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Imparting durable antimicrobial properties to cotton fabrics using alginate–quaternary ammonium complex nanoparticles

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ABSTRACT

A new type of nanoparticle composed of sodium alginate (SA) and 3-(trimethoxysilyl)propyl-octadecyldimethylammonium chloride (TSA) was prepared by ionic gelation. The average size of the SA–TSA nanoparticles was significantly affected by the initial mass ratio of SA and TSA used for the formation of the SA–TSA colloidal solution. SA–TSA nanoparticles with an average size of 99 nm were chosen and loaded onto cotton fabrics by a pad-dry-cure method. Scanning electron microscopy of the treated fabric indicated SA–TSA nanoparticles were well-dispersed on the fabric surface. Cotton fabrics treated with the nanoparticles at 70 ppm concentration demonstrated efficient antimicrobial activity (>99.99% reduction in viable cell counts) against a representative Gram-negative bacterium (*Escherichia coli*) and a Gram-positive bacterium (*Staphylococcus aureus*). The antibacterial efficacy was maintained even after 30 laundry cycles. The results indicate that the SA–TSA nanoparticles can be useful as a non-leaching agent imparting durable antimicrobial properties to cotton fabrics.

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1. Introduction

Clothing and other textile materials, especially those made of natural fibers such as cotton and wool, can act as media for the growth of microorganisms such as pathogenic or odor-generating bacteria and fungi. When in contact with the human body, such materials offer an ideal environment for microbial growth because of their large surface area and ability to retain oxygen, moisture and warmth, as well as nutrients from spillages and body exudates (Dev, Venugopal, Sudha, Deepika, & Ramakrishna, 2009). Therefore, with a rising interest in personal health and hygiene, textiles with antimicrobial properties are becoming an increasingly desirable aim of textile manufacturers.

Several different types of antimicrobial agents, such as oxidizing agents, coagulants, diphenyl ether (bis-phenyl) derivatives, heavy metals and metallic compounds, chitosan, and quaternary ammonium compounds (QACs) are used in the textile industry to confer antimicrobial properties (Hashem, Ibrahim, El-Sayed, El-Husseiny., & El-Enany, in press; Lim & Hudson, 2004; Ramachandran, Rajendrakumar, & Rajendran, 2004). In particular, QACs have been widely used as cationic disinfectants or biocidal coating to prevent the growth of microorganisms on the surface of materials including fibers, paints, filters, and packing films (Appendini & Hotchkiss, 2002; Kumar, Bhardwaj, Rawat, & Sabharwal, 2005; Son, Kim, Ravikumar, & Lee, 2006). This protective effect is achieved by the leaching of the bioactive QACs from the surface coating. However, ultimately the compounds will be exhausted and leaching will cease, rendering the material ineffective and limiting its long-term usefulness. To circumvent these problems, QACs could be anchored to a polymer backbone by a covalent non-hydrolysable bond. The resulting insoluble cationic polymer coating could exert antimicrobial activities merely by contact with water without requiring the release of the reactive agents. In fact, several insoluble QAC-containing polymers including polystyrene (Jiang, Wang, Yu, & Chen, 2005), chitosan derivatives (Kim, Lee, Lee, & Park, 2003), and poly(glycidyl methacrylate) (Kenawy, Abdel-Hay, El-Raheem, El-Shanshoury, & El-Newehy, 1998) have been synthesized and their unique properties as antimicrobial polymers reported.

In a previous study, we reported that a complex of alginate–quaternary ammonium in bead form (3 mm average diameter) can be easily prepared by the reaction of sodium alginate (SA) with 3-(trimethoxysilyl)propyl-octadecyldimethylammonium chloride (TSA) in acid solution, followed by crosslinking with calcium chloride ($CaCl_2$) (Kim et al., 2007). The SA–TSA complex beads are advantageous as a new type of insoluble antimicrobial polymer since they have greater antimicrobial activity and better durability in water than other conventional antimicrobial polymers. They effectively inactivate or kill a broad range of microorganisms with a short contact time and are relatively easier to produce. More importantly, the preparation process of the SA–TSA complex does not require organic solvents such as chloroform and dioxane, which carry toxicity and flammability concerns (Eknoian, Worley, Bickert, & Williams, 1999). These advantageous properties of the SA–TSA complex

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might be potentially useful for their applications in the textile industry as an alternative antimicrobial agent. To achieve this purpose, however, the SA–TSA polymer should be nanosized to confer the mechanical properties required for textile goods.

In this study, we describe the preparation of nanosized SA–TSA colloidal solution by manipulating the mass ratio of SA and TSA during the ionic gelation process. The resulting colloidal SA–TSA nanoparticles were coated on the surface of cotton fabrics by a pad-dry-cure method and the antimicrobial efficacy was evaluated.

2. Experimental

2.1. Materials

SA and TSA were purchased commercially (Sigma–Aldrich, St. Louis, MO) and used without further purification. As a test texture, bleached, desized, and mercerized 100% cotton fabric was supplied by the Korea Institute for Knit Industry. All other chemicals were analytical grade and were used as purchased.

2.2. Preparation of SA–TSA nanoparticles

SA–TSA nanoparticles were prepared by a two-step procedure based on the reaction between SA and TSA, followed by ionic gelation of the SA–TSA complex solution with $CaCl_2$. SA was dissolved in distilled water to a final concentration of 0.05%, and then various concentrations of TSA (0.05–2.5%) were added to the solution. The pH was adjusted to 4.0 with glacial acid at room temperature. The mixture was then stirred overnight at room temperature. Ten milliliters of 20 mM $CaCl_2$ was added drop-wise with gentle stirring into a beaker containing 100 ml of SA–TSA complex solution to generate SA–TSA nanoparticle colloidal solution. The colloidal SA–TSA nanoparticles were stirred for 3 h to improve curing prior to collection by centrifugation (6000 rpm, 30 min) at room temperature.

2.3. Nanoparticle size analysis

The average of 30 size readings were taken by photon correction spectroscopy using a Malvern Zetasizer and Particle Analyzer 5000 (Malvern Instruments, Malvern, UK). One milliliter of sample was gently shaken, placed into the analyzer chamber and readings were taken at 25 °C with a detected angle of 90°. Results are given as a *z*-average ± SD.

2.4. Antimicrobial treatment of cotton fabrics with SA–TSA nanoparticles

The cotton fabrics, cut in sizes of around 20 × 20 cm, were immersed in a finishing solution containing different concentrations of colloidal SA–TSA nanoparticles for 1 min and squeezed to 100% wet pick-up on a laboratory padding mangle. Samples were dried at 80 °C for 3 min and cured at 150 °C for 3 min. The morphology of treated cotton fabrics was observed by scanning electron microscopy (SEM) using a JEOL JSM-7000F scanning electron microscope (JEOL, Tokyo, Japan). Cotton samples that were untreated or treated with SA–TSA nanoparticles were dried at 105 °C for 1 h to reach constant weight. The add-on percentage (add-on%) of SA–TSA nanoparticles on the cotton samples was calculated by the following equation:

$$\text{add-on}\% = [(W_1 - W_0)/W_0] \times 100$$

where W_0 and W_1 are the weights of the cotton samples before and after treatment, respectively.

The rewetting time of the treated fabrics was determined according to AATCC Test Method 27–1994 (Ola et al., 2004) representing the time required for a droplet of water to be absorbed by a fibrous surface.

2.5. Antimicrobial test for cotton fabrics treated with SA–TSA nanoparticles

The antimicrobial properties of cotton fabrics treated with colloidal SA–TSA nanoparticles were evaluated by a quantitative shake-flask antimicrobial test method specially designed for specimens treated with non-releasing antimicrobial agents under dynamic contact conditions (Ye et al., 2005). *Escherichia coli* ATCC 25922, a Gram-negative bacterium, and *Staphylococcus aureus* ATCC X6538P, a Gram-positive bacterium, were used as the test organisms. *E. coli* and *S. aureus* were grown at 35 °C for 24 h on nutrient broth (Difco, Detroit, MI) and tryptic soy broth (Difco), respectively. Cultures of each organism were diluted with sterile distilled water to give a final concentration of 1.0×10^7 colony forming units (CFU)/ml representing the working bacterial dilution. One gram of fabric was cut into small pieces (1 × 1 cm) and transferred to a 250 ml Erlenmeyer flask containing 100 ml of the working bacterial dilution. All flasks were placed in the incubator, and continually shaken for 8 h at 35 °C and 200 rpm using a rotary shaker. Triplicate 1.0 ml volumes of sample solution from the sample/bacterial suspension were removed by pipetting, diluted with sterile distilled water, and spread onto separate agar plates. After incubation at 35 °C for 2 days, the number of colonies formed on the agar plates was counted. The average values of the triplicate determinations were converted to CFU/ml by multiplying by the dilution factor. The antimicrobial activity was expressed in terms of the percent reduction of the organism after contact with the test specimen compared to the number of bacterial cells surviving after contact with the control. The results were expressed as percent reduction of bacteria (R) by following equation:

$$R = [(B - A)/B] \times 100$$

where A and B are the surviving cells (CFU/ml) for the flasks containing test samples (treated cotton fabrics) and the control (untreated cotton fabrics), respectively.

2.6. Durability test

To evaluate the durability of the antimicrobial activity of the cotton fabrics treated with colloidal SA–TSA nanoparticles upon repeated launderings, the treated cotton fabrics were washed with an aqueous solution containing 3 g/L anionic detergent under vigorous magnetic stirring for 20 min at 25 °C and further rinsed in distilled water with magnetic stirring for 40 min 25 °C to remove residual anionic detergent from the fabric. Each fabric sample was air-dried at room temperature and the antimicrobial properties were quantitatively determined as described above.

3. Results and discussion

3.1. Preparation and characterization of SA–TSA nanoparticles

The formation of the SA–TSA complex occurs through covalent bonds formed between hydroxyl groups of SA and methoxysilyl groups of TSA, and the formation of particulate structures from the SA–TSA complex solution can be accomplished by ionic gelation due to Ca^{2+} (Kim et al., 2007). The sizes of particles made from polyelectrolyte complexation depend on the concentration and molecular weight of both polyelectrolytes, and conditions of mixing (Lertsutthiwong, Rojsitthisak, & Nimmannit, 2009; Sarmento,

Ferreira, Veiga, & Ribeiro, 2006). In the present study, the formation of SA–TSA nanoparticles was only achievable using 0.03–0.1% SA. No particle formation was observed in the complex solution when SA concentrations were <0.03%, while SA concentrations >0.1% led to the formation of micro-sized complex particles. Moreover, the size of the SA–TSA nanoparticles was significantly affected by the initial mass ratio of SA and TSA used for the formation of SA–TSA complex solution. At a final SA concentration of 0.05%, decreasing the SA:TSA mass ratio from 1:1 to 1:50 resulted in an increased particle size from 99 to 192 nm (Table 1). These relationships provide a processing window for manipulating nanoparticles and optimizing the nanosize for intended applications. Fig. 1 shows representative SEM images of the SA–TSA nanoparticles formed from the SA:TSA mass ratio of 1:1. The nanoparticles had spherical or elongated shapes with a relatively smooth surface.

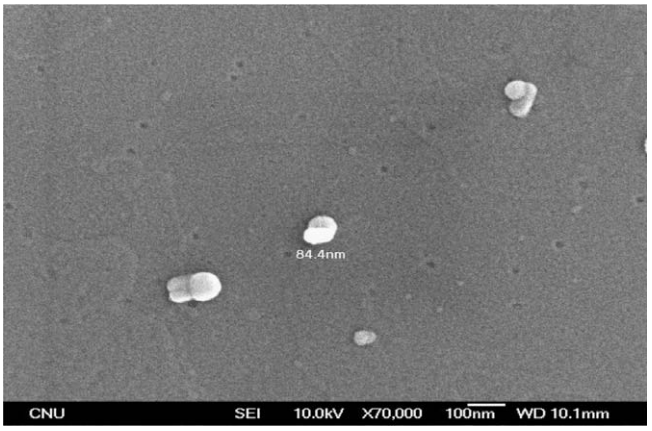

Fig. 1. SEM micrographs of SA–TSA nanoparticles produced with a SA:TSA mass ratio of 1:1.

3.2. Application of SA–TSA nanoparticles to cotton fabric

Padding is the most common finishing method for application of chemical formulation to textile materials in continuous processes. Padding consists of contacting the textile material with the formulation, usually by immersion, and squeezing the formulation out with squeeze rolls (Hong & Sun, 2008). In this study, cotton fabrics were immersed in the SA–TSA nanoparticle colloidal solution that was concentrated at 50, 70, and 100 ppm, and then squeezed between rollers to maintain the constant pickup of 100% based on the fabric weight. It is speculated that SA–TSA nanoparticles could adhere to the cotton fabric by chemical bonds between silanol groups formed by the partial hydrolysis of trimethoxysilyl groups in SA–TSA nanoparticles and fabric hydroxyl groups. The chemical binding of the nanoparticles to the cotton surface during the pad-dry-cure process is depicted in Fig. 2.

The content of SA–TSA nanoparticles adhering to the cotton fabric varied with the concentration of the colloidal SA–TSA nanoparticles in the finishing solution. The add-on% values of SA–TSA nanoparticles from 50, 70, and 100 ppm colloids were 1.8 ± 0.8%, 2.6 ± 0.5%, and 3.7 ± 0.9%, respectively, indicative of a linear relationship between the content of SA–TSA nanoparticles on cotton fabric and the concentration of colloidal SA–TSA nanoparticles in the finishing solution. Fig. 3 shows representative SEM images of both the untreated and the SA–TSA nanoparticles-treated cotton fabrics. The surface of treated fabrics was obviously coarser than that of the untreated fabric, indicating the presence of SA–TSA nanoparticles on the treated cotton fabrics. The majority of SA–TSA nanoparticles were well-dispersed and some nanoparticle aggregates were evident. In particular, the surface of the fabric treated with SA–TSA nanoparticles from 100 ppm colloid was uniformly coated with the nanoparticles.

Even though the surface of cotton fabric treated with SA–TSA nanoparticles did not show any visible changes, the rewetting time of the surface increased with increasing concentration of SA–TSA nanoparticles colloid. The rewetting time of the untreated cotton fabric was nearly instantaneous, at 2 s, while those of the cotton fabrics treated with SA–TSA nanoparticles from 50, 70, and 100 ppm colloids were 20, 50, 120 min, respectively. This implies

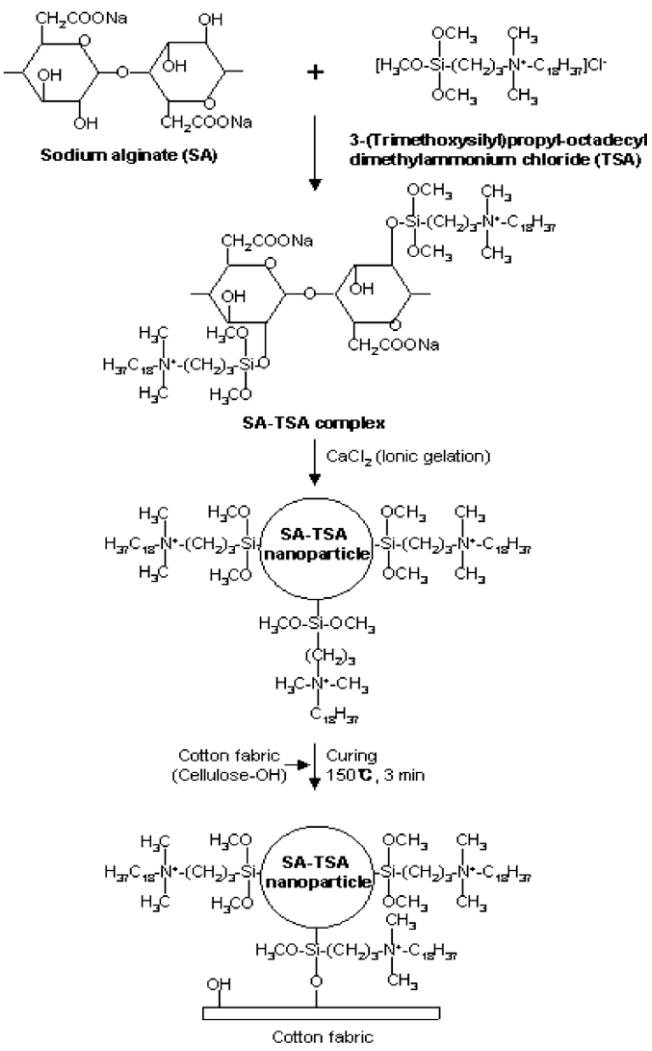

Fig. 2. Schematic diagram of reaction between cotton fabric and SA–TSA nanoparticles.

Table 1
Characterization of SA–TSA nanoparticles produced in terms of mean size as a function of SA/TSA mass ratio ($n = 3$).

SA:TSA mass ratio	Mean size (nm)
1:1	99 ± 19
1:5	109 ± 13
1:10	117 ± 10
1:20	159 ± 22
1:50	192 ± 25

that the surfaces of the treated cotton fabrics are relatively hydrophobic, probably due to the water-repellent property of TSA (Ola et al., 2004). Recently, as markets in leisure and outdoor sporting textiles have expanded, the need for superhydrophobic cotton fabrics has increased (Bae et al., 2009). The present results suggest

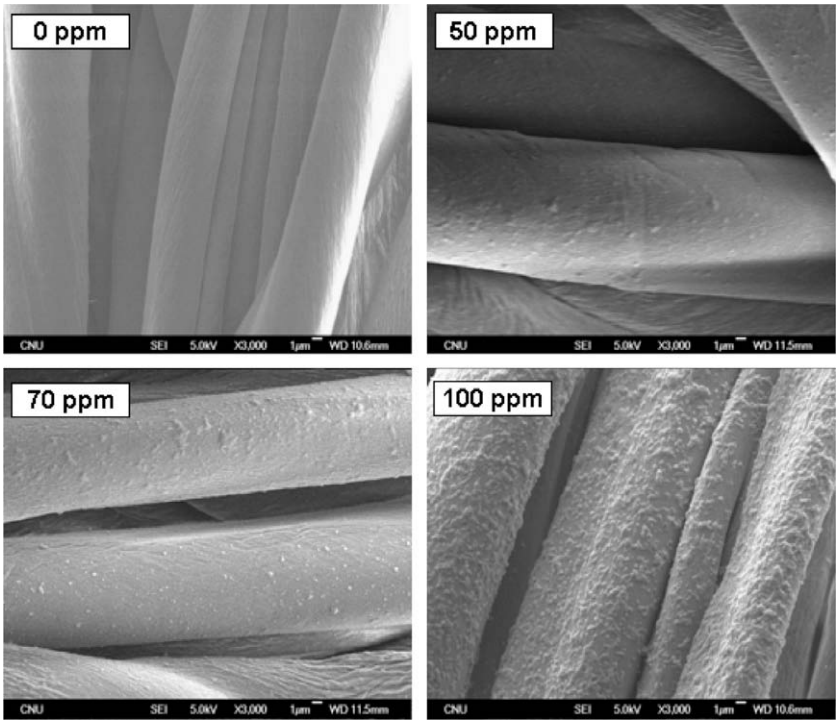

Fig. 3. SEM images of untreated and SA–TSA nanoparticle-treated cotton fabrics.

that the treatment of SA–TSA nanoparticles can be useful for imparting superhydrophobicity to hydrophilic cotton fabric.

3.3. Antimicrobial activity of cotton fabric treated with SA–TSA nanoparticles

The applications of QACs as antimicrobial agents are related to their very strong affinity for negatively charged surfaces of the microorganisms. QACs manifest their antimicrobial property in water by the following sequence of elementary processes: adsorption onto the microbial cell surface, diffusion through the cell wall, binding and disruption of the cytoplasmic membrane, and leakage of cytoplasmic constituents; the result is cell death (Massi, Guittard, Géribaldi, Levy, & Duccini, 2003).

The antimicrobial properties of cotton fabrics treated with SA–TSA nanoparticles were quantitatively evaluated against a representative Gram-negative bacterium (*E. coli*) and a representative Gram-positive bacterium (*S. aureus*) (Table 2). The antimicrobial activity increased with increasing concentration of SA–TSA nanoparticle colloids from 50 to 100 ppm. The percent reduction of bacteria (R) of the cotton fabrics treated with SA–TSA nanoparticles from 50 ppm colloid was 75% against *E. coli* and 90% against *S. aureus* after 8 h of exposure (contact) time. However, when the concentration of colloidal SA–TSA nanoparticles exceeded 70 ppm, *R* increased to >99.99% for both organisms. The present results show that SA–TSA nanoparticles are less toxic to *E. coli* than *S. aureus*. The lessened sensitivity of *E. coli* may be attributed to the presence of an additional wall layer (outer membrane) that shows a very low permeability toward hydrophobic compounds and, thus, functions as a barrier to hydrophobic TSA (Sikkema, De Bont, & Poolman, 1995).

Table 2
Antimicrobial activity of cotton fabrics treated with SA–TSA nanoparticles ($n = 3$).

Suspension concentration of SA–TSA nanoparticles (ppm)	*R* (%)[a]	
	S. aureus	*E. coli*
0	5.0 ± 2.0	4.7 ± 1.6
50	90.0 ± 1.8	75.0 ± 3.6
70	>99.99	>99.99
100	>99.99	>99.99

[a] For antimicrobial activity test, cotton fabrics were in contact with cell suspension at 35 °C for 8 h.

The effect of exposure time of treated cotton fabrics on the viability of the tested microorganisms is shown in Fig. 4. As expected, extension of treatment time increased the antimicrobial efficiency against the tested bacteria by providing more opportunities for contact between the nanoparticles and the bacterial cells. Treatment of bacterial culture suspension with cotton fabrics treated with SA–TSA nanoparticles from 70 ppm colloid for 8 h resulted in dramatic reduction in viable cell counts by 4–5 orders of magnitude. The complete elimination of bacterial colonies on agar plates was observed after exposure to the treated cotton fabrics for 12 h. In contrast, untreated cotton fabrics did not exhibit significant antimicrobial activity against any of the microorganisms tested, even when the treatment time was extended to 18 h. Therefore, it can be concluded that the treated cotton fabrics have good antimicrobial activity.

The positive charge (ammonium group) density and the length of the substituent chain are important factors determining the antimicrobial activity of insoluble polymeric ammonium salts (Jiang et al., 2005). High positive-charge density is thought to enhance the interaction of the ammonium group with the cytoplasmic membrane, while the long substituent chain may increase the hydrophobic interaction with the cytoplasmic membrane, which further strengthens the antimicrobial activity of the compounds (Jiang et al., 2005). Therefore, high density cationic groups and long alkyl chains in TSA may explain the high antimicrobial efficiency of the SA–TSA nanoparticles.

Antimicrobial agents applied to the surface of textile fabric could potentially be washed away when immersed in water. Thus,

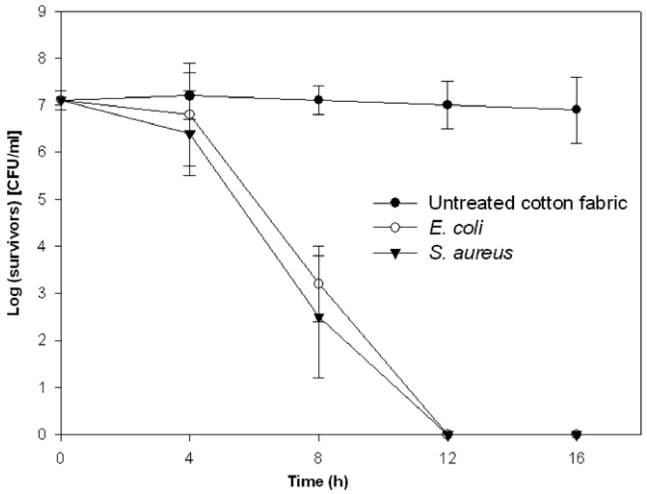

Fig. 4. Antimicrobial activity of cotton fabrics treated with SA–TSA nanoparticles from 70 ppm colloid against *E. coli* and *S. aureus* ($n = 3$).

the durability of antimicrobial activity to washing is a major consideration. To evaluate the durability of antimicrobial property, the antimicrobial efficacy of the treated cotton fabrics after repeated launderings was examined. Fig. 5 shows the effect of repeated washing on the antimicrobial activity of the cotton fabrics treated with SA–TSA nanoparticles. Even after 30 cycles of washing, the antimicrobial activity of the cotton fabrics remained at a high level. The good laundering durability demonstrated the stable adhesion of the SA–TSA nanoparticles on the surface of cotton fabric.

With the advent of bionanotechnology, the application of nano-sized antimicrobial agents in textile finishing has attracted a great deal of attention. Particularly, since silver is non-toxic and possesses good antimicrobial properties, silver nanoparticles are used in different textile fabrics (Perelshtein et al., 2008; Rai, Yadav, & Gade, 2009). Generally, smaller-sized silver nanoparticles are less toxic to animal skin and have a better antimicrobial efficacy than larger nanoparticles at the same level of concentration (Lee & Jeong, 2005). The present *in vitro* results indicate that the antimicrobial efficacy of cotton fabrics treated with SA–TSA nanoparticles is similar to that of cotton fabrics treated with 10 nm-diameter silver nanoparticles (Ilić et al., in press). However, in contrast to SA–TSA nanoparticles, silver nanoparticles can often induce a significant color change of cotton fabrics by the exposure to ultraviolet light. Moreover, silver nanoparticles can be unstable during repeated washing cycles and create effluents during manufacture and subsequent use that are harmful to the environment (Durán, Marcato, Souza, Alves, & Esposito, 2007; Ilić et al., in press), whereas SA–TSA nanoparticles form relatively stronger chemical linkages with hydroxyl groups of cotton fabric; thus, the release of the nanoparticles is less facile. Taking all above results into consideration, SA–TSA nanoparticles are judged to be potentially useful as the new type of agent imparting durable antimicrobial properties to cotton fabrics.

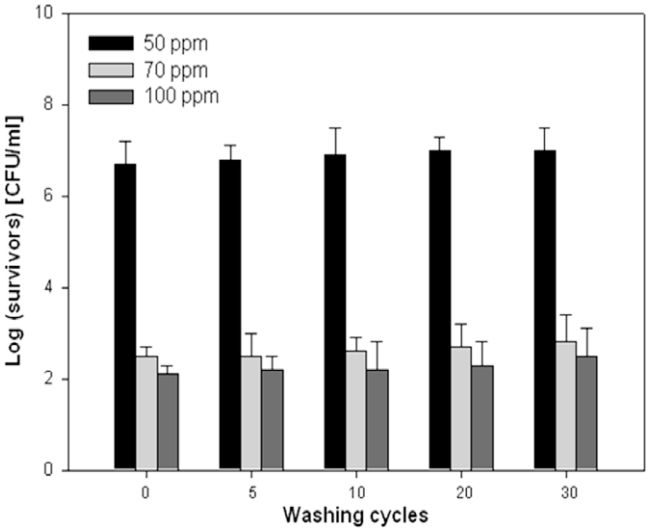

Fig. 5. Effect of repeated washing on the antimicrobial activity of cotton fabrics treated with SA–TSA nanoparticles against *E. coli* ($n = 3$).

4. Conclusions

SA–TSA nanoparticles with an average particle size of 99 nm were prepared by manipulating the mass ratio of SA and TSA at 1:1 during the ionic gelation process of SA–TSA complex and $CaCl_2$. The antimicrobial finishing of cotton fabrics using colloidal SA–TSA nanoparticles was performed by a pad-dry-cure method. The content of SA–TSA nanoparticles on the cotton fabrics had a linear relation with the concentration of colloidal SA–TSA nanoparticles in the finishing solution. The treated cotton fabrics showed a strong antimicrobial activity against both Gram-negative and Gram-positive bacteria. The antimicrobial activity was maintained over 99% even after being exposed to 30 consecutive laundering cycles. The present results suggest that SA–TSA nanoparticles would be advantageous as a new type of antimicrobial agent that can be used in various textile fields.

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