a, b), in very good agreement with the results obtained by UV–vis spectroscopy.

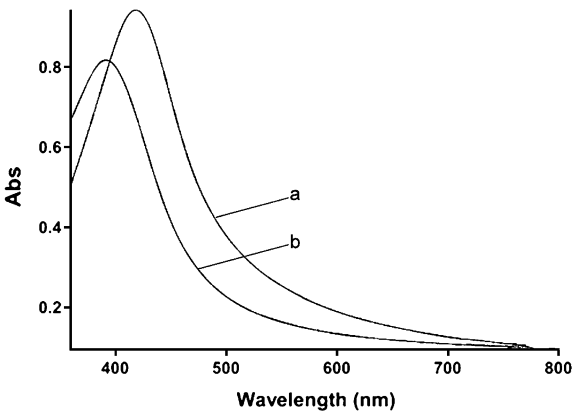


Fig. 1 UV–visible spectra of **a** diluted L (50 mg L^{-1}), **b** LS (4,000 mg L^{-1}) nanosilver colloid solutions

Interaction of cationic agent with cotton cellulose

In this work cotton fabric was cationized using CHPTAC in the presence of sodium hydroxide. Reaction of cationic agent with cotton cellulose produced cationized cotton (Montazer et al. 2007; Hyde et al. 2007), which can be represented as in Schemes 1; the cationization process includes two steps: (a) the chlorohydrin form of the reagent is converted to the epoxy intermediate (2,3-epoxypropyl trimethyl ammonium chloride; EPTAC), (b) the epoxy reacts with the cellulose fibers and converts it to the cationized cellulose, and (c) in a side-reaction the epoxy can be converted to the nonreactive 2,3-dihydroxy derivatives through a hydrolysis reaction (Hashem 2006).

FT-IR analysis

Fourier-transform infrared spectra were used to identify the presence of functional groups on the solid surface of the modified cotton. Figure 3 shows FT-IR spectra of normal (a), cationized cotton (b), normal cotton, and cationized cotton samples treated with L and LS colloid solutions (c, d, e, and f, respectively). FT-IR spectra of all samples showed characteristic cellulose peaks around 1,000–1,200 cm^{-1}. Other characteristic bands related to the chemical structure of cellulose were the hydrogen-bonded OH stretching at ca. 3,550–3,100 cm^{-1}, the CH stretching at 2,917 cm^{-1}, and the CH wagging at 1,316 cm^{-1}. Compared with normal cotton, cationized cotton has an obvious new peak at 1,491 cm^{-1} (CN), which

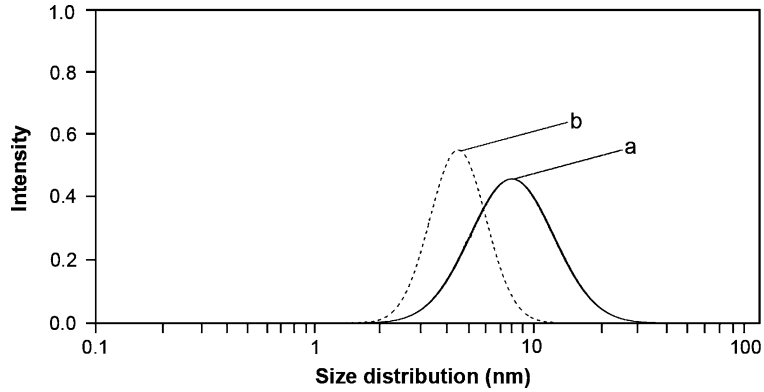
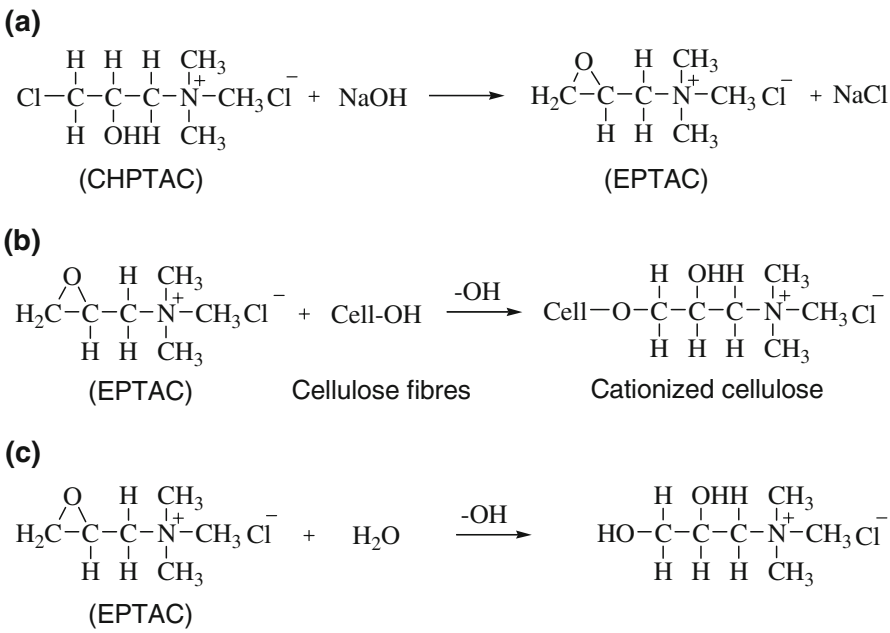


Fig. 2 Particle size distribution of **a** L and **b** LS colloid solutions

Scheme 1 Steps in cationization process



should be attributed to the quaternary ammonium groups (Zhang et al. 2007). These results indicate that the reaction has successfully converted cotton into cationic cotton. Analysis based on the determination of absorptions at 1,491 cm^{-1} (characteristic band of cationization agent attached to the fibers) to absorption at 1,648 cm^{-1} (absorption band related to the cellulose fibers) reveals that about 23% of the fibers have been cationized during the cationization process.

Fourier-transform infrared spectra of normal and modified cotton samples before and after treating with L and LS colloids are quite similar to untreated samples. No new peaks appear in the treated samples, indicating that no chemical reactions occurred between silver nanoparticles and cellulose fibers during the treatment of the normal or the cationized cotton with colloids. Therefore, silver adsorption on the surface of fibers cannot be related to the formation of chemical bonds between Ag particles and the functional groups on the surface of the fibers.

X-ray diffraction analysis

X-ray diffraction has been extensively used for the investigation of the supramolecular order (crystallinity) of cellulose and its derivatives (Cunha et al. 2007). XRD patterns of normal and cationized cotton are shown in Fig. 4a, b. It can be seen that the normal

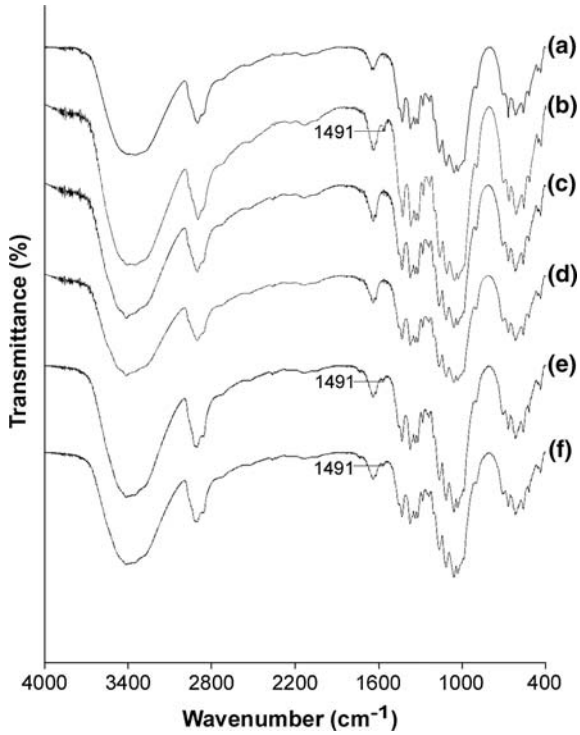


Fig. 3 FT-IR spectra of **a** normal cotton, **b** cationized cotton, **c** normal cotton treated with L and **d** LS colloids, **e** cationized cotton treated with L and **f** LS colloid solutions

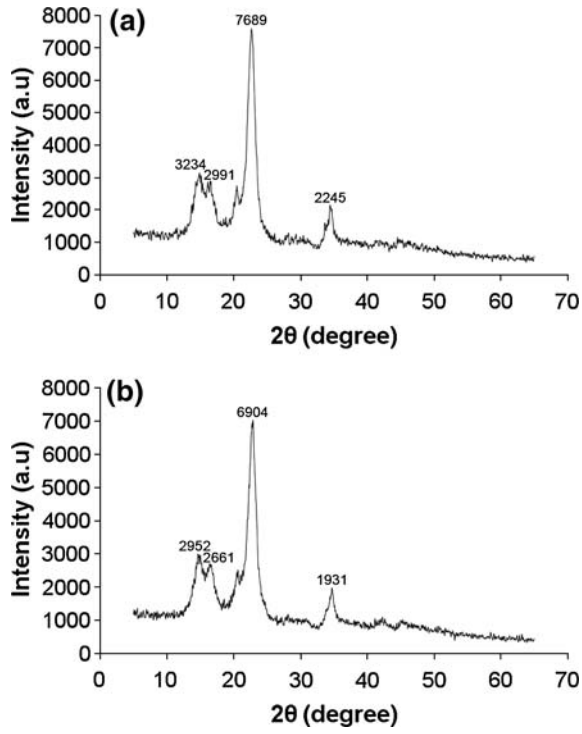


Fig. 4 XRD pattern of **a** normal, and **b** cationized cotton

cotton has main diffraction signals at $2\theta = 14.8°$ and 16.4° for the (101) plane, $2\theta = 22.6°$ for the (002) plane, and $2\theta = 34.5°$ for the (040) plane (Sun et al. 2007), which are typical for the cellulose I crystalline form (Yin et al. 2007). These characteristic peaks also appear in the XRD patterns of cationized cotton, which reveals that the cationization reaction does not change the main crystalline form of the cotton samples. Meanwhile, in comparison with normal cotton, the peak intensity of the cationized cotton declined due to the abundant –OH group in the texture of cotton being substituted by grafting of the cationic agent. The substitution of hydroxyl group reduces the density of hydrogen bands and thus partially destroys the crystalline structure of cotton fibers. So, the amorphous region is extended for the modified cotton, leading to lower crystallinity (Liu et al. 2007; Radosta et al. 2004; Xie et al. 2007; Zhang et al. 2007). The effects of these changes on adsorption of silver nanoparticles are discussed in the following sections.

SEM–EDS measurements

The cationization process influenced the morphology and structure of the cotton fibers. The morphologic changes of cotton samples after the cationization process and treatment with nanosilver colloids can be clearly observed from the SEM images. Figure 5a, b shows the morphology of normal and cationized cotton samples. Significant differences are clear between these cotton fibers; the former has a smooth surface and is uniform, whereas the latter is rough, which can be related to the imposition of ammonium groups onto the surface of the fibers. Figure 5c, d presents pictures of normal and modified cotton samples after treatment with L nanosilver colloid, and Fig. 5e, f presents normal and modified cotton pictures after treatment with LS nanosilver colloid, respectively. From the images it can be observed that the silver nanoparticles have been dispersed onto the surface of the fibers uniformly. Some of the nanoparticles have also agglomerated into clusters because of attractive forces bringing them together into groups.

Energy-dispersive X-ray spectroscopy (EDS) was employed to establish the chemical identity of the

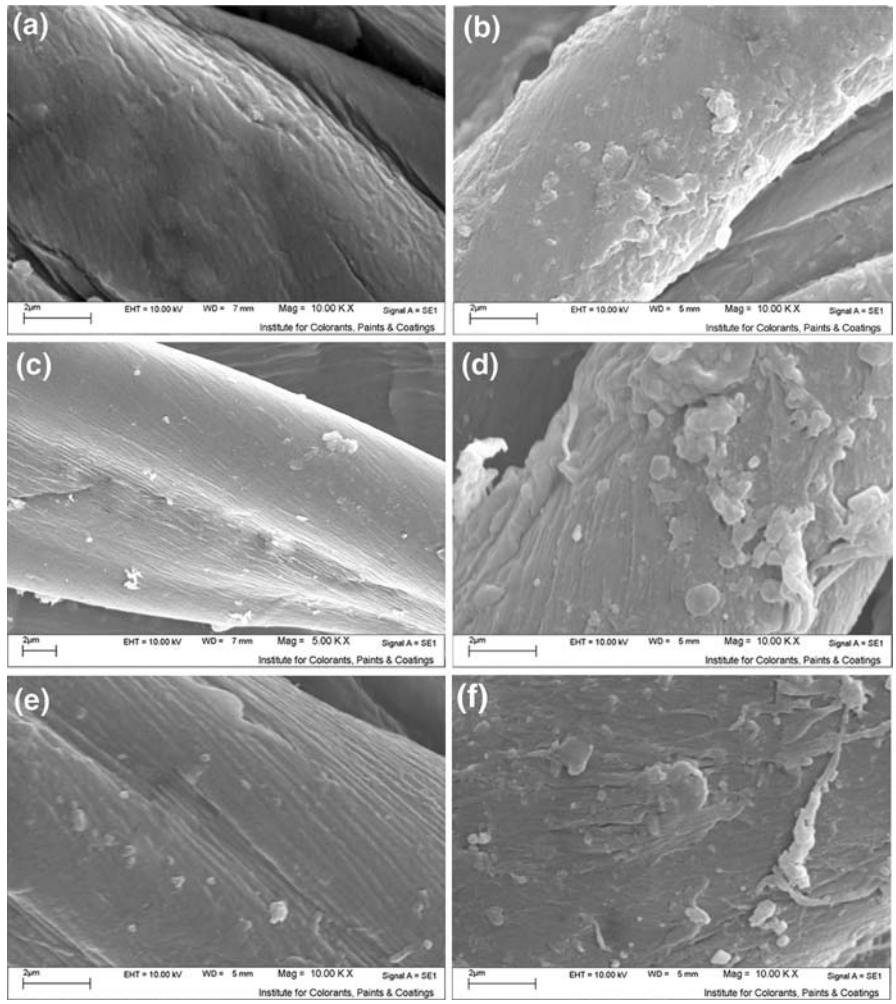


Fig. 5 SEM images of **a** normal cotton, **b** cationized cotton, **c** normal cotton treated with L colloid, **d** cationized cotton treated with L colloid, **e** normal cotton treated with LS colloid, and **f** cationized cotton treated with LS colloid solutions

observed particles. It can be clearly seen from the EDS analysis (Fig. 6a, b) that particles existing on the surfaces of the fibers are silver particles adsorbed onto fibers after treatment by L and LS colloid solutions. The Au signals are from the gold coating.

Study of adsorption of silver nanoparticles

Effects of cationization on adsorption of silver nanoparticles were studied by comparing the silver content of normal and cationized cotton fabric samples treated with L and LS colloids in different concentrations of nanosilver solutions at 80°C and 100°C. The quantity of silver adsorbed on the fabric samples was measured quantitatively by ICP-OES technique and the results are presented in Table 1. It is observed that the silver content on all cationized cotton is much greater than that of normal cotton. The much higher silver content of the cationized cotton samples may be explained by the following consideration. The maximum amount of nanoparticles adsorbed on the fibers is strongly dependent on the physical and chemical characteristics of the fibers. When cotton fibers are immersed in a nanosilver colloid bath, negative charges resulting from dissociation of the functional groups of cellulose repulse the anions on the surface of the nanoparticles. Silver nanoparticles dispersed in aqueous solutions usually have negative surface charge (Jones 2002) and then create a repulsive force against the cellulose fibres, which inhibits the sedimentation of silver nanoparticles on the surface of the fibres. Consequently, silver nanoparticle adsorption is much lower on the normal cotton than on cationized cotton fibres. In the case of

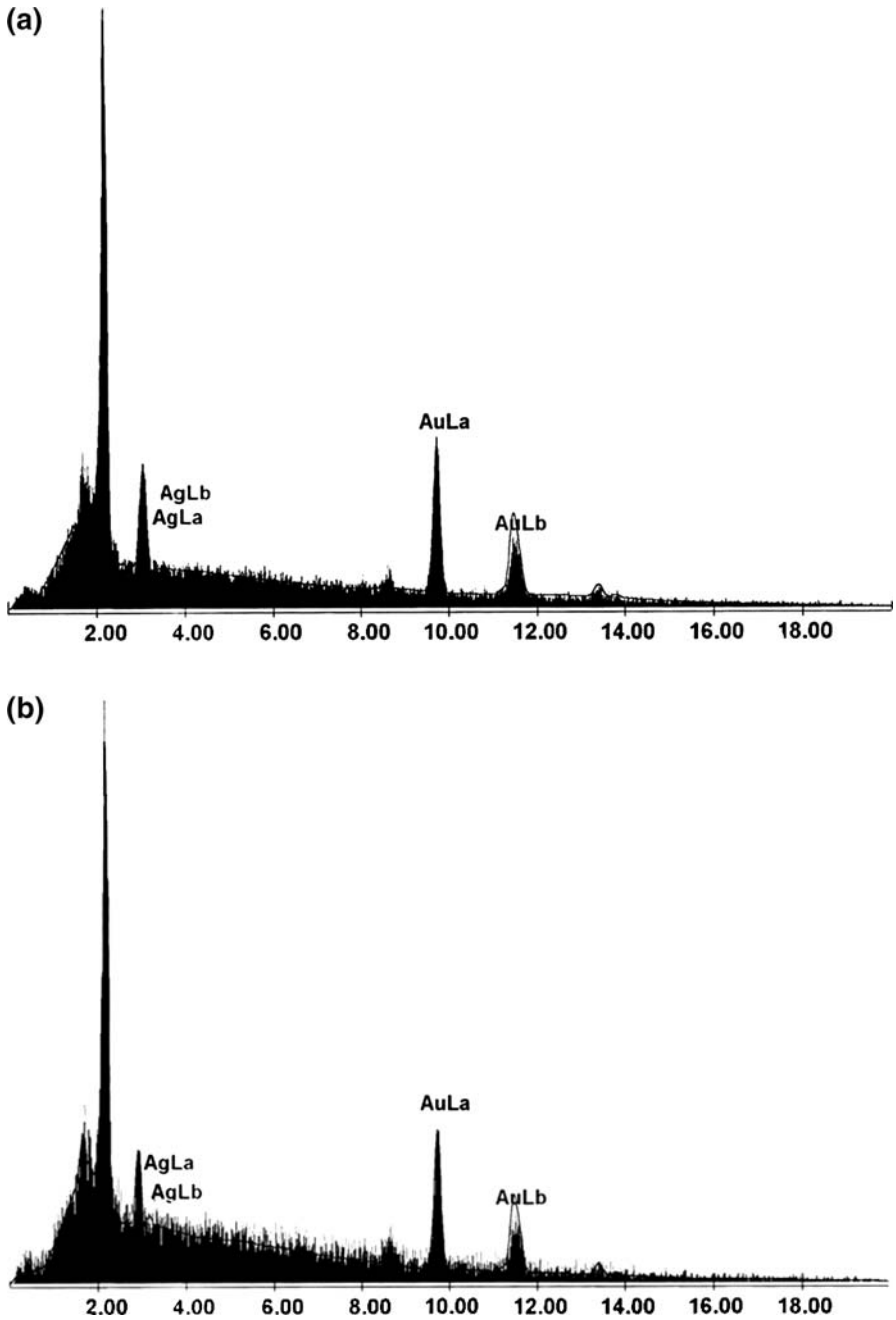


Fig. 6 EDS spectra of cotton treated with **a** L and **b** LS colloid solutions

the cationized cotton, large quantities of positive charges decrease the zeta potential of the fibre surfaces, which increases the sedimentation of silver particles because of the greater attractive forces between the fibres and the nanosilver (Liu et al. 2007). Also, the XRD patterns reveal that in modified cotton the crystalline phase decreases and, because amorphous structures have more vacancies than crystalline one, nanosilver adsorption increases (Zhang et al. 2007; Liu et al. 2007). Also from the SEM micrographs it is clear that the roughness of the surfaces of the fibres increases after cationization, which leads to the presence of more voids on the surfaces of the fibres, entrapping silver particles. Coating by other nanoparticles such as ZnO onto the surface of cellulose fibres due to the impaction of

Table 1 Silver content of normal and cationized cotton determined by ICP-OES technique

Silver concentration in exhaustion bath (mg L^{-1})	Temperature (°C)	Ag content (μg g^{-1})			
		Normal cotton treated by		Cationized cotton treated by	
		L	LS	L	LS
10	80	54.0 ± 0.9	92.0 ± 2.3	97.0 ± 1.4	151.0 ± 3.4
	100	61.0 ± 1.1	98.0 ± 1.6	89.0 ± 1.8	141.0 ± 1.3
25	80	78.0 ± 1.2	113.0 ± 3.1	305.0 ± 8.7	383.0 ± 4.6
	100	85.0 ± 1.4	121.0 ± 1.5	282.0 ± 6.3	351.0 ± 2.8
50	80	109.0 ± 2.2	164.0 ± 2.9	588.0 ± 3.2	686.0 ± 10.1
	100	117.0 ± 1.6	172.0 ± 2.6	527.0 ± 5.2	607.0 ± 5.6
100	80	213.0 ± 2.0	260.0 ± 4.6	792.0 ± 9.6	1,065.0 ± 17.8
	100	222.0 ± 2.4	271.0 ± 2.3	698.0 ± 4.8	973.0 ± 8.3
150	80	321.0 ± 7.8	379.0 ± 8.0	947.0 ± 13.4	1,387.0 ± 13.2
	100	336.0 ± 4.2	385.0 ± 6.1	894.0 ± 7.9	1,215.0 ± 9.8

particles onto the surface has been reported by other researchers (Ghule et al. 2006). The silver content of normal cotton samples treated at 100°C is greater than for those treated at 80°C, whereas in the case of modified samples the amount of silver adsorbed on the surface of the fibres treated at 80°C is greater than those treated at 100°C. This may be related to an increase of the rate of hydrolysis of the cationic reagent with increasing temperature, leading to a decrease in nanosilver adsorption. All samples treated with LS colloid had more silver content than those treated with L colloid solutions. To understand this effect, we need to consider the forces that small particles experience and how these forces affect their behavior. The presence of fixed or induced charges on particle surfaces affects most of the dynamic phenomena occurring in colloid systems as well as their stability (Toth 2001). L and LS nanosilver colloids have different stabilizers that have various surface characteristics, which may explain why samples treated with LS colloid adsorbed more silver.

Determination of inhibition zone

Antibacterial activity of fabric samples was determined in terms of inhibition zone formed on agar medium. The control samples were normal and cationized cotton without treatment with colloidal solutions, which did not show any antibacterial activity. Results of antibacterial activity tests are presented in Table 2. From these results it is observable that, the greater the concentration of

Table 2 Inhibition zones (diameter, in mm) of normal and cationized cotton samples against *Escherichia coli* bacteria

Silver concentration in exhaustion bath (mg L^{-1})	Temperature (°C)	Inhibition zone (mm)			
		Normal cotton treated by		Cationized cotton treated by	
		L	LS	L	LS
10	80	0.0	0.0	0.0	1–2
	100	0.0	0.0	0.0	1–2
25	80	0.0	1–2	2–3	3–4
	100	0.0	1–2	2–3	3–4
50	80	1–2	1–2	4–5	4–5
	100	1–2	1–2	4–5	4–5
100	80	1–2	2–3	5–6	5–6
	100	1–2	2–3	4–5	5–6
150	80	2–3	4–5	5–6	6–7
	100	2–3	4–5	5–6	6–7

nanosilver in the exhaustion bath, the more silver is adsorbed by the fibers and the larger the zone of inhibition that developed around the fabric samples. Inhibition zones around the cationized samples and samples treated with LS colloid solutions were greater than those around normal samples and samples treated by L solutions, respectively. Results illustrated that antibacterial efficiency against *E. coli* bacteria was dependent on silver content and that samples with greater silver content exhibited stronger antibacterial activity. Linear relationship between silver content and inhibition zone was not observed, which is due to the fact that only silver nanoparticles on the surface of samples can move and disperse around samples, forming larger inhibition zones.

Conclusions

Cationic groups were successfully formed on the surface of cotton using 3-chloro-2-hydroxy propyl trimethyl ammonium chloride. Adsorption of silver nanoparticles on cationized cotton is more than that on normal cotton, and modified samples treated at 80°C have more nanosilver than those treated at 100°C. The amount of nanosilver adsorbed on the cotton samples treated in L and LS colloid solutions are different, and cationization of fabrics strongly increases adsorption of nanosilver on the surface of the fibers due to the change of surface charge on the cellulose fibers. Cationized cotton treated with nanosilver colloids exhibited stronger antibacterial activity. Cationic modification can be used for modification of cellulosic fibers for increasing silver nanoparticle adsorption on their surfaces and producing stronger antibacterial activity.

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