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Highly effective antibacterial textiles containing green synthesized silver nanoparticles

A. Hebeish [b], M.E. El-Naggar [a,b], Moustafa M.G. Fouda [a,b,*], M.A. Ramadan [b], Salem S. Al-Deyab [c], M.H. El-Rafie [b]

[a] Strategic Center for Diabetes Research, Nanotechnology Department, King Saud University, P.O. Box 245, Riyadh 11411, Saudi Arabia
[b] Textile Research Division, National Research Center, Dokki, Cairo, Egypt, P.O. Box 12622, Giza 12522, Egypt
[c] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

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ABSTRACT

Nano-sized silver particles (AgNPs) (6–8 nm) at concentration of 500 ppm were synthesized using hydroxypropyl starch (HPS) as both reducing and stabilizing agent. A solution containing AgNPs (500 ppm) was diluted with distilled water to 100 and 50 ppm and applied to cotton fabrics in presence/absence of binder. The finished fabrics were examined for morphological features and surface characteristics by making use of scanning electron microscopy (SEM) which reveals that AgNPs are deposited on the surface of fibrils (fabric fibres). The antibacterial activity of the treated fabrics loaded with AgNPs was evaluated against *Escherichia coli* (gram −ve) and *Staphylococcus aureus* (gram +ve) bacteria. Results explored that, regardless of the concentration of AgNPs used, the bacterial reduction, in presence/absence of binder was always higher than 95% without washing. However, binder retains excellent antibacterial properties even after 20 washing cycles reflecting the significance of binder in fixation of AgNPs deposits on the surface of the fabrics.

1. Introduction

Nanotechnology is defined as the utilization of structures with at least one dimension of nanometer size for the construction of materials, devices or systems with novel or significantly improved properties due to their nano-size. Nanotechnology is an extremely powerful emerging technology which is expected to have a substantial impact on medical technology now and in the future. Nano-particles are commonly used in commercial products in the range of 1–100 nm (Russell, 2002). Nanoparticles have unique physical and chemical properties different from bulk materials based on specific characteristics, such as size, distribution, and morphology (Kamyar et al., 2010). New applications of nanoparticles and nanomaterials appear to be emerging rapidly (Kamyar et al., 2010; Suh, Suslick, & Stucky, 2009). One of those applications is antibacterial textile technology. Antibacterial finishes are applied to textiles for three major reasons: (a) to contain the spread of disease and avoid the danger of injury-induced infection, (b) to contain the development of odor from aspiration, stains and soil on textile materials, and (c) to contain the deterioration of textiles caused by mildew, particularly fabrics made of natural fibres (Gao & Cranston, 2008). Cotton may acts as a nutrient, becoming suitable medium for bacterial growth (Gao & Cranston, 2008; Goren˘Sek & Recelj, 2007). Therefore, cotton fibres are treated with numerous chemicals to get better antimicrobial textiles (Falletta et al., 2007; Lim & Hudson, 2004; Son, Kim, Ravikumar, & Lee, 2006; Son, Youk, & Park, 2006). Among the various antimicrobial agents, silver nanoparticles (AgNPs) which show strong inhibitory and antibacterial effects (Goren˘Sek & Recelj, 2007; Textor, Fouda, & Mahltig, 2010). Nanosilver based antimicrobial polymers represent a great challenge for both academia and industry (Kumar & 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, Yeo, & Yi, 2005). It is well known that silver has a broad antibacterial activity while exhibiting low toxicity towards mammalian cells (Lee, Karim, & Lee, 2007; Subhranshu, Jeyaraman, & Vinita, 2010; Wang, Wang, Hong, Wei, Gao, & Zhu, 2007; Yuranova et al., 2003). Thus, silver has the potential to be an excellent antibacterial agent. 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 (Raveendran, Fu, & Wallen, 2003).

* Corresponding author at: Strategic Center for Diabetes Research, Nanotechnology Department, King Saud University, P.O. Box 245, Riyadh 11411, Saudi Arabia. Tel.: +966 560773127, fax: +966 14725682.
E-mail addresses: mmfoudah@ksu.edu.sa, m_gaballa@yahoo.com (M.M.G. Fouda).

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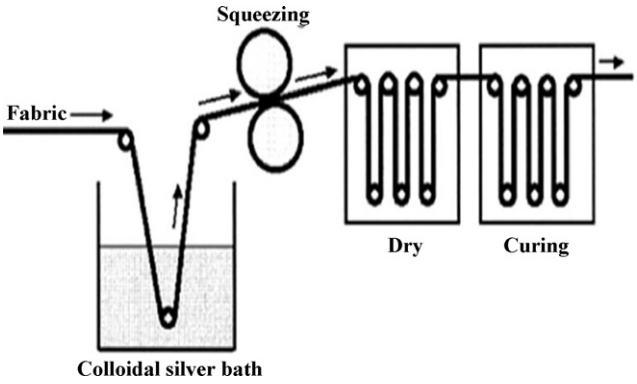

Fig. 1. Antibacterial finishing of cotton fabrics by pad-dry-cure.

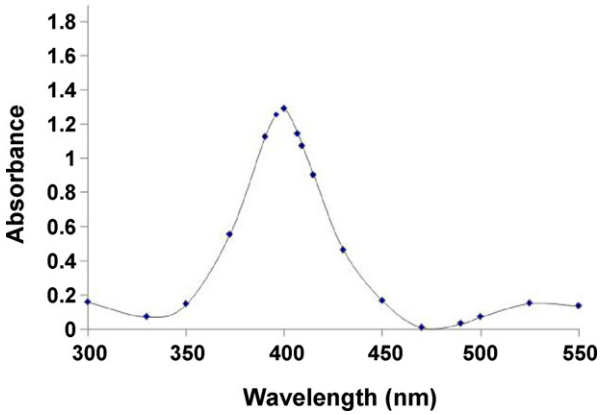

Fig. 2. UV–vis absorption spectroscopy of silver nanoparticles.

The present research article involves two major objectives: (1) green synthesis of nano-sized colloidal silver solution (AgNPs) using environmental, benign, economic and commercially viable polymer namely, hydroxypropyl starch (HPS) which act as both reducing for silver ions (Ag^+) and stabilizing agent for the formed AgNPs at optimum conditions previously studied by El-Rafie et al. (2) incorporation/deposition of AgNPs on to cotton fabrics with/without binder.

2. Experimental

2.1. Materials

Nano-sized silver colloidal solution with a concentration of 500 ppm was prepared according to the method described by El-Rafie (El-Rafie et al.,2011). Binder (Printofix® Binder MTB EG liquid (based on acrylate) was supplied by Clariant®, Cairo, Egypt. Mill desized-scoured-bleached cotton fabrics were supplied by El-Nasr Company for Spinning, Weaving and Dyeing, El-Mehallah El Kobra, Egypt. These fabrics were cut into identical squares (20 cm × 20 cm) and used for testing the antibacterial effect of colloidal silver as described below.

2.2. Antibacterial finishing of cotton fabrics

At first, the colloidal solution of AgNPs was diluted to two different concentrations 100 and 50 ppm with distilled water at room temperature (25 °C). Fabric samples were immersed independently in colloidal solutions of AgNPs at concentrations of 50 and 100 ppm for 30 s followed by squeezing to 100% wet pick-up using a laboratory pad at constant pressure. Samples were dried at 70 °C for 3 min and cured at 150 °C for 2 min. Durability of the treated fabrics against bacterial activity was performed as follows: the untreated/treated fabrics with AgNPs solution were evaluated quantitatively before and after repeated washing cycles (5, 10 and 20 cycles). Laundering was performed by a machine set with warm water containing sodium carbonate (2 g/l) and non wetting agent (5 g/l). Each laundering takes place around 45 min followed by tumble drying at 70 °C. The schematic representation of this finishing process is shown in Fig. 1.

2.3. Testing and analysis

Ultra violet–visible (UV–vis) spectra have been used as sensitive technique to prove the formation of AgNPs as it exhibits an intense absorption peak due to the surface plasmon excitation, which describes the collective excitation of conduction electrons in metal (Fryer, 1979). The green synthesized AgNPs were recorded in spectrophotometer from 300 to 550 nm. HPS solution was used as a blank. Particle shapes and sizes were obtained by transmission electron microscopy (TEM); JEOL-JEM-1230 (Fryer, 1979). Specimen measurements were prepared by placing drops of colloid solution on 400 mesh copper grid coated by an amorphous carbon film and the remaining solvent is evaporated at room temperature. By averaging the diameters of 100 AgNPs found in several arbitrarily chosen areas in enlarged microphotographs, the average diameter was obtained.

Scanning electron microscopy (SEM) was used to study the surface characteristics of fabrics treated with AgNPs in comparison with the untreated fabrics (Goldstein et al., 2003).

Antibacterial test was quantitatively evaluated against *Escherichia coli* (Gram −ve) and *Staphylococcus aureus* (Gram +ve) bacteria (Aramwit, Muangman, Namviriyachote, & Srichana, 2010). The antibacterial activity of the treated fabrics is performed as follow; squares of 1 cm of each fabric were prepared in an aseptic manner. Each square was placed in a sterile vial and the fabrics were pre-treated with 800 μl distilled water for 10 min. Tryptone soy broth (2.2 ml) was added to each vial to make a total volume of 3 ml. An aliquot (10 μl) of *S. aureus*/*E. coli* suspension was added to each fabric-containing vial (1.6 × 103/ml). Control broth with/without bacterial inoculation was also included. The vials were then incubated with agitation at 35 °C, 220 rpm. Aliquots of 10 μl broth were sampled at 24 h and serial dilution for the aliquots was prepared in broth. Duplicate aliquots (50 μl) of the serially diluted samples were spread onto plates. The plates were incubated at 35 °C and bacterial counts were performed. The bactericidal activity was evaluated after 24 h and the reduction percentage of bacteria was calculated by the following equation:

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

where R = the reduction rate, A = the number of bacterial colonies from untreated fabrics, and B = the number of bacterial colonies from treated fabrics.

3. Results and discussion

A well-stabilized AgNPs solution with a concentration of 500 ppm was prepared using HPS as reducing agent for silver ions as well as stabilizing for the formed AgNPs in the optimum conditions as follows: HPS, 0.9 g; silver nitrate, 0.078 g; pH, 12; temperature, 70 °C; duration, 15 min and total volume, 100 ml.

Fig. 2 shows the UV–vis absorption spectroscopy for AgNPs colloidal solution (concentration of 500 ppm) prepared in the above optimum conditions. It is clear that, the band becomes stronger and more symmetrical with a pronounced bell shape at λ max 405 nm. The band can be assigned to the plasmon resonance of AgNPs.

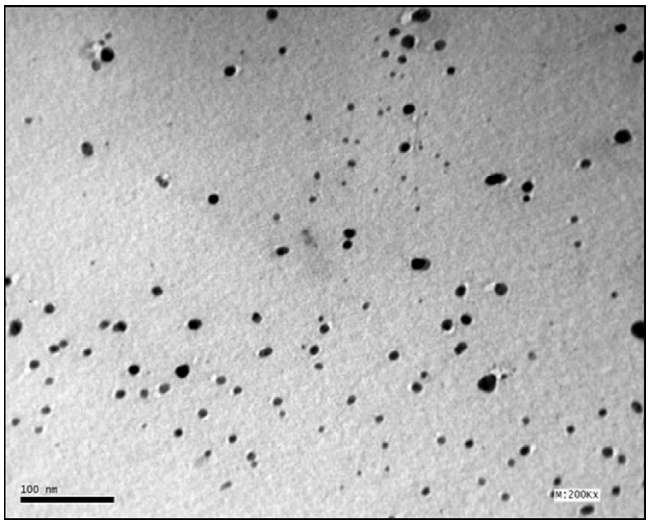

Fig. 3. TEM micrograph of silver nanoparticles with a concentration of 500 ppm.

Figs. 3 and 4 show the TEM image and the histogram of the size and size distribution of AgNPs in the aforementioned conditions. The obtained figures depict that the resultant product contains a well-stabilized AgNPs solution with a concentration of 500 ppm and a diameter range of (6–8 nm). AgNPs solutions with such unique characteristics are unequivocally feasible for industrial applications. The antibacterial activity of untreated/treated fabrics with colloidal solution of AgNPs is studied. Below are the proposed mechanism and the results and discussion.

3.1. Mechanism of bactericidal activity of silver nanoparticles

The bactericidal effect of silver ions on microorganisms is very well known. However, the mechanism of AgNPs is only partially understood. There are two proposed mechanism which can be explained as follows: (1) when AgNPs are prepared, the oxidation of zerovalent silver (Ag^0) to silver ion (Ag^+) occur to a great extent due to their extreme sensitivity to oxygen or to the interaction with water molecules (Mijakovic, Petranovic, Bottini, & Deutscher, 2005). Consequently, the high affinity of those silver ions to sulfur or phosphorous is the key element for the antibacterial effect. On the other hand, the abundance of sulfur-containing protein

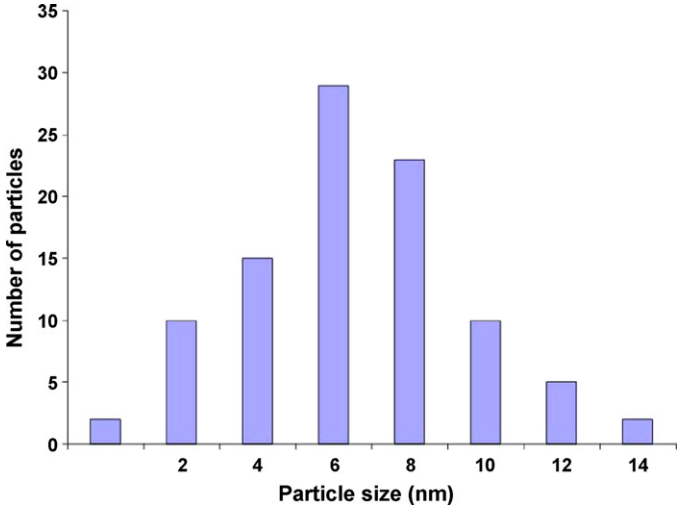

Fig. 4. Histogram of silver nanoparticles size distribution with a concentration of 500 ppm.

Table 1
The effect of repeated washing on the antibacterial properties of silver nanoparticle-treated cotton fabrics without binder.

Number of washing cycles	Bacterial reduction (%)			
	Nano-sized silver colloids concentration (ppm)			
	50 ppm		100 ppm	
	S. aureus	*E. coli*	*S. aureus*	*E. coli*
Before washing	96.4%	96%	98.3%	96%
After 5 cycles	73.6%	70.8%	74.7%	72.2%
After 10 cycles	67.7%	61.5%	68.1%	65.5%
After 20 cycles	60.9%	56.6%	62%	59%

on the bacterial cell membrane, AgNPs/Ag^+ can react with sulfur-containing proteins inside or outside the cell membrane, which in turn affects the bacterial cell viability (Mijakovic et al., 2005). It is also proposed that AgNPs/Ag^+ can interact with phosphorous moieties in DNA, resulting in inactivation of DNA replication leading to the inhibition of enzyme functions (Mijakovic, Petranovic, Mecek, Cepo, Mann, & Davies, 2006). (2). The Ag^+ released from AgNPs can also catalyze the production of oxygen radicals that oxidize molecular structure of bacteria (Wright, 2002). The formation of active oxygen occurs according to chemical reaction:

$$H_2O + \tfrac{1}{2}O_2 \xrightarrow{Ag^+} H_2O_2 \rightarrow H_2O + (O\cdot)$$

Such mechanism does not need any direct contact between antimicrobial agent (Ag^+) and bacteria, because the produced active oxygen diffuses from the fiber to the surrounding environment (Dastjerdi, Mojtahedi, Shoshtari, & Khosroshahi, 2010; Kim et al., 2007) Silver ions (Ag^+) can lead to denaturation of protein followed by cell death because of their reaction with nucleophilic amino acid residues in proteins, and attach to sulfhydryl, amino, imidazole, phosphate and carboxyl groups of membrane or enzyme proteins (Sathishkumar, Sneha, Won, Cho, Kim, & Yun, 2009).

3.2. Antibacterial efficacy of nano-sized colloidal silver based cotton fabrics

The interaction between fibres and metallic AgNPs results from: (1) formation of chemical bond between silver and alcoholic groups of cotton, and (2) physical adsorption of AgNPs on the fabric surface (Perelshtein, Applerot, & Perkas, 2008).

Fig. 5(a)–(c) shows the scanning electron microscope (SEM) images of cotton fabrics before/after treatment with AgNPs at two different concentrations (50 and 100 ppm).

Fig. 5b and c shows the homogeneous deposition of AgNPs on cotton fabrics after treatment with a solution containing 50 and 100 ppm of AgNPs. It is observed that the amount of AgNPs deposited on the fiber surface of cotton fabrics increases when the concentration of AgNPs colloids solution rises from 50 to 100 ppm.

Table 1 shows the antibacterial properties (bacterial reduction) of fabrics treated with AgNPs colloidal solution. This evaluation applies to untreated/treated fabrics, after repeated washing. Results of Table 1 show that, regardless of the concentration of AgNPs used for the treatment, the reduction of bacterial colonies was always higher than 95% against either *S. aureus* or *E. coli* for AgNPs-treated samples without washing. Subjecting the treated fabrics to 5 washing cycles leads to values slightly higher than 70%, which implies a decrement in the reduction of bacterial colonies. Subjecting the treated cotton fabrics to 10 or 20 washing cycles leads to a marginal reduction in the antibacterial properties. From Table 1, it can be concluded that, the treatment of cotton fabrics with a solution containing AgNPs at a concentration of 50 ppm is good enough to gain antibacterial properties. Nevertheless, repeated washing decreases the antibacterial effect

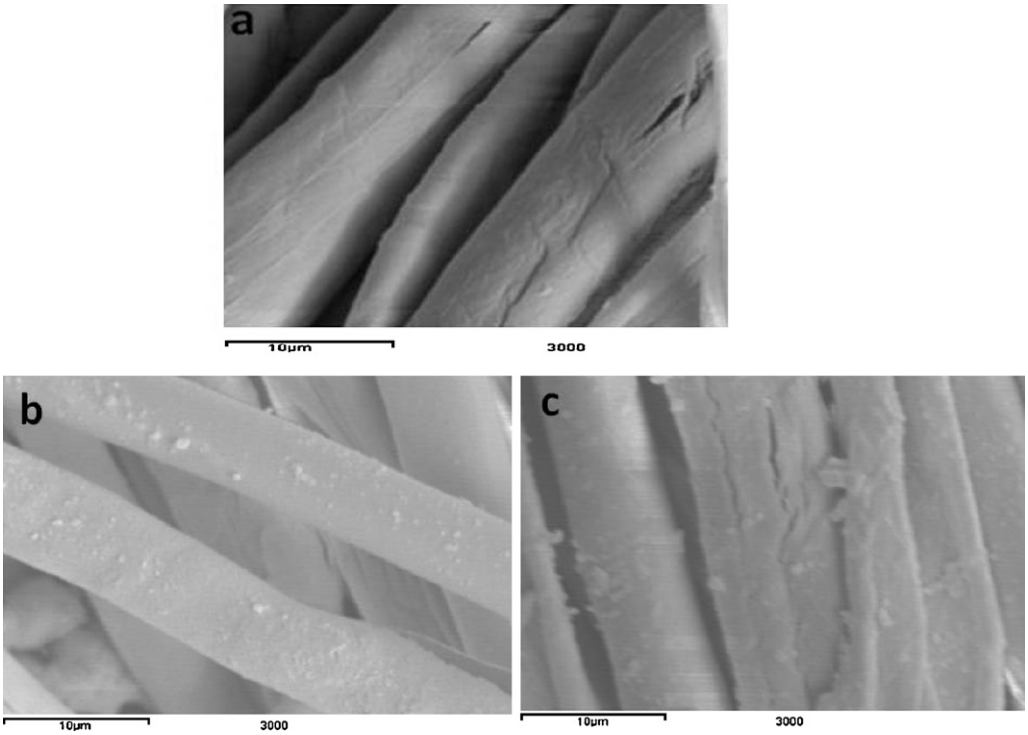

Fig. 5. SEM image of: (a) untreated cotton fabric, (b) nanosilver particles on cotton using 50 ppm, (c) nanosilver particles on cotton using 100 ppm.

Table 2
Effect of incorporation of binder with 50 ppm silver nanoparticle solution on antibacterial properties of treated cotton fabrics.

Number of washing	Bacterial reduction (%)	
	S. aureus	*E. coli*
Before washing	96.4%	95%
After 5 cycles	96%	93.1%
After 10 cycles	96%	92.8%
After 20 cycles	94.8%	92%

significantly, as a result incorporation of fixing agent such as binder; (Printofix® Binder MTB EG liquid) in the finishing bath formulation (AgNPs, 50 ppm; binder, 1%; padding pick up, 100%; drying, 70 °C/3 min; curing, 150 °C/2 min) is required.

Table 2 shows the effect of incorporation of binder into the finishing bath on the antibacterial properties (bacterial reduction) of the treated cotton fabrics before/after repeated washing cycles.

Results of Table 2 signify that fabrics treated with a solution containing nano-sized silver particles at a concentration of 50 ppm in the presence of binder retain excellent antibacterial properties. Bacterial reduction displays 96.4% and 95% in case of *S. aureus* and *E. coli* respectively. After 20 washing cycles, some fabric samples exhibited 94.8% and 92%, reflecting the significance of binder in the fixation of AgNPs deposits within the molecular structure of cotton. This situation becomes clearer when the fabrics were similarly treated without binder.

4. Conclusion

The present research shows the preparation of a well-stabilized AgNPs solution with a concentration of 500 ppm with a diameter of 6–8 nm using environmental benign polymer; HPS 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. The obtained AgNPs was successfully applied to cotton fabrics. It is found that, using 50 ppm of AgNPs is more enough to exhibit excellent antibacterial activity against *E. coli* and *S. aureus*. The SEM analysis indicates that the AgNPs are well dispersed on the cotton fibres. Binder was used successfully in this work to retain the antibacterial efficiency of the treated cotton fabrics. The result of durability to wash of the treated fabric also showed long-lasting bactericidal effect even after 20 washing cycles. The SEM analysis indicates that the AgNPs are well dispersed on the cotton fibres. 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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