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Color Data and Antibacterial Properties of Smart Ag/polypyrrole-Nanocoated Cotton Fabric

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SMART textiles are responsive fabrics for environmental changes, such as biological, electrical, thermal, mechanical, chemical, magnetic, optical, etc. It was envisioned that silver nanoparticles, in conjunction with polypyrrole, would render the cotton fabric colorful and antibacterial. Thus, cotton fabric was easily coated in situ while sliver nitrate gets reduced to silver (Ag), and pyrrole gets polymerized to polypyrrole (PPy). The Ag/PPy-nanocoated cotton fabric was characterized by ATR-FTIR and SEM-EDX, and the results obtained confirmed the structure of the coating layer in which the silver atomic content was 23.75%. The color strength of the nanocoated fabric was as high as 12.74. The color data indicated that the hue was dark gray, and the fastness properties revealed good to very good fastness properties. Antibacterial studies against antibiotic-resistant bacteria (*Escherichia coli* (gram-negative) and *Staphylococcus aureus* (gram-positive)) revealed the effectiveness of the Ag/PPy-nanocoated fabric and was even better than different antibiotics. The present work may pave the way for further development of medical textiles.

Keywords: Smart textile, Medical textile, Cotton, Polypyrrole, Silver nanoparticle, Coating.

Introduction

Textiles, especially those made of natural fibers such as cotton, can act as a medium for the growth of pathogenic bacteria. Cotton fabric in contact with the human body, it offers an environment for microbial growth as it has a large surface area, absorbs moisture and retains oxygen and other possible nutrients [1]. Thus, awareness has been growing for the production of medical textiles [2-5].

In this regard, smart textile could be an elegant approach in which organic-inorganic nanocomposites could be coated and thus imparting the fabric antimicrobial. The newly emerging nanocomposites are promising fields as they provide new materials with tailored functionality [6-10]. The coloration with cotton, silk, wool with silver, and gold nanoparticles to impart these fabric antimicrobial properties have been reported [11-17]. Polypyrrole (PPy) and polyaniline as they are electrically conductive polymers have been utilized for the production of smart textiles [18,19]. On the other hand,PPy has been reported to have biocidal effectsas a result of its positive charge that would ionically attract the negatively charged cell wall of bacteria, causing their death [9].

However, the in situ formed coated layer inside cotton fabrics using silver nitrate and pyrrole has not been reported. Herein, silver nitrate and pyrrole aqueous solution in the presence of dispersing and capping agent, cetyltrimethylammonium bromide, were used for the in situ coating of cotton fabrics with Ag/PPy-nanocoated layer. The characterization, the color data and fastness properties, and the antibacterials properties were investigated.

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Materials and Methods

Cotton fabric and Chemicals

Mill-scoured and bleached cotton fabric (130 g/m^2) was obtained from Misr El-Mehala Co. Egypt. The fabric was further treated with a solution containing 3 g/l nonionic detergent (Hostapal CV, Clariant) and 5 g/l sodium carbonate at a liquor ratio of 50:1 for 1 h at the boil, after which time it was thoroughly rinsed and dried at room temperature. Cetyltrimethylammonium bromide (CTAB), pyrrole, silver nitrate were purchased from Sigma-Aldrich and were used as received.

Coating method

Cotton fabric (1g) was treated with a mixture containing CTAB (5 ml, 25 x 10^{-3}M), 15 ml distilled water, silver nitrate (0.32 g, 1.88 mmol) and pyrrole (0.05 g, 0.75 mmol) in a LR 1:20 and at 50 ^{o}C for 40 h. The treated fabric was then thoroughly rinsed with water and air-dried to give 1.2 gram of Ag/PPy-nanocoated cotton fabric with 20% add on.

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

The fabric was well washed with distilled water to remove the loose particles and then dried before SEM determination. The fabric was measured on SEM (Quanta FEG 250, FEI Co.), working at 20 KV. Then, the fabric was coated with gold and fixed with stubs ofQuanta holders and examined under vacuum.

Attenuated total reflectance Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR –FTIR, PerkinElmer Spectrum 100) was used to study the chemical composition of the Ag/PPy-nanocoated and uncoated fabrics.

Color measurements

The colorimetric properties of Ag/PPy-nanocoated cotton fabrics were obtained using a Hunter Lab Ultra Scan® PRO (USA) in terms of CIELab and CIELch values (L*, a*, b*, c*,h^o) using a standard illuminant D65 and 10^o observer with specular radiation excluded on a Minolta CM-3600d visible spectrophotometer and provided with Spectramagic software. [20, 21] (Fig. 2). According to this system, three basic tristimulus components of color, namely, hue (h^o), chroma (C*) (also referred to as saturation), and Lightness (L*) (also referred to as luminance), were measured. The hue angle was measured from 0 to 360^o. The values of the two coordinates a* and b* were also determined. L* represents the lightness or darkness of a color (L*= 100 for white & L* = 0 for black) whereas a* = red to green (+a*= redder, -a*= greener) and b* = yellow to blue (+b* = yellower, -b*=bluer). Where the two"color" axes intersect = neutral grey.

The chroma (c*) and hue angle (h^o) were measured by using following equations :

$$\text{Chroma } c^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

$$\text{Hue angle } h^o = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (2)$$

The color strength expressed as (K⁄S) values of Ag/PPy-nanocoated cotton fabrics were measured by using a Hunter Lab Ultra Scan® PRO (USA) at the maximum wavelength of the coating layer (575 nm). The relative color strength (K/S values) was assessed using the Kubelka–Munk equation (3) [22]

$$\frac{K}{S} = \sqrt{\frac{(1-R)^2}{2R}} \quad (3)$$

where, R is the reflectance of colored samples and K and S are the absorption and scattering coefficients, respectively.

Antibacterial methods

Disk diffusion assay

Disk diffusion assay was performed on Mueller – Hinton agar (MHA). An equal diameter (7 mm) and weight (6μg) of Ag/PPy-nanocoated cotton fabric and cotton fabric were placed in intimate contact with nutrient agar, which has been previously seeded with an inoculum of each test organism. After incubation for 24 h in an incubator at 37 ^{o}C, a clear area of uninterrupted growth underneath and along the side of the test material indicates the antibacterial effectiveness of the fabric. *Escherichia coli ATCC 25922* (gram-negative) and *Staphylococcus aureus ATCC 25923* (gram-positive) were used. Additionally, the determination of the inhibition zone of Ag/PPy-nanocoated cotton fabric was similarly made in comparison with discs of different antibiotics. Six antibiotics were tested: Ampicillin (AP 10μg), Cephalothin (KF 30μg), Cotrimoxazole (TS 25μg), Penicillin G (PG10units), Erythromycin (E 15μg), clindamycin (CD 2μg) (Oxoid, Basingstoke, UK) (CLSI, 2010) [23-25].

Broth assay

In this procedure (AATCC 100- 1999 method), the disc is dipped into a test tube containing the bacteria culture solution in which the bacteria concentration is 1×108 CFU/ml with 0.5 McFarland. The suspension should have a final inoculum of 5 x 105 CFU/ml. The test tubes are shaken at 35 ˚C for 1 hr on a rotary shaker at 100 rpm, and serial dilutions of the test solutions were made. One ml of the dilute is poured onto Mueller – Hinton Agar (MHA) plate and incubated at 35±2 ˚C overnight, the number of colonies in agar plate is counted. The reduction rate in the number of colonies is calculated using the following equation reduction rate (%) in the number of the colonies = (A-B)/A× 100 Where A: number of colonies before shakingand B: number of colonies after shaking certain time.

Results and Discussion

Smart textiles are sensitive fabrics for environmental changes, such as biological, electrical, thermal, mechanical, chemical, magnetic, optical, etc. For this purpose, organic and inorganic nanocomposite would lead to the formation of new materials with new functions. Recent studies indicated the success of carbon nanotube/ silver nanoparticles/ polypyrrole nanocomposites with excellent bioactivity for the disinfection of polluted water. Thus, it was envisioned to coat cotton fabrics in situ after being impregnated with silver nitrate and pyrrole with the assistance CTAB as dispersing and capping agent. Fig. 1. Shows the in situ coating of cotton fabric with Ag/PPy nanocomposite. The coating proceeds by virtue of the oxidative polymerization of pyrrole by silver nitrate [9].

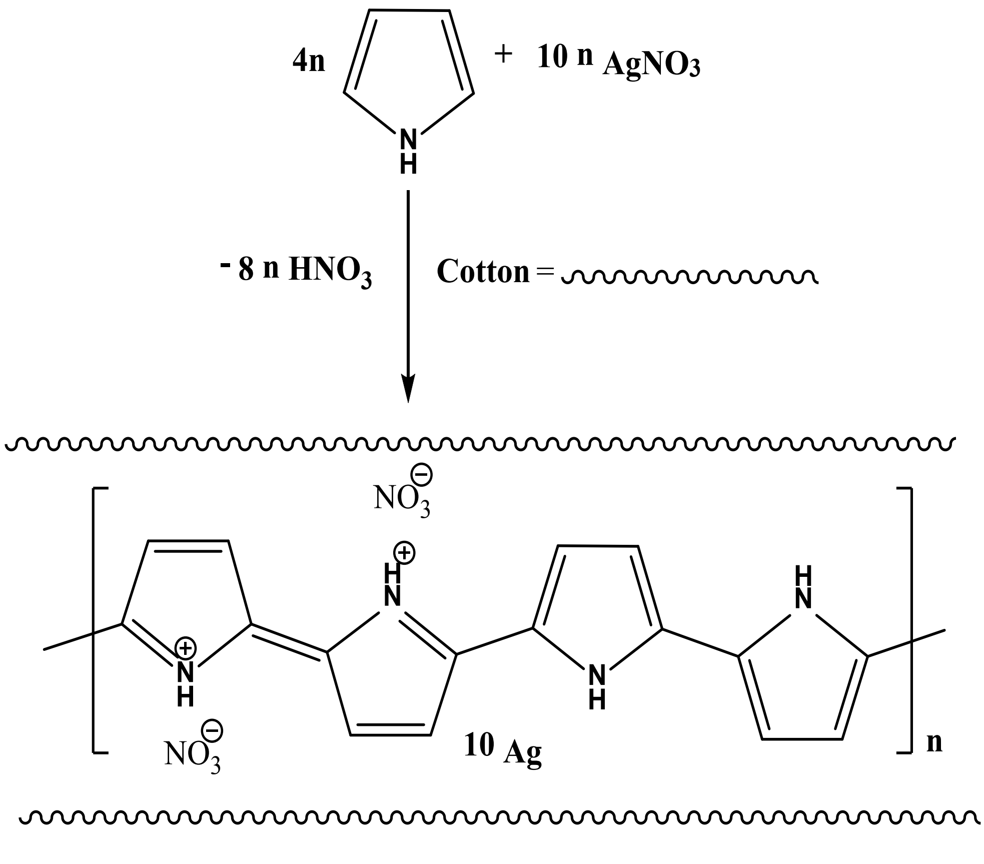

Fig 1. In situ coatinting of cotton fabric with Ag/PPy nanocomposite.

ATR-FTIR

The ATR-FTIR (Fig. 2) of cotton sample shows the characteristic peaks due to cellulose macromolecule at 3338 cm^{-1} (O–H stretching), 2905 cm^{-1} (C–H stretching), 1429 cm^{-1} (C–H wagging), 1364 cm^{-1} (C–H bending) and 1027 cm^{-1} (C–O stretching) [19]. These peaks have become weak, broad, and shifted after coating with Ag/PPy. Additionally, the characteristic peaks due to the PPy component are shown at 1576 cm^{-1} (C=C and C=N, skeletal vibration), 1315 cm^{-1} (C-N vibration), and at 910 cm^{-1} (C-H out of plane ring deformation) [26, 27]. The striking changes are clearly observed in the regions of hydroxyl and ether groups, indicating their involvement in the coating process where silver nanoparticles could be entrapped between cellulose macromolecule and polypyrrole.

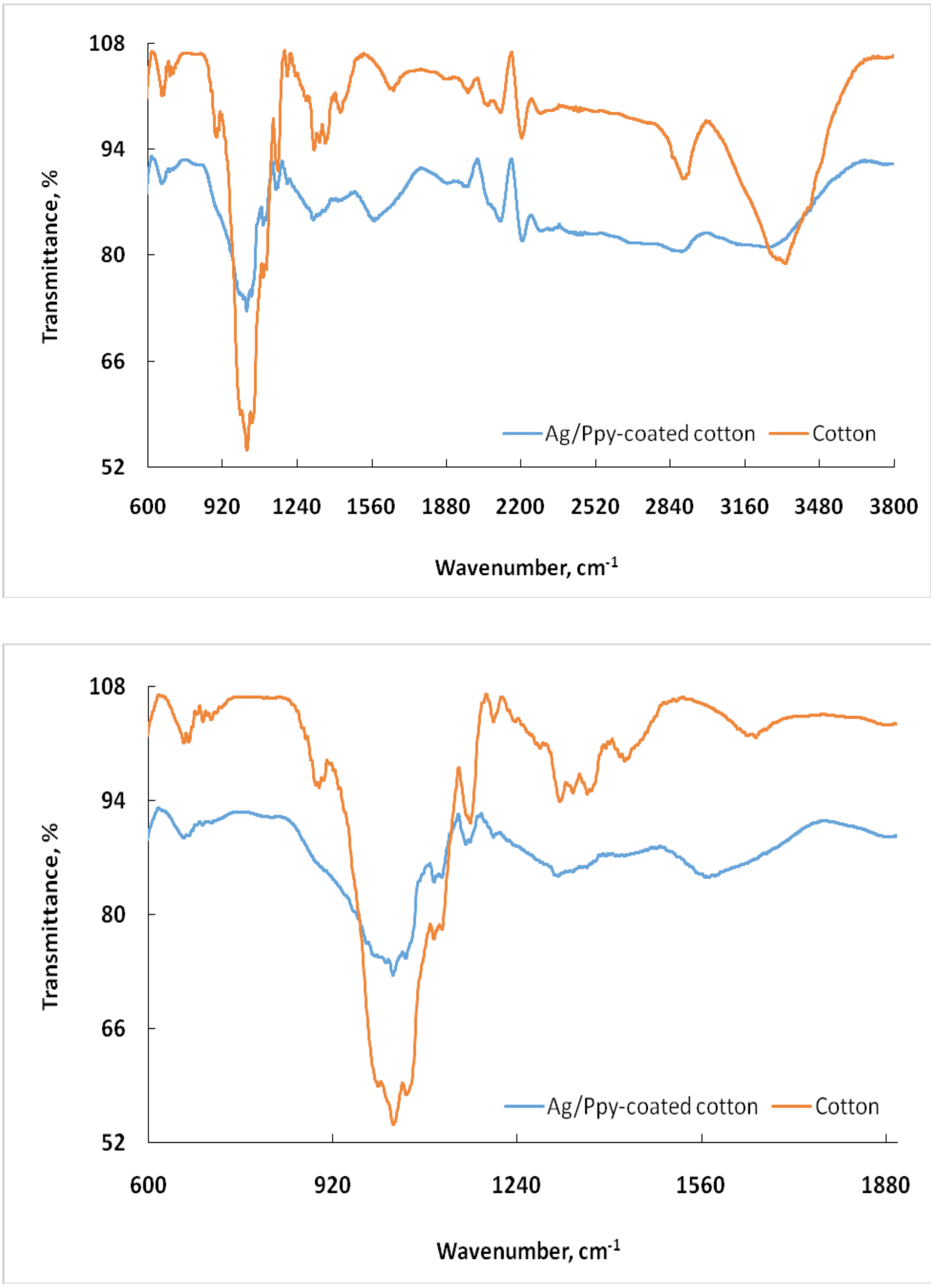

Fig. 2. ATR-FTIR spectra of Ag/PPy-nanocoated cotton and cotton fabrics. The upper figure is full scale and the lower one is an expanded region.

SEM-EDX

The texture of the cotton fabric, as it is known with a smooth surface, can easily be affected by chemical treatment. Thus, it was necessary to observe any changes in the texture after being coated with Ag/PPy nanocomposite. SEM images (Fig. 3) with different magnifications show clearly that the texture of cotton fibers have become rough and irregular with the appearance of dots on the fiber surface due to silver nanoparticles (less than 100 nm). Additional evidence was made by surface elemental analysis using the EDX technique. EDX analysis provides the percentage for the major elements present in the fabric sample. Fig. 3 also shows the EDX data at two different points in the surface of the coated fabric together with the spectrum of EDX at any point. Table 1 shows the elemental analysis at two different points of Ag/PPy-nanocoated cotton fabric, and the data obtained were almost similar, indicating the success of the homogeneous coating of cotton fabric.

A representative image of the excellent color observed for the Ag/PPy-nanocoated cotton fabric compared with the uncoated one is shown in Fig. 4.

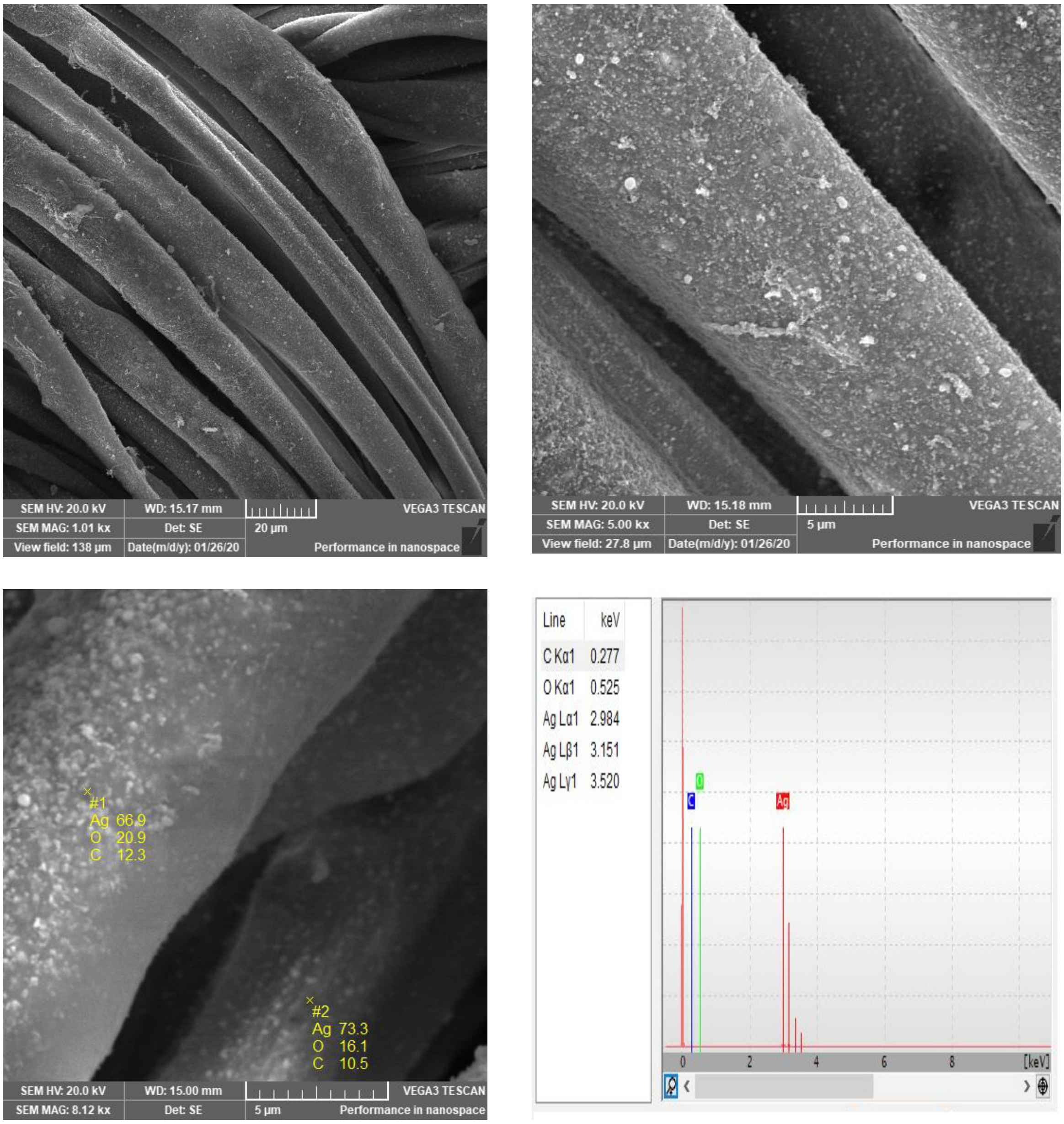

Fig. 3. SEM images of Ag/Ppy- nanocoated cotton fabrics with different magnifications. The images below from left to right show the EDX analysis at two different points and the spectrum at any point.

TABLE 1. EDX elemental analysis of Ag/Ppy-nanocoated cotton fabric.

Ag/Ppy-nanocoated cotton fabric	C		O		Ag	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
Point 1	10.5	34.1	16.2	39.45	73.3	26.45
Point 2	12.3	34.81	20.8	44.15	66.9	21.04
Average	11.4	34.45	18.5	41.8	70.1	23.75

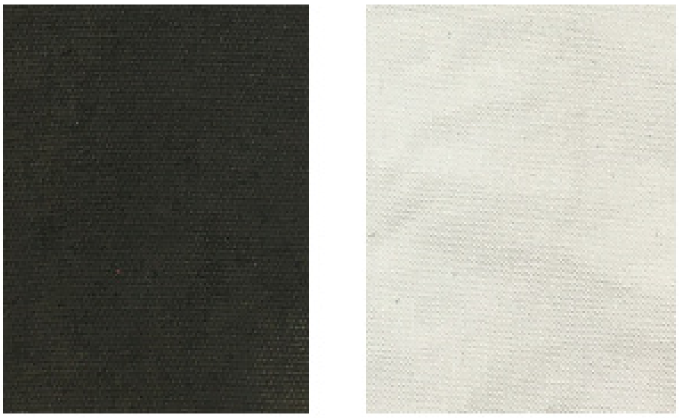

Fig.4. Images of Ag/PPy-nanocoatedcotton fabric (left) and cotton fabric right).

Color data and fastness properties

The color data values (L*, a*, b*, c*, h^o, K/S) were measured at the lambda maximum of the nanocoated fabric, and the results areshown in Table 2. The lambda maximum was 575 nm due to the high content of silver nanoparticles that absorb at 409 nm [28] and depend on the size. The larger the size of silver nanoparticles, the longer is the wavelength of absorption [29]. The absorption value of Ag/PPy is also a result of the interference with the absorption spectrum of polypyrrole (461 and 970 nm) [30]. The lower values of L*indicate that the sample is a dark color. Also, the chroma value c*, which is the distance from the gray color, is small, indicating the dull color of the sample, and as the hue angle is 84.5, thus, the color is dark gray. The fastness properties of the Ag/PPy-nanocoated sample are good to very good, indicating that the coating is intimate and with good binding interactions with the fabric.

Antibacterial studies

Smart textile made from cotton fabrics antibacterial of that antibiotic-resistant is of prime importance of a healthy environment. Thus, the success of coating cotton fabric with Ag/PPy necessitates the evaluation of the coated fabric in comparison with control and different antibiotics. The evaluation was made based on the formation of an inhibition zone on agar medium and broth essay for the kinetic of killing bacteria. Fig. 5 shows a representative antibacterial image of the inhibition zone anti-Escherichia *coli* for Ag/PPy-nanocoated cotton fabric compared with the uncoated one. It is clear that the Ag/PPy-nanocoated cotton fabric has a clear inhibition zone, whereas the cotton sample has zero plus an observed bacterial growth above the fabric. Table 3 shows a comparative inhibition zones anti-*Escherichia coli* (gram-negative) and *Staphylococcus aureus* (gram-positive) using Ag/PPy-nanocoated cotton fabric compared with the control and different antibiotics. Interestingly, the smart fabric showed potent against these bacteria and better than all antibiotics. Also, the broth essay indicated that the killing of bacteria is fast Fig. 6]. The effectiveness of the smart fabric presented is due to the rapture of the cell wall membrane of the bacteria with both silver nanoparticles and the cationic polypyrrole through physical and ionic bondings [9].

TABLE 2. Color data and fastness properties Ag/PPy-nanocoated cotton fabrics.

	L*	a*	b*	c*	h°	λ_{max}, nm	K/S
Color data	22.32	0.26	2.70	2.71	84.50	575	12.74

	Rubbing		Washing			Perspiration					
						Acid			Alkali		
Color fastness	**Dry**	**Wet**	**A**	**SC**	**SP**	**A**	**SC**	**SP**	**A**	**SC**	**SP**
	3-4	3-4	4	4	4	4	4	4	4	4	4

Alternation (A), Staining on polyester fabric (SP), Staining on cotton fabric (SC).
Wash & Rubbing and perspiration: 1, poor, 2, fair, 3, good, 4, very good, 5, excellent.

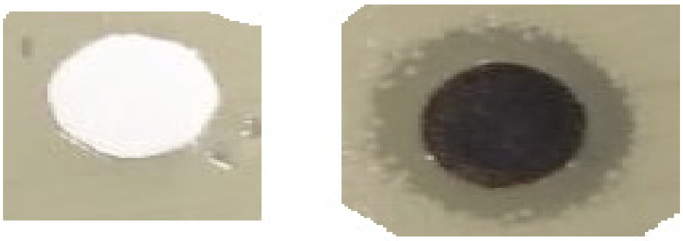

Fig. 5. A representative antibacterial image of the inhibition zone for Ag/PPy-nanocoated cotton fabric (right) compared with the uncoated one (left). The inhibition zone due to anti *Escherichia* coli.

TABLE 3. Antibacterial activity of Ag/PPy-nanocoated cotton fabric compared with uncoated and different antibiotics.

Sample	Sample weight, µg	Inhibition zone, mm	
		Escherichia coli	***Staphylococcus aureus***
Ag/PPy-coatedcotton	6	11±0.3	10±0.6
Uncoated cotton	5	0	0
Ampicillin	10	14±0.5	0
Cephalothin	30	13±0.6	0
Cotrimoxazole	25	25±0.5	0
Penicillin G	10	0	0
Erythromycin	15	0	0
clindamycin	2	0	0

*The values represent mean ± standard deviation of two replicates.

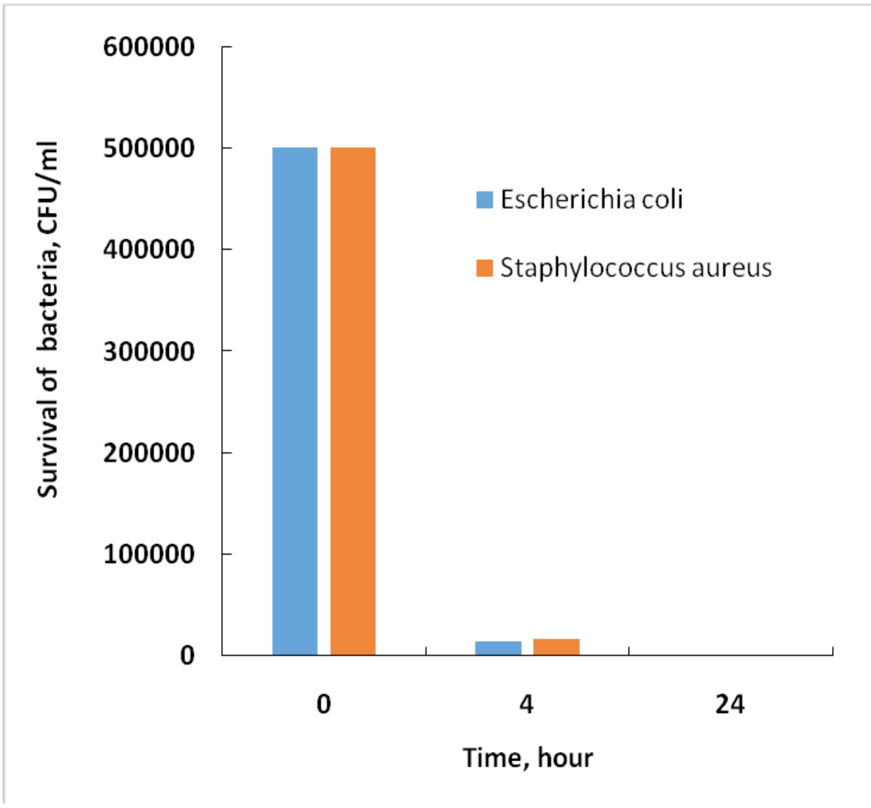

Fig. 6. Survival bacterial count versus time.

Conclusion

The present work provided a viable and facile method for the in situ coloration of cotton fabric with the antibacterial coating layer of Ag/PPy with good to very good color data. This smart nanocoated fabric revealed antibacterial activities better than different antibiotics.

This work might lead to further development in the field of medical textiles. Future work is in progress for process optimization and broader application in different textile fabrics.

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