Journal of Cleaner Production 101 (2015) 377–386

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Development of antibacterial cellulosic fabric via clean impregnation of silver nanoparticles

Zulfiqar Ali Raza [a, *], Asma Rehman [b], Muhammad Mohsin [c], Sadia Zafar Bajwa [b], Faiza Anwar [a], Abdul Naeem [d], Niaz Ahmad [a]

[a] Chemistry Research Laboratory, National Textile University, Faisalabad 37610, Pakistan
[b] Industrial Biotechnology Division, National Institute for Biotechnology and Genetic Engineering, Faisalabad, Pakistan
[c] Department of Textile Engineering, University of Engineering and Technology, Lahore, Faisalabad Campus, Pakistan
[d] National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form
28 March 2015
Accepted 30 March 2015
Available online 8 April 2015

Keywords:
Antibacterial activity
Cellulosic fabric
Silver nanoparticle
Textile

ABSTRACT

In the present study, we investigate single bath fabrication and impregnation of silver nanoparticles (SNPs) on enzymatic pretreated cotton fabric by using starch both as reducing as well as stabilizing agent under the autoclave conditions of 103.42 kPa, 121 °C for 15 min. The SNPs were characterized using UV–visible (UV–vis) spectroscopy, zetasizer nano and transmission electron microscopy. The UV–vis absorption spectra showed typical absorption peaks at ~420 nm corresponding to the surface plasmon resonance of SNPs. The hydrodynamic diameter of SNPs was as smaller as 20 nm with their respective zeta potential of −43.20 mV. Both scanning electron and atomic force microscopic analyses revealed that the surface of the treated cotton fabric was rougher than that of untreated fabric, and the SNPs were present on the surface of the treated fabric. Silver mapping and elemental analysis of the treated cotton fabric using energy dispersive X-ray spectroscopy confirmed the presence of SNPs in a homogeneous distribution. The textile properties of the fabric including wettability, whiteness, tensile strength and antibacterial activity were measured by using the standard methods. The SNPs impregnated cotton fabrics showed good durable antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* strains.

1. Introduction

In the current scenario, progressive and groundbreaking technologies are required, and the new textile products with interactive effects should be designed for high-tech and smart applications (Gupta et al., 2008; Lee et al., 2007). The antibacterial cellulose fabrics are well-demanded textile materials for clothing, technical, medical and hygienic purposes. Due to its biodegradable and hydrophilic nature, cellulose provides excellent media for pathogenic and odor producing microorganisms (Klemencic and Tomsic, 2012; Reijnders, 2006). To prevent it, a variety of antibacterial agents have been reported like metals and metal salts, quaternary ammonium compounds, triclosan, chitosan, peroxyacids and so on (Gao and Cranston, 2008); nevertheless, most of them being synthetic are non-biodegradable and toxic, which causes environmental and health concern including skin irritation, eco-toxicity and bacteria resistance (Gao and Cranston, 2008). The textile industry endures to search out eco-compatible process auxiliaries to replace the toxic ones. For that purpose, several antibacterial textile coatings, including metal nanoparticles, could be done (Gong et al., 2007; Gorjanc et al., 2012; Gouda, 2012). Again, amongst various types of nano-materials e.g., gold, zinc, copper, titanium, alginate etc., silver is by far the most widely used nano-material (Agarwal et al., 2010; Gao and Cranston, 2008; Gong et al., 2007), as they can be assembled into many different shapes, such as spheres, rods, cubes, wires, film, and coatings (Wijnhoven et al., 2009). The impregnation of silver nanoparticles (SNPs) on textiles brings interesting properties to the final apparel products and extends their use in

List of abbreviations: AATCC, American Association of Textile Chemists and Colorists; AFM, Atomic force microscope; ASTM, American Society for Testing and Materials; CIE, Commission International de L'éclairage; EDX, Energy dispersive X-ray; FE-SEM, Field emission scanning-electron microscope; SEM, Scanning electron microscope; SNPs, Silver nanoparticles; UV–vis, Ultraviolet–visible; TEM, Transmission electron microscope.

* Corresponding author. Tel.: +92 41 9230081; fax: +92 41 9230098.
E-mail address: zarazapk@yahoo.com (Z.A. Raza).

http://dx.doi.org/10.1016/j.jclepro.2015.03.091
0959-6526/

biomedical and advanced materials applications (Ahmad et al., 2006).

The chemical alteration of cellulosic fabric with a silver-based finish is of great technological significance particularly in imparting new functionalities in the cellulose. The treated cellulosic fabrics find multifunctional applications in clothing, undergarments, sportswear, fashion, and medical, smart and technical textiles. However, there are still several problems faced related to fabrication and application of SNPs, including their uneven impregnation onto the fabric surface (Gao and Cranston, 2008; Li et al., 2009). The most common protocol of manufacturing SNPs is the chemical reduction of Ag salts using various reductants such as $NaBH_4$, glucose, citrate, ascorbates and hydrazine (Gulrajani et al., 2008; Martinez-Castanon et al., 2009). A strong reductant leads to smaller monodisperse particles; in this case, the fabrication of larger particles could be hard to manage, whereas a weaker reductant induces slower reduction reactions; however, the nanoparticles hence obtained tend to be more polydisperse in size (Shirtcliffe et al., 1999). Since the reductants for SNPs fabrication are often considered toxic or hazardous, therefore the adaptation of clean methods is becoming primacy (Panacek et al., 2006). To solve above problems, much research in this decade has focused on the understanding the green synthesis of nanosilver and nanosilver compounds that include nontoxic chemicals, eco-friendly solvents and renewable materials rather than conventional synthesis with hazardous chemicals (Hebeish et al., 2011; Ravindra et al., 2010). Polysaccharides, for instance, are classically used as capping agents in SNPs fabrication, but they might also involve in the reduction of Ag^+ ions. The reduction of Ag^+ ions might be connected with the oxidation of aldehyde groups to give carboxylic acid groups (Manzi and van Halbeek, 1999). Generally, for above purposes, the polysaccharides in use include glucose, starch, heparin and so on (Manno et al., 2008; Singh et al., 2009).

The main objective of the study was to improve the textile fabric properties by incorporating the functionally important nanomaterials. Though many researchers worked on the coating of textile fabric with SNPS but there are few reports about the *in situ* fabrication of SNPs to improve the antimicrobial properties of particularly an enzymatic pretreated cellulosic fabric via a clean approach. Starch is used as reducing as well as stabilizing agent. The porous cellulose matrix of cotton fabric is used as the template for SNPs synthesis. This study is very useful to design the textile fabrics in order to enhance their inherent properties. The treated fabric and residual SNPs in the media were characterized by using various spectroscopic and microscopic techniques. The treated fabrics were, in addition, examined for antibacterial and other textile properties.

2. Materials and methods

2.1. Chemicals and reagents

Aquzaym SDL (an amylase), Scourzyme L (a pectinase) and Cellusoft L (a cellulase) were kindly donated by Novozymes. Hydrogen peroxide (H_2O_2, 34.5–36.5%) was obtained from Sigma–Aldrich, silver nitrate ($AgNO_3$, 99%) and starch ($C_6H_{10}O_{5x}$, GPG) from Fischer Scientific UK, nutrient agar from Merck, and nutrient broth from Lab. M. Ltd., UK. All the chemicals and reagents were used as received. All solutions used were made in distilled water of electrical conductivity below 3 μS/cm. Greige 100% cotton plain weave fabric was purchased from Ahmed Fine Textile Mills Ltd., Multan, Pakistan. Rhamnolipid surfactant, used as bioscouring agent, was obtained by using a bacterial strain of *Pseudomonas aeruginosa* (Raza et al., 2014).

2.2. Bacterial strains

The bacterial strains of *Escherichia coli* and *Staphylococcus aureus* were used for testing the antibacterial activity of treated fabric samples, as reported before (Mohsin et al., 2014). The bacteria were preserved at 4 °C on nutrient agar and refreshed weekly. The strains were exclusively streaked on nutrient agar and incubated (WIG-32, Daihan Scientic, Korea) at 37 °C for 24 h for a new growth. A sole colony was shifted to nutrient broth and incubated for 48 h. The cells were gathered by centrifugation (at 10,000 rpm and 4 °C for 15 min), washed in normal saline (0.9% w/v) and re-dispersed to an optical density of 0.7 at 600 nm. These cell dispersions were designated as inocula for antibacterial testing.

2.3. Pretreatments of cotton fabric

Enzymatic desizing of the greige cotton fabric was done by using 2 g amylase/L at 95 °C for 40 min. Bioscouring was done by using 6 gpectinease /L plus 100 mg rhamnolipid/L at 65 °C and pH 8 for 40 min of incubation on a lab scale launder-o-meter with fabric-to-liquor ratio of 1:30 (w/v) (Raza et al., 2014). The fabric was then bleached with hydrogen peroxide to achieve an optimum whiteness. All the above pre-treatments were carried out on a lab scale jigger machine. All samples prior to any treatments were washed to remove any degraded impurities. The washing was performed on a Roaches dyeing machine (Pyrotec S), at pH 8–9 using a non-ionic detergent of Triton X-100 (0.5 g/L) at 100 °C for 30 min. The non-ionic detergent was insensitive to hard water, exhibited a pronounced wetting action and was effective for removing the fatty residuals of bioscouring process. The samples were then washed off at 35–40 °C for 45 min, and finally rinsed with distilled water and air dried. The pretreated cotton fabric samples were subsequently air dried and then brought to a moisture equilibrium under conditions of relative humidity (65 ± 2%) and temperature (25 ± 1 °C) for 24 h.

2.4. In situ fabrication of silver nanoparticles

Silver nanoparticles were synthesized through a clean synthesis procedure using the starch both as reducing as well as stabilizing agent. For that purpose, various concentrations of $AgNO_3$ (0.1–1.0 mM) and starch (0.5–1.5% w/v) were dissolved in distilled water and vigorously stirred at room temperature. In a typical one-step synthesis protocol, 30 × 30 cm cotton fabric was immersed in a silver nitrate/starch aqueous solution in an Erlenmeyer flask. The fabric to liquor ratio was maintained at 1:20 (w/v). This flask was kept in an autoclave (Daihan Wisd, WAC-60) at 103.42 kPa (= 15 *psi*), 121 °C for 15 min. After autoclaving, the color of solution turned in a range from light yellow to deep brown depending upon the concentration and size of SNPs. Both treated fabric and solution were analyzed further for the presence and properties of SNPs. Digital photographs of treated fabrics and residual nano-silver colloids were captured by using Cyber-shot SONY digital camera (DSC-W310) of 12.1 Mega pixel.

2.5. UV–visible spectroscopy

The SNPs suspension was centrifuged (MSE Harrier 18/80, MSE, England) at 10,000 rpm and 4 °C for 15 min. The pellet of SNPs hence obtained was re-suspended in distilled water though sonication (BMS UC-D06). This aqueous colloidal suspension was subjected to UV–visible (UV–vis) spectrophotometry (BMS UV-2800, BMS, USA) in the range of 300–900 nm using distilled water containing starch and silver nitrate of respective concentrations as reference media.