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Production of antibacterial colored viscose fibers using in situ prepared spherical Ag nanoparticles

Hossam E. Emam*, Salwa Mowafi, Hamada M. Mashaly, Mohamed Rehan

Textile Research Division, National Research Centre, Dokki, Cairo 12622, Egypt

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ABSTRACT

In situ incorporation technique was used for coloration and acquiring excellent antibacterial properties for viscose fibers by silver nanoparticles (AgNPs). AgNPs were prepared in situ and incorporated in viscose matrix directly without using any other reducing and stabilizing agents. The main objective of this research was to successfully employ the reducing and stabilizing features of cellulose to produce nanosilver–viscose composites. Coloration of fibers after in situ AgNPs incorporation is related to surface plasmon resonance of silver. Colorimetric data were recorded as a function of washings to characterize the final colored fibers. Fastness properties and silver release were all measured to study the washable and wear off properties. Depending on the silver concentration, yellowish colored fibers with different shades were produced. Good fastness properties were obtained after 20 washings without using any crosslinker or binder. The colored fibers had excellent antibacterial activities against *Escherichia coli*, even after 20 washings.

1. Introduction

Nanoparticles of noble metals showed specific colors according to their surface plasmon resonance (SPR) absorption. Hence the examination of surface Plasmon resonance is taking a part of a huge research area, to investigate the properties on the nanometer scale (El-Sayed, 2001; Eustis, 2006; Eustis & El-Sayed, 2006). Numerous characteristics of nanometals, including their optical, electronic, catalytic, chemical and physical properties had shown to be related to size and shape of the precursor nanoparticles. The shape and crystallographic structure are the two major factors affecting on the SPR bands, the catalytic properties and surface activities of nanoparticles (Dick, McFarland, Haynes, & Van, 2002). On the other hand, the size of metal nanoparticles influences their optical properties (Qiaoling & Yahong, 2012).

The reducing and stabilizing agents used in the preparation process of nanomaterials play an important role in controlling both of size and shape of the resultant nanomaterials, and in turn, affects on the color of the net produced nanosilver colloidal solution. Kotelnikova et al. reported that, using of different reducing agents affects on the color of AgNPs incorporated cellulose. Using cellulose itself or sodium borohydride as reductant gave metallic silver with yellow color. By using ammonia or glycerol as reducers the red–brown color of Ag^0 was produced, while the grey color appeared when hydrogen potassium phosphate or hydroquinone were used (Kotelnikova, Demidov, Wegener, Windeisen, & Kotelnikov, 2003; Kotelnikova, Stoll, et al., 2003).

Silver nanoparticles (AgNPs) colloidal solution was prepared with different colors including yellow, red, green, blue and grey (Abdel-Mohsen, Abdel-Rahman et al., 2014; Bois et al., 2009; Gopinath et al., 2012; Harekrishna et al., 2009; Hebeish et al., 2010 Emam et al., 2013; Salprima et al., 2013) depending on their shape. In acidic medium, the preparation of silver nanoparticles by utilizing cellulose as reducing agent produced grey color (Emam et al., 2013). The yellowish color is corresponding to the spherical AgNPs which was easily produced by using carbohydrate materials as reducing agents (Abdel-Mohsen, Abdel-Rahman et al., 2014; Harekrishna et al., 2009; Hebeish et al., 2010). The triangular silver nanoplates and silver nanoprism have been obtained by several researchers with blue color, showing three absorbance beaks at 350, 450–500 and at 700–800 nm (Bin et al., 2011; Deivaraj, Lala, & Lee, 2005; Guoli, Wentao, Kai, & Zhanfang, 2011; Huiying et al., 2008; Jia et al., 2013; Sadhan, Priyanka, Santanu, Gobinda, & Ajay, 2012). Also, the silver nanodisc colloidal solution exhibited three absorbance beaks at 350, 400 nm and the maximum beak at 500–650 nm. These three beaks are contributing to the red color (Deivaraj et al., 2005; Sadhan et al., 2012). However, silver nanorods or nanoplates colloids had a greenish color (Deivaraj et al., 2005; Sadhan et al., 2012).

* Corresponding author. Tel.: +20 1008002487.
E-mail address: hossamelemam@yahoo.com (H.E. Emam).

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Antimicrobial activity of AgNPs was shown extensively in the literature, where many publications have studied the antibacterial activity of AgNPs coated fibers and/or fabrics (Abdel-Mohsen, Radim et al., 2012; Gorenšek et al., 2010; Ilić et al., 2009; Lee, Yeo, & Jeong, 2003; Maneerung, Tokura, & Rujiravanit, 2008; Maria et al., 2010; Matyjas-Zgondek, Bacciarelli, Rybicki, Szynkowska, & Kołodziejczyk, 2008; Ravindra, Murali, Narayana, & Mohana, 2010). Besides, anisotropic AgNPs colloidal solutions had also been used as a dye or a colorant for natural fibers and fabrics according to their color. The natural fibers and fabrics including wool, silk and cotton had been colored by different anisotropic AgNPs using wet chemistry process (Bin et al., 2011; Bin et al., 2013; Big et al., 2012; Watson, 2009). Different polymers were been used to achieve good washing fastness. Poly (diallyl dimethyl ammonium chloride) (PDDA) was used as crosslinker for cotton (Big et al., 2012), while poly-dimethyl siloxane was used for silk fibers (Bin et al., 2013).

Finally, based on literature, there are three different procedures for coloration of fibers or fabrics by using nanoparticles; firstly, metal nanoparticles colloidal solutions followed by impregnating the fabrics in the prepared colloidal solution process (Bin et al., 2011; Bin et al., 2013; Big et al., 2012; Watson, 2009). Secondly, the metal nanoparticles are prepared in situ the fabrics (Fern & James, 2011; Watson, 2009). In the third method, a polymer–nanoparticles composite is synthesized followed by spinning process to form colored fibers (Sreekumar, Arunashish, Lal, Anurage, & Bhasker, 2009).

Recently our group is started to use AgNPs as multifunctional agent for different fibers/fabric materials by in situ incorporation of AgNPs into fibers/fabric matrix. In the current work, we presented a simple procedure to produce the colored cellulose fibers based on viscose with excellent antibacterial action in one step using AgNPs. AgNPs were prepared and incorporated in cellulosic fibers matrix in situ by using cellulose itself as reducer and stabilizing agent. UV–vis spectra and transmission electron microscopy (TEM) images were both measured for the supernatant solutions. The colorimetric analyses (color strength, color difference and color space) of the colored cellulose fibers were all monitored up to 20 washings. Different fastness properties and silver release from fibers were studied after washing process. The antibacterial activity of the colored fibers was detected using the plate agar count method against gram negative bacteria *Escherichia coli*.

2. Experimental

2.1. Materials and chemicals

The regenerated cellulose fibers based on viscose 'CV' (Lenzing Viscose®) with linear density 1.3 dtex and length 38 mm, was kindly supported by Lenzing AG (Lenzing, Austria). The fibers did not contain any spin finishing and were used without further treatment.

Silver nitrate (99.5%, from Panreac, Barcelona, Spain), Sodium hydroxide (99%), Sodium carbonate monohydrate (>99%, from Merck, Darmstadt, Germany) Nitric acid (55%, from the Egyptian company for chemicals and pharmaceuticals, 10th of Ramadan-Egypt) were all used without any further purification.

2.2. Procedure

Colored/antibacterial viscose fibers were prepared in one step by using simple technique. The process was performed as follows: a 5 g of viscose fibers were stepwise immersed in 250 ml of 0.1N NaOH, the stirring was carried out for 10 min at room temperature. The silver nitrate solution with different concentration (0.4–8 mmol/l) was added dropwise to the container with stirring, then the temperature was raised to 70 ± 3 °C. After 45 min, the fibers were taken out, squeezed and rinsed by tap water for neutralization and then squeezed again. The fibers were dried at 75 ± 5 °C prior to analysis and characterization. The Absorbance of all supernatants was measured after the immersion time.

3. Measurements

3.1. UV–vis spectra

AgNPs solutions exhibit an intense absorption peak due to the surface plasmon resonance (SPR). Thus the UV–vis absorption spectra were used to measure the extinction of the residual solutions after the treatment step using a multi channel spectrophotometer (T80 UV/VIS, d = 10 mm, PG Instruments Ltd, Japan) at 250–600 nm.

3.2. Transmission electron microscope (TEM)

For more characterization of the prepared AgNPs, two drops of the supernatant colloidal solutions was placed on a 400 mesh copper grid coated by an amorphous carbon film. Then the solvent was evaporated in air at room temperature and then the grid was conducted to microscope equipment. The morphology was characterized by means of a JEOL-JEM-1200 transmission electron microscope. The diameter and size distribution of AgNPs were calculated by 4 pi analysis software using TEM photos.

3.3. Color measurements

The colorimetric analysis of the colored fibers was recorded using a spectrophotometer with pulsed xenon lamps as light source (UltraScan Pro, Hunter Lab, USA) 10° observer with D65 illuminant, $d/2$ viewing geometry and measurement area of 2 mm. All measurements were occurred at λ_{425}. The corresponding color strength value (K/S) was assessed by applying the Kubelka Munk (Menter & Hatch, 2003) (Eq. (1)).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where R is the decimal fraction of the reflection of the colored fabric, K the absorption coefficient and S is the scattering coefficient.

Now, in a lot of dye houses, there is a data match system which helps colorists to obtain different shades and to judge about the acceptance of these shades against a particular standard. The most widely used is the total color difference (ΔE) (Rupp, Bohringer, Yonenaga, & Hilden, 2001), which can be calculated from the CIE LAB color space data. The color space (L, a^*, b^*) of colored samples was measured by the same spectrophotometer used for measuring of color strength at the same set up, and then the color difference was calculated using.

$$\Delta E = L^2 + (a^2 + b^2)^{1/2} \quad (2)$$

where ΔE is the total difference between the sample and the standard, L the lightness from black (0) to white (100), a^* is a red (+)/green (−) ratio and b^* is yellow (+)/blue (−) ratio.

3.4. Fastness properties (Methods, 1990)

3.4.1. Color fastness to washing

The color fastness to washing was determined according to the method ISO 105-C02 (1989). The composite specimens were sewed between two pieces of bleached cotton and wool fabrics, and then immersed into an aqueous solution containing 5 g/l nonionic detergents at liquor ratio 1:50. The bath was thermostatically adjusted to 60 °C for 30 min. After the desired time, samples were removed, rinsed twice with occasional hand squeezing, and then

dried. Evaluation of the wash fastness was established using the grey-scale for color change.

3.4.2. Color fastness to rubbing

Color fastness to rubbing was determined according to the test method ISO 105-X12 (1987). The test is designed for determining the degree of color, which may transfer from the surface of the colored fibers to other surface, by rubbing. The current test can be carried out on dry and wet fibers.

3.4.2.1. Dry crocking test. The test specimen was placed flat on the base of the crock-meter. A white testing cloth was mounted. The covered finger was lowered on to the test specimen and caused to slide back and forth 20 times by making ten complete turns at a rate of 1 turn/s. The white test sample was then removed for evaluation using the grey-scale for staining.

3.4.2.2. Wet crocking test. The white test sample was thoroughly wetted out in water to a 65% and then picked up. The procedure was run as before. The white test samples were air dried before evaluation.

3.4.3. Color fastness to perspiration

Two artificial perspiration solutions were prepared as follows according to test method ISO 105-E04 (1989); acidic and alkaline solutions.

Acidic solution was prepared by dissolving of L-histidine monohydro-chloride monohydrate (0.5 g), sodium chloride (5 g) and sodium dihydrogen orthophosphate dihydrate (2.2 g) in one liter distilled water. Then the pH was finally adjusted to 5.5 using 0.1N NaOH. To prepare the alkaline solution, L-histidine monohydrochloride monohydrate (0.5 g), sodium chloride (5 g) and disodium hydrogen orthophosphate dihydrate (2.5 g) were all dissolved in 1 l distilled water. The pH was adjusted to 8 using 0.1N NaOH.

The fastness test was performed as follows. The colored specimen 5 cm × 4 cm was sewed between two pieces of uncolored specimens to form composite specimen. The composite samples were immersed for 15–30 min in both solutions with a proper agitation and squeezing to insure complete wetting. The test specimens were placed between two plates of glass or plastic under a force of about 4–5 kg. The plates containing the composite specimens were then held vertical in oven at 37 °C (±2 °C) for 4 h. The effect on the color of the tested specimens was expressed and defined by reference to grey-scale for color change.

3.4.4. Color fastness to light

The light fastness test was carried out in accordance with test method ISO 105-B02 (1988) using carbon arc lamp, continuous light, for 35 h. The effect on the color of the tested samples was recorded by reference to blue-scale for color change.

3.5. Detection of silver content

Silver content in the treated fibers was measured by extraction of silver from fibers as follows. A 0.2 g treated dried fibers was immersed in 20 ml of 15 wt% nitric acid for 2 h at 80 °C to extract silver. Silver concentrations in the extracted solutions were analysed with flame atomic absorption spectroscopy (AAS, SpectrAA, 220, Varian, Australian) equipped a silver lamp at 328.1 nm wavelength. The extracted silver from fibers was calculated using Eq. (3). A standard solution of $AgNO_3$ was used to make calibration solutions in range of 0.5–5 mg/l Ag^+. The extracted solutions were diluted to be in the calibration range.

$$Ag_f = \frac{Ag_s}{W(1 - MC/100)} \times V \quad (3)$$

where Ag_f is the silver content in fibers (g/kg) determined by extraction method, Ag_s the silver concentration (mg/l) in extracted solution, V the volume of extracted solution (0.02 l), W the weight of dried treated fibers (g) and MC is the moisture content in dried treated fibers (%).

3.6. Antibacterial test

The antibacterial activity of colored fibers was tested against *E. coli* AATCC 2666 as gram −ve bacteria. The antibacterial tests were performed quantitatively using the standard test method according to the AATCC test method 100–1999 for Bacterial Counting. All fibers samples were kept at controlled temperature 35 °C prior to test. After incubation step, weighted fibers were transferred into 100 mL of nutrient broth (1:500) (*ca.* 1.5×10^8 colony forming unit per ml) and then shaken vigorously for 1 min. A normal saline solution that prepared with 0.9% (w/v) was serial diluted and then plated onto eosin methylene blue (EMB) agar plates for *E. coli*. For all plates, the bacteria were incubated at 37 °C for 24 h and then the colonies were counted. The antibacterial activity of fibers was estimated by calculating the reduction percentage of bacterial colonies using Eq. (4).

$$R\% = \left[\frac{(B - A)}{B}\right] \times 100 \quad (4)$$

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

4. Results and discussion

4.1. Coloration mechanism

Basically, the coloration technique used in this study depends on the formation of in situ AgNPs in viscose fibers. Schematic diagram (Fig. 1) shows the mechanism of coloration technique which can be described in points as follows: (1) Immersion of cellulosic fibers in NaOH, caused swelling of cellulose fibers (Široký, Široká, & Bechtold, 2012), which in turn helped in distributing silver ions (Ag^+) inside the cellulosic matrix and hence improving the color homogeneity and fastness of the resultant fibers. In the swelling step, non-active cellulose transformed to alkali activated cellulose (Cell-COONa). (2) Besides, the alkali pretreatment raised the pH value to ≈12 which plays an important role in the reduction of Ag^+ to Ag^0. (3) When silver nitrate added to cellulose in alkaline solution, Ag^+ diffused well inside the swollen cellulose. The ion exchange interaction and/or complexation between Ag^+ and functional groups of cellulose (COO-Na and OH groups) are supposed to take a place (Abdel-Mohsen, Radim et al., 2012; Cai, Kimura, Wada, & Kuga, 2008; Emam et al., 2013; Ifuku, Tsuji, Morimoto, Saimoto, & Yano, 2009; Ju & Tallahassee, 2010; Saito & Isogai, 2005; Tajmir-Riahi, 1987). (4) By raising the temperature to 70 °C, the reducing end groups of cellulose are suggested to be more active for reducing Ag^+ to nanosized Ag^0 inside cellulosic matrix giving the yellow color. The reduction process of Ag^+ is catalyzed by the effect of light and heating (Cai et al., 2008; Ifuku et al., 2009; Ju & Tallahassee, 2010; Khanna & Subbarao, 2003). (5) Stabilization of the synthesized AgNPs could be related to the steric effect of the cellulosic chains. (6) Finally, the unbounded AgNPs were removed from the colored fibers by rinsing.

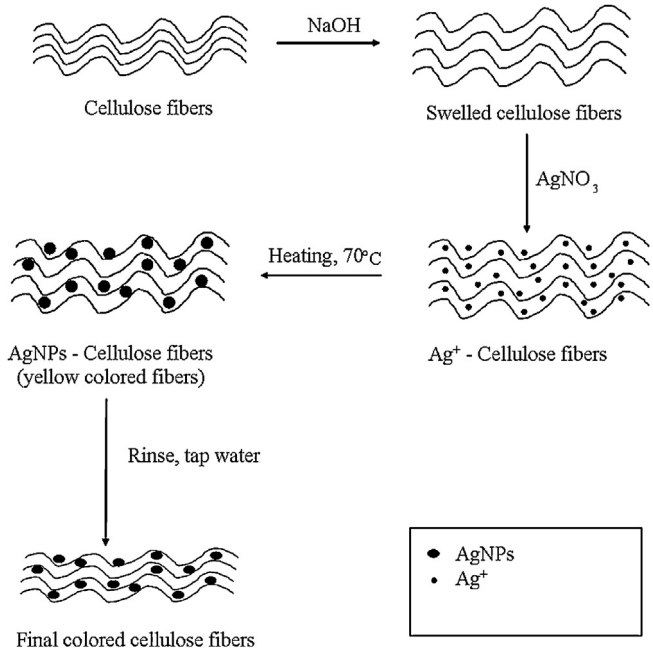

Fig. 1. Schematic diagram represents the proposed coloration mechanism of viscose as cellulosic fibers by forming in situ AgNPs.

4.2. UV–vis spectra

After the immersion step, the colored fibers were removed and the absorbance of supernatant solutions was measured. Fig. 2 shows the UV–vis spectra of supernatant solutions by using different concentrations of silver nitrate. It can be clarified that, due to the yellowish color of the supernatants, UV–vis spectra exhibited maximum absorbance peak at 398–406 nm, which could be described to be SPR of spherical AgNPs (Abdel-Mohsen, Radim et al., 2012; Harekrishna et al., 2009; Hebeish et al., 2010). Also, increasing concentration of silver nitrate is accompanied by appreciable change in the absorbance intensity. However, the shifting in the SPR was not significant to make observable change in color. On the left of SPR, there were very small peaks at 273–282 nm, which were related to the presence of silver ions (Ag^+) (Khanna & Subbarao, 2003).

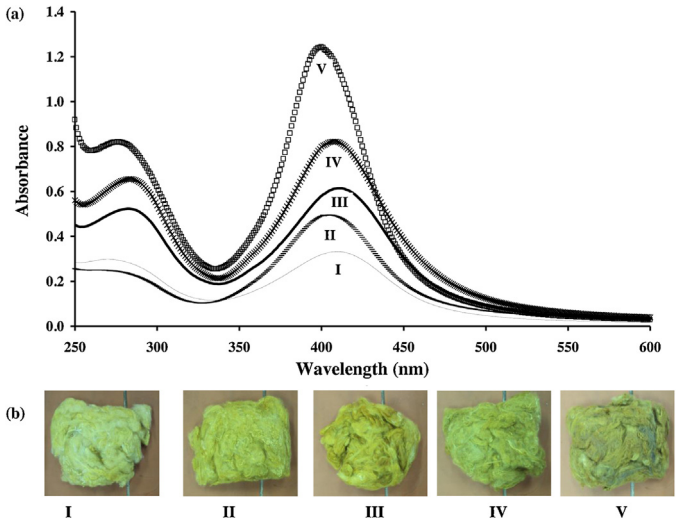

Fig. 2. (a) The UV–vis spectra of the supernatant solutions by using different concentrations of silver nitrate solutions (I) 0.4 mmol/l, (II) 1 mmol/l, (III) 2 mmol/l, (IV) 4 mmol/l, (V) 8 mmol/l, after 45 min immersion time at 70 °C using 1:50 M/L ratio. (b) Photographs of the corresponding treated fibers.

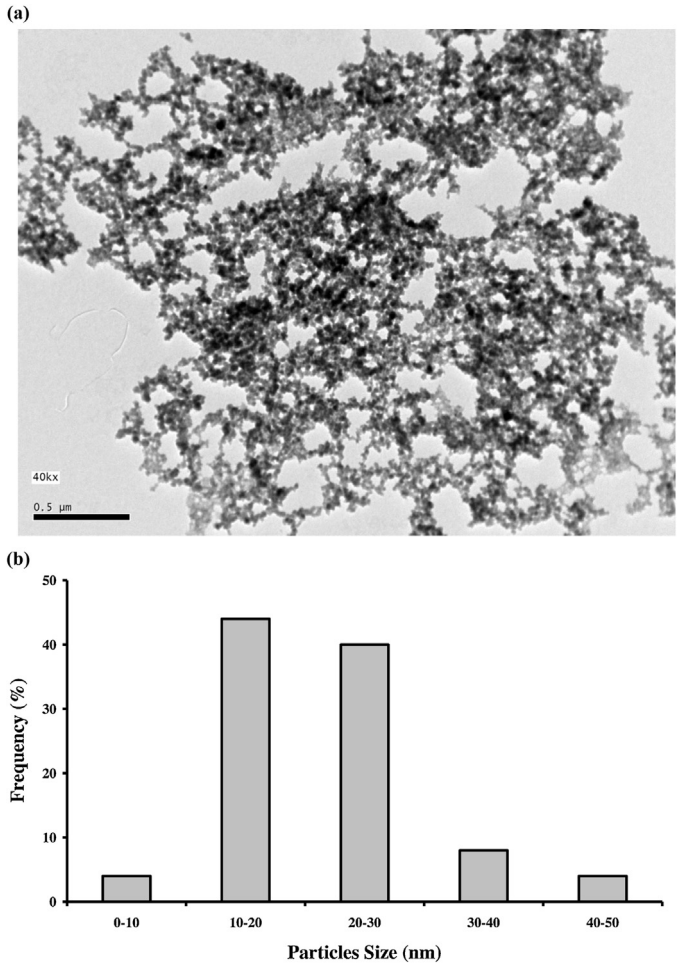

Fig. 3. (a) TEM graph of the supernatant solution which treated with 2 mmol/l $AgNO_3$. (b) Size distribution of particle size calculated from the corresponding TEM photo.

4.3. TEM images

TEM gave information regarding the size, shape and crystal structure of AgNPs. TEM of AgNPs in Fig. 3a shows that, Ag nanoparticles exhibited a spherical-like shape and are dispersed evenly. This result confirmed the supposed points explained according to UV–vis absorption spectra. Both results of UV–vis absorption (Fig. 2) and TEM (Fig. 3a) verified that, the yellow color of fibers is a result of presence of spherical AgNPs. AgNPs were observed sufficiently close to each other, which attributed to no reducing or stabilizing agent existed in solution. From TEM photos, the size average and size distribution of AgNPs were detected using analysis software. From Fig. 3b, size distribution of spherical AgNPs was in range of 0–50 nm. The majority of particles (80%) were located between 10 and 30 nm which is an indication for sufficient homogeneity and well dispersion of silver particles. Reduction of Ag^+ to Ag^0 was carried out by the action of cellulose reducing end groups (Emam et al., 2013). Cellulosic chains can be suggested to act in stabilizing of the produced nanosilver by steric effect. Thus, better homogeneity and dispersibility of AgNPs is expected in fibers compared to solution.

4.4. Color measurements

After removing the fibers from the impregnating solution, completely yellow colored fibers were obtained with good

Table 1
Colorimetric data for the viscose fibers treated with silver nitrate (light source D65).

$AgNO_3$ conc. (mmol/l)	L^*	a^*	b^*	K/S (at λ_{425})	ΔE
Untreated	95.90	−0.13	4.46	0.06	96
0.4	67.19	2.99	43.40	6.03	86.04
1	58.14	4.10	44.32	15.91	73.23
2	51.79	5.28	46.41	18.75	70.3
4	45.72	6.24	37.42	20.03	63.3
8	42.85	6.52	32.82	25.93	56.05

homogeneity. The yellow color of the so-obtained fibers became darker by using higher concentration of $AgNO_3$ as observed in Fig. 2b. This is could be due to the higher silver content in fibers by raising $AgNO_3$ concentration. This argument was supported by UV–vis spectra and TEM results (Figs. 2 and 3).

The colorimetric data were measured for untreated and treated viscose fibers to study the effect of AgNPs on the color of fibers, and are reported in Table 1. Lightness (L^*) is decreased from 95.9 for the untreated fibers to 67.19 for the fibers treated with 0.4 mmol/l of $AgNO_3$, and then gradually decreased to 42.85 for the fibers treated with 8 mmol/l $AgNO_3$. This decrement in L^* is a result of coloration of fibers, which become more deeply by using higher concentrations of $AgNO_3$. The red/green ratio (a^*) values are recorded to be −0.13, 2.99 and 6.52 for the untreated fibers, the fibers treated with 0.4 mmol/l $AgNO_3$ and the fibers treated with 8 mmol/l $AgNO_3$, respectively. The increment in a^* values is signing to some of redness color for the treated fibers. The yellow/blue ratio (b^*) value is raised from 4.46 for the untreated fibers to be in range of 32.82–46.41 for the treated fibers. The significant increasing in b^* values is attributed to the yellow color acquired after treatment.

Color strength (K/S) data were measured at $\lambda_{425\,nm}$ which is related to the yellow color. The K/S value is increased with increasing silver nitrate concentration, as it increased from 0.06 for the untreated fibers to 6.03 and 25.93 for fibers treated by using 0.4 and 8 mmol/l $AgNO_3$ respectively. The total color difference (ΔE) value of fibers is not changed significantly after treatment with 0.4 mmol/l of $AgNO_3$. However, ΔE value is changed from 96 for the untreated fibers to 86.04 for fibers treated with 0.4 mmol/l of $AgNO_3$. But ΔE is changed extensively to be 56.05 with increasing the concentration of silver nitrate to 8 mmol/l. The big difference in K/S and ΔE after treatment is corresponding to the change in yellow color shade.

Obviously, it can be summarized that: (1) the results of colorimetric data of fibers are agreed with UV–vis spectrophotometric data of the corresponding supernatant solutions. The treated fibers and corresponding supernatant solutions were both observed with the same yellowish color. (2) The darker yellow color of fibers is achieved by using higher concentrations of silver nitrate. This can be explained by the fact of high amount of spherical AgNPs is formed in fibers by using more concentrated silver nitrate solution. (3) The fibers had yellow color with different shades (from faint yellow to dark yellow), but the nature of color is not changed regardless to the concentration of $AgNO_3$. This is attributed to the production of AgNPs with only one shape (spherical).

4.5. Fastness properties

It is important for the colored fibers to be colorfast against washings or wear off. Thus the different color fastness properties of colored fibers were measured. Effect of the laundering durability up to 20 washings on the color fastness of the colored fibers was measured in the form of K/S and ΔE. Fig. 4a and b represents the K/S and ΔE values with washings up to 20 cycles. It was observed that, the K/S values were gradually decreased with washings. After 20 washing cycles, the K/S value was reduced from 6.03 to 2.02 and from 25.93 to 18.76 for fibers treated with 0.4 and 8 mmol/l of

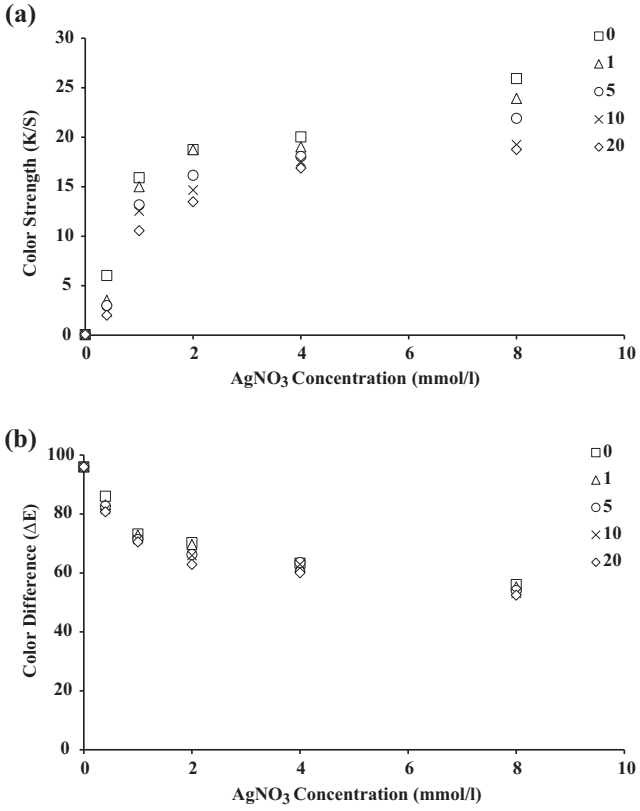

Fig. 4. Effect of washing cycle numbers on the color strength (a) and color difference (b) for fibers treated with different silver nitrate concentrations.

$AgNO_3$, respectively. After 20 washings, the K/S values of all treated fibers were still higher than that of the untreated fibers. The ΔE values were not changed significantly by washing process. It was changed from 86.04 for unwashed fibers to 80.74 after 20 washing cycles for fibers treated by using 0.4 mmol/l $AgNO_3$. While, it was changed from 56.05 to 52.47 for fibers treated with 8 mmol/l $AgNO_3$. The decrement in K/S values and changing of ΔE values explained as a result of washings, which in turn increases the rate of fading of the colored samples due to the release of AgNPs in the washing liquor.

Color fastness to washing, rubbing, perspiration and light were all detected for the colored fibers and listed in Table 2. All colored fibers have shown good light fastness except the fibers treated with lower concentration of $AgNO_3$ (0.4 and 1 mmol/l) which give moderate results. For all the colored samples, the wash fastness to staining on cotton and wool as well as the alteration of color during washing were all very good, regardless to the silver nitrate concentration used. The rubbing fastness generally was low for the fibers treated with 8 mmol/l $AgNO_3$. Dry rub fastness was found to be relatively higher than wet rub fastness. The perspiration fastness (acidic, alkaline solutions) were very good for all fibers treated with high $AgNO_3$ concentration (8 mmol/l), which gives relatively lower results compared to the others. The marginal lower fastness observed by using high concentration of $AgNO_3$ comparing to the lower concentration of $AgNO_3$, may be attributed to the higher release amount of AgNPs from the fibers due to washing or rubbing process. It can be concluded that, the net of color fastness results is good. This reflects the ability of the suggested technique to realize good coloration process with good fastness properties without using any more chemicals (e.g. crosslinkers, binder or coating materials).

Thereafter, in stead of using hazardous chemicals as reducers (Kotelnikova, Demidov, et al., 2003; Kotelnikova, Stoll, et al., 2003),

Table 2
Fastness properties of the colored fibers treated with different $AgNO_3$ concentration.

$AgNO_3$ conc. (mmol/l)	Rubbing fastness		Perspiration fastness						Washing fastness			Light fastness
			Acidic			Alkaline						
	Dry crocking	Wet crocking	St.*	St.**	Alt.	St.*	St.**	Alt.	St.*	St.**	Alt.	35 h
0.4	4	3–4	4–5	4–5	4	4	4–5	4	4	4–5	4	4
1	4	3–4	4	4	4	4	4	4	4	4–5	4	4
2	4	3	4	4	4	4	4	4	4	4–5	4	5–6
4	4	2–3	4	4	4	4	3–4	4	4	4–5	4	6
8	3–4	2–3	4	3–4	4	4	3–4	4	4	4–5	4	6

St.* = Staining on cotton; St.** = staining on wool; Alt. = alteration in color.

Table 3
Silver content and silver released from the treated fibers due to the washing process.

$AgNO_3$ conc. (mmol/l)	Ag content (mg Ag/g fiber)		Ag percent loss after washings (%)
	Unwashed	After 20 washings	
0.4	1.82	1.55	14.95
1	3.96	3.26	17.84
2	7.41	5.94	19.76
4	12.87	9.89	23.10
8	18.65	13.51	27.56

cellulose itself is preferred in the current research because of low chemical consumption. In addition to the homogeneity of fiber color and fastness of the colored fibers are both good due to in situ reduction of silver ions.

4.6. Silver content and silver release

The actual silver contents in the colored fibers were measured using AAS by extraction technique. The colored fibers were washed 20 times and then the silver content was measured to calculate silver release. From Table 3, it can be observed that, the silver content in fibers was increased by increasing silver nitrate concentration used in the treatment. Silver contents are recorded to be in the range of 1.82–18.65 mg/kg for fibers treated with 0.4–8 mmol/l $AgNO_3$. This could be attributed to the sorption capacity which is decreased by using higher concentration of $AgNO_3$. Increasing of the absorbance intensity (Fig. 2a) by increasing silver nitrate concentrations confirmed this observation.

The silver release by 20 washing cycles was calculated from the difference of silver contents of fibers before and after 20 washings. It was in range of 14.95–27.56% for all treated fibers. The amount of silver release is increased by increasing the silver content in fibers which means that, the higher silver content, the higher silver loss. Release property of silver suggests considerable binding between AgNPs and cellulose fibers, as more than 70% of silver was still remained in fibers after 20 washing cycles. Comparing to the coloration techniques using metal nanoparticles mentioned in literature (Bin et al., 2011; Bin et al, 2013; Big et al., 2012; Fern & James, 2011; Sreekumar et al., 2009; Watson, 2009), the coloration technique used in the presented work is much preferred. Because of the lower release of silver was achieved without using any more additional chemicals.

4.7. Antibacterial activity

Textiles made from natural fabrics provide an excellent environment for microorganisms to grow and hence reducing its exhaustion property, because of their ability to retain moisture. Therefore imparting the antibacterial property for natural fibers is a highly interested study. Thus, the antibacterial activity of unwashed and washed colored viscose fibers was tested against *E. coli* as an example of gram negative bacteria. The plate agar count method was used for the detection of antibacterial efficacy at different interval time (1 and 24 h) and data were reported in Table 4. From this table, it is quite clear that, the blank viscose fiber does not show any antibacterial effect. After incubation for 1 h, the reduction percent of bacterial colonies were not observed for all colored samples, which may be related to insufficient release of silver from fibers to the surrounding medium. Regardless of the concentration of silver on fibers, the bacterial colonies were almost reduced after incubation for 24 h. Subjecting the colored fibers to washing cycles leads to non-sense decrement in the bacterial reduction. Colored

Table 4
Antibacterial results of the treated fibers before and after 20 washing cycles.

Samples	$AgNO_3$ conc. (mmol/l)	Washing	Ag content (mg Ag/g fiber)	Bacterial reduction (%)	
				1 h	24 h
Untreated		0	0	0	
1	0.4		1.82	0	99.4
2	1		3.96	0	99.8
3	2	Unwashed	7.41	0	99.8
4	4		12.87	0	99.6
5	8		18.65	0	99.7
6	0.4		1.55	0	98.0
7	1		3.26	0	98.5
8	2	After 20 washing cycles	5.94	0	98.0
9	4		9.89	0	99.3
10	8		13.51	0	99.5

viscose fibers with low amount of silver content (1.55 mg/g) were enough to achieve excellent bacterial reduction.

The exact mechanism by which silver nanoparticles perform antibacterial function is still not identified, but there are four hypothesizes which principally depends on that, conversion of Ag^0 to Ag^+ by contact with moisture: (a) it is thought that Ag^+ interact with the thiol groups of enzyme and proteins that are important for the bacterial respiration. (b) The silver-catalyzed formation of disulfide bonds could possibly change the shape of cellular enzymes and subsequently affect their function. (c) Ag^+ can be bounded to the bacterial cell wall and outer bacterial cell, altering the function of the bacterial cell membrane; and (d) Preferential binding of Ag^+ with cells' DNA, preventing DNA from unwinding, an essential step for cellular replication (Batarseh, 2004; Cho, Park, Osaka, & Park, 2005; Davies & Etris, 1997; Klueh, Wagner, Kelly, Johnson, & Bryers, 2000; Mahendra, Alka, & Aniket, 2009; Percival, Bowler, & Russell, 2005).

5. Conclusions

The presented work introduces a successful simple method to produce colored viscose fibers with an excellent antibacterial property. The technique used here is based on the in situ incorporation of AgNPs into the viscose matrix without using any additional reducing or stabilizing agents. Cellulose itself acts as a reducer for Ag^+ and then stabilizes the produced AgNPs. Basically, the color of the produced AgNPs was used to impart a yellowish color to viscose fibers. The final colored fibers were characterized by different measurements: colorimetric data, fastness properties, silver content and silver release. The antibacterial activity of the colored fibers was also tested against common pathogenic bacteria: *E. coli* using plate agar count technique. The results showed that yellow colored fibers were obtained with different shades from faint yellow to dark yellow. The color of fibers became darker by using higher concentrations of silver ions. Good durable color to wash and wear off was obtained without using any more chemicals like crosslinker or binder. The colored viscose fibers were exhibited excellent antibacterial activities even after 20 washings. The technique used here provides industrial product with low cost, applicable in medical purposes, as well as it can be accomplished for other fibers. The applicatory potential of this technique for natural and synthetic fabrics is under investigation in ongoing research by our group.

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