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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 ΔE 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 ΔL^*, Δa^*, and Δb^* 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