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# Synthesis of nano silver on cellulosic denim fabric producing yellow colored garment with antibacterial properties

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ABSTRACT

In this study, an aged-look denim fabric with antibacterial property was prepared in one single step process. For this purpose, the simultaneous antibacterial finishing and discoloration of denim fabric was carried out through reduction of indigo dye and silver nitrate by glucose in alkaline media using a conventional garment washing machine. The uniform distribution of silver nanoparticles on the fiber surface was confirmed by scanning electron microscope and energy dispersive X-ray spectroscopy. The treated fabrics were also characterized by X-ray diffraction (XRD) and Raman spectroscopy. Due to the color changes during the process, the color coordinates of the treated samples were also measured. Findings suggest the potential of the proposed method in producing old-look denim fabric with desirable yellow appearance and reasonable antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* with low toxicity for human.



## 1. Introduction

Denim is an indigo-dyed cotton twill fabric in which the weft passes under two or more warp yarns. Warp yarns are dyed with indigo or blue dye and weft yarns remain white. The yarns are twisted so tightly that indigo dye usually colors only the surface, leaving the yarns center white (Montazer & Sadeghian Maryan, 2009).

Indigo dyed denim fabrics were traditionally washed with pumice stones soaked in sodium hypochlorite or potassium permanganate to obtain a desirable aged-look as well as a soft handle. Nowadays, old-look denim is produced by the cooperative action of the enzymes and mechanical forces. Cellulase as alternative to the pumice stone has been widely applied with an abrasive effect on the fiber surface producing worn-look. In addition, laccase has been reported to bleach the indigo dyed fabrics by degrading indigo both in solution and on denim producing various bleaching effects on the fabric (Cavaco-Paulo, 1997; Montazer & Sadeghian Maryan, 2008).

Different chemical agents such as sodium hypochlorite, potassium permanganate, sodium metabisulphite, sodium hydrosulphite and glucose have been used in the final stage of garment finishing reducing the back-staining during stone-washing (Cavaco-Paulo, 1998; Ibrahim, Abdel Momeim, Abdel Halim, & Hosni, 2008; Hebeish et al., 2009; Ibrahim, El-Badry, Eid, & Hassan, 2011; Montazer & Sadeghian Maryan, 2009; Saravanan, Vasanthi, & Ramachandran, 2009). Indigo dye is reduced to its water soluble leuco form before dyeing. Glucose and other reducing sugars can be used as green reducing agents for vat dyes in alkaline media (Hurry, 1930).

Due to the high moisture adsorption of cotton textile providing favorable medium for microorganism growth, many antibacterial agents have been used to control the growth of bacteria, fungi, molds, and algae to prevent rotting, staining and odor problems (El-tahlawy, El-bendary, Elhendawy, & Hudson, 2005; Yadav et al., 2006).

Nowadays, nano silver is widely used in antibacterial finishing of natural and synthetic textiles in commercial forms. Silver ions are released and reacted with sulfur groups in the proteins of bacteria and prevent the transfer of the nutrient causing death of the bacteria (Barani, Montazer, Samadi, & Toliyat, 2011). Adhesion of silver nanoparticles to the surface of bacteria altering the membrane properties, degrading lipopolysaccharide molecules, accumulating inside the membrane by forming pits and changing the membrane permeability (Lok, 2006; Sathishkumar et al., 2009) and penetrating inside bacterial cell, resulting in DNA damage (Ashkarran, Aghigh, Kavianipour, & Farahani, 2011) are some of the mechanisms have been reported for the antimicrobial property of silver nanoparticles.

In situ synthesis and stabilization of nano silver particles on cotton fabrics has been reported using starch as reducing agent. Also, sonochemical coating of nano silver particles using the

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ultrasound irradiation was reported by researchers (Barani et al., 2011; Perelshtein et al., 2008; Vigneshwaran et al., 2007). Synthesis of silver nanoparticles using polysaccharides, polyphenols, Tollens' reagent, UV irradiation, biological reduction, and polyoxometalate has been also investigated (Marambio-Jones & Hoek, 2010; Montazer, Alimohammadi, Shamei, & Rahimi, 2012; Sharma, Yngard, & Lin, 2009). Well-dispersed silver nanoparticles with size distribution of 20–80 nm were synthesized using glucose in presence of polyvinyl pyrrolidone (PVP) and sodium hydroxide, (Wang, Qiao, Chen, & Ding, 2005a; Wang, Qiao, Chen, Wang & Ding, 2005b). Silver nanowires with 30–60 nm diameter and 1–50 μm length were successfully prepared by poly (vinyl pyrrolidone) (Maity et al., 2011; Sun, Mayers, Herricks, & Xia, 2003). A facile method to synthesize silver nanoparticles using carboxymethyl chitosan as reducing and protecting agent has been reported which mixed with polyethylene oxide and subjected to electrospinning. The electrospun nanofiber showed excellent antibacterial activity against pathogenic bacteria (Fouda, El-Aassa, & Al-Deyab, 2013). Well stabilized silver nanoparticles nearly 6–8 nm were prepared using hydroxypropyl starch as reducing and stabilizing agent through a non-organic solvent method (El-Rafie et al., 2011). Besides, the prepared nano silver particles were applied to cotton fabrics in presence and absence of binder. Nano silver loaded fabrics exhibited excellent antibacterial activity even after 20 washing cycles in the presence of binder (Hebeish et al., 2011). Poly (acrylonitrile-*co*-methyl methacrylate) copolymer was grafted with silver nanoparticles biosynthesized using *Trichoderma viride* producing high antibacterial activity (El-Aassar, Hafez, Fouda, & Al-Deyab, 2013). Recently, non-toxic silver nanoparticles were synthesized using schizophyllan triple helical biopolymer as reducing and stabilizing agent (Abdel-Mohsen et al., 2014). Tollens' reaction was used to coat thin layers of silver on polyamide surfaces and the prepared textile showed an excellent durable antimicrobial activity even after 30 laundry cycles (Textor, Fouda, & Mahltig, 2010).

A novel method has been introduced to modify the coarse wool fineness along with synthesis of nano silver to impart antibacterial properties on wool using two sulphur-based reducing agents (Hosseinkhani, Montazer, Eskandarnejad, & Rahimi, 2012). Electrolessplating of silver nanolayer on polyester producing a conductive fabric has been reported using alkaline hydrolysis of polyester surface to enhance the fabric surface activity, improved nanoparticles adsorption, and produced ethylene glycol as a reducing agent (Montazer & Allahyarzadeh, 2013).

Moreover, in situ synthesis of silver nanoparticles on cotton fabric was carried out using Tollens' reagent. It was reported that the cellulosic chains of cotton act as reducing and stabilizer agents (Montazer et al., 2012). Silver nanoparticles were also prepared by sodium salt of carboxymethyl cellulose (CMC) as both reducing and stabilizing agent (Chen, Wang, Zhang, & Jin, 2008). Recently, *Keliab* has been used as a natural source for in situ synthesis of silver nanoparticles on cotton fabric producing excellent antibacterial properties against *Staphylococcus aureus* and *Escherichia coli* even at low silver content with negligible change of color and tensile strength (Aladpoosh, Montazer, & Samadi, 2014).

The main objective of this research is to study the in-situ synthesis and stabilization of nano silver particles on indigo dyed denim fabric imparting antibacterial property along with discoloration effect and reducing the back-staining.

## 2. Experimental

### 2.1. Materials

A 100% cellulosic denim fabric with twill 2/1 weave construction, weft and warp count of 15 nm with *z* twist, weft density of 20 cm$^{-1}$, warp density of 26 cm$^{-1}$, and fabric weight of 322 g/m$^2$ was used. In order to evaluate the back-staining occurred during discoloration process, a piece of 100% bleached woven cotton fabric weighing 166 g/m$^2$ with weft and warp density of 26 cm$^{-1}$ was sewed on the denim fabric and labeled as white pocket. Silver nitrate with 99% purity, glucose as a reducing agent and sodium hydroxide for preparing the alkaline media were all provided by Merck Co., Germany.

**Table 1**
Conditions of different sample preparation.

| Sample code | $AgNO_3$ (mg/L) | Glucose (mg/L) | NaOH (g/L) | Time (h) |
|---|---|---|---|---|
| NS1 | 0.2 | – | 0.25 | 1 |
| NS2 | 0.2 | – | 0.25 | 2 |
| NSG1 | 0.2 | 0.5 | 0.25 | 1 |
| NSG2 | 0.2 | 0.5 | 0.25 | 2 |

### 2.2. Methods

Prior to the finishing treatment, the denim fabric was desized at 70 °C by 1 mL/L amylase for 15 min under pH = 7. The desized samples were treated in aqueous solutions containing distilled water, $AgNO_3$ and NaOH at boil for 1 h and 2 h with liquor-to-good ratio (L:G = 40:1) using a conventional garment washing machine. The process was carried out in presence and absence of glucose, regarding its effects on silver nanoparticles synthesis. After the treatment, samples were rinsed with distilled water in the same conventional garment washing machine with L:G = 40:1 for 10 min. Samples are labeled as NS1, NS2, NSG1 and NSG2 in which G refers to the presence of glucose in the preparation procedure and 1 and 2 correspond to the treatment time, 1 h and 2 h, respectively (Table 1).

### 2.3. Test methods

The surface morphology of the samples and particle size of the synthesized nanoparticles were analyzed by scanning electron microscope (Philips Co, XL30, SEM). Samples were coated by a thin layer of gold to minimize charging effects. X-ray studies were performed using a Siemens D5000 X-ray diffractometer (Cu *K*a, 1.5418 Å, operation voltage 40 kV). Raman spectra were obtained by the Raman spectroscopy Thermo Nicolet 960 Es (USA) model 1064.

$L^*$ (Lightness), $a^*$ (redness–greenness) and $b^*$ (yellowness–blueness) color values of the samples were obtained by data color spectrophotometer (microflash 200d) and CIELAB $\Delta E$ color difference values under illuminant D65 for 1964 standard observer were calculated according to the following equation:

$$\Delta E = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{0.5} \quad (1)$$

where $\Delta L^*$, $\Delta a^*$, and $\Delta b^*$ are differences between color coordinates of treated and untreated samples.

Furthermore, the whiteness index (WI) of the white pocket was measured.

The antibacterial properties of treated fabrics were evaluated by quantitative experiments according to AATCC test method 100-2004. *S. aureus*, a Gram-positive bacterium, and *E. coli*, a Gram-negative bacterium, were used as the test organisms. The antibacterial activity was expressed in terms of the percentage reduction of the organism after contact with the test specimen compared to the number of colonies of bacteria surviving after contact with control. The results were reported as percent reduction of bacteria (R) by the following equation:

$$R = \left[\frac{(M_1 - M_2)}{M_1}\right] \times 100 \quad (2)$$

where $M_1$ and $M_2$ are the number of bacteria colonies recovered from the untreated and treated fabrics after inoculation and incubation, respectively.

AATCC 61(2A)-1996 test method was used for evaluating the washing durability of the treated samples, in which each cycle of the washing process is equivalent to five cycles of home laundries at 38 °C. The antibacterial activity of the treated samples was observed after 5 washing cycle, indicating the stability of the synthesized Ag nanoparticles adsorbed on denim fabrics.

To determine cell toxicity of untreated and selected treated cellulosic denim, the normal primary human skin fibroblast at passage 3 were cultured in Dulbecco's modified Eagle's medium supplemented with fetal calf serum (10%) and L-glutamine (2 mM) and incubated at 37 °C in a fully humidified, 5% $CO_2$ Incubator. Cellulosic denim fabrics were cut into 1 cm × 1 cm pieces and soaked in 2 mL culture medium for 24 h. The samples in each dilution was added to the cells and incubated for 24 h. The test samples were removed from the cell cultures, and the cells were incubated for 24 h in fresh

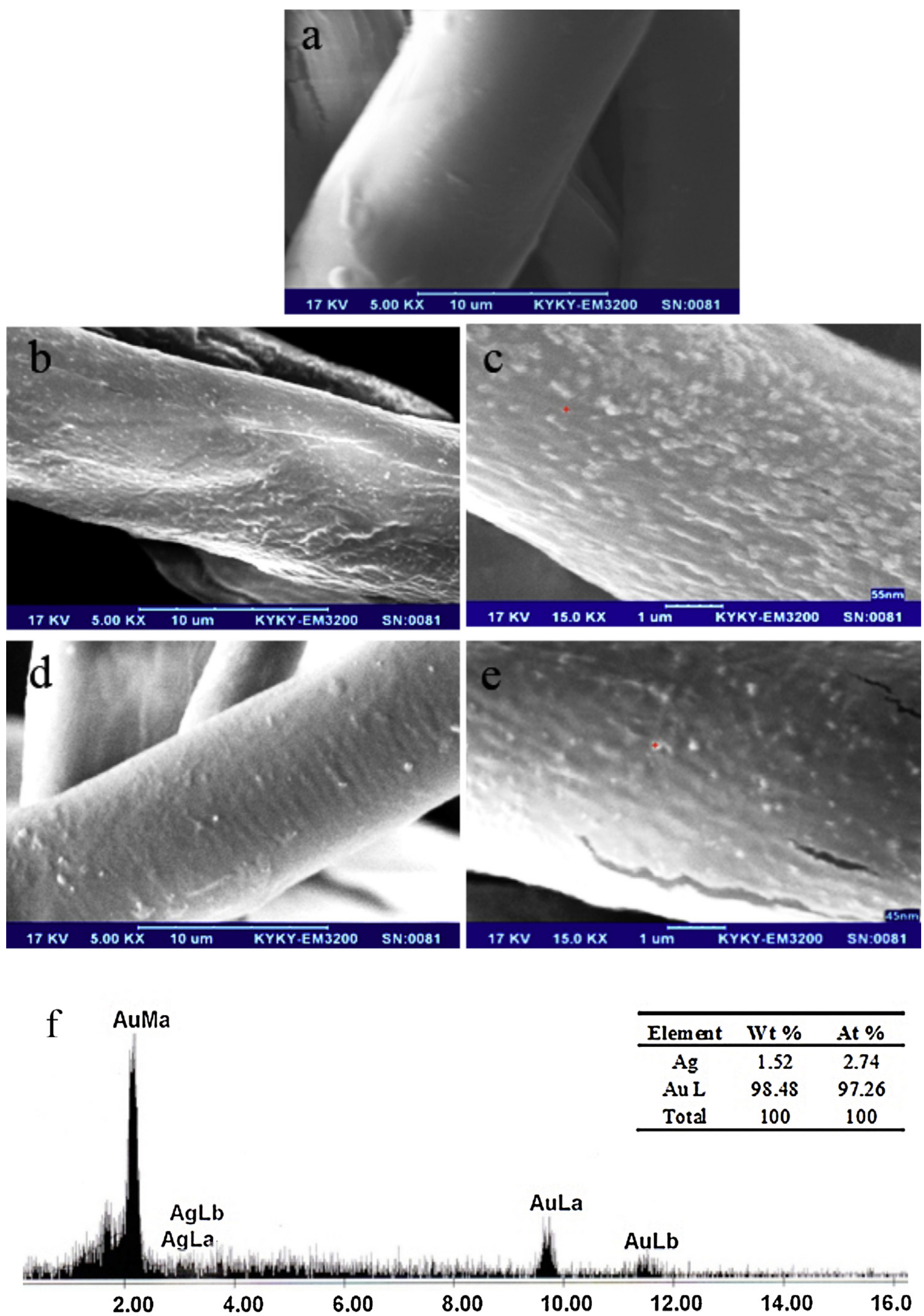



**Fig. 1.** SEM images of different samples, (a) Untreated cellulosic denim, (b) NS2 (5000×), (c) NS2 (15,000×); (d) NSG2 (5000×); (e) NSG2 (15,000×); (f) EDAX spectrum of treated cellulosic denim fiber (NSG2).

medium and then tested with 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay (Kangwansupamonkon, Lauruengtan, Surassmo, & Ruktanonchai, 2009). The absorbance was read with a Tecan Sunrise™ microplate reader at a wavelength of 492 nm. Results were recorded as percentage absorbance relative to untreated control cells. The cytotoxicity results were used to calculate percentage relative cell viability after incubation with the samples by using the following equation:

$$\text{cell-viability} \quad (\%) = \left[\frac{\text{abs}_{\text{sample}}}{\text{abs}_{\text{control}}}\right] \times 100 \tag{3}$$

where $\text{abs}_{\text{sample}}$ is the absorbance in a well containing sample and $\text{abs}_{\text{control}}$ is the absorbance for untreated control cells.

## 3. Results and discussion

### 3.1. Morphological studies

The SEM images of untreated cotton denim fabric (a), sample NS2 (b, c) and sample NSG2 (d, e) are shown in Fig. 1. While the surface of the untreated fabric is smooth with no particles (Fig. 1a), the synthesized nano silver particles are well distributed on the surface of fibers treated with silver nitrate in presence or absence of glucose (Fig. 1b–e). The deposition of nano silver particles on the fiber surface (45 nm and 55 nm in presence and absence of glucose, respectively) was further confirmed by SEM pictures of treated fabrics (NS2 and NSG2) at higher magnification (15,000×, Fig. 1c and e). No agglomeration can be observed on sample NSG2 (Fig. 1d and e), indicating the synthesis of silver nano particles with smaller size due to the stabilizing effect of glucose. This is in agreement with previous findings (Wang et al., 2005a,b) suggesting the effective role of glucose in synthesis of smaller nano silver particles with no agglomeration.

### 3.2. Elemental analysis

The elemental composition of the treated fabric was characterized by Energy dispersive spectroscopy. An EDX spectrum of sample NSG2 along with weight and atomic percentages indicated the presence of Ag on the surface of the treated fabric. As the treated sample was coated by gold before the EDX experiment, Au peaks are also included in the spectrum.

### 3.3. Crystalline structure studies

Fig. 2 shows the XRD spectra of untreated cotton fabric and sample NS2. The X-ray diffraction pattern of NS2 differed from the untreated sample, especially at 2$\theta$ values greater than 60°. Two prominent peaks appeared at 2$\theta$ = 66° and 72°, indicating the presence of silver metal on fabric as confirmed by SEM and EDX. Also, the sharp peak at 35° is related to the crystal of cellulose substrate.

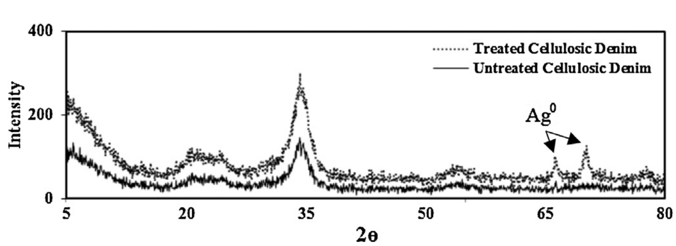



**Fig. 2.** XRD patterns of untreated cotton fabric and cotton denim fabric treated with silver nitrate (NS2).

### 3.4. Chemical structure studies

During the reduction of silver ions into silver nanoparticles, cellulose chains of cotton denim can be oxidized (Montazer et al., 2012), which was confirmed by Raman spectroscopy (Fig. 3). In comparison to Raman spectrum of raw cotton fabric (Yongliang, Serge, & Tryphone, 1998; Adebajo, Frost, Kloprogge, & Kokot, 2006; Montazer et al., 2012), the main peak in the region of 2700–2900 cm$^{-1}$ belongs to the C—H groups of aldehyde for the treated denim (Tipson, 1968). Also, a peak around 1360–1550 cm$^{-1}$ corresponds to COO$^-$ compounds (carboxylic acids group) (Jenkins, Almond, Atkinson, Hollinsm, & Knowles, 2005). The peak appears at 1550–1650 cm$^{-1}$ relates to the C═O due to cellulose oxidation (Jenkins et al., 2005; Montazer et al., 2012; Wang et al., 2005a,b). Silver ions can be reduced into silver metal through glucose and/or cellulose oxidation (Scheme 1). The hydroxyl group (—OH) in cellulose can be changed into aldehyde group (—CHO) and further oxidation led to —COOH group formation. The alkaline condition has been proved to enhance the reaction rate, resulting in higher reducing ability. It has been reported that cellulose chains of cotton denim can be oxidized through reduction of silver ions into silver nanoparticles (Montazer et al., 2012).

### 3.5. Color changes

Table 2 shows the colorimetric coordinates of the treated samples obtained by spectrophotometer. Furthermore, in order to evaluate the back-staining occurred during the discoloration process, the color coordinates were also measured on back of samples and white pocket. Ten measurements were carried out for each sample to check the reproducibility of the results and found to be within the acceptable limit.

The $L^*$ values of the treated samples (in presence or absence of glucose) were more than the untreated fabric due to the discoloration of indigo dye during the treatment. Also, samples treated for 1 h were lighter than the identical specimens treated for 2 h, indicating the adverse effect of the higher treatment time on lightness. Synthesis of nano silver on the treated denim fabrics resulted in yellowing, possibly due to the Plasmon effect of nano silver produced by silver nitrate reduction process. The yellowness ($b^*$) of the samples NS1 and NS2 was slightly higher than the treated fabrics NSG1 and NSG2 and untreated sample, which was related to the discoloration effect of glucose as a result of partial reduction.

The yellowness of NS2 and NSG2 fabrics was slightly more than samples NS1 and NSG1, possibly due to longer process time. Prolong treatment time to 2 h led to more indigo and silver nitrate reduction, enhancing nano particles synthesis and adsorption. According to Table 2, the $L^*$ values of white pocket for untreated fabric was more than samples treated with silver nitrate alone and along with glucose. In addition, lightness of the sample pockets decreased after longer treatment time. Due to synthesis and adsorption of nano silver particles the yellowness of all the treated samples increased. Moreover, samples treated in presence of glucose were bluer due to discoloration effect of glucose. Yellowing effect of silver synthesis on treated samples (NS1, NS2) resulted in negative WI values. In this regard, presence of glucose in the process increased the WI values of the pockets of samples NSG1 and NSG2, as a result of glucose discoloration effect.

Reduced back-staining of the treated samples in comparison to the untreated fabric was observed possibly due to the synthesis of nano silver particles. In this regard, samples treated in presence of glucose (NSG1 and NSG2) were bluer comparing to NS1 and NS2, due to the ability of glucose to reduce indigo dye.

Considering the yellowing effect of silver nanoparticles synthesis, the $a^*$ values of the treated fabrics indicated higher greenness

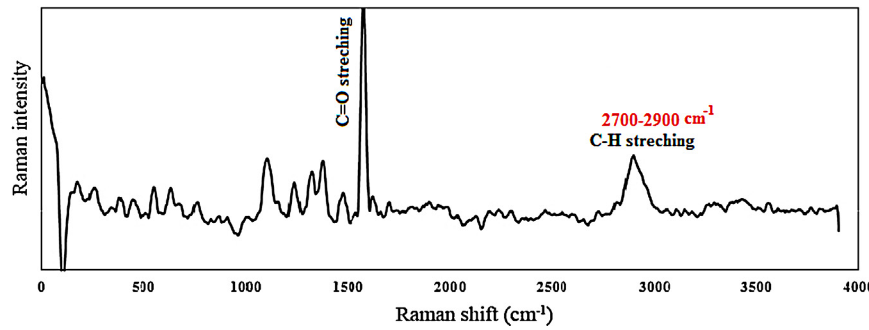
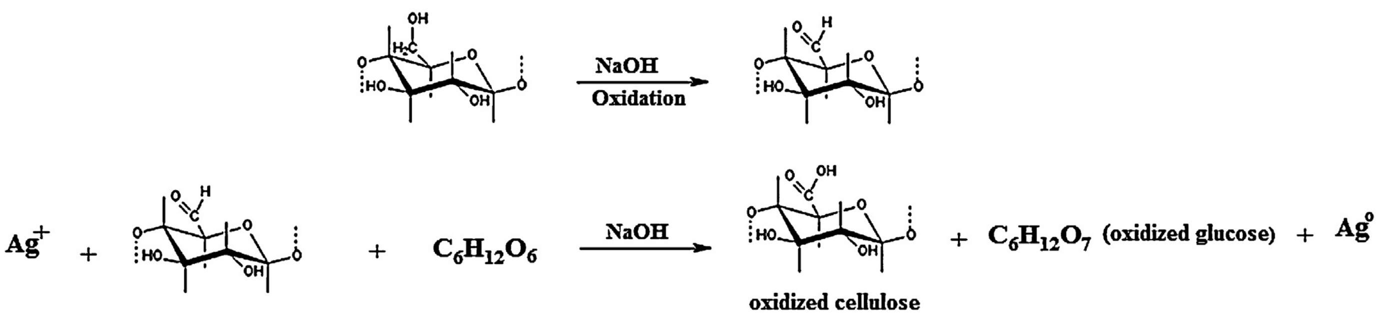



**Fig. 3.** Raman spectrum of treated denim fabric (NS2).




**Scheme 1.** Possible reactions of nano silver synthesis.

in comparison to the untreated sample and the change was more prominent for samples back and white pocket.

### 3.6. Antibacterial activity

According to Table 3, the silver nitrate treated denim fabrics showed reasonable antibacterial activity against Gram-negative and Gram-positive bacteria. Although the silver nitrate/glucose treated samples reduced the number of bacteria colonies to some extent, they were not as effective as the treated samples without glucose. Glucose as a suitable nutrient for the growth of bacteria led to decrease in antibacterial ability from 89.1% and 97.6% to 71.2% and 77.9%, respectively. Residues of glucose on the fabric surface showed detrimental effect on antibacterial efficiency, resulting in higher bacteria growth. The highest antibacterial activity was obtained for sample NS2, as a result of more silver nanoparticles synthesized on the sample due to longer treatment time.

### 3.7. Durability

The washing stability of silver nanoparticles adsorbed on treated denim fabrics was evaluated and the change in antibacterial efficiency of the washed samples after each cycle of laundry was recorded (Table 3). The washed samples showed appropriate antibacterial activity even after 40 washing cycles. Formation of negative charges on cellulose chain, attraction of $Ag^+$ to chemical active groups of cellulose, oxidization of cellulose during silver ions reduction to silver nanoparticles and fiber swelling during the synthesis process at boil led to adsorption of synthesized silver nano particles into the intra molecular structure of cellulose, producing durable antibacterial properties.

### 3.8. Cytotoxicity

Cytotoxicity test was carried out to investigate any harmful effects of the treated fabrics on human dermal fibroblasts. The extraction medium was cultured with normal human dermal fibroblasts and its viability was determined by MTT assay. Cells without a treatment of the sample were considered as a control with a cell viability of 100%. The cell viability of untreated and treated samples after 24 h of incubation is shown in Fig. 4a. No significant change was observed in the viability of normal human dermal fibroblasts cultured with denim fabrics treated by silver nitrate (NS2, NSG2) and the untreated sample. The average elative cell viability was over 70%, indicating good biocompatibility of the treated fabrics (Kangwansupamonkon, Lauruengtan, Surassmo, & Ruktanonchai, 2009). Therefore, the treated cellulosic denims (NS2 or NSG2) indicated low toxicity with suitable antibacterial activity similar to the untreated denim.

**Table 2**
Color coordinates of untreated and treated denim.

| Properties | Color coordinates | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Face | | | | Back | | | White pocket | | | |
| Sample | $L^*$ | $a^*$ | $b^*$ | $\Delta E$ | $L^*$ | $a^*$ | $b^*$ | $L^*$ | $a^*$ | $b^*$ | WI |
| Untreated | 21.7 | 1.1 | −8.5 | 0.0 | 42.0 | −1.3 | −4.9 | 80.0 | −1.9 | 6.0 | 30.0 |
| NS1 | 22.3 | 1.0 | −6.7 | 1.8 | 43.9 | −2.1 | −1.9 | 77.2 | −3.9 | 10.6 | −5.5 |
| NS2 | 21.9 | 0.9 | −6.6 | 1.9 | 43.0 | −4.8 | 1.5 | 75.3 | −5.8 | 11.5 | −9.2 |
| NSG1 | 23.1 | 0.9 | −7.7 | 1.3 | 43.0 | −3.2 | −3.0 | 81.1 | −4.6 | 8.6 | 13.6 |
| NSG2 | 23.0 | 1.1 | −7.0 | 1.9 | 42.7 | −3.9 | −2.8 | 77.8 | −5.8 | 7.9 | 26.1 |

**Table 3**
Antibacterial activities of different fabrics before and after laundering.

| Sample | Number of laundering | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | | 5 | | 10 | | 20 | | 30 | | 40 | |
| | *E. coli* | *S. aureus* | *E. coli* | *S. aureus* | *E. coli* | *S. aureus* | *E. coli* | *S. aureus* | *E. coli* | *S. aureus* | *E. coli* | *S. aureus* |
| Untreated | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| NS1 | 89.1 | 90.4 | 89.0 | 90.3 | 88.9 | 90.2 | 88.0 | 90.0 | 88.0 | 90.0 | 87.9 | 89.3 |
| NS2 | 97.6 | 96.2 | 97.6 | 96.2 | 97.6 | 96.2 | 97.5 | 96.2 | 97.5 | 96.0 | 97.1 | 96.0 |
| NSG1 | 71.2 | 71.6 | 71.0 | 71.3 | 70.8 | 70.1 | 70.0 | 69.9 | 70.0 | 69.8 | 70.0 | 69.7 |
| NSG2 | 77.9 | 78.3 | 77.9 | 78.3 | 77.7 | 78.3 | 77.5 | 78.0 | 77.5 | 77.9 | 77.3 | 77.9 |

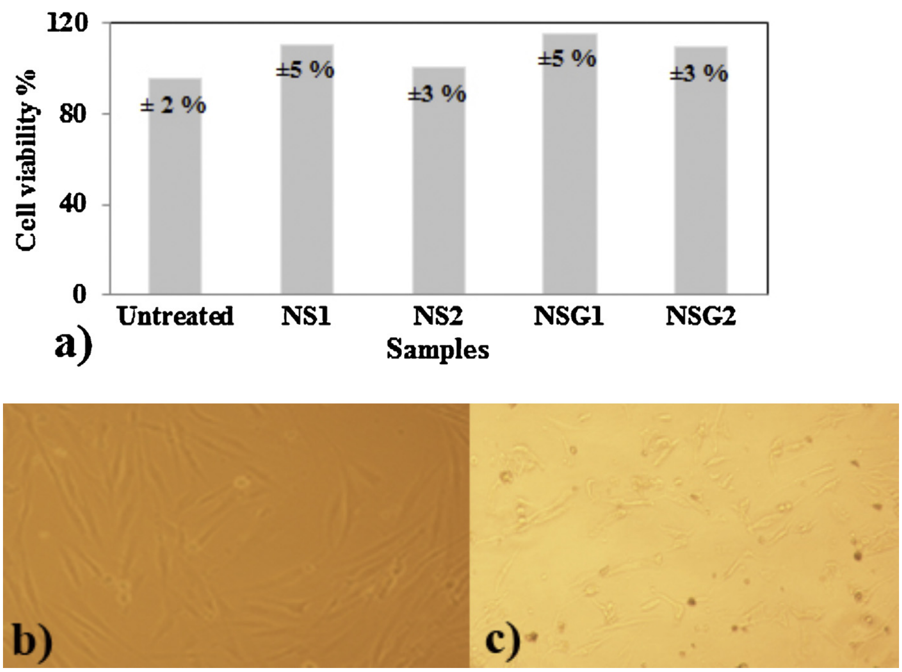



**Fig. 4.** Cell viability after 24 (h) of incubation with the untreated and treated samples (a), Photograph of dermal fibroblasts cells of control (b) and treated samples (c).

The alteration in the shape or morphology of the cells after exposure to toxic materials was further observed by the optical microscopy pictures of dermal fibroblasts cells (Fig, 4b and c). Morphology of fibroblast cells in presence of treated fabrics was normal and similar to the morphology of the control sample, indicating negligible harmful effects on human skin.

## 4. Conclusions

This research designed a novel route for producing aged-look denim fabric with desirable yellowing appearance and durable antibacterial activity by simultaneous silver nanoparticles synthesis and denim fabric discoloration. Silver nanoparticles with smaller size and less agglomeration were prepared using glucose as a reducing agent and the back side of the treated fabrics was yellower in comparison to the untreated denim fabric due to the silver nanoparticles synthesis and discoloration effect of glucose. Although glucose as a suitable nutrient for the growth of bacteria had detrimental effect on the antibacterial efficiency, the treated fabrics had no adverse impact on human dermal fibroblasts (low toxicity).

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