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Development and antibacterial performance of silver nanoparticles incorporated polydopamine–polyester-knitted fabric

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Abstract. **Metallization is one of the finishing processes in textile treatment that can produce multifunctional effects. The present study dealt with the development of an antibacterial polyester-knitted fabric via facile and green impregnation of silver nanoparticles (SNPs). This was done by applying a polymeric foundation on the polyester-knitted fabric by simply dip-coating in the aqueous solution of dopamine. Then the SNPs were *in situ* fabricated and impregnated on the surface of polydopamine-modified polyester-knitted fabric in an aqueous solution of $AgNO_3$ at room temperature. Thus, a multi-functional finishing of polyester-knitted fabric was done. The Fourier transform infrared spectroscopy was done to confirm the polymer attachment. Scanning electron microscopy equipped with energy dispersive X-ray was done to confirm the presence of SNPs on treated fabric. The crystallography of the treated surface was examined by X-ray diffraction. The antibacterial properties of treated fabrics against broad spectrum bacterial strains were investigated and found significant.**

Keywords. **Antibacterial activity; *in situ* fabrication; polyester fabric; silver nanoparticle.**

1. Introduction

Textile materials and clothing are known to be susceptible to bacterial attack, as they provide large surface area and absorb moisture required for bacterial growth. This often leads to objectionable odour, dermal infection, product deterioration, allergic responses and other related issues [1]. This necessitates the development of clothing that could provide a desired antibacterial activity. The antibacterial agents are protective agents that being bactericidal, bacteriostatic, fungicidal and fungistatic, offer special protection against the various forms of textile deterioration. A number of chemicals have been employed to impart antimicrobial activity to textile goods. Those chemicals include inorganic salts, organometallics, iodophors, phenols and thiophenols, onium salts, antibiotics, nitro compounds, urea and related compounds, formaldehyde derivatives, amines, etc. [2,3]. These chemicals are non-biodegradable and toxic, which causes environmental and health concerns. The textile industry continues to look for eco-friendly processes that substitute for toxic textile chemicals. Hence, several antibacterial coatings could be achieved to manufacture antimicrobial textiles [2,4,5].

Silver has been used in many applications in pure free metal or compound forms because it possesses antimicrobial activity against pathogens but is nontoxic to humans. The silver ions are very reactive leading to inhibition of microbial respiration and metabolism as well as physical damage. Moreover, it has been suggested that silver ions intercalate into bacterial DNA once entering the cell, which prevents further proliferation of the pathogen. Recently, nanotechnology has amplified the effectiveness of silver nanoparticles (SNPs) as antimicrobial agents [5]. The larger surface area-to-volume ratio of SNPs increases their contact with microbes and their ability to permeate cells [6]. Nanoparticles can also endow fabrics with improved performances and functionality. Recently, the use of polyester in protective wear, sports and in medical sector has been increased, but the problem is with its hydrophobic nature and low surface energy [7]. Mostly its SNPs treatment requires multi-steps or complex reagents which make the process expensive and laborious and most of the times they are toxic. Therefore, it is required to exploit some facile and clean protocols to form and apply SNPs on the polyester fabric.

Dopamine (3,4-dihydroxyphenethylamine) is a neurotransmitter found in central nervous system which has a vital role in human health. It is a kind of low molecular-weight catecholamine that mimics the adhesive protein, can spontaneously self-polymerize on various inorganic and organic surfaces and uniformly form films under mild conditions [8,9]. Dopamine containing two hydroxyl groups at the ortho positions to one another had been proved to have the abilities to reduce metal ions to metal nanoparticles such as Au^+ and Ag^+ [10].

In this study, first polyester-knitted fabrics were modified with dopamine and then treated with silver nitrate ($AgNO_3$) in an aqueous medium under room temperature. The dopamine was used both as binding agent and reductant.

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This is the first report on the *in situ* impregnation of SNPs on polyester-knitted fabric.

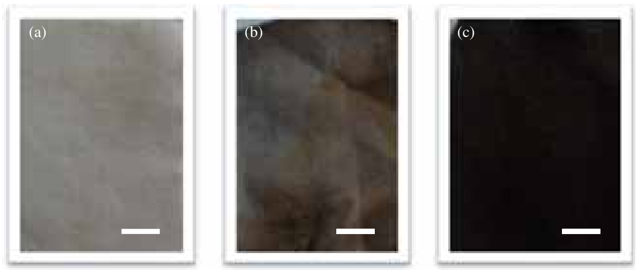

Figure 1. Digital images of (**a**) untreated polyester, (**b**) dopa-polyester and (**c**) SNPs-treated dopa-polyester fabrics. Bar = 1 cm.

2. Materials and methods

2.1 *Materials*

An interlocked knitted 100% greige polyester-knitted fabric was purchased from a local textile industry. The construction properties of fabric included: count 84 denier, 49 courses per inch, 36 wales per inch and 115 g m^{-2} areal density. The fabric was washed in diethyl ether anhydrous prior to use. All chemicals and reagents used in this study are mentioned herein with their respective manufacturer: $AgNO_3$, potassium phosphate monobasic (KH_2PO_4) and sodium phosphate dibasic (Na_2HPO_4), dopamine hydrochloride ($C_8H_{11}NO_2{\cdot}HCl$) from Sigma-Aldrich, Tris-hydrochloride

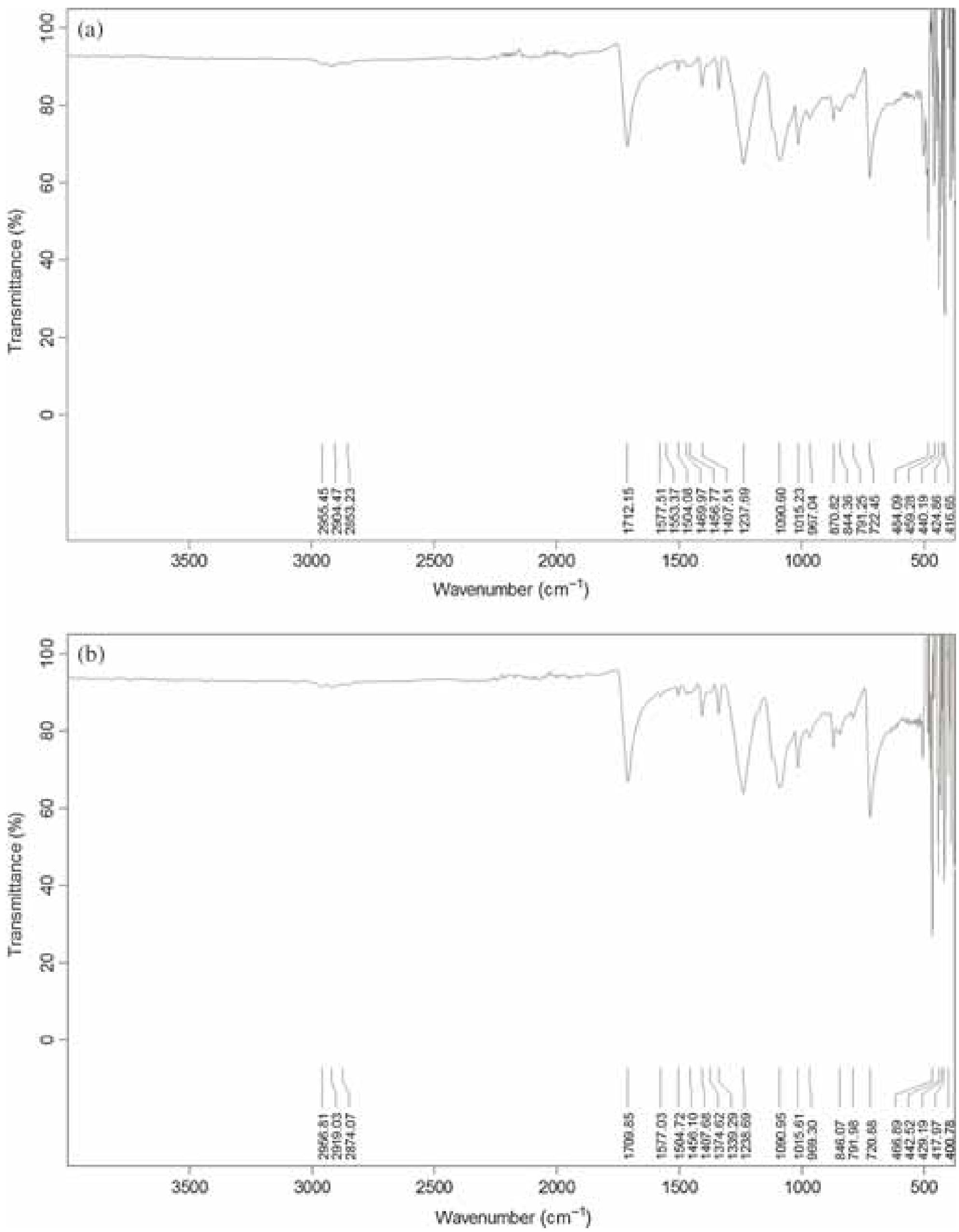

Figure 2. FTIR spectra of (**a**) untreated polyester and (**b**) dopa-polyester fabrics.

(Amresco), sodium hydroxide (Merck) and hydrochloric acid (RDH). All the chemicals and reagents were of analytical grade and used as received without further purification. Deionized water was obtained from Millipore Milli-Q water deionization system.

2.2 *Preparation of polydopamine polyester*

The dopamine with the concentration of 0.001 mol l^{-1} was dissolved in the buffer solution, prepared by using the Tris method [11]. The pH value of the prepared solution was set at 8.5, and polyester specimens were dipped into it with constant stirring at room temperature for 24 h. The fabric specimens were then taken out and rinsed with distilled water until the residual water turned clear. The polyester-knitted fabric treated with polydopamine was later named as dopa-polyester fabric.

2.3 *In situ impregnation of SNPs on dopa-polyester fabric*

The dopa-polyester fabric specimens were dipped into $AgNO_3$ solution of desired concentration at room temperature for 8 h. The specimens were then rinsed with distilled water for 10 min and dried at 40°C in a vacuum oven for 6 h.

2.4 *Fabric characterization*

To confirm the impregnation of finish on the polyester fabric, the attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, Bruker Tensor 27) was recorded at a wavenumber range of 4000–500 cm^{-1}. The ATR-FTIR was equipped with ZnSe grid that allowed recording of the FTIR spectrum directly on a specimen placed on grid. The X-ray diffraction patterns of polyester fabrics were obtained with an X'Pert XRD diffractometer, using CuKα (1.5406 Å) radiation operating with 40 mA and 45 kV in the 2θ range of 10–70°, at a scan rate of 1° min^{-1}. The water contact angle of polyester fabric specimen was measured by using Theta Lite tensiometer (TL 100 and TL101). The surface morphologies of the both treated and untreated polyester-knitted fabrics were characterized by using a field emission scanning-electron microscope (FE-SEM, JSM 7500F) equipped with a transmission electron (TE) and energy dispersive X-ray (EDX) detectors at an accelerating voltage of 13 kV. The surface topographies of both untreated and treated polyester-knitted fabrics were investigated by using atomic force microscope (AFM, Shimadzu, SPS-9600). To get scans, silicon nitride probes (model NCHR-10 POINTPROBE®-Silicon SPM-Sensor) having micro cantilever with 4 μm thickness, 125 μm and 30 μm width; with force constants of 42 N m^{-1} were used. The resonance frequency was adjusted to 320 kHz. All the scans were carried out in an ambient temperature in noncontact mode. The SPM Manager Software provided by the AFM system supplier was used for the data analysis. The surface roughness R_a was calculated directly from the AFM image using the SPM software. The antibacterial activity of the fabric specimens was determined according to clear zone of inhibition test [12]. Briefly, the test bacterial strains of *Escherichia coli* and *Staphylococcus aureus* were separately streaked on nutrient agar Petri plates and incubated at 37°C for 24 h for fresh growth. The single colonies of test bacteria were separately transferred onto nutrient broth for 48 h. The cells were collected by centrifugation at 10000 rpm at 4°C for 15 min, washed with normal saline and re-suspended to an absorbance of 0.7 at 600 nm. These cell suspensions were used as inocula for antibacterial testing. The fabric specimens were placed onto nutrient agar and incubated at 37°C for 24 h. The antibacterial activity of the fabric was tested by the inhibition zone method [13].

3. Result and discussion

The digital images of polyester-knitted fabrics are shown in figure 1. The timeline of treatment process shows that the untreated polyester was whitish which turned to light grey as dopa-polyester and finally become dark grey on further impregnation of SNPs on it. In this research work, a facile procedure for binding of SNPs on polyester-knitted fabric has been reported. First, the polyester-knitted fabric was modified with polydopamine. The polydopamine coating formed on the surface of polyester fabrics after treating with polydopamine in the Tris buffer solution. Then $AgNO_3$ was applied on this modified polyester in an aqueous medium under room temperature. The dopamine acted both as binding agent and reductant, so it could *in situ* reduce the Ag^+ to Ag^0 without adding any further reducing agent. The SNPs could be generated and distributed homogeneously on the surface of polydopamine-modified polyester fabrics [14].

3.1 *Spectroscopic characterization*

Figure 2 shows the FTIR spectra of all the polyester systems. There were some characteristic peaks of the functional groups which could explain that crosslinking occurs between

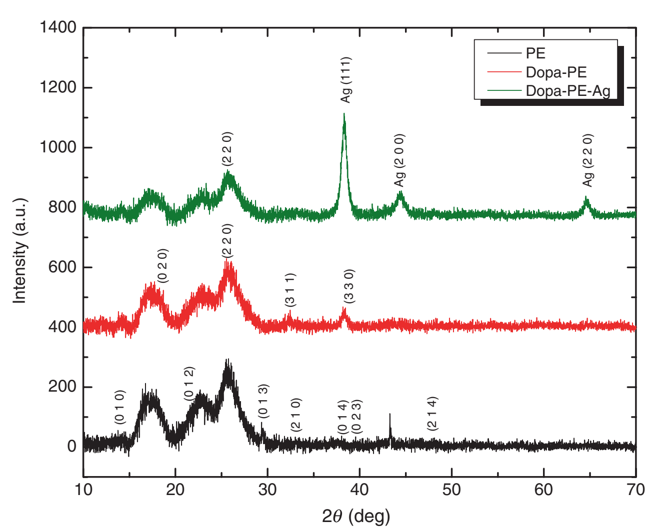

Figure 3. XRD spectra of knitted-polyester fabrics.

the polydopamine and polyester and then between SNPs and polyester. In the case of polyester-knitted fabric (figure 2a), the ester (C=O) band was observed at 1712 cm^{-1}, while with dopa-polyester, C–NH_2 asymmetric stretching was observed at 1339 cm^{-1} (figure 2b).

Figure 3 presents the combined XRD patterns of the polyester-knitted fabrics. The characteristic peaks at 14.32, 22.39, 29.73, 32.62, 37.76, 39.47 and 47.99° corresponding to (010), (012), (013), (210), (014), (023) and (214), respective lattice planes. The first three peaks correspond to the high degree of crystallinity of the unfinished polyester fabric. It was observed that due to the presence of low atomic number elements in the polyester, the number of peaks and their intensity are limited. The average crystallite size of untreated polyester fabric estimated from the Debye-Scherrer equation, $D = 0.89\lambda/\beta \cos\theta$ is 17.23 nm. The crystal structure is tetragonal. The polydopamine treatment of polyester-knitted fabric altered the geometry of the fabric as orthohombic. Then, characteristic peaks were observed at 18.32, 25.55, 32.29 and 38.38° corresponding to (020), (220), (311) and (330) lattice planes, respectively. Now, the average crystallite size was 13.3 nm. On the SNPs treatment of dopa-polyester, the crystal structure of orthorhombic retained. Then, the characteristic peaks observed for Ag space group fm-3m (face-centered-cubic) at 38.28, 44.41 and 64.50° corrresponding to the respective lattice planes of (111), (200) and (220). The arverage particle size observed was 14.30 nm. The intensity level and number of peaks in the case of finished fabric were higher due to the presence of higher atomic number element of silver in the finish.

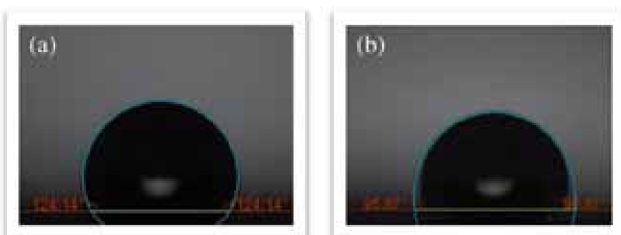

Figure 4. Contact angle changes in knitted-polyester fabrics: (**a**) untreated polyester and (**b**) SNPs-treated dopa-polyester.

3.2 *Surface characterization*

Contact angle is a quantitative measure of the wetting of a solid (polyester-knitted fabric here) by a liquid (water here). Low value of θ indicates that the liquid spreads, or wets,

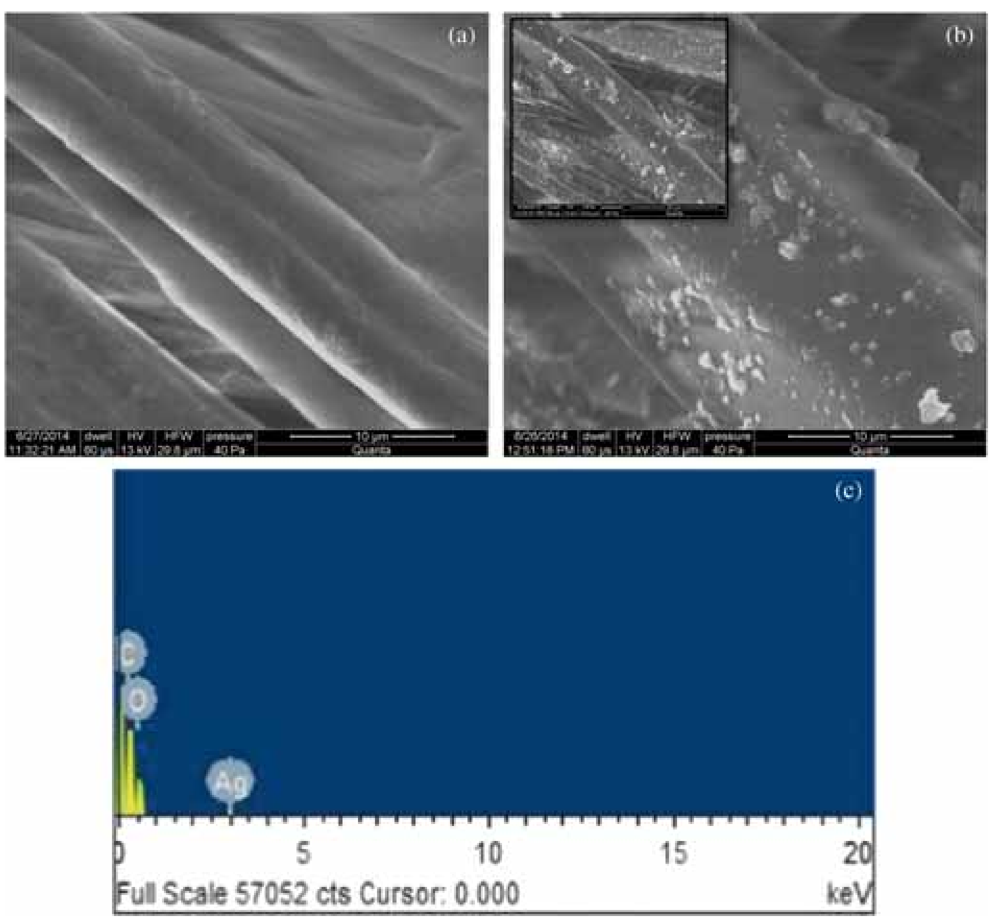

Figure 5. SEM images of (**a**) untreated and (**b**) SNPs-treated knitted-polyester fabrics and (**c**) EDX of latter.

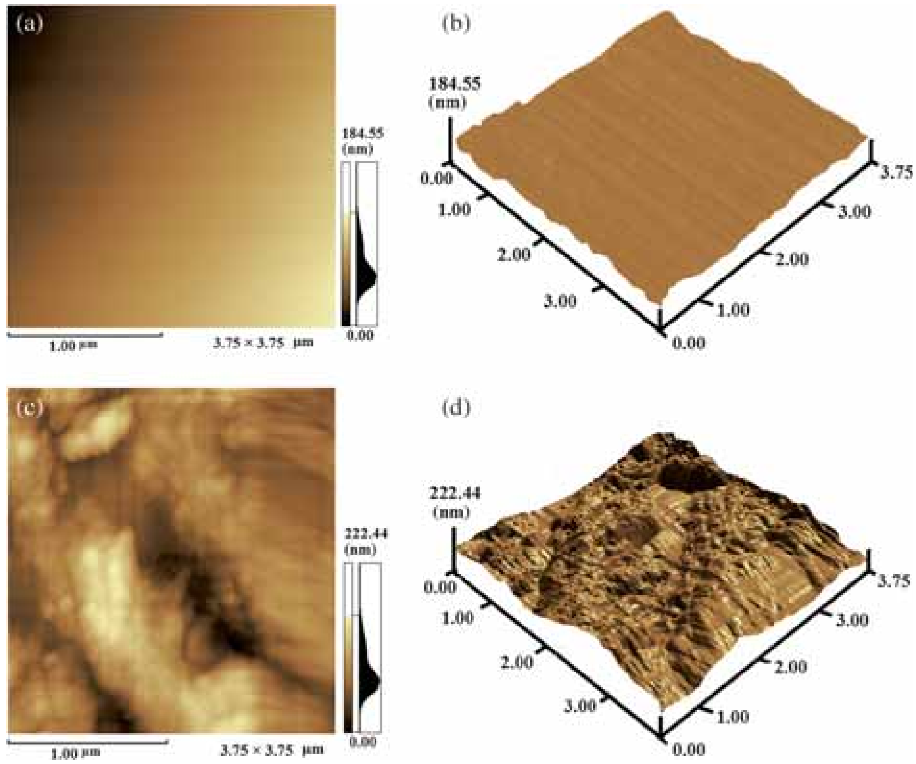

Figure 6. AFM image of cotton fabric, topography and (**a**, **b**) 3D of untreated and (**c**, **d**) SNP-treated polyester fabrics.

while high values indicate the poor wetting. If the angle is less than 90°, the liquid is set to wet the solid. If it is greater than 90°, it is said to be non-wetting. A zero contact angle represents a complete wetting. The digital images of water drop on both untreated and treated polyesterknitted fabrics are shown in figure 4. After treatment the contact angle of treated fabric decreased than that of untreated fabric, which meant that the treated fabric moved towards hydrophilic domain. This alteration in behaviour might be due to the application of polydopamine coatings which have ability to alter super hydrophobic surfaces into hydrophilic ones [15].

The SEM images of both untreated and SNPs-treated dopa-polyester-knitted fabrics are shown in figure 5a and b. The surface of untreated fabric is quite uniform and plane, whereas that of the SNPs-treated dopa-polyester is embedded with polydispersed SNPs indicating a lustrous coating on the fabric surface. EDX analysis confirmed the presence of a silver-based finish on the treated polyester-knitted fabric (figure 5c).

AFM observation reveals the surface topography of both untreated and SNPs-treated dopa-polyester fabrics as shown in figure 6. The untreated fabric shows a smooth surface as shown in figure 6a (topography) and b (three-dimensional image). The SNPs treated fabric, however, shows a rougher surface with visible SNPs embedded on the fabric matrix (figure 6c, d). It was also observed that the treated fabric losses its native surface structure and is disguised by the SNPs layer. Interestingly, the surface roughness R_a of control fabric increased from 10 to 29 nm after deposition of SNPs.

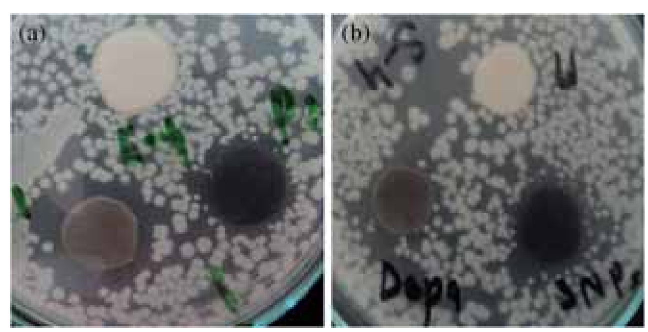

Figure 7. Antibacterial activity of treated knitted-polyester fabric against (**a**) *E. coli* and (**b**) *S. aureus* species.

In the case of dopa-polyester and SNP-treated dopa-polyester fabrics, the zones of inhibition were observed as shown in figure 7. No direct bacterial growth underneath the treated fabric specimens indicated the presence of antimicrobial activity. Sileika *et al* [16] also observed the antibacterial activity on polydopamine-modified polymer surfaces. It is generally believed that SNPs have a high affinity to react with the sulfur- and phosphorus-containing compounds in the bacterial cells. Therefore, they could attach to the surfaces of the bacterial cells and even penetrate into them leading to bacterial death [17,18].

4. Conclusions

In the present study, polyester-knitted fabrics were modified with polydopamine which is acting both as binding as well as reducing agent. The dopa-polyester was then *in situ* impregnated with silver nanoparticles in an aqueous medium under ambient conditions. The silver nanoparticles were homogeneously distributed on the surface of dopa-polyester fabric as illustrated by SEM results. The impregnation of silver nanoparticles on dopa-polyester fabric was also confirmed by EDX and FTIR spectroscopy, and the geometric orientation of nanofinish on the treated fabrics was investigated by XRD spectroscopy. The treated fabric exhibited broad-spectrum antibacterial activity against the test bacterial stains of *E. coli* and *S. aureus*. The devolved antibacterial fabric might find potential applications in biomedical, environmental, catalysis and sensing fields.

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