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Surface modification of cotton fabrics for antibacterial application by coating with AgNPs–alginate composite

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ABSTRACT

In recent years nano-sized particles have been focused on bacteriostasis. We investigated antimicrobial activities by applying AgNPs–alginate composite on cotton fabric, using a simple one-step rapid synthetic route by reduction of silver nitrate using alkali hydrolyzed alginate solution which acts as both reducing and capping agent. FTIR spectra, color coordinates, silver content, silver release percent and SEM images of treated fabric samples confirmed the successful physical deposition of AgNPs–alginate composite on the fabric. The treated fabrics demonstrated an excellent antibacterial activity against the tested bacteria, *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*. A slight decrease in the antibacterial feature of the cotton fabrics was observed after successive washings. However, an efficient antibacterial activity still remained on the fabrics.

1. Introduction

The development of materials containing substances with antimicrobial activity has been implicated in a variety of biomedical applications (Djoric & Burrell, 1998; Feng et al., 2000; Kraft, Hansis, Arens, Menger, & Vollmar, 2000). Silver or silver ions have long been known to exhibit powerful antimicrobial activity (Slawson, Van Dyke, Lee, & Trevors, 1992; Zhao & Stevens, 1998) and strong biocidal effects against as many as 16 species of bacteria including *Staphylococcus aureus* and *Escherichia coli* (Spadaro, Berger, Barranco, Chapin, & Becker, 1974).

For this reason, silver-based compounds have been used extensively in many bactericidal applications, including the formulation of dental resin composites (Yoshida, Tanagawa, & Atsuta, 1999; Yoshida, Tanagawa, Matsumoto, Yamada, & Atsuta, 1999), ion exchange fibers (Nonaka, Node, & Kurihara, 2000), and coatings of medical devices (Bosetti, Masse, Tobin, & Cannas, 2002; Schierholz, Lucas, Rump, & Pulverer, 1998). The synthesis protocols for nanostructured materials have been developed (Andrew, Mirkin, & Letsinger, 2000; Duan, Cai, Luo, Li, & Lei, 2006).

Recently, the preparation of ultrafine metal particles has attracted considerable attention because they can offer highly promising and novel options for a wide range of technical applications (Henglein, 1993; Hayward, Saville, & Aksay, 2000; Henglein, 1993; Hossam et al., 2013). The large specific surface area and high fraction of surface atoms on silver nanoparticles (AgNPs) leads to enhanced antibacterial activity compared to bulk silver metal.

Silver nanoparticles (AgNPs) in combination with hydrophilic, biocompatible polymers can be a basis of new generation of antimicrobial materials (El-Rafie, Mohamed, Shaheen, & Hebeish, 2010; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010; Hebeish et al., 2011; Varaprasad et al., 2011). Silver is a historically well known metal for its broad antimicrobial activity while nanocrystalline silver was reported to extinguish microbes more rapidly and completely than its cationic form (Bhattacharya & Mukherjee, 2008). Polymers in solutions and as hydrogels were shown to be effective capping agents for AgNPs providing in the same time biocompatibility and diversity of forms and structures, and thus possibilities for variety of biomedical applications such as antimicrobial coatings, wound dressings and, potentially, tissue implants (Monteiro et al., 2009).

Hydrogels, in specific, can act as efficient donors of AgNPs and Ag ions as well as other immobilized biologically active substances, while blends of different polymers may provide desired stability or degradation rate and biomechanical properties (Varaprasad et al., 2011). Alginate, poly(vinyl alcohol) (PVA) and poly(N-vinyl-2-pyrrolidone) (PVP) are among mostly studied polymers for biomedical applications in general, including also immobilization of AgNPs (Armentano, Dottori, Fortunati, Mattioli, & Kenny, 2010;

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Sharma, Yngard, & Lin, 2009). All three polymers form biocompatible hydrogels, which differ in mechanical strength.

Alginate is a naturally derived linear copolymer that forms hydrogels in the presence of divalent cations such as Ca^{2+} *via* ionic interactions. Ca-alginate gels are generally weak with mechanical and structural properties that depend on alginate composition (Drury, Dennis, & Mooney, 2004; Martinsen, Skjak-Braek, & Smidsrod, 1989). Alginate, mostly as Ca–alginate hydrogel, is already commercially used in wound dressings some of which provide antimicrobial activity by the release of silver ions.

Alginate is widely used in industry and medicine for many applications such as scaffolds and wound dressings due to low toxicity, favorable mechanical properties, and capacity for bioresorption of the constituent materials (Boontheekul, Kong, & Mooney, 2005; Kim et al., 2005).

Alginate dressings are widely used in the treatment of exuding wounds, as the ion exchange occurring between the calcium ions of the dressing and the sodium ions in the exudates results in the formation of a gel on the surface of the wound. This gel maintains an appropriate moist environment (Winter, 1962). Alginate non-woven fabrics are clinically applied for moisture wound healing. According to Anna, Alicja, and Ewa (2011), alginate itself has not antimicrobial activities, but the hydrocolloids like alginate could be used as edible coating films, which can improve shelf life and food quality by serving as selective barriers to moisture transfer, oxygen uptake, lipid oxidation, losses of volatile aromas and flavors, and so this will protect from bacterial growth. Their use is gaining importance in food protection and preservation as they provide advantages compared with films made from synthetic materials.

Wound infection contributes to the formation of a nonhealing wound (Warrier & Burrell, 2005). Bacterial load on the surface of a wound amplifies and/or perpetuates a pro-inflammatory environment. Therefore, antimicrobial agents, such as silver-based formulations, are often used for wound healing. Silver-coated dressings are commonly used because they are effective in killing a broad range of bacteria.

Recently, AgNPs were synthesized in alginate solutions using gamma irradiation (Liu, Chen, Zhong, & Wu, 2009), electrochemical synthesis (Obradovic et al., 2010) and on the surfaces of alginate microbeads using photochemical reduction (Saha et al., 2009; Saha, Pal, Kundu, Basu, & Pal, 2010). However, the utility of AgNPs depends on the efficiency of nanoparticle stabilization due to their high tendency to agglomerate. A general mechanism of AgNPs formation and growth was proposed recently and consists of consecutive steps of classical nucleation and growth, aggregative nucleation and growth, and Ostwald ripening (Richards, Rath, & Buhro, 2010).

The goal of this work is the production of cotton fabrics with excellent biocidal properties through two major steps: (1) Preparation of colloidal solution of silver nanoparticles by ecological and viable method using alkali hydrolyzed sodium alginate as a biocompatible and biodegradable polymer which acts as both a reducer for silver nitrate which acts as a generator for nanosilver and a stabilizing agent for the produced silver nanoparticles during the reaction, (2) Physical deposition of AgNPs–alginate composite on the surface of cotton fabrics with/without using binder.

2. Experimental

2.1. Materials

Silver nitrate (99.5%), sodium alginate supplied from (Egyptian Starch and Glucose Company, Cairo, Egypt), sodium hydroxide, sodium carbonate monohydrate and nitric acid (55%) were all used without further purification. Bleached plain cotton fabrics were used as received without any treatments.

2.2. Coating process

Incorporation of silver nanoparticles in cotton fabrics was performed by pad – dry – cure method. Ag-cellulosic fabrics was prepared by immersing of fabrics (20 cm × 20 cm) in a colloidal solution bath of silver nanoparticles (50 ppm and 100 ppm) for 30 seconds and squeezed to 100% wet pick up using laboratory pad at constant pressure. The samples were dried at 75 °C for 15 min and cured at 120 °C for 3 min for thermal fixation of nanoparticles on fabrics surface.

Table 1 shows synthesis process and characterization of AgNPs-alginate composite. 50 and 100 ppm AgNPs colloidal solutions are prepared as follows: 3 g/l alginate was hydrolyzed by 20 g/l NaOH at 70 °C then $AgNO_3$ (0.5 mmole/l in case of preparing 50 ppm, and 1 mmole/l in case of preparing 100 ppm AgNPs) was gradually added, and then left for 15 min to complete the preparation process. In case of presence of binder, the binder (10 g/l) was added after $AgNO_3$ then the solution is left at 70 °C for 15 min.

3. Measurements

3.1. Scanning electron microscopy (SEM)

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, Netherlands).

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- 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 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 the initial weight (g) and B the weight of dried fabric (g).

3.4. Detection of silver content

Silver content in the coated cotton fabrics was measured 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).

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

where C_s is the silver concentration (mmole/l) in extracted solution which is detected by atomic absorption spectroscopy; V the volume

Table 1
Synthesis process and characterization of the produced AgNPs.

AgNPs (ppm)	$AgNO_3$ (mmol/l)	Reducing agent	Temperature/time	AgNPs shape	Size distribution
50	0.5	3 g/l alginate	70 (°C)/1 min	Spherical	–
100	1	3 g/l alginate	70 (°C)/1 min	Spherical	1–4 nm

of extracted solution; W_d the weight of dried coated fabric (g); MC the moisture content of coated fabrics (%) (Hossam et al., 2013).

3.5. Washings and silver release

The washing process (Hossam et al., 2013) 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).

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

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 previously.

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–alginate composite coated cotton fabrics were tested by using two different techniques; qualitative method (inhibition zone technique) and quantitative method (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 separately with Gram (+) bacteria as *S. aureus* and Gram (−) bacteria as *E. coli* and *Pseudomonas aeruginosa*, 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 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, 1993). The average width for zone of inhibition along a streak on either side of the tested fabric was calculated using Eq. (4):

$$W = \frac{T - D}{2} \tag{4}$$

where W is the width of clear zone of inhibition in mm, T the total diameter of tested fabric and clear zone in mm, and D the diameter of the tested fabric in mm.

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).

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

where $R\%$ is the reduction percentage of bacterial colonies, A is the number of bacterial colonies on the agar plate with the coated fabric, and B is the number of bacterial colonies on the agar plate for control.

4. Results and discussion

In comparison with other water-soluble polymers, polyelectrolytes can stabilize nanocolloids better due to electrostatic repulsion (Kim et al., 2011; Lee et al., 2011). Alginate is an anionic polymer with a high charge density. Alginate fragments contain carboxylate groups which can provide well dispersed nanoparticles which are stable against agglomeration. In the present study, AgNPs–alginate composite have been synthesized in a 'green' method using alginate as a natural biopolymer, simply heating an aqueous mixture of sodium alginate and $AgNO_3$. As, in this method, alginate is playing the dual role as a reducing agent for nanosilver generator ($AgNO_3$) and a stabilizer for the net produced nanoparticles.

In the presence of alginate, a possible chelation of Ag^+ by the adjacent hydroxyl and carboxylic groups of alginate may be supposed, and then Ag^+ chelate produces Ag^0 on heating. This method was found to produce AgNPs–alginate composite reproducibly. To determine the reduction efficacy of Ag, a set of experiments were carried out, and the obtained data could be discussed as follows.

4.1. SEM micrographs

The morphological changes of cotton fabrics caused by deposition of AgNPs–alginate composite were followed by SEM. SEM images of cotton fabrics loaded with 100 ppm (AgNPs–alginate composite) colloids are presented in Fig. 1a and b. Through the

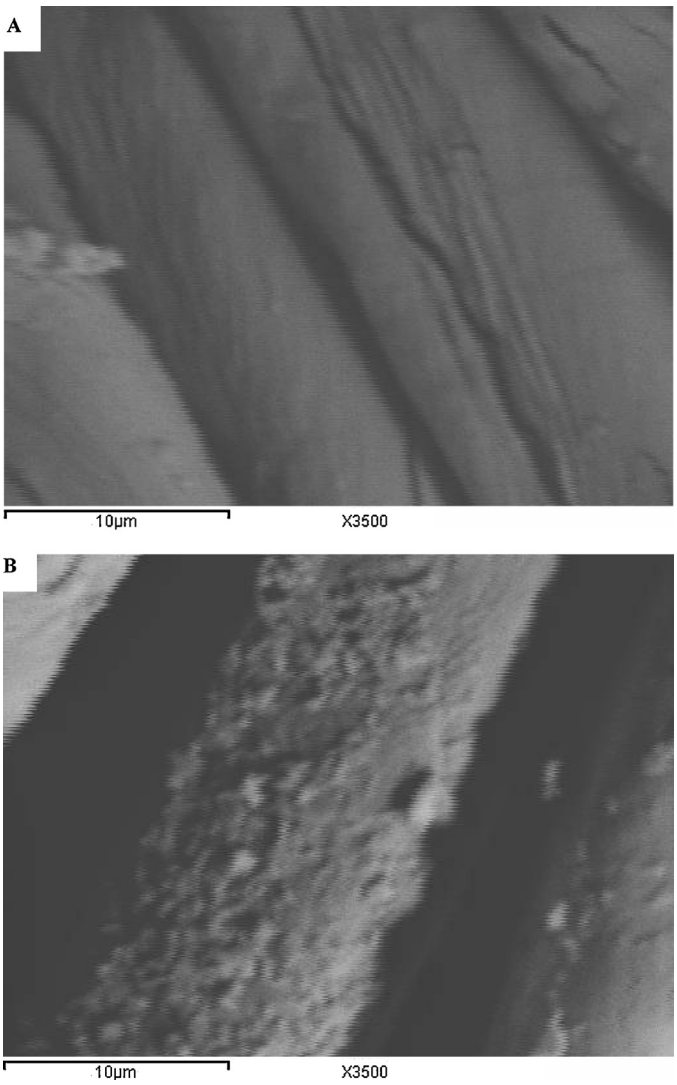

Fig. 1. SEM images for (A) untreated cotton fabric and (B) cotton fabric treated with 100 ppm AgNPs.

achieved SEM images the presence of alginate–AgNPs composite on the surface of the coated fabrics was confirmed. It could be supposed that the AgNPs coated on the surface of fabrics could not be seen with SEM, due to their small size and the fact that they are embedded in the polymer matrix of the alkali hydrolyzed alginate, so it could be decided that SEM images reveal aggregates of somewhat larger units of the nanosilver–polysaccharide composite.

4.2. FTIR-analysis of the uncoated and AgNPs–alginate composite coated cotton fabrics

The presence of AgNPs on cotton fabric was further confirmed by the FTIR measurement. Fig. 2 shows the FTIR spectra of untreated cotton fabric and AgNPs coated cotton fabric. The characteristic peaks of cotton due to cellulose macromolecule, which appear at 3334 cm^{-1} (O—H stretching), 2900 cm^{-1} (C—H stretching), 1430 cm^{-1} (C—H wagging), 1368 cm^{-1} (C—H bending) and 1029 cm^{-1} (C—O stretching) (Chinkap, Myunghee, & Eun, 2004) have become red shifted and with stronger intensity for silver nanocoated cotton fabric. But, the spectra of silver nanocoated cotton fabric does not reveal new peaks different from the case of untreated sample, which means that no chemical reaction on cellulose takes place during the coating of AgNPs, and this may clarify

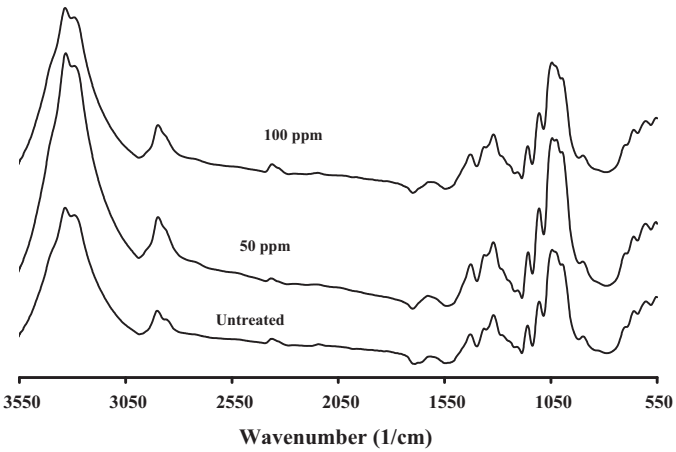

Fig. 2. ATR–FTIR spectra of untreated and AgNPs treated cotton fabrics.

that, loading of AgNPs on the fabric surface only results from physical deposition process.

4.3. Silver contents and silver release

The amount of silver released during washing was quantitatively evaluated by atomic absorption spectroscopy. The amounts of silver content for 0.5 g cotton fabrics loaded with AgNPs–alginate composite and silver released from fabrics into the washing bath after each washing cycle are shown in Fig. 3.

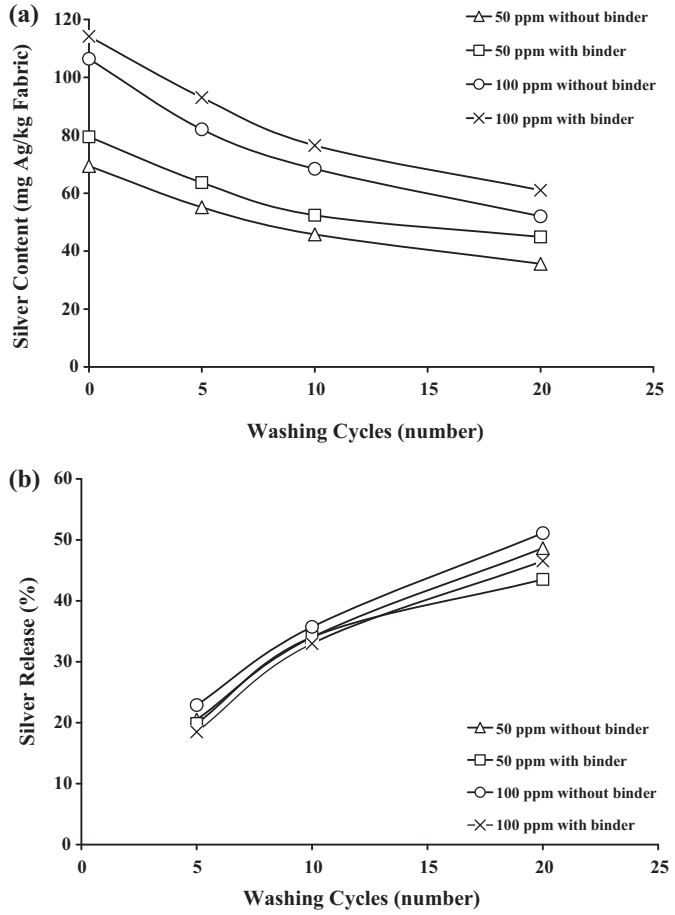

Fig. 3. (a) Silver contents on the treated fabrics with different treatment conditions with number of washing cycles. (b) Silver release from the treated cotton fabrics in the washing liquor.

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	−0.27 ± 0.08	1.59 ± 0.09
A	1	69.40	80.29 ± 0.26	0.56 ± 0.01	4.62 ± 0.02
	2	55.17	81.19 ± 0.18	0.22 ± 0.08	3.00 ± 0.16
	3	45.79	81.47 ± 0.08	0.08 ± 0.01	3.59 ± 0.30
	4	35.64	83.29 ± 0.04	0.06 ± 0.01	1.81 ± 0.04
B	1	79.44	80.46 ± 0.04	0.01 ± 0.03	4.03 ± 0.26
	2	63.66	81.62 ± 0.47	−0.02 ± 0.01	2.06 ± 0.33
	3	52.40	83.97 ± 0.37	0.09 ± 0.06	2.03 ± 0.03
	4	44.88	85.57 ± 0.01	−0.08 ± 0.05	1.29 ± 0.28
C	1	106.40	79.08 ± 0.06	0.18 ± 0.09	3.09 ± 0.14
	2	82.06	80.73 ± 0.27	−0.03 ± 0.04	2.20 ± 0.11
	3	68.41	80.98 ± 0.18	0.05 ± 0.03	1.73 ± 0.07
	4	52.03	82.78 ± 0.00	0.06 ± 0.01	1.27 ± 0.00
D	1	114.17	81.06 ± 0.17	0.03 ± 0.01	3.31 ± 0.35
	2	93.05	81.49 ± 0.02	0.03 ± 0.04	1.53 ± 0.25
	3	76.50	82.48 ± 0.18	−0.04 ± 0.02	2.10 ± 0.05
	4	61.03	83.62 ± 0.26	0.03 ± 0.03	1.48 ± 0.09

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

Table 3
Effect of washing cycles and silver content on the antibacterial activities of nanosilver treated cotton fabrics against three different bacterial strains.

Samples		Silver content (mg/kg)	Inhibition zone diameter (mm)		
			Staphylococcus aureus (gram +ve)	*Escherichia coli* (gram −ve)	*Pseudomonas aeruginosa* (gram −ve)
Blank (untreated)		0	0	0	0
A	1	69.40	1.5	1.5	2
	2	55.17	1.5	1	1
	3	45.79	0.5	0.5	1
	4	35.64	0.5	0	0
B	1	79.44	2	1.5	1.5
	2	63.66	1.5	1	1.5
	3	52.40	1	1	1.5
	4	44.88	0.5	0.5	0.5
C	1	106.40	2.5	2	2.5
	2	82.06	1.5	1.5	2
	3	68.41	1.5	1	1
	4	52.03	1	0.5	1
D	1	114.17	3	2	2.5
	2	93.05	2	1.5	2
	3	76.50	2	1	1.5
	4	61.03	1	0.5	1

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

The results pointed out that certain amount of silver were released from cotton fabrics after applying the washing procedures, and it could be supposed that, the nanoparticles are probably physically bound to fabrics.

The results indicated that the lowest silver content was obtained for those samples loaded with 50 ppm (AgNPs–alginate composite) colloid without binder. However, the highest silver content was obtained for those samples coated with 100 ppm AgNPs in the presence of binder (114.17 mg/kg), but, after 20 washing cycle it becomes 61.03 mg/kg, and this confirms the necessity of using a binder in the coating process for nanosilver fixation.

Additionally, the results clarified that, the amounts of silver released in the washing bath, were increased during the washing process. After 20 washings, for fabrics coated with 100 ppm nanosilver colloidal solution without binder, nearly 50% of AgNPs were released in the washing bath, however for that coated with 50 ppm silver colloid with binder, 38% were released in the washing bath.

Evidently, the higher amount of retained silver provides desirable laundering durability, but, it is noticeable that the release of silver from the cotton fabrics treated with nanosilver colloid without binder was considerably faster than that with binder, which might be indirectly reflected in poor laundering durability of the obtained antimicrobial properties. But, in spite of small amount of silver left after washings, this quantity is sufficient to provide the required bactericidal activity.

4.4. Color coordinates

The color changes of cotton fabrics after deposition of AgNPs–alginate composite were quantitatively determined using the CIE $L^*a^*b^*$ coordinates (Table 2). The obtained data clarified

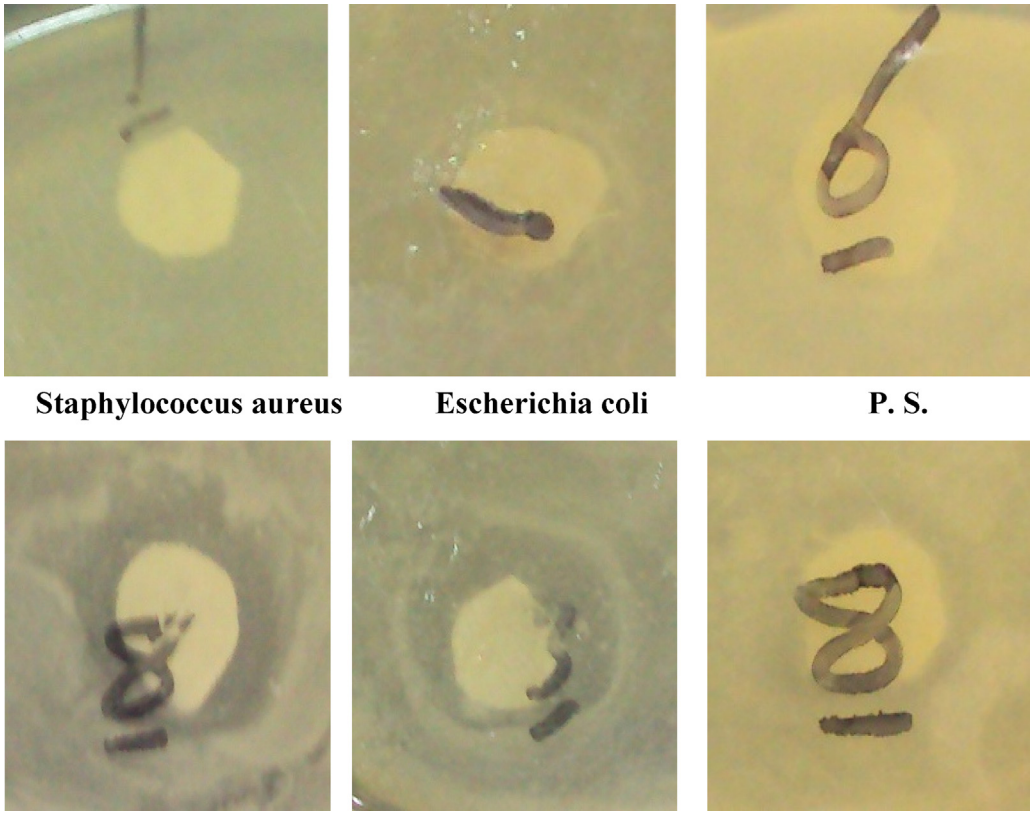

Fig. 4. Photos represent the inhibition zone for three different bacterial strains; top photos for untreated fabrics and bottom photos for AgNPs treated fabrics.

the effect of deposition of AgNPs–alginate composite with two different concentrations in the presence and absence of binder, on the change of color for the coated cotton fabrics. The data showed that, The AgNPs–alginate composite coated cotton fabric turned to creamy white due to the surface Plasmon absorption of AgNPs. The color became deeper with the increase of AgNPs content in the fabric (Kelly & Johnston, 2011), as b^* value which reflects the yellowness of fabrics indicates that, for uncoated fabrics $b^* = 1.59$, treated fabrics with 50 ppm AgNPs without binder, $b^* = 4.03$, and with binder $b^* = 4.62$, coated fabrics with 100 ppm AgNPs without binder, $b^* = 3.09$, with binder $b^* = 3.31$. Thus the yellowness of AgNPs treated cotton fabrics is related to the Ag content of the fabrics, and also is considerably affected by the using of binder in the loading process, as by increasing the concentration of nanosilver colloid, and by the addition of binder, the yellowness is increased, which confirmed that higher concentration of the loaded nanoparticles is achieved, and this indicated the important role of binder in fixing the loaded AgNPs on the fabric surface. Also, by increasing the number of washings, the yellowness is decreased, which could be explained as, by washing, the amount of nanoparticles released to the surrounding bath was increased, however the presence of binder declined silver release in washing bath and in turn increased fabric yellowness.

Also, from L^* values which expresses the change in lightness by using different concentrations of AgNPs, in the presence and absence of binder, and assured the suggestions supposed from the change of b^* values. The results revealed that, by using higher concentrations of nanosilver colloidal solution in the presence of binder, the lightness of the coated fabrics is decreased, which indicates that more AgNPs are loaded on the fabric surface, and this also reflected the efficiency of binder in AgNPs fixation, and by washing, the lightness was increased, and this confirmed that more AgNPs are released from the coated fabrics to the bath, and this supports the essential use of binder in the loading process.

Table 4
Quantitative analysis of antibacterial activities for AgNPs treated cotton fabrics after 20 washing cycles.

Samples	Silver content (mg/kg)	Bacterial reduction (%) *Staphylococcus aureus* (gram +ve)
Blank (untreated)	0	0
A	35.64	90
B	44.88	92
C	52.03	95
D	61.03	95

A: Cotton treated with 50 ppm AgNPs solution; B: Cotton treated with 50 ppm AgNPs solution in presence of binder; C: Cotton treated with 100 ppm AgNPs solution; D: Cotton treated with 100 ppm AgNPs solution in presence of binder.

4.5. Antibacterial activity

Two colloidal solutions containing 50 and 100 ppm of AgNPs–alginate composite were prepared as previously described. Each solution (S) was applied in the presence and absence of binder, and after treatment, fabrics thus loaded with nano-sized silver particles were laundered 5, 10 and 20 cycles. This was done to clarify the durability of the silver nanoparticles as antibacterial finish which was realized through investigating the bacterial reduction rates of *E. coli, P. aeruginosa and S. scherichia coli, Pseudomonas aeruginosa and Staphylococcus aureus*, after washing of the coated fabrics.

Results of Tables 3 and 4 and Fig. 4, signified the following features: (a) the untreated cotton fabric (blank) exhibited no inhibition zone indicating no antibacterial activity; (b) treatment

of the fabrics using the two concentrations of silver nanoparticles render the fabric antibacterial irrespective of the bacteria used, (c) resistance of the treated fabric to *S. aureus* is, however, greater than that for the others as evidenced by comparing the inhibition zone for all the used bacteria, (d) similarly, the higher concentration of silver nanoparticles is accompanied by higher inhibition zone than the lower concentration reflecting the key role played by greater silver content within the fabric in the bacterial activity of the latter, (e) fabrics treated with AgNPs in the presence of binder display higher antibacterial activity than those obtained for fabrics coated in the absence of binder, indicating greater fixation in concomitant with higher accessibility of the silver nanoparticles by coating in the presence of binder, (f) the inhibition zones are lower upon giving 5 washing cycles implying partial removal of the silver nanoparticles under repeated washing, (g) the retained antibacterial activity – after 20 washing cycles – as measured by quantitive method advocated current treatment as durable finishing for production of antibacterial cotton, as the bacterial reduction percent was 95% by coating with 100 ppm AgNPs in the presence of binder and, (h) the finishing treatment under investigation is so effective that fabrics finished using current treatment formulation at silver content as low as 35.64 mg/kg acquired significant ability for bacterial reduction (90%) even after 20 washing cycles.

5. Conclusion

This study showed excellent technique for the preparation of a well-stabilized AgNPs–alginate composite using environmental benign polymer; alginate which plays an important dual rule as both reducing for Ag^+ and stabilizing agent for the formed AgNPs in aqueous solution without using an extra reducing agent and without any complex steps, as maximum concentration of AgNPs–alginate composite was obtained from the first minute of adding nanosilver generator to the alkali hydrolyzed alginate. The obtained AgNPs–alginate composite was successfully applied to cotton fabrics. It is found that, using 50 ppm of AgNPs–alginate composite is sufficient to exhibit excellent antibacterial activity against *E. coli*, *P. aeruginosa* and *S. aureus*. The data shown by FTIR spectra, color coordinates, silver content and SEM analysis indicates that the AgNPs–alginate composite are well deposited on the cotton fabrics. Binder was used successfully in this suggested procedure to retain the antibacterial efficiency of the coated cotton fabrics. The result of durability to wash of the coated fabric also showed good bactericidal effect even after 20 washing cycles and in the absence of binder. Therefore, this kind of treatment is considered to be safe, cost effective and environmental friendly process in the fabrication of antibacterial finishing and textiles.

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