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Characterization of nanosilver coated cotton fabrics and evaluation of its antibacterial efficacy

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ABSTRACT

An ecological and viable method for coating of cotton fabrics with silver nanoparticles (AgNPs) has been carried out. Nanocoated fabrics were characterized by scanning electron microscopy, energy dispersive X-ray and infrared spectroscopy. Color coordinates and silver release were assessed and the impact of repeated washings was evaluated. Silver contents were measured using atomic absorption spectroscopy and were 109.07 and 97.85 mg/kg for the fabrics treated with 100 ppm of AgNPs in presence and absence of binder respectively. Antibacterial activities of the cotton fabrics coated by AgNPs were evaluated qualitatively and quantatively, and the results explored that, regardless of the concentration of AgNPs used, the biocidability was always higher without washing. However, for all coated fabrics, a sufficient antibacterial action still observed after 20 washings. The results revealed that valuable antibacterial textiles which are required in different medical textile fields could be successfully produced.

1. Introduction

Particular attention is oriented nowadays about how to reduce or eliminate infections completely, especially those caused by antibiotic-resistant bacterial strains. These bacteria have been shown to have long survival times on commonly used hospital fabrics, such as hospital privacy drapes, scrub suits, and lab coats (Neely & Maley, 2000; Slaughter et al., 1996). The survival and transfer of microorganisms between patients and health care workers have been documented (Ransjo, 1979). The medical gowns and uniforms used currently have been proven to provide ineffective barriers for health care workers in numerous studies (Granzow, Smith, Nichols, Waterman, & Muzik, 1998; Lovitt, Nichols, Smith, Muzik, & Pearce, 1992; Quebbeman et al., 1991; Smith & Nichols, 1991).

This demonstrates a great need for antimicrobial textiles and polymers that are able to protect against all major pathogens (Liang et al., 2006; Worley & Sun, 1996; Worley & Williams, 1988). Clothing and other textile materials, especially those made of natural fibers such as cotton and wool, can act as media for the growth of microorganisms such as pathogenic or odor-generating bacteria and fungi. When in contact with the human body, such materials offer an ideal environment for microbial growth because of their large surface area and ability to retain oxygen, moisture and warmth, as well as nutrients from spillages and body exudates (Dev, Venugopal, Sudha, Deepika, & Ramakrishna, 2009).

Therefore, with a rising interest in personal health and hygiene, textiles with antimicrobial properties are becoming an increasingly desirable aim of textile manufacturers. Therefore, many antibacterial agents have been applied to fabricate antibacterial textiles, such as quaternary ammonium compounds (Sun, Li, Qiu, & Qing, 2005), chitosan (Ali, Joshi, & Rajendran, 2011), triclosan (Kalyon & Olgun, 2001), nanoparticles of noble metals and metal oxides (Jiang, Liu, & Yao, 2011; Joshi, Ali, & Rajendran, 2007; Mary, Bajpai, & Chand, 2009; Montazer & Seifollahzadeh, 2011; Vasilev et al., 2010; Xia, Cai, Jiang, & Yao, 2011) and bioactive plant-based products (Alemdar & Agaoglu, 2009), in which silver nanoparticle (AgNPs) has been widely used due to its broad spectrum of antibacterial activity and low toxicity toward mammalian cells (Hebeish et al., 2011), (Mahendra, Alka, & Aniket, 2009; Virender, Ria, & Yekaterina, 2009).

Using AgNPs leads to increasing the number of particles per unit area and, thus, antibacterial effects can be maximized (Yeo & Jeong, 2003). It has been proven that fibers that contain silver nanoparticles in the core-part (inside the fiber) had no significant antibacterial activity (Yeo & Jeong, 2003). However, fibers that have silver nanoparticles in the sheath-part showed excellent antibacterial effects.

However, Ag NPs are lack of chemical bonds to link with natural fibers which will bring about unsatisfied laundering durability of Ag NPs treated antibacterial textiles. Moreover, when Ag NPs

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release in great number into natural environment, the antibacterial ability of them could potentially compromise the health of organisms, e.g. alga in river, microorganisms especially vital bacteria that are important in the support and continuation of all forms of life, such as the degradation of organic matter, transformation of elements, and recycle of nutrients (Bradford, Handy, Readman, Atfield, & Mühling, 2009; Miao et al., 2010). Hence, some binders were applied to fix Ag NPs on the fibers to provide durability of antibacterial properties (El-Rafie, Mohamed, Shaheen, & Hebeish, 2010).

The antibacterial properties of the loaded AgNPs could be discussed in terms of their surface interaction with the cell membrane and/or inside interaction, especially smaller particle size, thereby decreasing permeability, disturbing respiration as well as causing damage of the cell (Ibrahim, Eid, Youssef, El-Sayed, & Salah, 2012; Jones & Hock, 2010; Mahapatra & Karak, 2008).

It is believed that the high affinity of silver toward sulfur or phosphorus is the key element of this effect. Due to the abundance of sulfur containing proteins on the bacterial cell membrane, AgNPs can react with sulfur-containing proteins inside or outside the cell membrane, which in turn affects bacterial cell viability (Morones et al., 2005). It was also proposed that silver ions (particularly Ag^+) released from AgNPs can interact with phosphorus moieties in DNA, resulting in inactivation of DNA replication, or can react with sulfur containing proteins, leading to the inhibition of enzyme functions (Mastsumure, Yoshikata, Kunisaki, & Tsuchido, 2003).

These properties allow the incorporation of AgNPs into various matrices such as textiles and wound dressing materials (El-Rafie et al., 2010; El-Rafie, Shaheen, Mohamed, & Hebeish, 2012; Gupta, Bajpai, & Bajpai, 2008; Hee, Jong, Soon, & Sung, 2007; Hermans, 2006; Hyang, Hyoung, Yoon, Kwan, & Seung, 2007; Hyung, Bo, & Young, 2010; Lee, Yeo, & Jeong, 2003; Marija & Petra, 2009; Mohammad, Mohammad, & Mohammad, 2009; Pollini, Russo, Licciulli, Sannino, & Maffezzoli, 2009; Purwar & Joshi, 2004; Williams, Halo Source, & Cho, 2005).

However, most of the loading processes were based on using commercial AgNPs or require multiple steps and complex reagents to prepare Ag-coated matrices (Vesna et al., 2009). Also, preparation of AgNPs using synthetic reducing agents is normally associated with environmental toxicity or biological hazards. Therefore the development of AgNPs based on environmental benign natural polymers is considered as most appropriate method for environmental reasons. The present emphasis is on use of starch as stabilizing agent in the green synthesis of silver nanoparticles (AshaRani, Mun, Hande, & Valiyaveettil, 2009; Raveendran, Fu, & Wallen, 2003; Singh, Sinha, & Mandal, 2009) and also as an efficient reducer by the action of alkali, since these can be easily integrated into systems for biological and pharmaceutical applications. Starch has been shown to act as a reductant as well as capping material (Sreeram, Nidhin, & Nair, 2008; Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006) and yields highly stable and water-soluble nanoparticles suspensions. Synthesis of metal nanoparticles has also been reported under surfactantless conditions, where different sugar molecules have been exploited for the syntheses and stabilization of metal nanoparticles (Panigrahi et al., 2006).

The presented work was undertaken with applying the ecofreindly prepared AgNPs colloidal solution in the finishing process of cotton fabrics to impart antibacterial activity. The coating process was carried out using two different concentrations of AgNPs (50 and 100 ppm) with/without binder. The treated fabrics were analyzed by scanning electron microscope (SEM), energy dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FTIR). Silver contents in fabrics were measured using atomic absorption spectroscopy (AAS). Color coordinates and silver release for the treated fabrics were both detected. Finally, the antibacterial action of the coated fabrics was tested against two types of bacteria; *Staphylococcus aureus* as Gram +ve and *Escherichia coli* as Gram −ve by using two different techniques; qualitatively by inhibition zone (ZI) method and quantitatively by plate count agar method.

2. Experimental

2.1. Materials

Silver nitrate (99.5%), Maize starch supplied from (Egyptian Starch and Glucose Company, Cairo, Egypt), Sodium hydroxide, Sodium carbonate monohydrate and Nitric acid (55%) were all used as received. Desized, scoured, and bleached 100% cotton fabrics, were kindly supplied from El-Mahalla Company for Spinning and Weaving, El-Mahalla El-Kubra, Egypt.

2.2. Coating process

Experiments were performed on samples with maximum dimension of 20 cm × 20 cm. The cotton samples were subjected to four separated treatments. In the first one, the fabrics were treated with Ag-NPs colloidal solution at concentration of 54 ppm with1% Binder (printo® FX based on acrylate) solutions. The second treatment embraced treating of cotton fabrics with 108 ppm Ag-NPs colloidal solution containing 1% Binder. Then, the third and forth ones were carried out like the first and the second ones but without using binder. After padding, all treated samples; encompassing, AgNPs-cotton and Binder/AgNPs-cotton were squeezed to 100% wet pick up at constant pressure, then dried at 70 °C for 3 min, followed by curing at 150 °C for 2 min.

Table 1 shows synthesis method and characterization of the produced AgNPs. 50 and 100 ppm AgNPs colloidal solutions were prepared as follows: 1 g/l of alkali hydrolyzed maize starch is prepared and $AgNO_3$ (0.5 mmol/l and 1 mmol/l) was gradually added, then 10 g/l of binder was finally added to the colloidal solutions and left for 1 h at 60 °C.

3. Measurements

3.1. Scanning electron microscopy (ESEM) and energy dispersive X-ray (EDX)

Scanning electron microscopy (SEM) was used to study the surface characteristics of fabrics treated with AgNPs in comparison with the untreated fabrics (ESEM FEG, XL 30, Philips, Netherland). For chemical characterizations of treated fabrics energy dispersive X-ray (EDX) analyses were carried out using the same instrument.

3.2. Attenuated total reflection–Fourier transform infrared spectroscopy (ATR-FTIR)

Nanosilver coated cotton fabrics and the uncoated fabrics were both characterized by ATR-FTIR spectrophotometer (Bruker Vector 22 Spectrometer GmbH, Germany), with a diamond crystal. Scanning area was in range of 3750–500 cm^{-1}, repetitious scans average was 128 with 2 cm^{-1} interval scanning and the spectra resolution was adjusted at 4 cm^{-1}. All spectra were manipulated using 9 points smoothing and were all normalized.

3.3. Moisture content

Moisture content was measured as follows: 1 g of sample was weighed accurately and then dried at 105 °C for 4 h. The dried

Table 1
Synthesis process and characterization of AgNPs.

AgNPs	$AgNO_3$	Polysaccharide	Temperature/time	AgNPs shape	Size distribution
50 ppm	0.5 mmol/l	1 g/l starch	60 °C/1 h	Spherical	–
100 ppm	1 mmol/l	1 g/l starch	60 °C/1 h	Spherical	2–30 nm

sample was reweighed; then, moisture content was calculated according to Eq. (1), which was found to be 4.54%.

$$\mathrm{MC} = \left[\frac{A-B}{A}\right] \times 100 \quad (1)$$

where MC is moisture content (%), A, initial weight (g) and B, weight of dried fabric (g).

3.4. Detection of silver content

Silver content in the coated cotton fabrics was measured according to the method suggested by Hossam et al. (2013) as follows: 0.2 g of coated dried fabrics was immersed in 30 ml of 15 wt% nitric acid for 2 h at 80 °C. Silver concentration was recorded by using flame atomic absorption spectroscopy (AAS, SpectrAA, 220, Varian, Australian) equipped with silver lamp (328.1 nm). The silver content was calculated by Eq. (2).

$$\text{Silver content (mmol/kg)} = \frac{C_s}{W_d/(1-\mathrm{MC}/100)} \times V \quad (2)$$

where C_s, silver concentration (mmol/l) in extracted solution which is detected by atomic absorption spectroscopy; V, volume of extracted solution; W_d, weight of dried coated fabric (g); MC, moisture content of coated fabrics (%) (Hossam et al., 2013).

3.5. Washings and silver release

The washing process of AgNPs coated fabrics can be described briefly as follows: treated fabric was immersed in washing solution which contained 2 g/l Na_2CO_3 and 2 g/l commercial detergent, using material to liquor ratio 1:50.Then, the samples were stirred and left for 15 min at 55 ± 5 °C. Finally, the fabrics were gently squeezed and rinsed with tap water. This process was repeated 5, 10 and 20 times to get 5, 10 and 20 washings. The silver release was calculated with Eq. (3).

$$\text{Silver release (\%)} = \left[\frac{C_b - C_a}{C_b}\right] \times 100 \quad (3)$$

C_b is the silver content in treated fabrics before washing, and C_a is the silver content in treated fabrics after washing. C_a and C_b were measured by extraction method which is described below.

3.6. Color measurements

Color measurements of AgNPs coated fabrics were recorded with a colorimeter with pulsed xenon lamps as light source (UltraScan Pro, Hunter Lab, USA). The equipment could be characterized as follows: CIE LAB color space, 10° observer with D65 illuminant, d/2 viewing geometry and measurement area of 2 mm. Color measurement parameters are lightness (L^*) from black (0) to white (100), a^* is a red (+)/green (−) ratio, b^* is yellow (+)/blue (−) ratio. Each data point was the average of two independent measurements.

3.7. Antibacterial test

The antimicrobial activity of AgNPs coated cotton fabrics were tested by using two different techniques; qualitative method by using inhibition zone technique and quantitative method by using plate count agar method.

The qualitative method was carried out by using a modified Kirby–Bauer disk diffusion technique (Bauer, Kirby, Sherris, & Turck, 1966). Briefly, 100 μl of the tested bacteria were grown in 10 ml of fresh media until they reached a count of approximately 108 cells/ml (Pfaller, Burmeister, Bartlett, & Rinaldi, 1988). A 100 μl of microbial suspension was spread onto agar plates corresponding to the broth in which they were maintained. Plates inoculated with Gram (+) bacteria as *S. aureus* and Gram (−) bacteria as *E. coli*, were incubated at 35–37 °C for 24–48 h, then the diameters of the inhibition zones were measured in millimeters (Bauer et al., 1966). Standard discs of *Tetracycline* (Antibacterial agent), served as positive controls for antimicrobial activity, however, filter discs impregnated with 10 μl of solvent (distilled water, chloroform, DMSO) were used as a negative control.

When a part of the AgNPs coated fabrics is placed on agar media, AgNPs will diffuse from fabric into the surrounding. The solubility of nanosilver and its particle size will determine the size of the area of silver infiltration around the fabric. If an organism is placed on the agar it will not grow in the area around the fabric if it is susceptible to the AgNPs. This area of no growth around the coated fabric is known as a "*Zone of inhibition*" or "*Clear zone*".

For AgNPs diffusion, the zone diameters were measured with slipping calipers of the National Committee for Clinical Laboratory Standards (NCCLS, 1997). The average width of a zone of inhibition along a streak on either side of the test fabric is calculated using Eq. (4):

$$W = \frac{T-D}{2} \quad (4)$$

where W, width of clear zone of inhibition in mm; T, total diameter of test fabric and clear zone in mm, and D, diameter of the test fabric in mm (Fig. 1).

The quantitative method was performed for the washed samples against *S. aureus* (AATCC 6538) as Gram +ve bacteria according to the AATCC test method 100–1999 for Bacterial Counting. Briefly all treated fabrics were kept at 35 °C prior to test. Then, 0.5 g fabrics were transferred into 100 ml of nutrient broth (ca. 1.5×10^8 colony forming unit per ml), and shaked vigorously for 1 min. A normal saline solution was prepared with 0.9% (w/v), was exposed to serial dilution and then plated onto Mannitol salt agar plates. Plates were incubated at 37 °C for 24 h and then the colonies were counted. The reduction percentage of bacterial colonies was calculated using Eq. (5).

$$R\% = \left[\frac{B-A}{B}\right] \times 100 \quad (5)$$

where R% is the reduction percentage of bacterial colonies; A is the number of bacterial colonies on the agar plate with coated

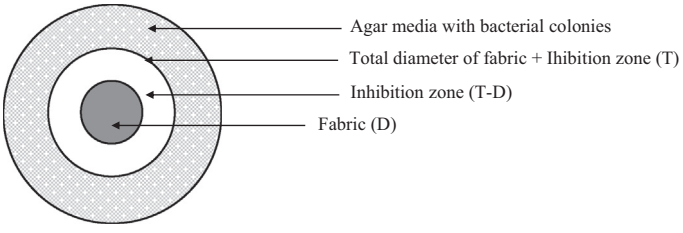

Fig. 1. Schematic diagram represents test of antibacterial activity using inhibition zone technique.

fabric, and *B* is the number of bacterial colonies on the agar plate for control.

4. Results and discussion

Briefly, the mechanism of how alkali hydrolyzed starch can act as both a reducer for nanoparticles generator and a stabilizing agent for the net produced NPs could be explained as follows: alkali treatment is thought to increase the solubility of starch by rupturing the granules, and then degrading starch macromolecules to give smaller fragments with higher reducing power, also it acts in increasing the affinity of the free hydroxyl groups of sugars by removing the protons which in turns assist the formation of silver nanoparticles.

For synthesis of AgNPs, the generally accepted mechanism suggested a two-step process, i.e. atom formation and then polymerization of the atoms. In the first step, a portion of metal ions in a solution is reduced by the reducing agent (starch fragments). In the second step, the atoms produced act as nucleation centers and catalyze the reduction of the remaining metal ions present in the bulk solution. Subsequently, the atoms coalesce leading to the formation of metal clusters.

4.1. SEM micrographs and EDX spectrum

As it has been mentioned by Navzer et al., that cotton fabrics are better materials for silver deposition with good durability, robustness, and smoothness of hand (Navzer et al., 2007). Therefore, finished cotton fabrics are chosen in this work for coating process.

The interaction between the fabrics and the metallic silver nanoparticles results from: the physical adsorption of silver nanoparticles on the surface of the fabrics (Perelshtein et al., 2008). The morphological changes of cotton fabrics caused by deposition of AgNPs were monitored by scanning electron microscope (SEM). The SEM images of cotton fabrics before and after treatment with silver nanoparticles with two different concentrations (50 and 100 ppm), at two different magnifications are shown in Fig. 2.

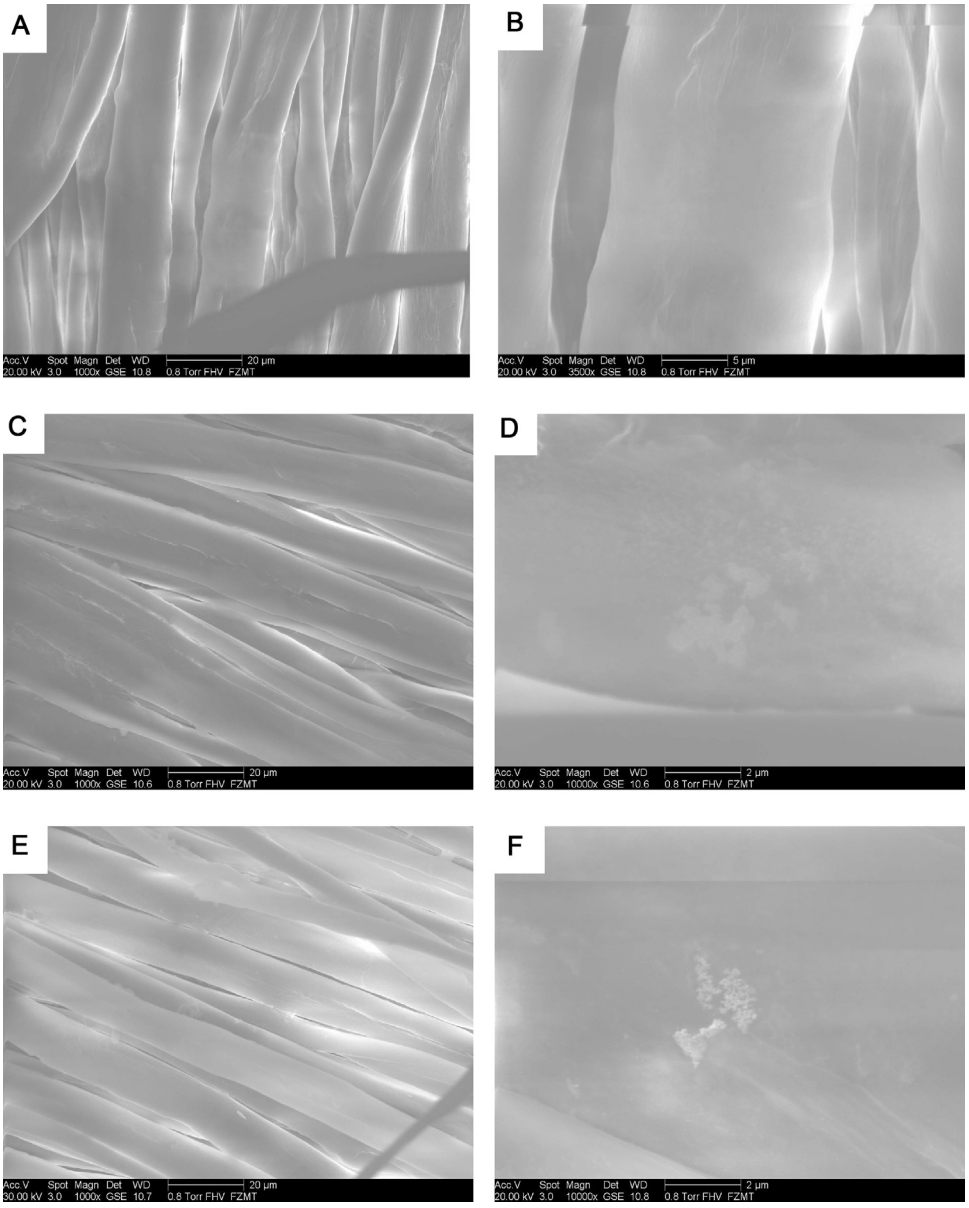

Fig. 2. SEM images: (A and B) untreated cotton fabric (C and D) cotton fabric coated with 50 ppm AgNPs, (E and F) cotton fabric coated with 100 ppm AgNPs.

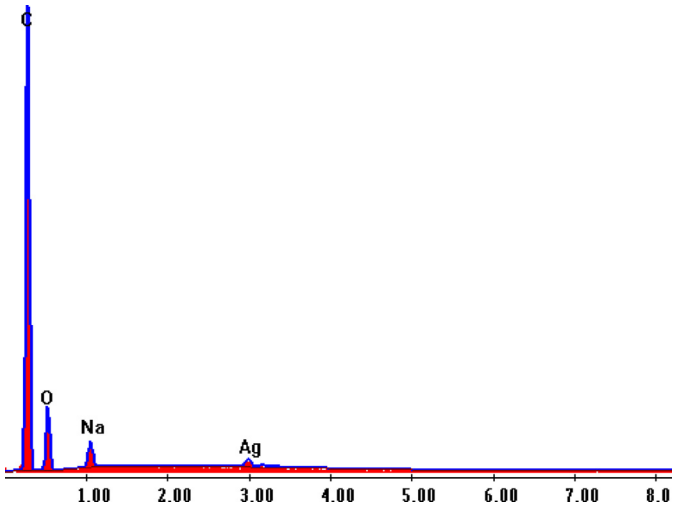

Fig. 3. EDX image for cotton coated fabric with 100 ppm AgNPs.

The microscopic images in Fig. 2(A and B) demonstrate the smooth surface of cotton fabric before coating with nanosilver. The presence of AgNPs cannot be observed on cotton fiber coated by 50 ppm AgNPs colloidal solution due to low concentration of precursor solution (Fig. 2C and D). On the contrary, the cotton fabrics loaded with 100 ppm of AgNPs colloidal solution is covered with well dispersed quite uniform AgNPs (Fig. 2E and F). Aggregates consisting of smaller particles are also noticeable.

Fig. 3 shows the EDX spectrum of a treated sample confirming the existence of silver element on the surface of the fabric treated with 100 ppm of AgNPs. Also, it confirms the existence of the low amount of nanosilver particles on the surface of the treated fabrics as tiny peak of silver was observed. The presence of sodium element in the EDX spectrum is related to the alkaline solution of AgNPs which contains sodium hydroxide.

4.2. ATR-FTIR analysis of AgNPs coated cotton fabrics

Fig. 4 shows the ATR-FTIR spectra of the aforementioned untreated and finished treated cotton fabrics with starch–nanosilver colloidal solutions under different conditions.

It is obvious that the most characteristic peaks in Fig. 4 are the main functional groups attributable to cellulosic molecular structure of cotton fabrics. These include: the absorption bands at 3414 cm^{-1} (OH, stretching), 2906 cm^{-1} (CH, aliphatic, stretching), 1164 cm^{-1} (C—O, stretching) and 1114 cm^{-1} (C—O—C, asymmetric bridge stretching). The band at 2390 cm^{-1} is characterized for CO_2 of air.

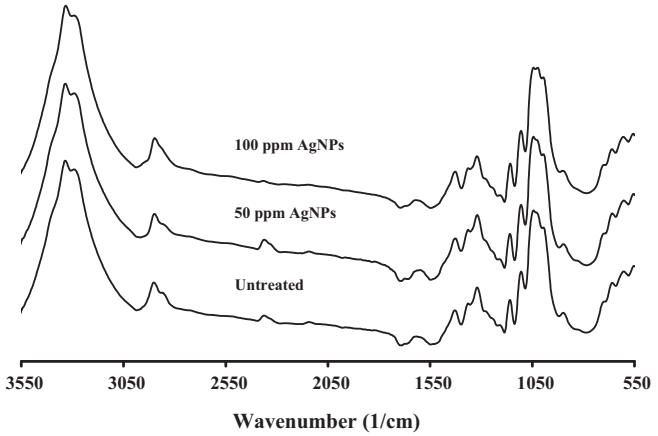

Fig. 4. ATR–FTIR spectra of untreated and coated cotton samples.

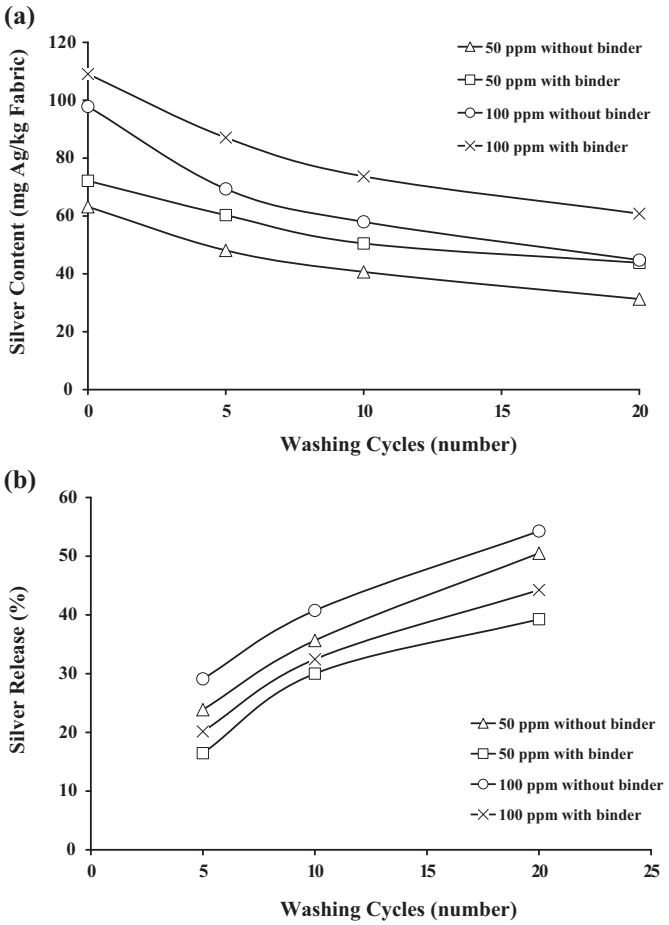

Fig. 5. (a) Silver content for the coated fabrics with different treatment conditions as a function of washing cycles. (b) Silver release from coated cotton fabrics by washing.

From Fig. 4, it could be clarified that, all charts are superimposible. Therefore it is safe to state that; treatment of cotton fabrics with starch–nanosilver solutions does not affect on the molecular structure of fabrics, and this confirms that there is no chemical interaction between Cellulosic chains of fabric and starch–silver nanocomposite, as, the interaction between fibers and metallic silver nanoparticles only results from physical adsorption of silver nanoparticles on surface of treated fabrics.

4.3. Silver content in AgNPs coated cotton fabrics and silver release

Total silver content in treated fabrics was determined by atomic absorption spectrophotometer. From Fig. 5a, obviously, it could be observed that the actual amount of silver content on the surface of fabrics increased by increasing the concentration of the AgNPs colloids, as it increased from 63.20 mg/kg by using 50 ppm to 97.85 mg/kg by using 100 ppm of nanosilver colloidal solutions. It is a point which could be associated with higher deposition of AgNPs, which is suggested to take a place with fixation therein through physical bonding.

The data also highlighted that, higher concentrations of AgNPs with binder improved nanosilver loading. As by treating fabrics with 100 ppm AgNPs colloidal solution using binder, silver content reaches 109.07 mg/kg. The treatment of cotton fabrics with 100 ppm AgNPs colloidal solution by using binder results in giving the best value of nanosilver loading. This confirms the role of

Table 2
Color coordinates data (CIE lab) for AgNPs treated fabrics as a function of silver content.

Samples		Silver content (mg/kg)	L^*	a^*	b^*
Blank (untreated)		0	93.47 ± 0.15	−0.26 ± 0.08	1.59 ± 0.09
A	1	63.20	87.27 ± 0.33	0.08 ± 0.12	5.93 ± 0.09
	2	48.11	87.10 ± 1.31	0.39 ± 0.09	2.55 ± 0.18
	3	40.67	88.20 ± 0.25	0.47 ± 0.23	2.61 ± 0.47
	4	31.29	88.94 ± 0.44	0.22 ± 0.13	3.00 ± 0.80
B	1	72.15	83.76 ± 0.06	0.31 ± 0.21	10.07 ± 0.82
	2	60.29	85.48 ± 0.38	0.48 ± 0.19	6.57 ± 1.05
	3	50.51	86.01 ± 0.20	0.55 ± 0.11	6.55 ± 0.40
	4	43.83	86.18 ± 0.11	0.55 ± 0.21	5.79 ± 0.45
C	1	97.85	83.51 ± 0.07	0.36 ± 0.21	14.53 ± 0.01
	2	69.36	86.48 ± 0.04	0.36 ± 0.05	7.55 ± 0.51
	3	57.98	87.64 ± 0.04	0.07 ± 0.09	6.62 ± 0.01
	4	44.75	87.96 ± 0.11	0.68 ± 0.23	5.34 ± 1.31
D	1	109.07	86.72 ± 0.04	−0.12 ± 0.05	7.58 ± 0.25
	2	87.10	87.70 ± 0.06	−0.63 ± 0.04	6.17 ± 0.30
	3	73.68	87.95 ± 0.24	0.03 ± 0.02	4.82 ± 0.02
	4	60.81	88.76 ± 0.25	0.13 ± 0.02	3.82 ± 0.18

A: Cotton treated with 50 ppm AgNPs solution.
B: Cotton treated with 50 ppm AgNPs solution in the presence of binder.
C: Cotton treated with 100 ppm AgNPs solution.
D: Cotton treated with 100 ppm AgNPs solution in the presence of binder.
1, before washing; 2, after 5 washing cycles.
3, after 10 washing cycles and 4, after 20 washing cycles.

binder in fixation of the deposits of silver nanoparticles within the molecular structure of cotton.

To evaluate the laundering durability of nanosilver coated cotton fabrics, Ag content and silver release percent were both measured after different washings. Fig. 5b shows the silver release from fabrics after repeated washings. Silver release percent is increased by increasing the concentration of nanosilver colloidal solution which was used in coating process, as it was 39.3% and 44.2% after 20 washing cycles for fabrics treated with 50 and 100 ppm AgNPs, in the presence of binder respectively. Silver release percent was higher in case of using AgNPs colloidal solution without binder rather than that with binder. As in case of coated fabrics treated with 100 ppm AgNPs in absence of binder, silver release percent was 29.1%, and became 54.3% after 5 washings. However, in the presence of binder, silver release percent was 20.1%, and reached 44.2% after 20 washings. So, it could be concluded that, subjecting the coated cotton fabrics to washings resulted in a decrement of silver content and this created the idea of incorporating fixing agent in the finishing bath.

Also, it could be suggested that, as 31.92 mg/kg of silver was released after 20 washings for fabrics coated with 50 ppm AgNPs, the silver release in waste water in one washing cycle could be calculated to be 32.1 μg/l. This amount of silver is lower than the permitted value for silver content in waste water (100 μg/l) for the Austrian legal regulations (April 1996, 58. Stück, 462 Bundesministerium für Land- und Forstwirtschaft). Also, according to Juyoung Kim, the cytotoxicity for human cell was not observed for Ag-impregnated cellulose with 0.035 Ag (wt/v)% or lower (Kim et al., 2009). Thus, 31.29 mg/kg as silver amounts, released after coating fabrics with our suggested colloidal nanosilver solution, could be described to be saved for human beings.

4.4. Color coordinates

Results of the foregoing section clarified the effect of applying the nanosized silver colloidal solutions on the color of cotton fabrics, in case of coating fabrics with two different concentrations of nanosilver solution (50 and 100 ppm) in the presence and absence of binder. The color coordinates were expressed by, L^* (black (0) and white (100)), a^* (red (+) and green (−)) and b^* (yellow (+)/blue (−)) (Gulrajani, 2010).

The achieved results are proposed in Table 2. From the previous studies (Gulrajani, 2010) which shows the change of color related to the values of color coordinates, it could be summarized that, decreasing of L^* and increasing of b^* values reflected the increment of yellowness for the coated fabrics. It evident from the results of Table 2 that, b^* value is higher for coated fabrics rather than uncoated fabrics. However, b^* value is gradually decreased with washing. Also it can be observed that, the treatment in the presence of binder resulted in increasing of b^* value. As for uncoated fabric $b^* = 1.59$, for fabric coated with 50 ppm nanosilver solution $b^* = 5.93$, for fabrics coated with 50 ppm in the presence of binder = 10.07, however, for fabrics treated with 50 ppm exposed to 20 washings $b^* = 3.00$. The b^* value was increased by increasing the AgNPs concentration used from 50 ppm to 100 ppm, which is attributed to the higher silver content for the coated fabrics. This means that higher concentrations of AgNPs are deposited on the fabrics which in turn increase yellowish appearance of coated fabrics.a^* value was not changed significantly, as for untreated fabric $a^* = -0.26$, for 50 ppm AgNPs coated fabric in the presence of binder, $a^* = 0.31$, and for 100 ppm AgNPs treated fabric in the presence of binder, $a^* = -0.12$.

However, for L^* values, the uncoated fabric (=93.47) with higher value than that for fabric coated with 50 ppm (=87.27). However, after 20 washings, L^* became 88.94. This means that the application of nanosized silver particles decreased whiteness appearance of coated cotton fabrics. Also by washings, yellowish staining caused by nanosilver treatment started to decrease as some of nanosilver particles were removed in washing liquor.

Obviously, it could be concluded that, by coating fabrics with colloidal nanosized silver solution, yellowness increased and lightness decreased. Also, by addition of binder, yellowish staining caused by nanosilver deposition was increased. This indicated the important role of binder in fixation of nanosilver deposits on the molecular structure of the coated cotton fabrics. However, by washing, yellowness decreased, as the fabrics started to turn back to white color because of releasing AgNPs to the surrounding washing bath.

4.5. Antibacterial efficacy

Textile goods, especially those made from natural fabrics can provide an excellent environment for microorganisms to grow,

Table 3
Effect of washing cycles and silver content on the antibacterial activities of nanosilver coated cotton fabrics.

Samples		Silver content (mg/kg)	Inhibition zone diameter (mm)		Bacterial reduction (%)
			Staphylococcus aureus (Gram +ve)	*Escherichia coli* (Gram −ve)	*Staphylococcus aureus* (Gram +ve)
Blank (untreated)		0	0	0	0
A	1	63.20	1.5	1	
	2	48.11	1	1	
	3	40.67	0.5	1	
	4	31.29	0	0	87
B	1	72.15	1.5	1.5	
	2	60.29	1.5	1	
	3	50.51	1	0.5	
	4	43.83	0.5	0.5	90
C	1	97.85	2	2	
	2	69.36	1	1.5	
	3	57.98	1	1	
	4	44.75	0.5	0.5	90
D	1	109.07	1.5	2	
	2	87.10	2	1.5	
	3	73.68	1.5	1.5	
	4	60.81	1	1	95

A: Cotton treated with 50 ppm AgNPs solution.
B: Cotton treated with 50 ppm AgNPs solution in the presence of binder.
C: Cotton treated with 100 ppm AgNPs solution.
D: Cotton treated with 100 ppm AgNPs solution in the presence of binder.
1, before washing; 2, after 5 washing cycles.
3, after 10 washing cycles and 4, after 20 washing cycles.

because of their large surface area and ability to retain moisture. Therefore to impart the natural fabrics, a high antimicrobial activity and its chemical modification has been found to be a highly effective field of study (Holme, 1993).

Thus, the current study focuses on improving the antibacterial activity of cotton fabrics via individual inclusion of certain bioactive nanosilver–starch composite. To evaluate the durability of the imparted antibacterial activity after repeated washings, the antibacterial activities were studied with washings.

The antibacterial activity was tested qualitatively against two different bacterial strains; *S. aureus* as an example of Gram positive bacteria and *E. coli* as an example of Gram negative bacteria, and results were reported in Table 3. The data shown in Table 3 reveals that: (i) all the coated samples performed splendid antibacterial activities owing to the presence of AgNPs. (ii) The higher AgNPs concentration, the higher silver content in fabric and hence, the better the imparted antibacterial activity. However, coating of cotton fabrics with 50 ppm colloidal nanosilver solution was enough to gain excellent antibacterial properties. (iii) The antibacterial activity of nanosilver coated fabrics decreased slightly after several washings, as after 20 washings, the coated fabrics still exhibited excellent durability. (iv) Regardless of the concentration of AgNPs used, inclusion of a binder has a positive effect on antibacterial performance properties.

From the data, it could be concluded that, fabrics coated with a solution containing 50 ppm AgNPs in presence of binder retain excellent antibacterial action. This is clarifying the important role of binder in fixation of AgNPs deposits within the molecular structure of cotton (Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010). This phenomenon becomes clearer when the fabrics were similarly coated without binder.

The bacterial (*S. aureus*) counting method was used as quantitative method for the detection of antibacterial efficacy and data was reported in Table 3. The test was done only for the coated fabrics exposed to 20 washings. Results of Table 3 also showed that, regardless of the concentration of AgNPs used or silver content of fabrics, the reduction of bacterial colonies was always higher than 85%. An excellent antibacterial property was gained for the fabrics coated with 50 ppm AgNPs solution in the presence of binder, as it caused a reduction of bacterial colonies by 90%. Subjecting the treated fabrics to washings leads to non sense decrement in the reduction of bacterial colonies, as after 20 washings, fabrics coated with 100 ppm AgNPs colloidal solution (with binder) caused a bacterial reduction reached to 95%. Thus, it still exhibited excellent antibacterial properties.

5. Conclusion

Excellent antibacterial cotton fabrics were produced by coating with low concentration of AgNPs using environmentally easy method. SEM micrographs and EDX analysis confirmed the existence of AgNPs on the surface of cotton fabrics. The fabrics were coated and exposed to multiple washings in order to determine the amount of silver leached into the washing bath. It can be inferred from the study that, fundamental differences in the concentration of AgNPs and the presence or absence of binder controlled the amount of Ag loaded on the fabrics' surfaces, and also the amount of nanoparticles released into the washing liquor. The obtained color coordinates data revealed that, through increasing the AgNPs loaded on the surface of the cotton fabrics, the color turned to yellow. The yellowish color is become deeper in the presence of binder which confirms the significant role of binder in fixing the loaded nanoparticles. The AgNPs imparted an excellent antibacterial property to the cotton fabric with an excellent washing durability. The nanosilver coated cotton fabrics still retain excellent antibacterial activity after 20 washings. Application of AgNPs based on these findings may lead to produce valuable medical and antiseptic dressing or bandage which are required in different medical purposes.

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