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A New Method Based on Exhaustion for Immobilization of Silver Nanoparticles on The Surface of Cotton Fabrics

M.E. YAZDANSHENAS*, M. SHATERI KHALILABAD† and M.R. NATEGHI‡
Department of Textile Engineering, Islamic Azad University, Yazd Branch, Yazd, Iran
Fax: (98)(21)88741058; Tel: (98)(21)88741057
E-mail: dr.yazdanshenas@gmail.com

This work explores the antibacterial activity, yellowness and whiteness indices of cotton fabric pretreated with nano-silver colloidal solution. A new method based on exhaustion is introduced to deposit nano-silver particles on the surface of cotton fabric samples. By this way, the antibacterial properties of the fabrics due to the binding of silver nanoparticles are conserved for long time. Nano-silver colloidal solution has been used to treat the fabric samples by exhaustion method at 80 ºC in various concentration of nano-silver. Effect of radiation at different exposition time durations on the yellowness and whiteness indices has been studied. Present study showed that antibacterial activities of fabric samples depend on the amount of silver deposited on the surface of the fabric and it was recognized that even at low concentration of silver, samples showed good antibacterial effect and very good durability to washing. Yellowness index was increased with increasing of silver content and irradiation time intervals but whiteness index decreased. These deficiencies can be reduced by washing samples before exposing to light.

Key Words: Silver nanoparticles, Yellowness index, Whiteness index, Stabilizer, Antibacterial activity, Exhaustion.

INTRODUCTION

Many antimicrobial products that were formerly used with textiles are now strictly regulated because of their toxicity and potential for environmental damage. Products such as copper naphthenate, copper-8-quinolinate and numerous organo mercury compounds fall into this category[1]. Other materials that still have limited use in specialized areas include tributyl tin oxide, dichlorophene and 3-iodopropynylbutyl carbamate[1]. These products typically show a broad spectrum of activity against bacteria and fungi, but suffer from application and durability problems[1]. Silver based antimicrobial captures received attention only because of the non-toxicity of the active Ag^+ to human cells[2] but also because of their novelty being a long lasting biocide with high temperature stability and low volatility[3]. Moreover, it was reported that silver does not introduce any of the delivery problems encountered with anti-

† Young Researchers Club, Islamic Azad University, Yazd Branch, Yazd, Iran.
‡Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran.

bacterial drugs[4]. The silver that has been mainly used for antibacterial finishing during the past few decades has been in the form of chemical compounds because of technical difficulties dealing with the elemental form. Beside development of technologies for producing silver nanoparticles, an attempt has been made to apply them to textile antibacterial finishing.

The research interest in this field of material science stems from the fact that there are different methods to incorporate silver in various polymeric substrates. One conventional approach is by the deposition of metallic silver directly onto the surface of the substrate, for example by vapour coating, sputter coating[5], ion beam coating or RF-plasma and vacuum deposition[6]. However, this technique generally suffers from many demerits, which include poor adhesion, lack of coating uniformity, add time, cost and complexity to the overall process of fabrication of the antimicrobial material and the need for special processing conditions and long term activity. Another method of coating silver nanoparticles onto a substrate involves electrochemical deposition of silver from solution and layer by layer deposition[7]. These methods also have some drawbacks because of the low silver pick up onto the substrate and requirement of special technique for the surface preparation. In the textile industry various methods used for finishing of different goods and are applicable for silver nanoparticles finishing of textiles. Some of researchers used padding[8,9] and pad-dry-cure[10,11] methods for treating nano-silver colloidal solution on textile fabric. They demonstrated that treated fabrics have good antibacterial effect and good durability to washing whereas these methods are simple, fast and inexpensive and can be used in commercial textiles[8-11].

In this article, for the first time, the conventional exhaustion method for treatment of cotton textile is used with two kinds of nano-silver colloidal solutions with different stabilizers. Antibacterial activity of the particles treated samples was tested against *Escherichia coli* bacteria.

EXPERIMENTAL

Gray plain woven cotton fabric weighing 120 g/m^2 were obtained from Yazd Baf Textile Co. Ltd, Iran. Two commercial water based nano-silver colloids with two different stabilizers and concentration of 2000 mg L^{-1} (L) and 4000 mg L^{-1} (LS) were supplied by Pars Nano Nasb Co., Ltd. Iran.

Finishing process by exhaustion method: Before the finishing process, gray cotton fabric were desized, scoured, bleached and then equilibrated in conditioned room (20 ºC, 60 % RH). Fabric samples were treated with nano-silver colloids by a conventional exhaustion method, at 30:1 liquor ratio. The silver concentration was varied as 10, 25, 50, 100 and 150 mg L^{-1} of nano-sized silver particle in the exhaustion bath. Samples were immersed in a fresh colloidal bath for 5 min at ambient temperature and then the temperature of bath was increased to 80 ºC during 20 min and held at final temperature for 0.5 h. Finally, the samples were taken out of the bath, rinsed with water and dried in dark at room temperature.

Scanning electron microscopy (SEM) measurements: Microscopic investigations on fabric samples were carried out using a Philips XL30 scanning electron microscope (SEM) equipped with a LaB6 electron gun and an EDS (EDS Philips-EDAX/DX4) spectroscopy. Images were taken at different magnifications (from 150 × to 3000 ×), using secondary electrons (SE) in accordance with the clarity of the images. Fabric samples were fixed with carbon glue and metalized by gold vapour deposition to record images.

Inductively coupled plasma optical emission spectrometry: Inductively coupled plasma-optical emission spectrometery (ICP-OES) CCD simultaneous was used on Varian Vista Pro (Argon plasma, Ag 328.068 nm excitation, Ag sensivity of 0.004 mg L^{-1}), Australia to measure the quantity of silver concentration on fabric samples. Fabric samples (0.5 g) were incinerated in a digitally controlled furnace. Temperature was gradually increased to 600 ºC and then maintained for 0.5 h. Remained ashes were dissolved in concentrated nitric acid in a 50 mL volumetric flask and then filled by doubly distilled water to indication line. All solutions were stored in plastic containers at room temperatures unless otherwise mentioned.

Antimicrobial assessment: Two test methods were used to determine the efficacy of antimicrobial fabric samples. The agar diffusion (qualitative) and suspension test (quantitative). *Escherichia coli*, ATCC 1533, a gram negative bacterium, was used as a test microorganism which can be cultured and handled in a standard laboratory with minimal health risk. The bactericidal effect of the fabric samples was evaluated qualitatively according to AATCC 147-2004. An *ca.* 10^5 colony-forming units of *Escherichia coli* bacteria were inoculated on nutrient agar plates and then 2 × 2 cm of each fabric samples were planted onto the agar plates. The plates are then incubated at 37 °C for 18-24 h and examined for growth of bacteria directly underneath the fabric samples and immediately around the edges of the samples (zone of inhibition). The antimicrobial activity of the samples was also evaluated quantitatively according to AATCC 100-2004. The colonies of the bacterium on the agar plate were counted and the reduction in numbers of bacterium was calculated using the following equation:

$$\text{Percentage reduction of bacteria (\%)} = (A - B)/A \times 100 \qquad (1)$$

where A is the number of bacterial colonies from an untreated samples and B is the number of bacterial colonies from the silver nanoparticles-treated samples.

Reflectance spectrophotometric analysis: The fabric samples were wrapped onto a holder and analyzed using an X-Rite CA22 spectrophotometer. The instrument parameters of the spectrophotometer were selected as follows: 2 from observer, C illuminant and colour guide spectro, ASTM D1925 equation (for yellowness index) and 10 from observer, D65 illuminant, colour guide spectro, Stephenson equation (for whiteness index) and UV-vis reflectance included. The reflectance of the treated fabric samples was measured in the 360-750 nm and yellowness and whiteness indices values were instrumentally determined from the reflectance measurements. We also studied the effect of light irradiation (500 MBTL, Mercury Ballast, Tungsten

Filament Lamps and internally Phosphorus coated, mounted centrally so that the light distribution constant around the Circumference) at different times (15, 30 and 60 h) on yellowness and whiteness indices of all fabric samples.

RESULTS AND DISCUSSION

Exhaustion is an inexpensive and the easiest dyeing method which has been used extensively for colouring of various textile samples[12]. In this method the goods are immersed into dye solution for a definite time in order to let the dye penetrate into the goods. However it seems that this method can also be a suitable and facile manner for immobilization of silver particles on cotton fabrics. The cotton samples treated by exhaustion method using L and LS nano-silver colloids were examined by SEM to investigate the presence and distribution of the particles on the surface of the fabrics. Figs. 1 (a,b) and 1 (c,d) represent the pictures of cotton samples after treating with L and LS nano-silver colloids, respectively. Presence of nanoparticles on the surface of cotton samples can be observed clearly from SEM images. In addition, from SEM images can be recognized that the silver nanoparticles have been dispersed on the surface of the fibers uniformly. Silver nanoparticles are well

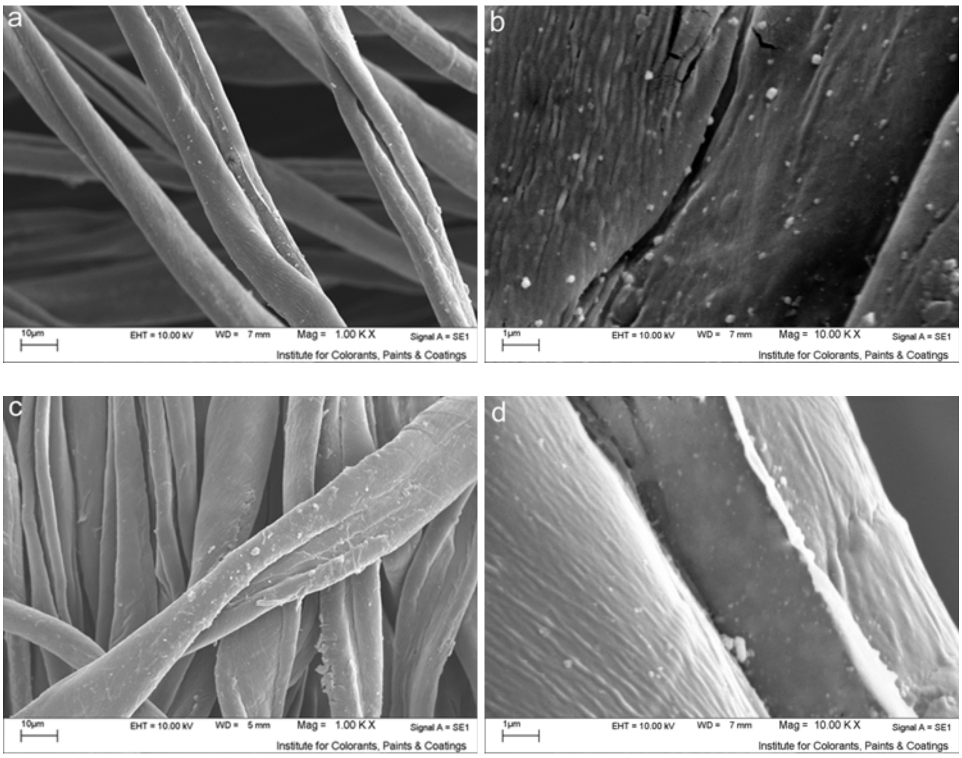

Fig. 1. SEM images of cotton treated with L (a,b) and LS (c,d) nano-silver colloids in different magnification

dispersed on the surface of the cotton samples and a part also has diffused into the pores of the cotton fibers. Some of nanoparticles had also agglomerated into clusters because attractive forces bring them together into a group. These samples were used to study the antibacterial activities against the *Escherichia coli* bacteria according to the procedures mentioned in experimental section.

The size of the zones of inhibition for different fabric samples treated with L and LS nano-silver colloids before and after 1 cycle washing is given in Table-2. It was observed that with increasing of silver nanoparticles on exhaustion bath, the zone of inhibition of samples increased. Samples treated with LS nano-silver colloid have stronger antibacterial activity, than those treated by L solution, because of the more silver content in the first treated samples (Table-1). After washing, zone of inhibition on the around of all samples was not observed which is due to reason that only silver nanoparticles on the surface of the samples can move and disperse around of samples, forming zone of inhibition. Tables 3 and 4 show the bactericidal effect of fabric samples treated with L and LS nano-silver colloidal solutions before and after 1, 5, 10 and 20 cycles washing. The reduction of bacterial colonies was found to be 99.99 % for all samples before and after washing unless the samples treated with nano-silver colloidal solution at 10 and 25 mg L^{-1} was decreased somewhat after 10 and 20 washing cycles (Tables 3 and 4). These high antibacterial activities can be attributed to the diffusion of nano-silver particles into the pores of cotton fabrics during the finishing process. These particles are trapped inside the pores and are not able to move out to the surface of the fabrics and remove from it. Therefore, excellent bacteriostatic durability after multiple washing is achieved.

TABLE-1
AMOUNT OF SILVER NANOPARTICLES DEPOSITED ON THE SAMPLES TREATED WITH L AND LS NANO-SILVER COLLOIDS, BEFORE AND AFTER WASHING

Washing	Nano-silver colloid	Silver concentration in exhaustion bath (mg L^{-1})				
		10	25	50	100	150
0 cycle	L	51	76	111	214	321
	LS	91	116	161	265	384
1 cycle	L	40	61	98	169	258
	LS	69	93	129	215	309
5 cycles	L	32	44	66	128	189
	LS	55	71	94	157	231
10 cycles	L	27	37	56	104	163
	LS	44	59	77	130	188
20 cycles	L	23	34	52	92	147
	LS	41	51	71	117	171

In critical applications, yellowness of coated fabrics may be undesirable[13]. In nano-Ag coated fabrics application, the yellowness can be due to surface plasmon absorbance of the nano silver and light[12,14-16].

TABLE-2
INHIBITION ZONES (DIAMETER) IN mm OF FABRIC SAMPLES TREATED WITH L AND LS NANO-SILVER COLLOIDS, BEFORE AND AFTER 1 CYCLE WASHING

Nano-silver colloid	Silver concentration in exhaustion bath (mg L^{-1})				
	10	25	50	100	150
L*	0.0	0.0	1-2	2-3	3-4
L**	0.0	0.0	0.0	0.0	0.0
LS*	0.0	1-2	2-3	3-4	4-5
LS**	0.0	0.0	0.0	0.0	0.0

*Before washing, **After 1 cycle washing.

TABLE-3
EVALUATION DATA RELATIVE TO THE ANTIBACTERIAL EFFECTS OF FABRIC SAMPLES TREATED WITH L NANO-SILVER COLLOID, BEFORE AND AFTER WASHING

Washing	Bacteria	Silver concentration in exhaustion bath (mg L^{-1})					
		0.0	10	25	50	100	150
	Start	1.2×10^5	1.2×10^5	1.2×10^5	1.2×10^5	1.2×10^5	1.2×10^5
0 cycles	After 24 h	6.3×10^5	<10	<10	<10	<10	<10
	% reduction	-	99.99	99.99	99.99	99.99	99.99
1 cycles	After 24 h	7.3×10^5	<10	<10	<10	<10	<10
	% reduction	-	99.99	99.99	99.99	99.99	99.99
5 cycles	After 24 h	6.8×10^5	<10	<10	<10	<10	<10
	% reduction	-	99.99	99.99	99.99	99.99	99.99
10 cycles	After 24 h	7.5×10^5	5.4×10^3	2.1×10^3	<10	<10	<10
	% reduction	-	95.5	98.25	99.99	99.99	99.99
20 cycles	After 24 h	7.7×10^5	4.5×10^4	4.3×10^3	<10	<10	<10
	% reduction	-	62.5	96.42	99.99	99.99	99.99

TABLE-4
EVALUATION DATA RELATIVE TO THE ANTIBACTERIAL EFFECTS OF FABRIC SAMPLES TREATED WITH LS NANO-SILVER COLLOID, BEFORE AND AFTER WASHING

Washing	Bacteria	Silver concentration in exhaustion bath (mg L^{-1})					
		0.0	10	25	50	100	150
	Start	1.2×10^5	1.2×10^5	1.2×10^5	1.2×10^5	1.2×10^5	1.2×10^5
0 cycles	After 24 h	6.3×10^5	<10	<10	<10	<10	<10
	% reduction	-	99.99	99.99	99.99	99.99	99.99
1 cycles	After 24 h	7.3×10^5	<10	<10	<10	<10	<10
	% reduction	-	99.99	99.99	99.99	99.99	99.99
5 cycles	After 24 h	6.8×10^5	<10	<10	<10	<10	<10
	% reduction	-	99.99	99.99	99.99	99.99	99.99
10 cycles	After 24 h	7.5×10^5	3.1×10^3	<10	<10	<10	<10
	% reduction	-	97.45	99.99	99.99	99.99	99.99
20 cycles	After 24 h	7.7×10^5	2.6×10^4	8.7×10^2	<10	<10	<10
	% reduction	-	78.33	99.27	99.99	99.99	99.99

The yellowness and whiteness indices of all the samples treated with nano-silver colloids before washing are presented in Table-5. As it is clear from resulted data, the both indices have been affected by increasing the concentration of nano-silver colloids in the bath solution. L solution has more effect on yellowness of the fabrics than LS and by increasing the concentration of nanoparticles in exhaustion bath the yellowness was also increased. The pattern of change in whiteness index varies conversely to yellowness index of the treated cotton samples. Table-5 shows the yellowness and whiteness indices of fabric samples after irradiation by Tungsten Filament lamp at different times (15, 30 and 60 h). Yellowness index increased in all treated samples in the first 15 h after irradiation times. Changes in the yellowness index after 30 and 60 h are not so much and are the same for both solutions. LS type has significant effect on these changes and has been increased more than L type. This effect can be related to stabilizers of silver nanoparticles in colloidal solutions.

TABLE-5
YELLOWNESS AND WHITENESS INDICES OF FABRIC SAMPLES

Silver concentration in exhaustion bath (mg L^{-1})	Irradiation times (h)	Yellowness index (%)*	Whiteness index (%)*	Yellowness index (%)**	Whiteness index (%)**
0.0	0.0	4.531	72.216	4.531	72.216
10	0.0	4.788	68.445	5.311	70.317
	15	5.502	66.173	6.416	67.442
	30	6.354	63.380	7.042	66.787
	60	7.619	58.407	7.461	65.531
25	0.0	5.285	67.601	5.362	69.996
	15	6.621	64.118	9.237	55.740
	30	7.816	61.014	10.965	52.930
	60	9.721	55.411	11.673	48.201
50	0.0	6.503	65.089	5.258	69.704
	15	7.813	60.620	12.294	47.673
	30	9.443	56.518	15.317	44.116
	60	11.843	50.348	16.934	41.559
100	0.0	9.186	56.566	5.611	68.562
	15	11.125	49.034	17.637	45.065
	30	13.319	45.864	23.813	35.141
	60	17.141	39.719	25.819	29.319
150	0.0	12.731	54.132	5.802	67.469
	15	15.028	47.229	29.018	20.803
	30	18.219	40.784	35.731	16.764
	60	22.840	29.618	38.065	9.528

*Fabric samples treated with L nano-silver colloid.
**Fabric samples treated with LS nano-silver colloid.

Conclusion

Exhaustion method has been used for the first time for antibacterial finishing of cotton fabric with silver nanoparticles. SEM images shows that the silver nanoparticles have been dispersed on the surface of the fibers uniformly. Treated fabric samples showed good antibacterial effect, even at low concentration of nano-silver and excellent bacteriostatic durability after multiple washing due to immobilization of nanoparticles to cotton fabric. Spectrophotometeric data showed that using silver nanoparticles as an antibacterial agent for cotton causes fabric yellowness and yellowness increases as irradiation time and silver nanoparticles concentration increases.

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