

# Simultaneous Antimicrobial and Dyeing of Wool: A Facial Method

Panthea Sepahi Rad,<sup>1</sup> Majid Montazer,<sup>2</sup> Mohammad Karim Rahimi<sup>3</sup>

<sup>1</sup>Textile Department, Researches and Sciences Unit, Azad University, Tehran, Iran

<sup>2</sup>Textile Department, Amirkabir University of Technology, Center of Excellence in Textile, Tehran, Iran

<sup>3</sup>Medical Science, Tehran North Azad University, Tehran, Iran

Received 17 October 2010; accepted 3 January 2011

DOI 10.1002/app.34089

Published online 23 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** This study is carried out to examine the effects of simultaneous dyeing and antimicrobial finishing of wool yarns. Wool yarns were dyed with acid dye along with colloidal silver nanoparticles through the exhaustion method in a one-bath. Different concentrations of nanosilver were examined to evaluate its influences on the color and the antibacterial properties of the yarns. The antibacterial property of the sample has been tested by a Gram-negative bacterium *Escherichia coli* and a Gram-positive bacterium *Staphylococcus aureus*. Also, the tenacity of wool yarns, color, and rubbing fastness of the dyed yarns has been measured. The color fastness against washing and

antibacterial property of the dyed yarns after 10 laundering cycles was also considered. The fiber morphology was studied by SEM pattern, EDX, and X-ray diffractometer. The results showed that the wool yarns dyed with acid dye along with 25 ppm of silver nanoparticles exhibited a very good antimicrobial effect even after 10 laundering cycles on *S. aureus* while the rubbing fastness remained unchanged, and the color fastness and tenacity were even improved. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1405–1411, 2011

**Key words:** wool; acid dye; antimicrobial; exhaustion; laundering

## INTRODUCTION

Textile, as known, is a good media and suitable nutrient source for generating and propagating of microorganisms. Microorganisms are found everywhere and under optimal conditions of nutrients (protein and hydrocarbon), moisture, pH or temperature, and they can grow enormously. Growth of microorganism on textile causes unpleasant effects, such as deterioration, color change, bad smell, and loss of mechanical properties. Furthermore, textiles are suitable media for growing pathogenic microorganism. This makes the antimicrobial process a highly important stage of textile processing.<sup>1–5</sup>

The antimicrobial finishing needs to be compatible with other finishing processes, agents, and dyeing in particular. In this research, the compatibility of this process with dyeing has been precisely verified.<sup>3,5</sup>

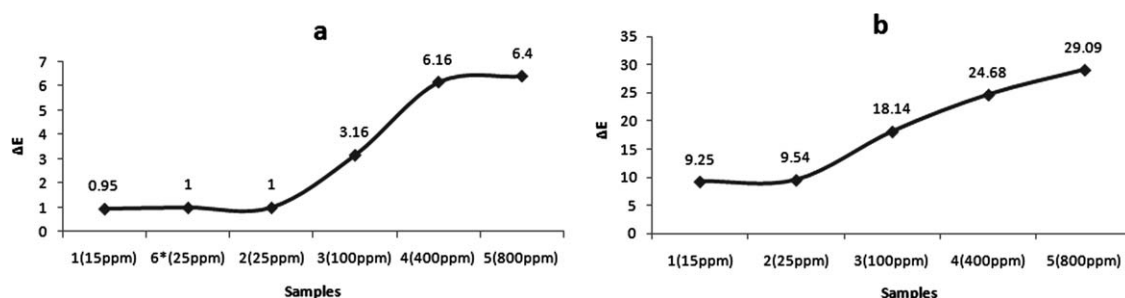
Wool is an excellent media for generating and propagating of microorganisms and insects due to the moisture absorption properties and the richness of protein as a nutrient source. This fact underscores antimicrobial property of wool. The wool keratin is very sensitive to heat, pH, oxidation agents, and

other conditions. Then, it should avoid any additional processing in regular practices to maintain the structure of wool. This makes the idea of using multifunctional finishing and combining different steps of wool processing valuable and critical.<sup>6–8</sup>

Antimicrobial finishing is considered to be applied either separately or with other operations.<sup>9</sup> However, the compatibility of chemicals and application conditions is more important. There are also some natural dyes such as Acacia catechu, Kerria lacca, Quercus infectoria, Rubia cordifolia, and Rumex maritimus, Curcuma henna, Cochineal that have inherent antimicrobial activity and are applied on wool and silk. Antimicrobial effects of these dyes depend on their concentration. Quercus infectoria can be regarded as the most effective and shows maximum zone of inhibition, thereby indicating best antimicrobial activity against all the microbes tested. As a matter of fact, the usages of natural dyes are limited due to certain commercial restrictions like lack of standards, not easy to process, and limited spectra of color.<sup>4,10–13</sup>

Chitosan and henna are recently used to treat wool fabric in two separate steps. It has been proved that the chitosan-treated wool fabrics shows increased dye uptake, sweat, and light fastness. The treated fabrics are found to be antimicrobial, and the chitosan treatment enhances the antimicrobial characteristics of the dyes. Color change has been occurred by increasing chitosan.<sup>11</sup>

Correspondence to: M. Montazer (tex5mm@aut.ac.ir).



**Figure 1** Color differences after various concentration of nanosilver. (a) Nanosilver and dye before laundering; (b) nanosilver without dye. \*Nanosilver and dye were applied on sample 6 separately in different bath.

Furthermore, a new antimicrobial method for wool fabrics based on immobilization of lysozymes has been introduced. The wool fabric has been initially activated with glutaraldehyde and then has been used to covalently immobilize lysozymes. Wool fabric immobilizing lysozymes presents a higher ratio of bacteriostatics against *Staphylococcus aureus*. Moreover, lysozymes are nontoxic with ecofriendly characteristic.<sup>14</sup> Cotton fabrics have also been used by chitosan and *N*-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride as a crosslinking agent including citric acid, butane tetra carboxylic acid, and citric acid. The antibacterial effect becomes apparent after several laundering improvement in wrinkle recovery. Therefore, it could be called antimicrobial functionalization method.<sup>15</sup>

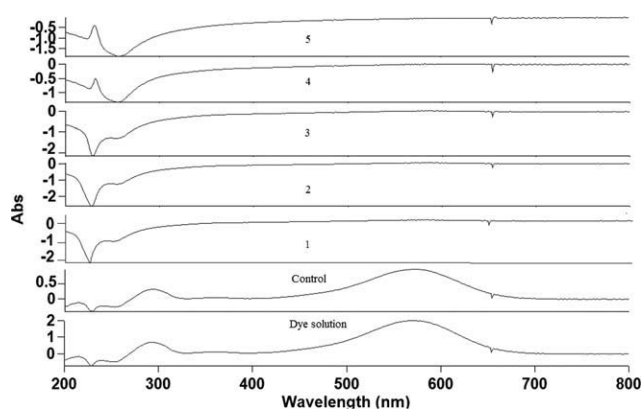
Many metal cations such as copper, zinc, gold, silver, and their nanoparticles in the size range of 1–100 nm have antimicrobial activities. Nowadays, nanoparticles are very important role for the modification of textile products.<sup>16–21</sup>

Although heavy metals such as copper and chromium have been used with acid mordant dyes on wool for several years, their antimicrobial activities are being observed recently. Different heavy metal cations have several oxidation states, and they are

able to form a coordinate covalent bond. They can form a combination with different ligand and cause color fastness. Although silver has an excellent antimicrobial characteristic, but it is not used as a mordant in dyeing because of the low chemical activity and low oxidation state. The most likely oxidation state of silver is +1. The cost might have been also considered as a negative point as well.<sup>3,16–23</sup>

Silver kills more than 650 types of germs with high laundering durability. It is nontoxic and ecofriendly especially in nanosize and its application has been widely recommended.<sup>4,24</sup>

Nanosize silver is applied on different types of fiber, yarn, and fabric through different stages of several methods. For instance, antimicrobial silver nanoparticles have been immobilized on nylon and silk fibers by following the layer-by-layer deposition method. PET fabric has also been treated by nanosilver with crosslinkable poly siloxane via different methods, simultaneous, or after treatment with various concentrations of nanosized silver. A remarkable biostatic efficacy against *S. aureus* and *K. pneumonia* has been appeared. Wool has been treated by a sulfur nanosilver colloidal solution-containing Ag/S complex. This had a perfect antimicrobial efficacy against *S. aureus* and *K. pneumonia*.<sup>20,25–27</sup>



**Figure 2** Absorbance spectra of dye bath waste water for dyed samples 1–5 that have been treated with different amount of nanosilver, control sample, and a sample of solved dye.

**TABLE I**  
Color Fastness Evaluated by Gray Scale After 10 Laundering Cycles and Rubbing Fastness in Dry and Wet Conditions

Samples	Color fastness to washing	Rubbing fastness wet	Rubbing fastness dry
1	4	5	5
2	4	5	5
3	4–5	5	5
4	4–5	5	5
5	4–5	5	5
1 <sup>a</sup>	2	5	5
2 <sup>a</sup>	2	5	5
3 <sup>a</sup>	2–3	5	5
4 <sup>a</sup>	2–3	5	5
5 <sup>a</sup>	2–3	5	5
Control	2	5	5

<sup>a</sup> Nanosilver and dye were applied separately.

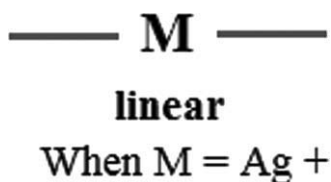


Figure 3 Formation of linear complex by silver ion.

Taking all the above-mentioned facts into account, in this study, dyeing and antimicrobial finishing of wool yarns with acid dye and nanosilver colloidal solution has been considered through a facial method, that is, simple exhaustion method in one bath. The color and tenacity of dyed yarns and size and shape of the nanoparticles have been considered and evaluated.

### MATERIALS AND METHODS

The wool yarns with 10 Nm count including 25–35- $\mu\text{m}$  fibers diameter (Kashan Kork industrials Co., Iran), nanosilver colloidal solution 8000 ppm with 5 nm particles and sphere shape (Narmin Chimi Co., Iran), acetic acid from Merck (Germany), ammonium citrate from Merck (Germany), Acid Blue 92 (Alvan Sabet Co., Iran), *E. coli* ATCC11303, *S. aureus* ATCC 6538, and distilled water were used in this research.

#### Dyeing with acid dye and nanosilver

The wool yarns (1 g) were initially washed with detergent at 60°C for 20 min and then dyed with acid dye (2% o.w.f), acetic acid (2% o.w.f), and different concentration of nanosilver (0.0015%, 0.0025%, 0.01%, 0.04%, and 0.08% o.w.f). The liquor to goods ratio (L.R.) was 100 : 1 for all specimens.

#### Dyeing process

The wool yarns were added to the dyeing bath at 40°C and left for 5 min. Then, the acetic acid and

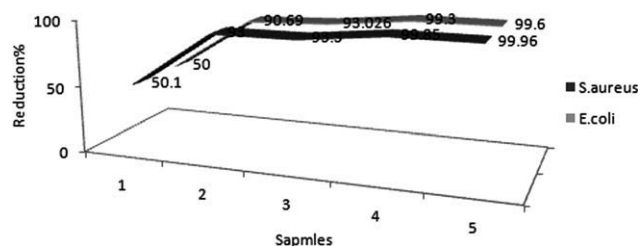


Figure 4 Reduction of bacteria against various concentrations of nanosilver.

nanosilver was added and the wool yarns treated for 10 min. The acid dye was added to the dye bath, and the temperature increase to boil within 15 min and kept boiling for reached to the boiling for 45–60 min. The samples were finally washed and dried at room temperature. The pH of dye bath was dependant on the concentration of nanosilver as it was 6–6.5 for the bath with 0, 0.0015%, 0.0025%, and 0.01% of nanosilver and 5–5.5 for the bath with 0.04% and 0.08% nanosilver.

#### Color differences

The color of samples has been compared to the dyed sample without nanosilver. The color difference has been measured according to the following formula:

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

$$\begin{aligned} \Delta L &= L_s - L_c, \Delta a = a_s - a_c, \Delta b \\ &= b_s - b_c (s = \text{sample}, c = \text{control}) \end{aligned}$$

#### Rubbing fastness

The rubbing fastness has been measured by a manual crock meter according to ISIRI 204 (ISO 150-X12 textiles 2001) after conditioning the samples at 20°C and 65% relative humidity for 24 h.

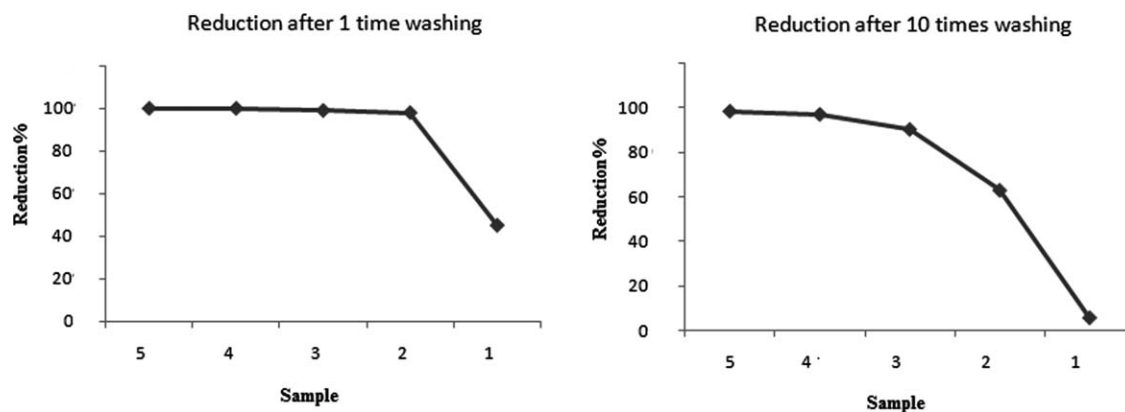


Figure 5 Reduction of *S. aureus* against nano silver 1 and 10 washing cycles.

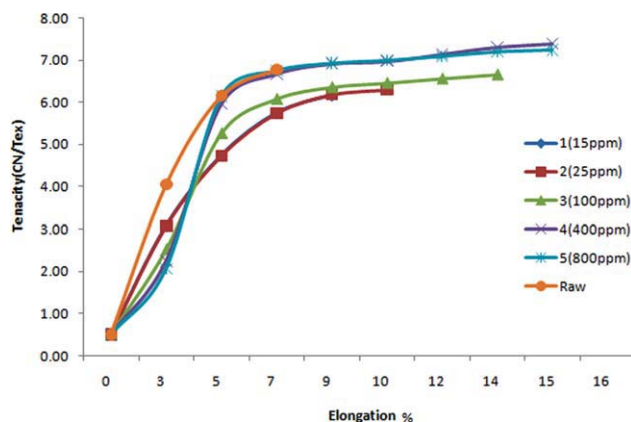


Figure 6 Plots of tenacity-elongation of samples.

### Antimicrobial test

Nanosilver antibacterial activity has been evaluated by a quantitative method AATCC100, 2004. The organisms taken for this study were *S. aureus* and *Escherichia coli*. The reduction in colony number between the treated and untreated fabrics after incubation has been determined. The percentage of the reduction has been calculated according to the following equation.

$$\text{Reduction}(\%) = \frac{(B - A)}{B} \times 100$$

Antimicrobial activity, expressed as the percentage of reduction, 'B and A' representing the numbers of bacteria recovered from the untreated and the treated wool yarns, after inoculation and incubation, respectively.

### Tenacity

Elongation and yarn tenacity have been tested in accordance with the Iranian standard 29 by Uster Tensorapid 3. Wool yarn has been conditioned at 20°C and 65% RH for 24 h. Each specimen has been examined 10 times.

### Washing fastness

The samples have been washed according to ISIRI 10076 (ISO 150-C10 color fastness to washing with soap or soap and soda). Each washing cycle was taking 20 min, and, for each sample, 10 washing cycles have been applied. Each specimen has been examined five times.

### SEM, EDX, and XRD

"LEO 440i scanning electron microscope with IMIX EDX chemical analysis" and "X'Pert PRO X-ray diffractometer (XRD)" has been used.

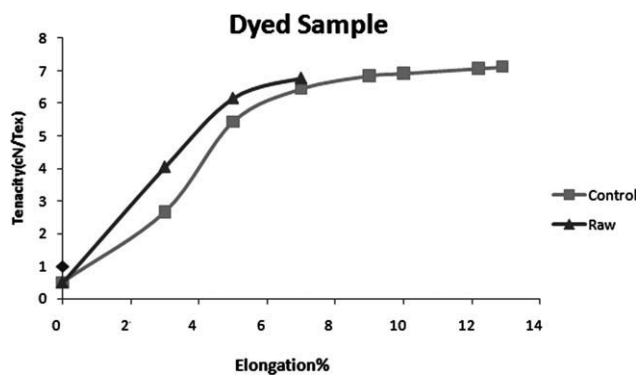


Figure 7 Tenacity-elongation of control and raw yarn.

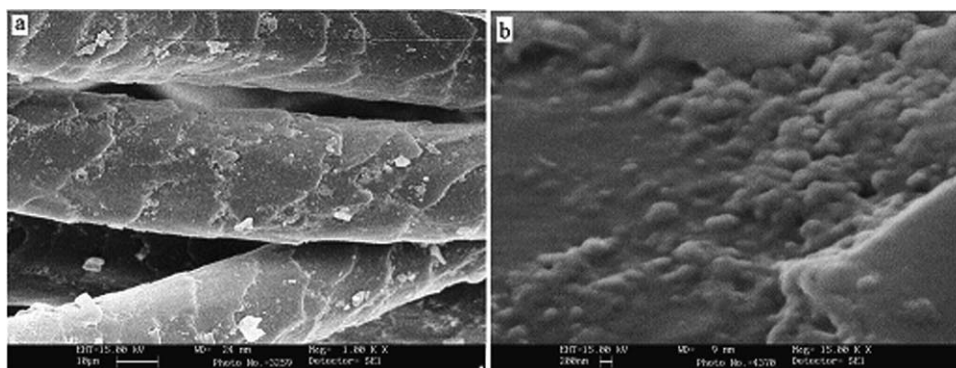
## RESULTS AND DISCUSSION

To evaluate the color changes occurred as results of existence of nanosilver in the dye bath, the color of the acid dyed samples along with the nanosilver was compared to the dyed sample without the nanosilver, and also the nanosilver-treated samples were compared to the raw wool yarn. Because the concentration of the dye was constant, then the color differences can be related to the concentration of the nanosilver. This is illustrated in Figure 1. It is indicated that increasing of the concentration of nanosilver up to 400 ppm led to increase the color difference. However, there is no noticeable color change between the 400 and 800 ppm. The color of nanosilver-treated samples without dye was differed from light yellow to light brown by increasing the concentration of nanosilver. The color difference of samples 1 and 2 (15 and 25 ppm) is very low, and it can be considered negligible.

Figure 1(b) illustrates the color difference for the only nanosilver-treated samples with different concentrations of nanosilver. By increasing the nanosilver concentration, the rate of color difference was reduced. It can be concluded from the Figure 1(a,b) that with increasing in the nanosilver, the dyed samples show about two times more color changes comparing with undyed samples. Specifically, the color changes for the sample 5 is six times bigger than the sample 1 for the dyed samples while this is three times for the same undyed samples [Fig. 1(b)].

TABLE II  
Average and Standard Deviation of Tenacity at Break

Samples	Average of tenacity at the break ( $\pm$ SD)
1	6.16 ( $\pm$ 0.20)
2	6.3 ( $\pm$ 0.49)
3	6.65 ( $\pm$ 0.34)
4	7.39 ( $\pm$ 0.34)
5	7.25 ( $\pm$ 0.90)
Control	6.92 ( $\pm$ 0.20)
Raw	6.78 ( $\pm$ 0.29)



**Figure 8** Surface images of wool fiber having 400 ppm silver particles; (a) 1,000 and (b) 15,000 magnifications.

It is remarkable that almost the whole dye has been adsorbed to the wool yarn in the presence of nanosilver, whereas a considerable amount of the dye remained in the dye bath for the sample without nanosilver Figure 2.

For the purpose of study the remaining dye in the dye bath after dyeing, the UV spectroscopy<sup>1</sup> has been used. Figure 2 shows the UV absorption spectrum of the dye bath of the dyed samples 1–5, which have been treated with the different concentration of nanosilver, the control sample, and also a dye solution. As it shows, the absorption value is nonsense for samples 1–5, which mean there is no residual dye in bath for the samples treated with nanosilver, while the control sample has got the same spectra as the solved dye only with lower intensity. It is also considerable that even with a very small amount of nanosilver (15 ppm in sample 1), all dyes have been absorbed, having in mind that the amount of dye has been constant for all samples.

High dye uptake in nanosilver finishing samples can be justified by the fact that nanosilver has the ability to release silver ions, which have strong affinity to such anions like carboxyl, hydroxyl, and, specially, thiol groups of protein. These anions could bind with silver ions while cationic site of fiber like amino groups could be accessible by dye anionic.<sup>27–29</sup> This phenomenon could be a good reason for complete dye absorption.

The improvement of washing fastness has been proved to be another effect of the presence of nanosilver in dye bath as shown in Table I. Although control sample seems to have poor color fastness after 10 washing cycle evaluated by gray scale, samples 1, 2, 3, 4, and 5 with 15, 25, 100, 400, and 800 ppm nanosilver have shown excellent color fastness after 10 washing cycle. Nanosilver and dye have been applied on samples 1\*, 2\*, 3\*, 4\*, and 5\* separately in different baths. The color fastness of these

samples has been almost the same as the control sample after 10 cycles of washing. Rubbing fastness has remained constant. All samples are showing excellent rubbing fastness in dry and wet, exactly the same as control sample (Table I).

To describe the concluded facts more theoretically, it can be considered that silver (I) ions form a linear complex with one ligand in either side with a 180° angle (Fig. 3). Therefore, it sounds reasonable to form silver complex either between two molecules of dye or a molecule of fiber and a molecule of dye.<sup>30</sup> This can justify high color fastness after 10 washing cycle and constant rubbing fastness (dry and wet), for the sample with nanosilver, whereas acid dye Blue 92 has poor color fastness according to the color index Part 1.

### Antimicrobial results

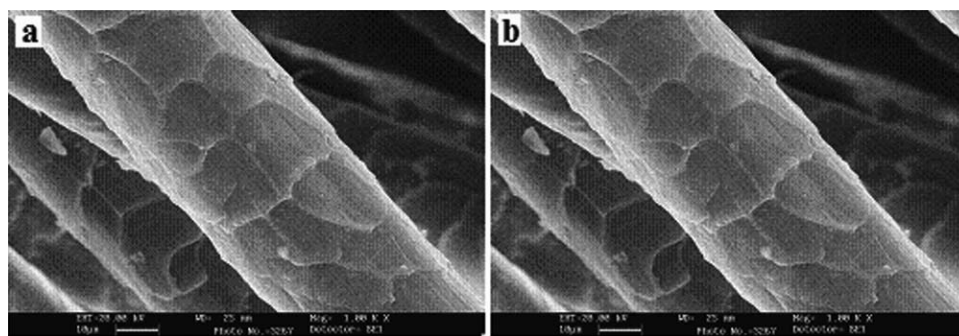
Figure 4 shows that antimicrobial effects of nanosilver against *E. coli* and *S. aureus* on wool are almost the same.

The bacteriocidal effect has been maintained against *S. aureus* after several laundering cycles. This could be related to attraction of nanosilver to protein of the wool. Nanosilver could be penetrated to fiber and made bound to anionic sites (Fig. 5).

### Tenacity results

Plots of tenacity-elongation illustrate that by increasing of nanosilver concentration, tenacity and elongation of specimens have been increased (Fig. 6). The reason is not known yet. The raw yarn is shown with black color. Comparing the raw sample with the others, one might conclude that the curve for the raw yarn is influenced by applying nanosilver. This is not true. As illustrated in Figure 7(a), similar change in curve has happened between the control sample with no nanosilver, and the raw yarn that shows that it relates to the dyeing process. Considering the tenacity, as shown in both Figures 6 and 7, it

<sup>1</sup>Using a 'Cary 300 UV-vis spectrophotometer' produced by Varian Company.



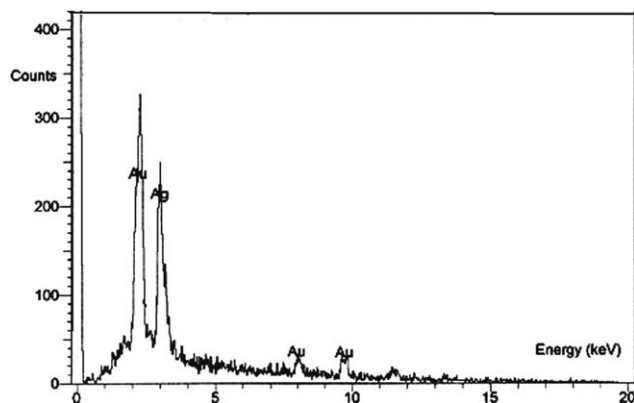
**Figure 9** Surface images of wool untreated by nano silver; (a) 500 and (b) 1000 magnifications.

can be derived that applying nanosilver has caused an increase in tenacity for the bigger amount of nanosilver (samples 4 and 5).

Each sample has been examined for six times. The average has been taken for all samples according to which the Figures 6 and 7 have been illustrated. Table II shows that the standard deviation is low enough to validate the results.

### SEM and EDX

The acid-dyed wool yarn along with nanosilver has been observed by the SEM. The wool yarn surface treated with 400 ppm colloidal nanosilver can be seen in Figure 8. The silver particles can be detected as white spots on the surface of the silver-treated fibers. There is no white spots on the picture of the raw yarn as seen in Figure 9. The EDX analysis has also been used to support this claim. It can be observed that the silver metal existed in Figure 10, while there is no sign of silver spectrum in the raw yarn in Figure 11. As it can be found from Figure 8(b), the nanosilver particles have been spread all over the fiber surface. This can be a reason of the yarn tenacity improvement after dyeing along with nanosilver. The existing of the nanosilver particles on the fiber surface is of the size of 7.5–13  $\mu\text{m}$  as observed in the SEM pictures while



**Figure 10** EDX analysis of 400 ppm nanosilver has been applied on wool.

the initial size of the nanoparticles was 5 nm. This can be due to the agglomeration of the nanosilver on the wool surfaces. The agglomeration of particles could be happened during dyeing process, which may cause reducing the chemical and antimicrobial activity of the silver nanoparticles.<sup>29,31,32</sup>

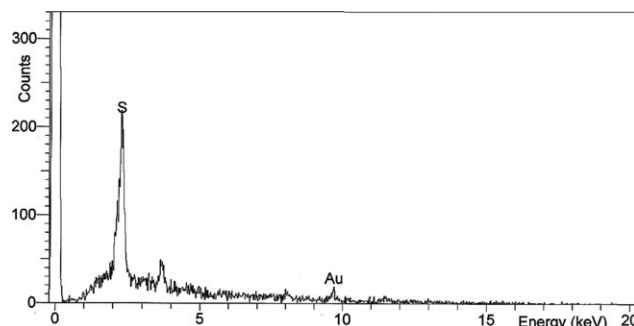
### XRD results

The X-ray diffractometer (XRD) pattern shows a weak peak of Ag for the sample treated with 400 ppm nanosilver. This is good enough to prove the crystalline formation of nanosilver on the wool surface in Figure 12. It has also been shown through XRD analysis that these crystals are cubic-shaped, whereas the initial crystalline structure of nanosilver was sphere. It means that the crystalline structure has been altered during dyeing process.

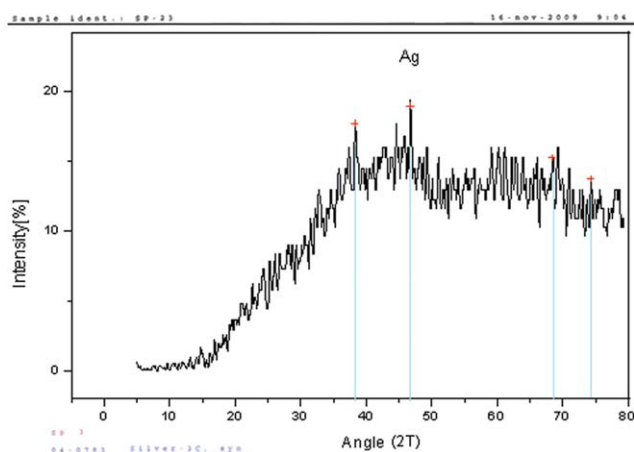
The antibacterial activity of silver nanoparticles depends on the size and shape of the nanoparticles. The bactericidal activity of the triangular nanosilver is more than the other shapes.<sup>31,32</sup> Therefore, the antibacterial activity of nanosilver with cubic crystals is expected to be less than that of the triangular nanosilvers.

### CONCLUSIONS

A simultaneous antimicrobial and dyeing process of wool yarns can be adapted scientifically and



**Figure 11** EDX analysis of untreated wool.



**Figure 12** XRD pattern of nanosilver on wool.

practically by using a colloidal nanosilver solution and acid dye through an exhaustion method. The existence of nanosilver during dyeing of wool yarns with acid dyes leads to produce a wool yarn with antibacterial properties and also increases the dye absorption and improves both the color fastness against washing and the tenacity of the wool yarns. Meanwhile, increasing the concentration of the nanosilver alters the sample color. However, a small amount of the silver nanoparticles induces an excellent antimicrobial property to the wool yarn against *E. coli* and *S. aureus*, which are maintained after several launderings, particularly against *S. aureus*.

## References

- Mitchell, R.; McNamara, C. J. *Cultural Heritage Microbiology Fundamental Studies in Conservation Science*; American Society for Microbiology, ASM Press: Washington, DC, 2010; p 97–105.
- Purwar, R.; Joshi, M. *AATCC Rev* 2004, 4, 22.
- Schindler, W. D.; Hauser, P. J. *Chemical Finishing of Textile*; Wood Head Publishing: UK, 2004; p 165–174.
- Gao, Y.; Cranston, R. *Text Res J* 2008, 60–72.
- Holme, I. *Rev Prog Color Relat Top* 2003, 33, 85.
- Kotowa, J. S. *Int Biodeterior Biodegrad* 2004, 53, 165.
- Tonin, C.; Aluigi, A.; Songia, M. B.; Arrigo, C. D.; Mormino, M.; Vineis, C. *J Therm Anal Springer* 2005, 77, 987.
- Hsieh, S.; Ciou, J.; Wang, J. *J Appl Polym Sci* 2007, 103, 4080.
- Sayed, A. Z.; El-Gaby, M. S. A. *Color Technol* 2001, 117, 293.
- Giri Dev, V. R.; Venugopal, J.; Sudha, S.; Deepika, G.; Ramakrishna, S. *Carbohydr Polym* 2009, 75, 646.
- Bird, C. L. *Theory and Practice of Wool Dyeing*, 4th ed; Society of Dyers and Colourists: Bradford, 1972.
- Joshi, M.; Wazed, S.; Purwar, R. *Ind J Fibre Text Res* 2009, 34, 295.
- Han, Sh.; Yang, Y. *Dyes Pigm* 2005, 64, 157.
- Wang, Q.; Fan, X.; Hu, Y.; Yuan, J.; Cui, L.; Wang, P. *Bioprocess Biosyst Eng* 2009, 633–639.
- Montazer, M.; Afjeh, M. G. *J Appl Polym Sci* 2006, 103, 178.
- Trotman, E. R. *Dyeing and Chemical Technology of Textile Fibers*, 6th ed. Wiley: New York. p 67–100.
- Mary, G.; Bajpai, S. K.; Chand, N. *J Appl Polym Sci* 2009, 113, 757.
- Nazari, A.; Montazer, M.; Rashidi, A.; Yazdanshenas, M. E.; Moghadam, M. B. *J Appl Polym Sci* 2010, 117, 2740.
- Arai, T.; Freddi, G.; Colonna, G. M.; Scotti, E.; Boschi, A.; Murakami, R.; Tsukada, M. *J Appl Polym Sci* 2001, 80, 297–3–3.
- Dastjerdi, R.; Montazer, M.; Shahsavan, S. *Colloids Surf A* 2009, 345, 202.
- Tsukada, M.; Katoh, H.; Wilson, D.; Shin, B.; Arai, T.; Murakami, R.; Freddi, G. *J Appl Polym Sci* 2002, 86, 1181.
- Kobayashi, Y.; Nakanishi, T.; Komiyama, J. *J Text Res* 2002, 72, 1088.
- Dixit, Y. C.; Patel, H.; Desai, D. J. *J Serb Chem Soc* 2007, 72, 119.
- Gorenssek, M.; Recel, P. *J Text Res* 2007, 77, 138.
- Cheng, J.; Jixiong, J. U. S. Pat. 6,979,491 (2005).
- Dubas, S. T.; Kumlangdudsana, P.; Potiyaraj, P. *Colloids Surf A* 2006, 289, 105.
- Yeon, H.; Jong, K.; Kim, H.; Chul, S.; Sung, K.; Jeong, H. *J Mater Sci* 2007, 42, 8020.
- Nies, D. H.; Silver, S. *Molecular Microbiology of Heavy Metals*; Springer-Verlag: Berlin, 2007; p 343–352.
- Rai, M.; Yadav, A.; Gade, A. *Biotechnol Adv* 2008, 72, 76.
- <http://scienceaid.co.uk/chemistry/inorganic/complex.html> (2006–2009).
- Morrison, R. T., Boyd, R. N. *Organic Chemistry*, 5th ed; Allyn and Bacon Inc.: New York, 1987; p 5–72.
- Pal, S.; Tak, Y. K.; Song, J. M. *Appl Environ Microbiol* 2007, 73, 1712.