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Study of Antibacterial Activity and Dyeability Property of PET/Cotton Fabrics Coated Ag/SiO_2 Nanocomposites

Laleh Maleknia[1*], Eelaheh Ahmadi[2]

Department of Textile Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
[1,*] *Department of Biomedical Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran*

[2] *Nanotechnology Research Center, South Tehran Branch, Islamic Azad University, Tehran, Iran*

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Abstract

In the present study, two components of Ag/SiO_2 nanocomposite were prepared by the Sonochemical method and then the PET/cotton fabric was treated with Ag/ SiO_2 nanoparticles (Ag/ SiO_2 NPs) by a pad-dry method. The treated fabric is dyed at the optimum condition with direct dyes. The influence of the Ag/ SiO_2 nanocomposite on the performance of PET/cotton fabric was investigated by the use of X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscope (SEM), electron dispersive X-ray spectroscope (EDX) and reflectance spectrophotometer (RS). TEM images of Ag/ SiO_2 showed the particle size was 30-70 nm. SEM results of Ag/SiO_2 nanocomposite powders show that nanoscale particles are well formed, also SEM micrographs of treated fabrics indicated that the nanoparticles were well dispersed on the surface of the sample. EDX results showed the presence of nanoparticles increased on the surface of samples with increased concentration of colloid solution nanoparticles. The antibacterial properties were determined by the reduction growth of a Gram-negative Bacterium E. coli and a Gram-positive Bacterium Staphylococcus aureus. Photo-catalytic activities of the coated PET/cotton fabric were evaluated through the degradation of methylene blue under UV irradiation.

Keywords: PET/Cotton, Nano Ag/SiO_2, Sonochemical method, Antibacterial, Dyeability.

[*] Corresponding author. Tel: +98 -9124239573
E-mail address: maleknia.nrc@azad.ac.ir

1. Introduction

In recent years, the demand for antibacterial fabrics in domestic and abroad markets has grown significantly because of more awareness of the potential threat of spreading diseases. Bio-protective fabrics such as medical clothes, protective garments, and hygienic textiles are the main applications of antibacterial fibers [1]. The main antimicrobial agents used in textiles include organo-metallic compounds, phenols, quaternary ammonium salts, and organo-silicons. To be successful in the marketplace, these finishing agents should be durable and have selective activity towards undesirable organisms. Safety, non-toxicity, and biodegradability are required for antimicrobial agents, and the active ingredients used in antimicrobial finish need to be registered after they have been demonstrated effective and safe to use [2]. Nanotechnology has real commercial potential for the textile industry. This is mainly because conventional methods used to impart different properties to fabrics often do not lead to permanent effects, and will lose their functions after laundering or wearing. Nanotechnology also can provide high durability for fabrics, because Nano-particles have a large surface area-to-volume ratio and high Surface energy, thus presenting better affinity for fabrics and leading to an increase in the durability of the function[3].The general methods of preparing antibacterial fibers are adsorbing or grafting some antibacterial materials such as silver, metal complex, and quaternary ammonium group on the fiber's surface, but up to now, few reports can be found about the grafting of the Ag/SiO2 Nano-antibacterial agent on the textile fiber's surface[4–7]. Furthermore, silver is a non-toxic and non-tolerant disinfectant that can reduce many bacterial infections significantly. As a natural renewable resource that has several unique properties, silver now attracts an increasing amount of scientific and industrial interest from fields as diverse as chemistry, medicine, biotechnology, food science, and textile science. Nano-silver particles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness [3]. The properties of Nano silver particles may change depending on their size hindering, therefore, the correct assessment of such dose relations. Smaller Nano silver particles are more toxic than larger ones especially when oxidized [8]. The antibacterial activity of small (<10 nm) Nanosilver particles is dominated by Ag+ ions, while for larger ones (>15 nm) the antibacterial contribution by Ag+ ions and particles is comparable. Such a behavior implies a surface area dependency of the antibacterial activity especially for small Nano silver sizes since the Ag+ ion release is proportional to the exposed Nano silver surface area [9]. This dependency could not be proven when evaluating data from plasma-made Nanosilver and macrophage cells [10]. These limitations prevent a quantitative assessment of the antibacterial activity of Nano silver to determine correct dose relations. To overcome that, Nano silver particles with limited agglomeration and closely controlled size are needed [8]. Silver particles on bulk matrixes have weak washing resistance so it can cause a fast release of silver ions and a short lifetime for the antimicrobial process [11]. Therefore, two key points should be considered to further improve the bactericidal activities of silver-based materials; (1) silver-based materials should be based on silver nanostructures providing a high surface area to volume ratio and so a high fraction of surface atoms [12,13], which enhances the antimicrobial activity of silver, even at a low concentration [14], and (2) the washing resistance of the Ag nanostructures should be improved by immobilizing them in the pores of porous hosts to gain a long-term antimicrobial activity [15,16].One way to address this is to immobilize Nanosilver on a support material. That way, Nano silver is stabilized and retains its nanostructure since it is anchored on an inert support. Furthermore, having such immobilized Nanosilver inhibits its flocculation in aqueous suspensions[8].In particular, it was found that silver-supported silica materials, such as silica glass, silica thin film, silica shell, silica Nanospheres, Nanotubes, and silica nanoparticles can be suitable candidates for antibacterial materials due to their excellent chemical stability and high bactericidal properties [17].Silver-supported silica materials are expected to be good candidates for antibacterial materials due to their good chemical durability and high antibacterial activity. Moreover, these hybrid materials can prevent metal nanoparticles from agglomerating without the use of a stabilizer and be easily retrieved owing to the relatively large size of supporting materials. As a result, they make it easy to handle metal nanoparticles. On the other

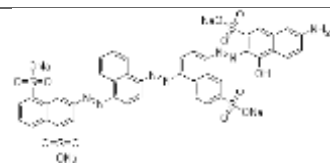
hand, hollow structure often exhibits properties that are substantially different from those of general particles (low density, large specific surface area, stability, and surface permeability), thus making them has been also attractive from both scientific and technological viewpoints [18]. The purpose of this research is to study the antibacterial activity of PET/cotton fabrics treated with Ag/SiO_2 nano-antibacterial agent. The relation of NP concentration and its antibacterial activity on fabrics was investigated. Moreover, the dyeability and photocatalyst properties were also examined.

2. Materials and Methods

2-1 Materials

The materials and chemical reagents included: Tetra ethylorthosilicate (TEOS, 98 %) ammonia (NH3), ethanol (99.9%), NaBH4, and silver nitrate ($AgNO_3$) (Merk). The direct dye, Direct Blue 71 and Methylene Blue (MB) was kindly provided by Alvan Sabet Co.Ltd (Iran) and used as received without further purification. The molecular structure of DB71 in non-hydrolyzed form is illustrated in Table 1. The PET/Cotton fabric (serge, 295 gm^{-2}) was provided by Ardekan Co. Yazd, Iran.

Table 1 Chemical structure, molecular formula, and molecular weight of DB71

Name	Molecular Structure	Molecular Formula	Molecular Weight
Direct Blue 71		$C_{40}H_{23}N_7Na_4O_{13}S_4$	1029.86

2.2 Method

For the synthesis of nanoparticles SiO_2, 2.79 *mL* of tetraethyl ortho silica and 22.2 *ml* of ethanol were mixed. Then the above solution, using a syringe, a drip into a container of materials that contain ammonia, water, and ethanol was added under ultrasonic for an hour. And for 2 *h*, ultrasonic treatment, to reduce the average particle size continues. Then the solution containing the nanoparticles was washed, filtered, and dried. Another part of the solution prepared for two-component nanoparticles in SiO_2/Ag was used. The synthesis of nano-composite two-component SiO_2/Ag, 7 *mM* solution of $AgNO_3$ was prepared. A solution containing SiO_2 nanoparticles under ultrasound was applied for 5 *min*. Then proceed with ultrasound, 7 *mM* $AgNO_3$ solution is added drop by drop to the above solution. Then the homogeneous solution, the time was 15 *min*. Then, for the recovery of silver and formation of a two-component composite, 15.8 *mM* solution of

$NaBH_4$ was prepared and was added drop by drop to a solution under ultrasonic. The stirring was continued for 1 *h* and then, the solution was filtered, washed, and dried.

The concentration of colloidal Ag/SiO_2 was diluted with distilled water and dispersant agent by 200, 400, and 800 *ppm* for our experimentation. The PET/Cotton fabric samples were padded with each concentration of colloid solutions and then were immediately dried at 110°*C*.

After the pre-treatment stage, the samples were soaked in a dye bath comprising 1.5 % dye, a liquor ratio of 20:1. The dye bath temperature was raised from 40 °*C* to 98 °*C* for 40 *min* and then kept at 98 °*C* for 45 *min*. The samples were then thoroughly rinsed and air-dried (Fig. 1) [22].

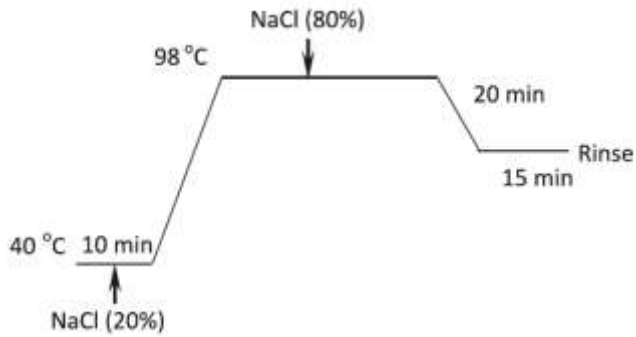


Fig. 1 Dyeing diagram

2.3 Instruments

To produce nanoparticles and disperse them, the ultrasonic device was used. Pad-drying was performed using an EVAC padding machine (L. & W. machine works, McConnells highway, SC). A washing machine (Kenmore, Heavy duty 70 series) and a tumble dryer (Kenmore, Heavy duty 70 series soft heat) were used for wash fastness tests. The morphology and structures of the samples were characterized by scanning electron microscopy (SEM) (Stereo Scan S360, Oxford) and X-ray diffraction (Y-2000 diffractometer; Dandong, China) using Ni-filtered Cu-Kα incident radiation. FEG Philips CM 200 transmission electron microscope (TEM) was used to observe the size and distribution of loaded silver on the SiO_2 surface. All dyeing was carried out in sealed stainless steel dye pots of 300 cm^3 capacity, dyeing machine using a liquor ratio of 20:1. Cultures of the following microorganisms were used in this research work: Staphylococcus aureus ATCC 6538 and Escherichia coli ATCC 4157.

The antimicrobial properties of fabrics were quantitatively evaluated against S. aureus, a gram-positive bacterium, and E. coli, a gram-negative bacterium, according to AATCC 100-1993 test method. Circular fabric swatches (about 1 *g*) were challenged with 1.0 ± 0.1 *ml* of bacterial inoculums in a 250 *ml* container. The inoculum was a nutrient broth culture containing $1.0 \times 10^4 - 1.0 \times 10^6$ colony-forming units (CFU)/*ml* of bacteria. After bringing the control (untreated sample) and test swatches in contact with bacteria for 24 *h*, 100 *ml* of sterilized distilled water was poured into the vessel and vigorously shaken before the dilution of the supernatant to 10^3 *ml*. The diluted solution aliquots were placed on a nutrient agar and incubated for 18 *h* at 37 °*C*. Viable colonies of bacteria on the agar plate were counted, and the reduction in the number of bacteria was calculated by using equation (1):

$$\text{Reduction rate (\%)} = (A - B)/A*100 \quad (1)$$

Where A and B are the number of bacterial colonies from untreated and treated fabrics, respectively [20].

The color strength of the dyed samples was determined from the sample reflectance (*R*). The reflectance (*R*) of the dyed samples was measured on a color measurement system, at the wavelength of minimum reflectance, under CIE Illuminant D65 and d/8° illumination/observation. In addition to visual assessments, the samples were also evaluated objectively by measuring the CIE LAB values (L*, a*, and b*) of the dyed samples using the above system, and then calculating the color change, ΔE. Illuminant D65 and 10° observer geometry were used throughout for the color measurement.

Test for color removal, Nano-composites, and Nano-particles with concentrations of 200, 400, and 600 *ppm* were prepared. Nanoparticles and nanocomposites were placed on the fabric by pad/ dry method. 100*ppm* concentration of methylene- blue (merck) and reactive- black (wastewater factory Toranj - Iran) were prepared. The two sides of the fabric, produced by the wastewater, were spotting. Then, the fabric, in the presence of sunlight during times of 1, 2, 3, and 12 *h* respectively. Images were prepared for comparison by a camera.

3. Result

3.1. Characterization of Nanoparticles

3.1.1. XRD analysis

Powder XRD patterns of SiO_2 and Ag/SiO_2 nanocomposites are shown in Figure 2. Figure 2 shows the XRD pattern of the samples that is quite identical to SiO_2 and Ag/SiO_2 nanocomposites. We can see that no characteristic peaks of impurities were observed.

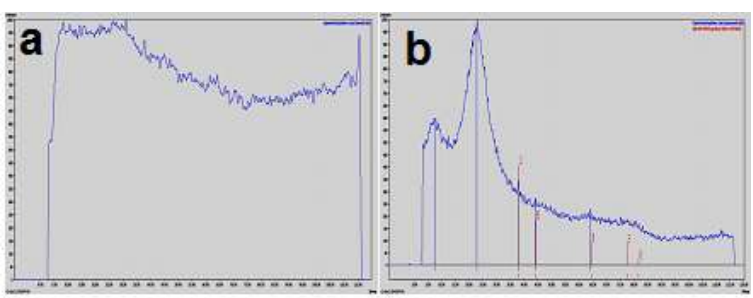


Fig. 2. XRD pattern of nanoparticles of (a) SiO_2 and (b) Ag/SiO_2

3.1.2. SEM analysis

Morphological properties of Ag/SiO_2 were investigated using SEM analysis. Figure 3 shows the SEM micrograph of SiO_2 Nanoparticles and Ag/SiO_2 nanocomposite. The images show that the nanoparticles and nanocomposites produced by the ultrasonic method, the proper size, and good uniformity are important.

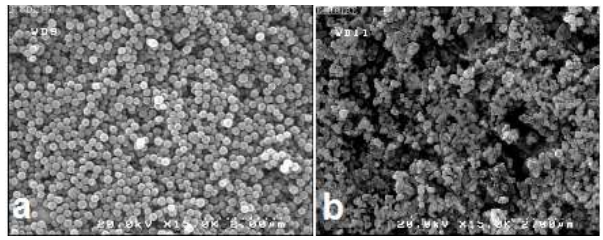
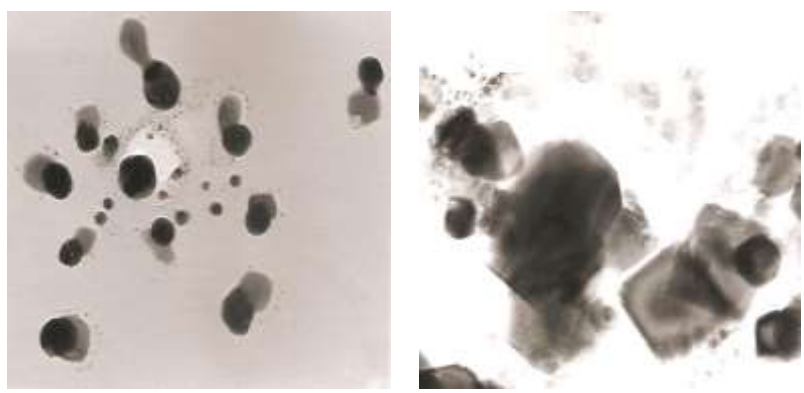


Fig 3. SEM micrograph of Nano SiO_2 and Ag/SiO_2 Nanocomposites (1500 KX)

3.1.3. TEM analysis

Figure 4 shows the TEM images of Nano Ag/SiO_2. It can be seen the nano-SiO_2 powder is almost round. The spherical nano-Ag particles are distributed on the SiO_2 grain surface.



a **B**

Fig 4. TEM image of the Ag/SiO_2 nanoparticles: a) 100KX , b) 200KX.

With this regard, the average size of Ag/TiO_2 particles is mostly less than 30-70 *nm* deposited with very fine Ag nanoparticles (less than 10 *nm*). It was obvious that Ag/SiO_2 aggregated heavily. However, Ag/SiO_2 was well dispersed. As a result, Ag/SiO_2 could be dispersed evenly and steadily.

3.2. Study of treated fabrics

3.2.1. SEM analysis

Figure 5, SEM taken from the fabric is processed with Ag/SiO_2 Nanocomposites. It is observed that nanoparticles of Ag/SiO_2 are depressively deposited on the surface of PET/Cotton samples. As shown in the 3. a – 3.d images, the surface is mostly of fibers and no agglomeration of particles is observed. Also, the sizes of Ag/SiO_2 particles are obvious here and the results are by TEM results.

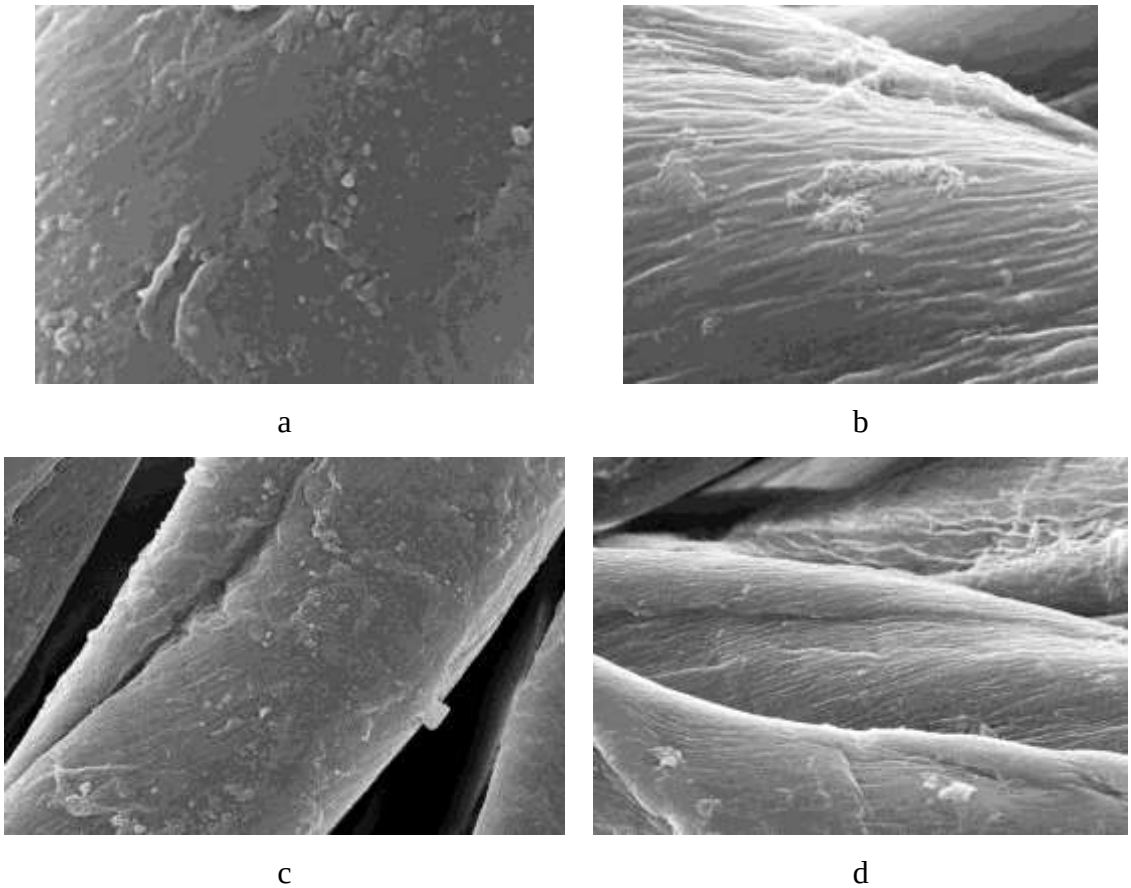


Fig 5. SEM micrograph of PET/Cotton fabric treated with Ag/SiO_2 antibacterial agent: a)200 ppm at 10.00KX, b)400 ppm at 10.00KX, c) 800 ppm at 3.00KX, d) un-treated at 10.00KX

EDX analysis has also been carried out on the modified samples. Ag/SiO_2 NPs synthesized on PET/Cotton fabric, in different regions have been studied by the instrument. They are presented in Figure 6.

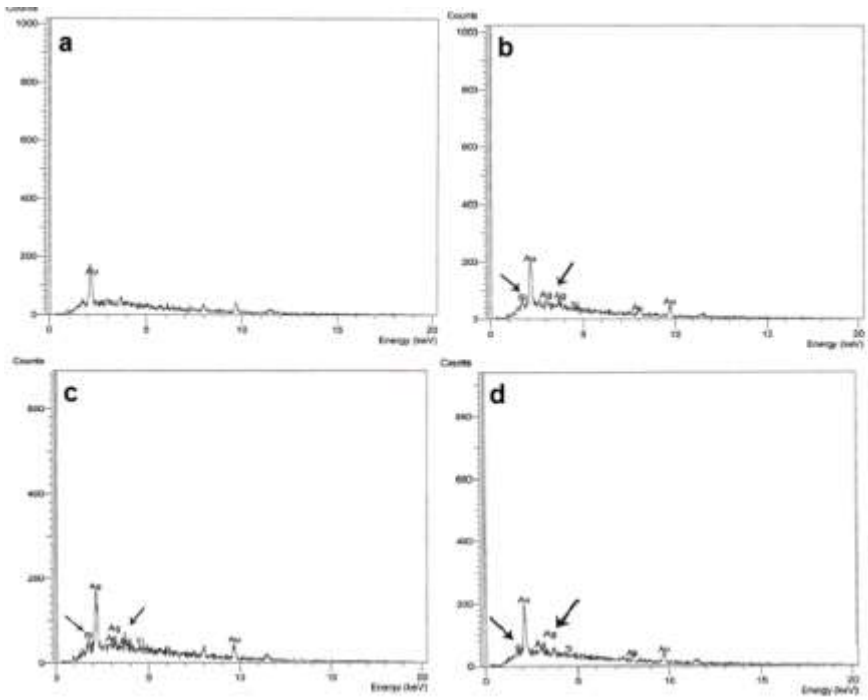


Fig 6. EDX spectra pattern of PET/cotton fabric treated with Ag/SiO_2 antibacterial agent:

a) un-treated b) 200 ppm c) 400 ppm d) 800 ppm

From Figures 6b and 6d, it has been noticed that, the Ag content of 10.80*wt*.% (200 *ppm*) raises to 24.11 *wt*.% in the 800 *ppm* and the Si content of 16.97 *wt.*% (200 *ppm*) falls to 10.11 *wt*% in the 800 *ppm*. This means that the deposition of Ag/SiO_2 on the PET/Cotton fabric is almost uniform. In this work, when the Ag/SiO_2 molar ratio is low, the silver cluster is detected by EDX, which implies that most of the silver is located in the body of SiO_2. Even with the increase in the molar ratio of Ag/SiO_2, though some large silver cluster was formed on the surface, more silver still existed as a small cluster.

3.2.2. Antibacterial *activity of Ag/SiO_2*

The antibacterial activity of PET/cotton fabrics resulted from the presence of nanoparticles of Ag/SiO_2 antibacterial agent grafted on their surface. The effect of the suspension concentration of the antibacterial agent on the antibacterial activity of samples before and after washing is shown in Figure 7 and Figure 8. It can be seen that the antibacterial ratio increased with increasing suspension concentration of the antibacterial agent, and consequently with the grafting content.

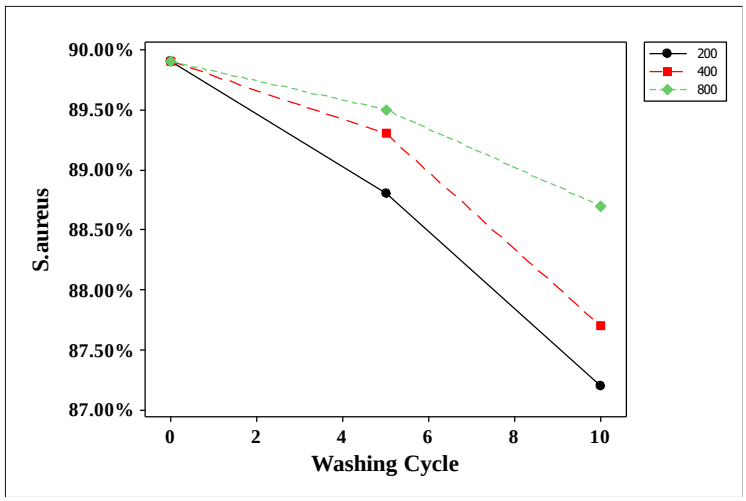


Fig 7. The antibacterial ratios of PET/Cotton in different concentrations of Ag/SiO_2 against S. aureus.

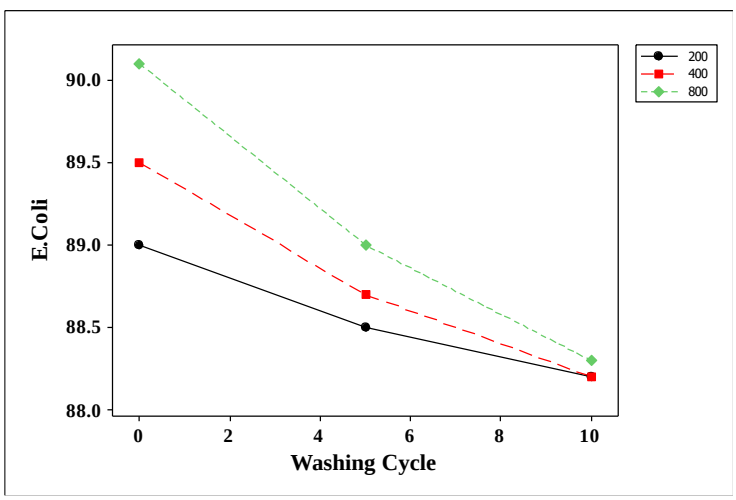


Fig. 8 The antibacterial ratios of PET/Cotton in different concentrations of Ag/SiO_2 against E. coli

When the concentration was 200 ppm, the antibacterial ratio was up to 89.60% against *E. coli* and 89.70% against *S. aureus*, respectively. However, when the concentration was over 800 *ppm*, the antibacterial ratio only showed a slow increase. The above results suggest that an adequate antibacterial agent on fabric surfaces is necessary for the inhibition of bacterial growth.

3.2.3. Effect *of Ag/SiO_2 concentration on dye uptake of treated samples*

Figure 9 shows the effect of Ag/SiO_2 concentration on the dyeability of PET/Cotton fabrics. The maximum *R* (%) values were obtained in 750 *nm*. It is extremely difficult to evaluate the treatment [21]. However, in this research, to evaluate the effect of Ag/SiO_2 concentration, samples that were treated with different amounts of

Ag/SiO_2, were dyed by C.I Direct Blue 71 Special. Figure 9 shows the results for untreated and different treated samples. The *R* (%) values for treated fabrics were significantly higher than untreated ones. The dye-binding properties of Ag/SiO_2 have been studied and it is reported that Ag/SiO_2 NPs have an extremely high affinity for many classes of dyes including direct dyes.

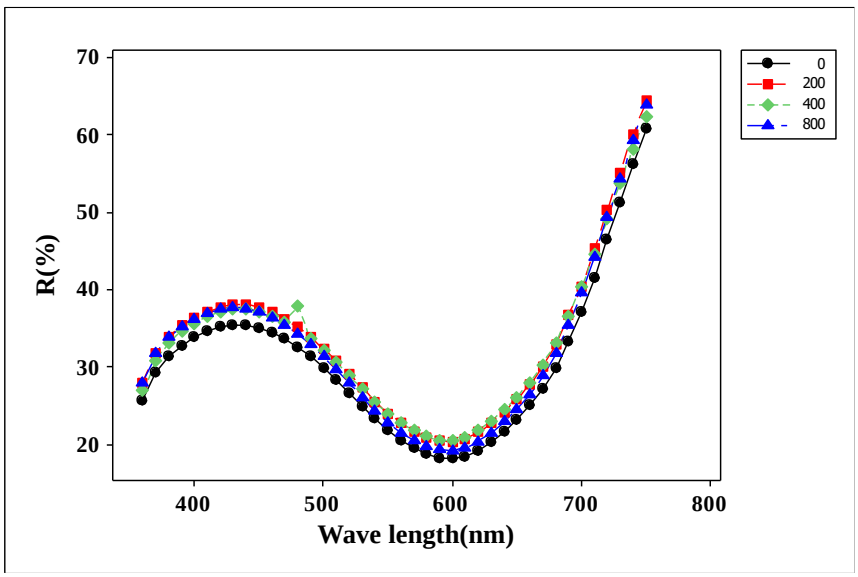


Fig. 9. The effect of NP concentration on the colorimetric data (R%) of PET/cotton fabrics dyed with DB7.

3.2.4. Stain *removal experiments in the presence of visible light*

Degradation of dye by visible light of the sun at different periods was analyzed. With increasing exposure time in the presence of sunlight, the color removal was done well. A fabric containing two-component nanoparticles showed the best result, and the colors were almost completely broken down and destroyed. Figure 10 shows that although industrial wastewater contains textile materials such as paint, oil, etc., the photocatalytic properties of two-component nanoparticles, show good performance. The images showed that the nanoparticles Ag/SiO_2 have the photocatalytic properties of SiO_2 nanoparticles better than the methylene blue dye and industrial waste has been removed.

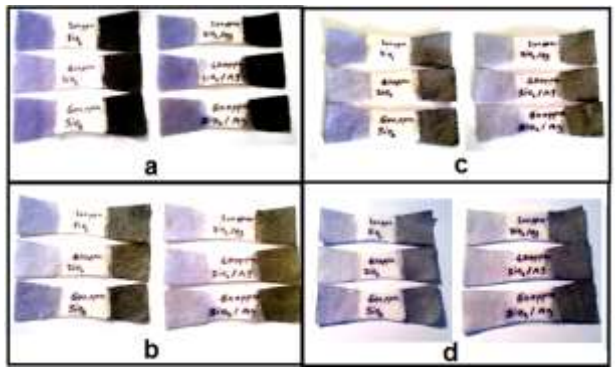


Fig. 10 Images taken from fabric with SiO_2 nanoparticles and Ag /SiO_2 nanocomposites processed by methylene blue and reactive black spotting concentrations of 200, 400, and ppm under the sunlight in the time of a) 0 h, b) 1 h, c) 2 h, d) 3 h.

4. Conclusions

A composite antibacterial agent of Ag/SiO_2 nanoparticles was prepared by the adsorption, the as-obtained antibacterial agent was a nearly spherical particle with an average particle size of about 30 -70 *nm*. The Ag/SiO_2 nanocomposite antibacterial agent is well dispersed on the surface of the PET/Cotton fabrics. The antibacterial fabrics showed excellent antibacterial activity against the tested germs. Grafting content and the antibacterial ratio were adjustable by controlling the suspension concentration of the Ag/SiO_2 nanocomposite antibacterial agent during grafting. When the concentration was 800*ppm*, the antibacterial ratio was 90.12% against *E. coli* and 89.24% against *S. aureus*, respectively. With the increased suspension concentration during treatment, especially for the concentration over 400*ppm*, the particles of Ag/SiO_2 nanocomposite antibacterial agent became agglomerated on the PET/cotton surface. Treatment of PET/Cotton with Ag/SiO_2 NPs increased the dye absorption of direct dyestuff. The concentration of NPs played a noticeable effect on fabrics' dyeability. Also, the photocatalytic properties of the nanocomposites showed that the color of the sun degradation of done shortly.

References

[1] Wang S., Hou W., Wei L., Jia H., Liu X., Xu B., Surface & Coatings Technology 202 (2007) 460–465.

[2] Han, S., and Yang, Y., Dyes Pigments 64, (2005) 157–161.

[3] Mirkazemi A., Maleknia L., Yousefi K,. Ghoreishian M., and Eshghi S., Proceedings of the International Conference on Nanotechnology: Fundamentals and Applications Ottawa, Ontario, Canada, 483 (2010) 4-6.

[4] Wang J., Li J.X., Ren L., Zhao A.S., Li P., Leng Y.X., Sun H., Huang N., Surf. Coat. Technol. 15, (2007) 6893.

[5] Gray J.E., Norton P.R., Alnouno R., Marolda C.L., Valvano M.A., Griffiths K., Biomaterials 24, (2003) 2759.
[6] Xiao Y.N., Zeng H.M., Zhang J.M., Guo W.P., Wu Q.P., China synthetic fibers industry, 24(2001) 5.
[7] Yoshinari M., Oda Y., Kato T., Okuda K., Biomaterials 22, (2001) 2043.
[8] Sotiriou G.A., Teleki A.., Camenzind A, Krumeich F., Meyer A., Panke S., Pratsinis S., Chemical Engineering Journal 170 (2011) 547–554.
[9] G.A. Sotiriou, S.E. Pratsinis, Environ. Sci. Technol. 44 (2010) 5649–5654.
[10]C. Carlson, S.M. Hussain, A.M. Schrand, L.K. Braydich-Stolle, K.L. Hess, R.L. Jones, J.J. Schlager, J. Phys. Chem. B 112 (2008) 13608–13619.
[11]Y.L. Wang, Y.Z. Wan, X.H. Dong, G.X. Cheng, H.M. Tao, T.Y. Wen, Carbon 36 (1998)1567.
[12]N. Ichinose, Y. Ozaki, S. Kashu, Superfine Particle Technology, Springer Verlag, New York, 1992.
[13]O. Akhavan, E. Ghaderi, Sci. Technol. Adv. Mater. 10 (2009) 15003.
[14]H.J. Lee, S.Y. Yeo, S.H. Jeong, J. Mater. Sci. 38 (2003) 2199.
[15]C.N. Lok, C.M. Ho, R. Chen, Q.Y. He, W.Y. Yu, H. Sun, P.K.H. Tam, J.F. Chiu, C.M. Che, J. Proteome Res. 5 (2006) 916.
[16]J.R. Morones, J.L. Elechiguerra, A. Camacho, K. Holt, J.B. Kouri, J.T. Ramirez, M.J. Yacaman, Nanotechnology 16 (2005) 2346 .
[17]Akhavan O., Ghaderi E., Current Appl Phy 9, 1381–1385 (2009).
[18]D.L. Wilcox, M. Berg, T. Bernat, D. Kellerman, J.K. Cochran (Eds.), Proc Mat Res Soc Symp, vol. 372, Boston, MA, USA (1995).
[19]Mei N., Xuguang L., Jinming D., Husheng J., Liqiao W., Bingshe X., Carb Polym 78, (2009) 54–59.
[20]Son, Y. A., and Sun, G., J. Appl. Polym. Sci. 90(2003)2194–2199.
[21]Jocic D., Julia M.R., and Erra P., J. Soc. Dyers Colour, 113 (1997) 25-31.
[22]Liu X., Wang W., Xu P, FIBRES & TEXTILES in Eastern Europe, 18, (2010) 93-96.