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Durable Antibacterial Functionality of Cotton/Polyester Blended Fabrics Using Antibiotic/MONPs Composite

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Abstract: To fulfil the ever-growing demand for durable and multi-resistant textile fabrics against pathogenic bacteria, this work is aim to investigate the dual effect of coating cotton/polyester fabrics by composite of antibiotics/metal oxide nanoparticles. To carry out this study, cotton/polyester blended fabrics with different constructions were coated with ZnONPs, ZrO_2NPs, antibiotics namely doxymycin, cefadroxil, and ciprofloxacin (1 % w/v) individually and combined in presence of citric acid and sodium hypophosphite as a crosslinking agent and a catalyst respectively. Nitrogen content (%N), metal content, and antibacterial activity as well as performance and physical properties were assessed. Full characterization of untreated and treated fabrics by FTIR, SEM and EDX analysis were also carried out to confirm the binding and fixation of the used antibiotics and/or MONPs onto/within the fabric structure. The results revealed that the coated fabric samples by antibiotic/MONPs exhibited high nitrogen and metal contents as well as excellent antibacterial activity compared to the coated fabrics by the nominated MONPs and antibiotics individually. The results also showed that the variation in the antibacterial functionality, performance and physical properties of the treated fabrics are governed by the type of substrate, type of construction and type of additives. Additionally, coated fabrics evinced satisfactory antibacterial efficacy even after 15 washing cycles.

Keywords: Cotton/PET fabrics, Coatings, Antibiotics, MONPs, Durable antibacterial functionality

Introduction

Cotton based textiles still play a vital role in textile industry e.g. medical textiles, sport wear, work wear, casual wear, bed sheets, upholstery, etc. This is due to its beneficial advantages including breathability, biodegradability, softness, and comfortability. However, cotton fabrics suffer from undesirable physico-mechanical properties such as easy wrinkle, low strength, and dimension stability in addition to its low resistance toward microbes [1]. Therefore blending cotton fibers with synthetic ones is always preferable, from economic point of view, to overcome some of these drawbacks [2]. Additionally, cotton containing fabrics whether bleached, dyed or printed with new desirable functionalities and performance properties including UV-protection, electromagnetic shielding, antibacterial activity, self-cleaning, wrinkle free, etc. are greatly appreciated by consumer market for their high added-value taking into account product quality, cost and environment [3-8].

Antimicrobial finishing has become one of the most popular finishing, from users' point of view, since it eliminates the negative effect of microbes towards both the wearer and fabric itself namely cross-infection, unpleasant odor, staining, discoloration, mechanical strength reduction, etc. Therefore many research works have been dedicated to imparting an efficient and durable antimicrobial functionality to textile fabrics by utilization and development of eco-friendly finishing formulations taking into consideration type of antimicrobial agents, fabric type and construction, and method of fixation [5]. The antimicrobial agents that have been investigated during these studies include but not limited to: antibiotics [9-11], biopolymers [12], N-halmine [13], natural dyes [14,15], plant extract [16], metal salts [17], and inorganic nanoparticles and nanocomposites [18-26].

Therefore, The main task of the present work is to study the dual effect of coating cotton/polyester fabrics with different composites of metal oxides nanoparticles (MONPs) and antibiotics namely doxymycin, ciprofloxacin and cefadroxil on: i) the efficiency of loading MONPs on the surface of treated substrates, and ii) durability and effectiveness of antimicrobial functionality of treated substrates against the tested bacteria. To achieve our goal, different construction type of cotton/polyester fabrics namely plain 1/1, twill 2/2 and satin 4 were coated by the nominated MONPs and antibiotics individually and combined in presence of citric acid as a crosslinking agent and sodium hypophosphite as a catalyst with the aid of low frequency ultrasound.

Experimental

Materials

Mill-scoured and bleached cotton/polyester fabrics with different type of weave were used. The warp direction for all the used substrates are cotton/polyester blended yarn (55/45, Ne 38). The details specifications for the used substrates are given below:

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No.	Weave type	Type of substrate (weft direction)	Yarn count	Weight (kg/m^2)
1	Plain 1/1	Cotton	Ne 20	159.5
2		Cotton/PET (50/50)		
3	Twill 2/2	Cotton		167.5
4		Cotton/PET (50/50)		
5	Sateen 4	Cotton		162.5
6		Cotton/PET (50/50)		

Nano-metal oxides namely zinc-oxide (ZnONPs, 20 wt. % in water, ≤40 nm avg., Sigma-Aldrich, USA), and Zirconium (IV) oxide (ZrO_2NPs, 5 wt. % in water, ≤100 nm avg., Sigma-Aldrich, USA) were of commercial grades. Doxymycin (Nile Pharma Co., Egypt), Cefadroxil (SmithKline Beecham, Egypt), and Ciprofloxacin (Ameria Pharm Ind., Egypt) were all purchased in pure state (Figure 1). Citric acid (CA), sodium hypophosphite monohydrate (SHP, $NaH_2PO_2 \cdot H_2O$), and nonionic wetting agent were all of laboratory reagent grade.

Methods

Coating Cotton Containing Fabrics with the Nominated Active Ingredients

Samples of the nominated fabrics were coated by immersing them in aqueous solution containing: citric acid (25 g/*l*) as a crosslinking agent, sodium hypophosphite (12.5 g/*l*) as a catalyst, noninonic wetting agent (2 g/*l*) in presence of ZnONPs, ZrO_2NPs, Doxymycin, Cefadroxil, and Ciprofloxacin (1 % w/v) individually or in combination using low frequency ultrasound bath at room temperature for 15 min. The samples were then squeezed to pick up 80 %, dried at 100 °C/3 min and finally cured at 160 °C for 2 min.

Tests and Analysis

Nitrogen content of coated samples with antibiotics was determined by Kjeldahl method [27].

Zinc content of the coated fabric samples with ZnONPs were determined by a flame atomic spectrophotometer GBC Avanta, Australia. While zirconium content of coated samples with ZrO_2NPS was determined using inductively coupled plasma emission spectrometer (ICP-OES-720) (Agilent technologies).

X-ray diffraction (XRD) The X-ray diffraction method was used to identify ZnO and ZrO_2 nanoparticles coated fabric samples. XRD patterns recorded on a Philips PW 3050/10 model. The diffractometer was controlled and operated by a PC computer with the programs P Rofit and used a MoK (source with wavelength 0.70930 Å, operating with Mo-tube radiation at 50 kV and 40 mA.

FTIR analysis was performed on untreated substrate No. 1 and its corresponding fabric samples coated with the nominated antibiotics. The analysis was carried out using Nicolet Magna-IR 560 spectrometer.

Scanning electron microscope (SEM) and energy - dispersive X-ray spectroscope (EDX) for selected fabric samples were used to record the morphology changes and determine the elemental composition of the fabrics surface. SEM and EDX analysis were carried out using Quanta™ 250 FEG (Field Emission Gun) attached with an accelerating voltage - 30 kV, FEI Co., Netherland.

Antibacterial against pathogenic *S. aureus* (Gram positive: G+ve) and *E. coli* (Gram negative: G-ve) bacterial was evaluated qualitatively and expressed as zone of growth inhibition (ZI, mm) according to AATCC Test Method: 147-1988.

Air permeability (AP) was tested according to DIN Test Method: 53887 using Air Permeability Tester model M021A, SDLATLAS.

Wrinkle recovery angle for untreated and treated samples at dry state [WRA (w+f) °] was assessed according to ASTM Method D-1296-199.

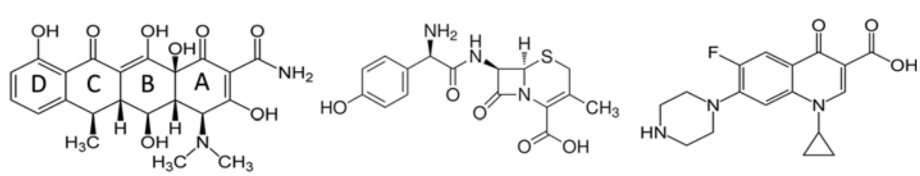
Breaking strength of untreated and treated samples at warp direction was determined by the strip method according to ASTM D5035-11 (2015), using Tennius Olsen Tensile machine model ST5. The Retained Strength (RS) was calculated according to the following equation: RS (%)= $(TS_2/TS_1)\times 100$, where TS_1 and TS_2 equal to tensile strength of untreated and treated samples respectively.

Durability to wash (after 15 washing) was evaluated, for selected samples, according to AATCC Test Method 61(2A)-1996.

Results and Discussion

Effect of Crosslinking Agent

Table 1 showed the effect of treatment of cotton/PET fabrics with citric acid (25 g/*l*), as a crosslinking agent, in presence of SHP (12.5 g/*l*), as a catalyst, on the performance properties of treated fabrics. It is worth noted that the



Doxymycin Cefadroxil Ciprofloxacin

Figure 1. Chemical structure of the used antibiotics.

Table 1. Effect of crosslinking agent on performance properties of treated fabric samples

Type of weave	Type of substrate (weft direction)		AP (l/m^2/s)	WRA (W+F)^o	TS (kg)
Plain	Cotton	Untreated	285	189	56
		CA/SHP	276	202 (6.8↑)*	50 (89.3)**
	Cotton/ PET	Untreated	296	215	60
		CA/SHP	280	222 (2.3↑)	55 (91.7)
Twill 2/2	Cotton	Untreated	403	203	73
		CA/SHP	384	234 (15.3↑)	55 (75.3)
	Cotton/ PET	Untreated	457	236	70
		CA/SHP	454	249 (5.5↑)	55 (78.6)
Satin 4	Cotton	Untreated	464	210	70
		CA/SHP	454	244 (16.2↑)	52 (74.2)
	Cotton/ PET	Untreated	486	243	68
		CA/SHP	460	257 (5.7↑)	53 (77.9)

Finishing formulation: CA (25 g/l), SHP (12.5 g/l), Wet pick-up (80 %), drying at 100 °C/3 min, thermofixation at 160 °C/2 min, WRA (w+f)^o: wrinkle recovery angle (warp and weft), TS: Tensile strength. *Values between brackets show the percent increase in WRA and **values between brackets show the RS (%): retained strength.

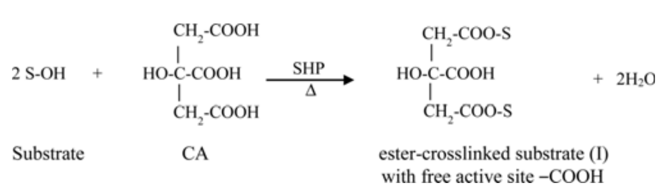
untreated and treated substrates with CA/SHP did not show any antibacterial activity whatsoever against pathogenic bacteria, G+ve (*S. aureus*) and G-ve (*E. coli*). On the other hand, the results demonstrated a significant improvement in CRA value of the treated fabric samples accompanied by decrease in tensile strength regardless of the type of the treated substrates. The change in the aforementioned properties is due to the role of the used crosslinking agent in the stabilization of cellulose chains thus inhibit their movements in the amorphous and intermediate regions. On the other hand, all the treated substrates showed decrease in their air permeability which may be attributed to the deposition of the crosslinking agent onto/within the fabric structures which in turn prevent the air from passing through. The extent of variation in the tested performance properties is governed by the type of fabric and type of weave.

Regarding the type of substrate at the weft direction, cotton/PET showed better results in CRA, air permeability and tensile strength compared to cotton containing fabrics. However cotton containing fabrics were higher in the percent improvement in CRA accompanied by decrease in both air permeability and tensile strength. This may be due to the increase in the extent of ester-crosslinks between CA/SHP and cellulose cotton fibers at weft direction [4,19,28].

Regarding the type of weave, the enhancement in the air permeability and wrinkle recovery angle showed the following decreasing order: satin 4 > twill 2/2 > plain due to the fact that the fewer numbers of fiber interlacements per unit area are, the greater the air permeability values are, while the retained strength of the crosslinked fabric samples showed the following decreasing order: plain > twill 2/2 > satin 4 that may be attributed to the higher number of interlacements in plain weave compared with twill and satin, which in turn assist the fabric samples to withstand the chemical modification [29-31].

Effect of MONPs Type

The effect of incorporation of ZnONPs and ZrO_2NPs (1 % w/v) individually into the coating formulation in presence of CA (20 g/l) as a crosslinking agent and SHP (12.5 g/l) as a catalyst on the antibacterial properties of the treated cotton/PET blended fabrics was studied and the obtained results are presented in Figure 2. The treated cotton/PET fabric samples with the nominated metal oxide nanoparticles in presence of CA/SHP as an eco-friendly ester crosslinking agent resulted in creation of -COOH active sites onto the ester-crosslinked fabric samples which in turn enhanced the extent of loading and immobilization of the nominated MONPs during the thermofixation step (equations (1), (2)). Accordingly, the treated cotton/PET fabric samples with the nominated MONPs showed a significant improvement in their antibacterial activity against the tested pathogens regardless of the used MONPs. The improvement in the antibacterial activity of the treated fabric samples is a direct consequence to the photocatalytic properties and semi-conductor behavior for both ZnONPs and ZrO_2NPs and their capability to generate reactive oxygen species (ROS) such as $^{\bullet}OH$, O_2^{-}, and H_2O_2 as it was extensively explained and reported elsewhere [19,24,32,33]. These species have the ability to penetrate and destroy the cell membrane of the tested bacterial and hence inhibiting the growth of these bacteria and eventually causing their death. Additionally, the antibacterial activity of the coated fabrics showed better inhibition zone against G+ve (*S. aureus*) bacteria than G-ve (*E. coli*) which is probably due to the differences in their cell walls structures [34].



(1)

(I) + MONPs → MONPs loaded cotton/PET fabric (2)

where S-OH: Substrate (cotton at weft direction, Cell.OH, or cotton/PET, HO.Cell/PET, at weft or warp direction); MONPs:

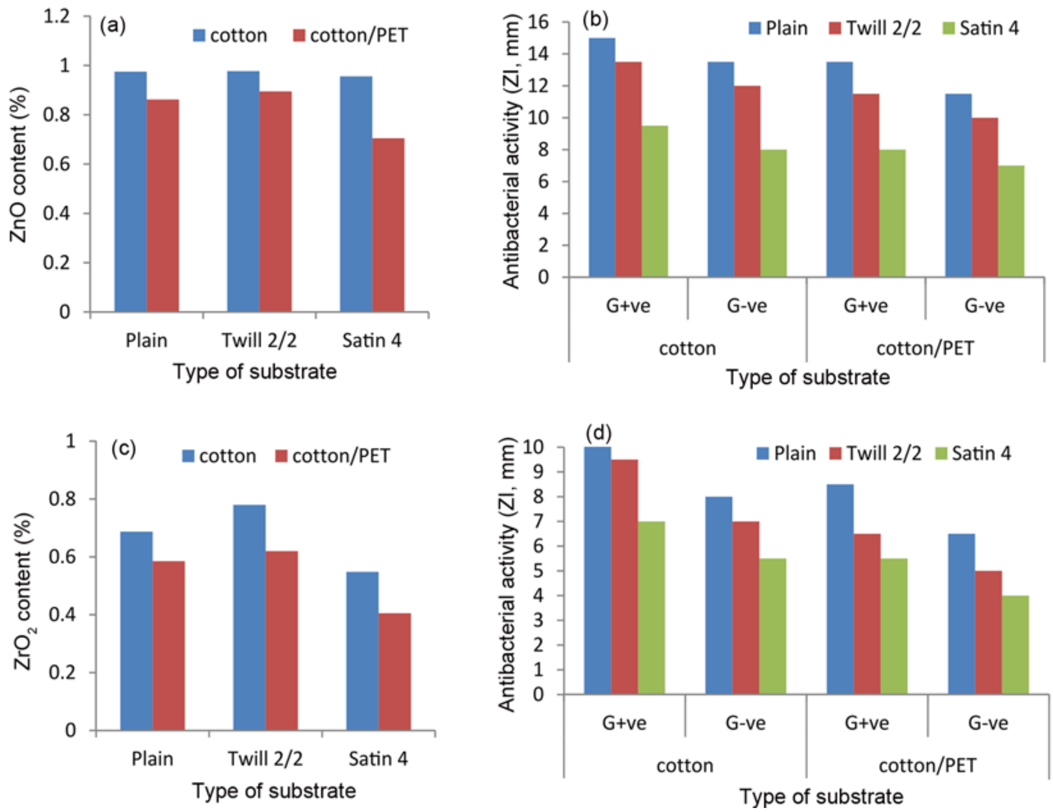


Figure 2. Metal content and antibacterial activity of treated fabric samples with different MONPs; (a, b) ZnONPs and (c, d) ZrO_2NPs respectively.

ZnONPs or ZrO_2NPs

Additionally, the results obtained in Figure 2 also revealed that the increase in metal content along with the improvement in the antibacterial activity of the treated fabric samples towards the tested bacteria were governed by the type of MONPs. Cotton/PET fabric samples coated with ZnONPs showed higher metal content and better antibacterial activity compared with ZrO_2NPs treated ones. The difference between the effects of the two types of MONPs can be attributed to the differences between their sizes, the extent of penetration, loading, distribution and fixation onto and within the treated fabric samples structure as well as differences in their photocatalytic behavior [19].

Moreover, Figure 3 illustrated the XRD for the coated fabric samples, [cotton weft/(C/PET) warp], coated by the nominated MONPs. All XRD patterns exhibited peaks at 2θ 15 °, 16.5 ° and 22.5 ° corresponding to cellulose structure. Additional peaks were recorded at 2θ 33.9 ° and a small peak at 39 ° for ZnO nanoparticles (Figure 3(a)), while additional peaks were recorded at 2θ 35 ° and small peak at 30 ° (Figure 3(b)) corresponding to ZrO_2 nanoparticles [35,36].

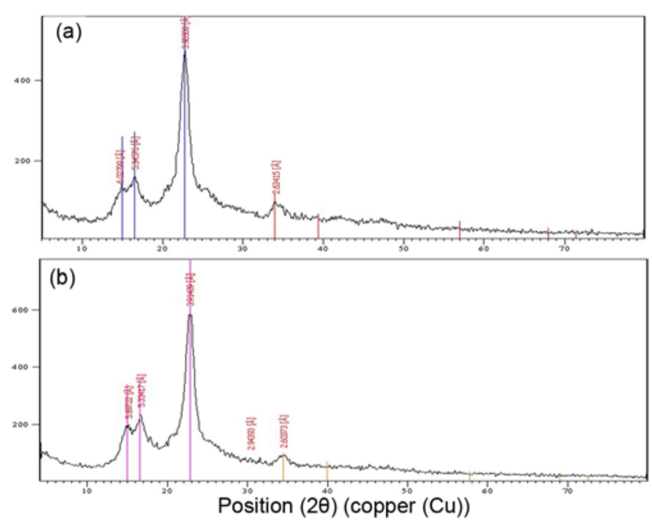


Figure 3. XRD patterns of coated fabrics by the nominated MONPs; (a) ZnONPs and (b) ZrO_2NPs.

On the other hand, Figure 4(a, b) revealed that all the treated fabrics with the nominated MONPs showed an improvement in WRA, along with a marginal decrease in tensile strength compared with the untreated ones as follow: CA/SHP + ZrO_2NPs > CA/SHP + ZnONPs > CA/SHP >> None, and CA/SHP > CA/SHP + ZnONPs > CA/SHP + ZrO_2NPs >> None, regarding WRA and tensile strength, respectively Figure 4(a, b) and Table 1. The changes in these properties reflected the positive role of MONPs to act as a co-catalyst to enhance the extent of crosslinking of the treated fabrics with CA/SHP therefore improve the anti-creasing properties along with slight decrease in tensile strength [4,37]. Additionally, all the coated fabric samples with MONPs showed a decrease in the air permeability compared to the untreated ones Figure 4(c). This can be attributed to the deposition of the nanoparticles onto the fabric surface and into the pores between the fibers thereby prevent the air to pass through freely. However, minimal reduction in air permeability and tensile strength was observed in case of coating by ZnONPs.

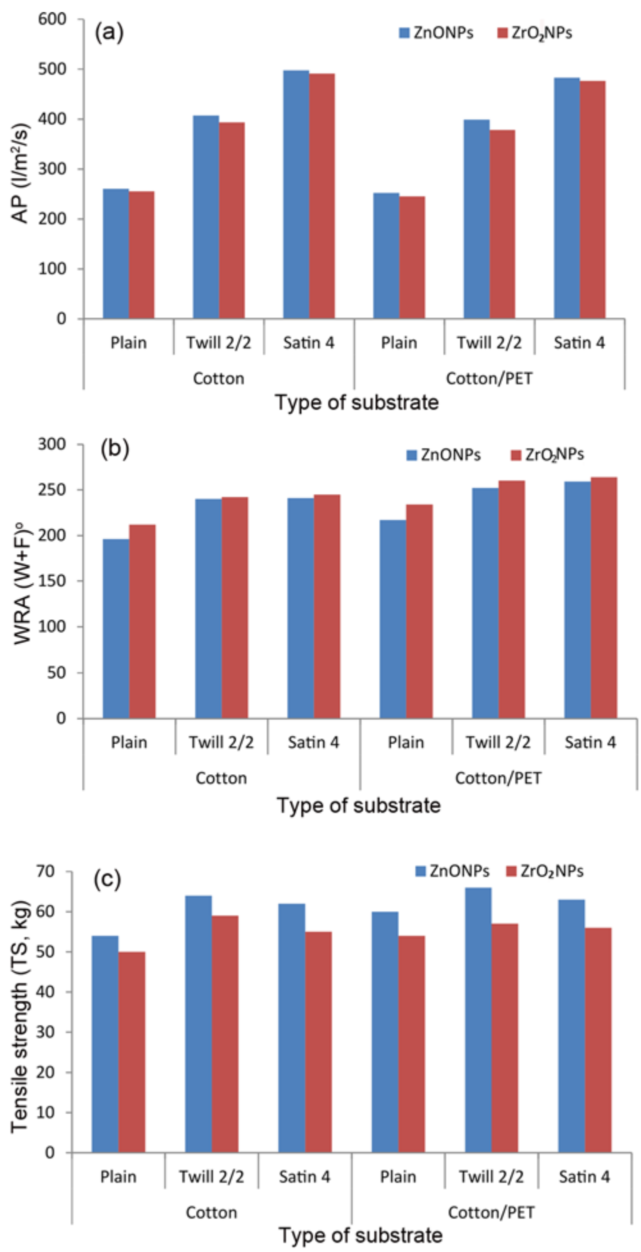


Figure 4. Effect of MONPs type on performance properties of treated fabric samples; (a) AP: air permeability, (b) WRA (W+F)^{o}: wrinkle recovery angle (warp+weft), and (c) TS: tensile strength. *Footnote*: Finishing formulation: CA (25 g/*l*), SHP (12.5 g/*l*), nanoparticles (1 % w/v), wet pick-up (80 %), drying at 100 ^{o}C/3 min, thermofixation at 160 ^{o}C/2 min.

Effect of Antibiotic Type

Three types of antibiotics namely doxymycin, cefadroxil and ciprofloxacin (1 % w/v) were added individually to the coating formulation in presence of CA/SHP (20/12.5 g/*l*), as an ester-crosslinking system, to impart antibacterial activity to the coated cotton/PET fabrics. The impact of the nominated antibiotics on %N and the antibacterial functionality of treated fabric samples are presented in Figure 5. Figure 5 showed an increase in %N along with remarkable improvement in antibacterial activity of treated fabric samples. The increase in %N was governed by the type of the used antibiotics and followed the decreasing order: ciprofloxacin > cefadroxil > doxymycin. While the extent improvement in antibacterial activity of treated fabric samples followed the decreasing order: doxymycin > ciprofloxacin > cefadroxil. The variation in %N and antibacterial activity of the treated fabrics can be attributed to the extent of penetration, distribution and fixation of antibiotics onto the fabrics surface and within the intermolecular of cotton/polyester samples (equations (3), (4)), as well as nature of the used

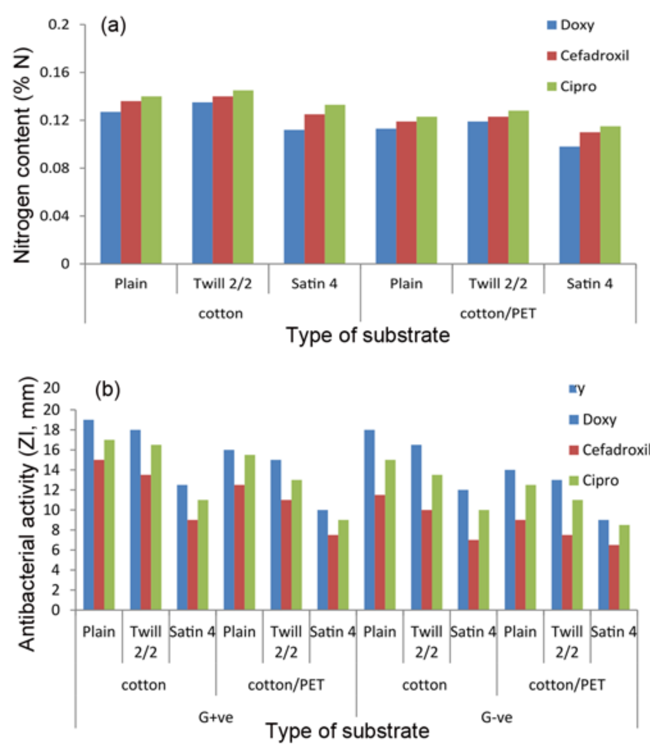
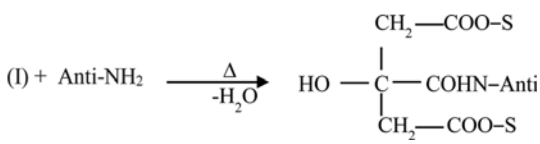


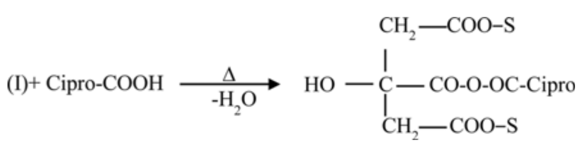
Figure 5. Nitrogen content (a) and antibacterial activity (b) of treated fabric samples with different antibiotics.

antibiotics and their mode of action. Doxymycin as tetracyclines antibiotic can inhibit bacterial protein synthesis by preventing the association of aminoacyl-tRNA with the bacterial ribosome [38,39]. While cefadroxil exhibits antibacterial activity by interfering with the later stages of bacterial cell wall synthesis through inactivation of one or more penicillin-binding proteins and inhibits cross-linking of the peptidoglycan structure [40,41]. Ciprofloxacin inhibits DNA gyrase, topoisomerase II, and topoisomerase IV that necessary to separate bacterial DNA, thereby inhibits cell division [42,43].



(3)

where: Anti-NH_2: Doxymycin or Cefadroxil



(4)

Moreover, Figure 6 represents The FTIR spectra of untreated sample [Cotton weft/(C/PET) warp] and the treated samples with different types of antibiotics in presence of CA/SHP as crosslinking agent. The comparisons between the untreated sample and treated ones reveal new peaks as follow: in case of treated with doxymycin, new characteristic peaks can be seen at 1614 cm^{-1} and 1583 cm^{-1} corresponded to carbonyl group in ring A and C respectively. Also, it can be observed peaks at 1665 cm^{-1} and 1532 cm^{-1} that are related to carbonyl and amino groups of the amide [39]. While in case of cefadroxil, the intensity of C=O vibration at 1713 cm^{-1} has noticeably increased and additional peaks at 1353 cm^{-1} and 815 cm^{-1} assigned for C-N and N-H groups respectively were observed [44]. On the other hand, in case of treated with ciprofloxacin, new characteristic peaks at 1626 cm^{-1} and 1596 cm^{-1} assigned for C=O vibration and aromatic C-C stretch were clearly seen, another peaks were also observed at 1484 cm^{-1} and 1386 cm^{-1} corresponding to C-H and aromatic C=C respectively. Also, an additional peak was found at 812 cm^{-1} assigned for N-H group [45].

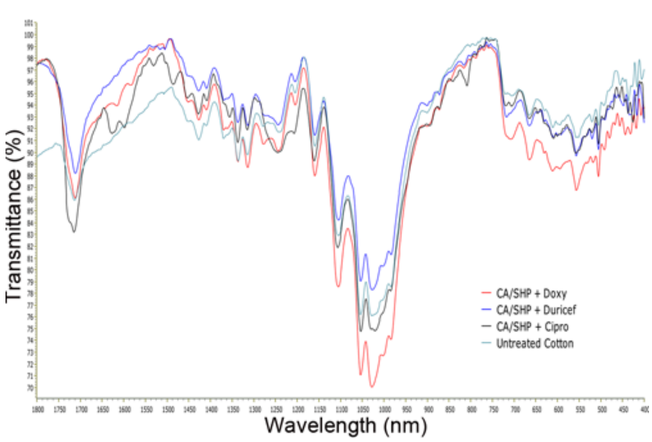


Figure 6. IR spectra of untreated and treated fabric samples with nominated antibiotics.

Moreover, the results obtained from Figure 7(a-c) showed an improvement in WRA values (a) along with decrease in

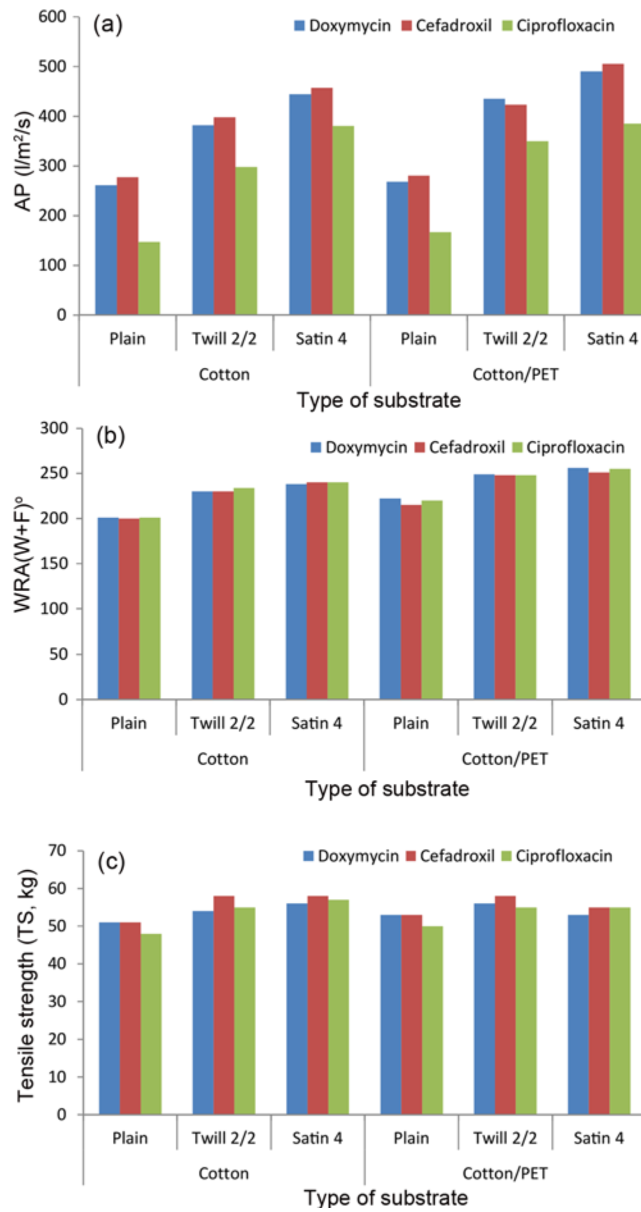


Figure 7. Effect of antibiotics types on performance properties of treated fabric samples; (a) AP: air permeability, (b) WRA $(W+F)^o$: wrinkle recovery angle (warp+weft), and (c) TS: tensile strength. *Footnote*: Finishing formulation: CA (25 g/*l*), SHP (12.5 g/*l*), antibiotic (1 % w/v), Wet pick-up (80 %), drying at 100 °C/3 min, thermofixation at 160 °C/2 min.

air permeability (b) and tensile strength (c) of the coated fabric samples compared with the untreated ones, regardless of the type of antibiotic and type of substrate. However, there are no significant differences in WRA or tensile strength for the coated fabric samples by the used antibiotics. On the other hand, air permeability of the coated fabric samples by the used antibiotics decreased according to the following order: Ciprofloxacin >> Doxymycin > Cefadroxil, which may be due to the differences in their molecule sizes and the extent of their penetration within the fabric structure.

Effect of Antibiotic/MONPs Composite

Figure 8 and Figure 9 signified that coating fabrics samples with antibiotic/MONPs composite along with CA/SHP, as eco-friendly ester-crosslinking system, resulted in a significant increase in nitrogen content (%N) Figure 8(a) and metal content (%) Figure 8(b), along with excellent improvement in antibacterial functionality Figure 9(a, b), expressed as zone of inhibition (mm), for all treated substrates. The remarkable enhancement in the tested properties is attributed to the synergistic effect of both MONPs and the used antibiotics. The improvement in %N along with the improvement in antibacterial activity showed the following order: antibiotic/ZnONPs > antibiotic/ZrO_2NPs > antibiotic alone, regardless of the used antibiotic. The variation in the %N reflected the differences in the ability of the used MONPs to act as co-catalyst for SHP and enhanced the extent of ester-crosslinking of the treated fabric samples which in turn enhanced the extent of fixation of antibiotics onto/into the fabric structure and accordingly improved the efficiency of the used antibiotics against the tested pathogens by inhibiting the cell growth of these bacteria.

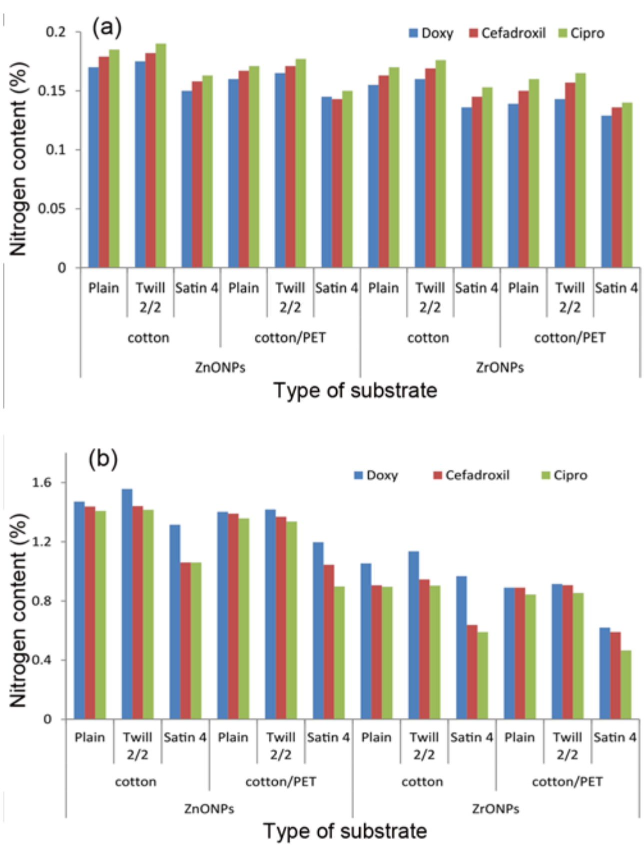


Figure 8. Nitrogen content (a) and metal content (b) of treated fabric samples with different types of antibiotic/MONPs composites.

On the other hand the increase in metal content and the remarkable improvement in the antibacterial functionality showed the following order: Doxymycin/MONPs > Cefadroxil/MONPs > Ciprofloxacin/MONPs >> MONPs alone. The extent increase in the metal content of coated fabrics is attributed to the creation of more active sites namely -COOH, -OH, -NH, as a result of antibiotics fixation onto/into the coated fabrics samples, thus increased the extent of loading and binding of MONPs onto the coated fabric samples, which in turn improved the photo catalytic activity of the loaded MONPs and their antibacterial activity against the tested G+ve and G-ve bacteria. The data also revealed that coated fabric samples by antibiotic/ZnONPs composite showed better antibacterial activity than corresponding antibiotic/ZrO_2NPs treated ones Figure 9(a, b) which reflect the difference between them in their photocatalytic activity.

Conclusively, among all the used antibiotic/MONPs composites, doxymycin/ZnONPs composite showed the highest %N, metal content and antibacterial functionality. The presence of ZnONPs improved the extent ester-crosslinking and the fixation of doxymycin onto/within the coated fabric samples and at the same time, doxymycin, as tetracyclines, has the ability to form strong complexes with nano-metal oxides resulted in increasing the extent of loading of ZnONPs onto the coated fabrics, which in turn enhanced the photocatalytic activity and the antibacterial functionality remarkably [19,39,46].

On the other hand, data from Figure 10 showed that the performance and physical properties varied depending on the used antibiotic/MONPs composite. Coated fabric samples by antibiotic/ZrO_2NPs showed higher wrinkle recovery angle than antibiotic/ZnONPs, whereas coated fabric samples by antibiotic/ZnONPs showed better air permeability and tensile strength than antibiotic/ZrO_2NPs, irrespective to the type of antibiotic, type of fabric and type of weave. The changes in the aforementioned properties, as function in MONPs, reflected the difference between the nominated MONPs in their particle size, concentration, distribution, extend of loading/fixation and their photo catalytic activity [4,19,28]. Regarding the type of antibiotic used in the composite, both WRA and tensile strength did not significantly affected by the type of antibiotic. While air permeability decreased according to the following order: ciprofloxacin/MONPs > cefadroxil/MONPs > doxymycin/MONPs. This may due to the size and extent of penetration and fixation of the nominated antibiotics within the fabric

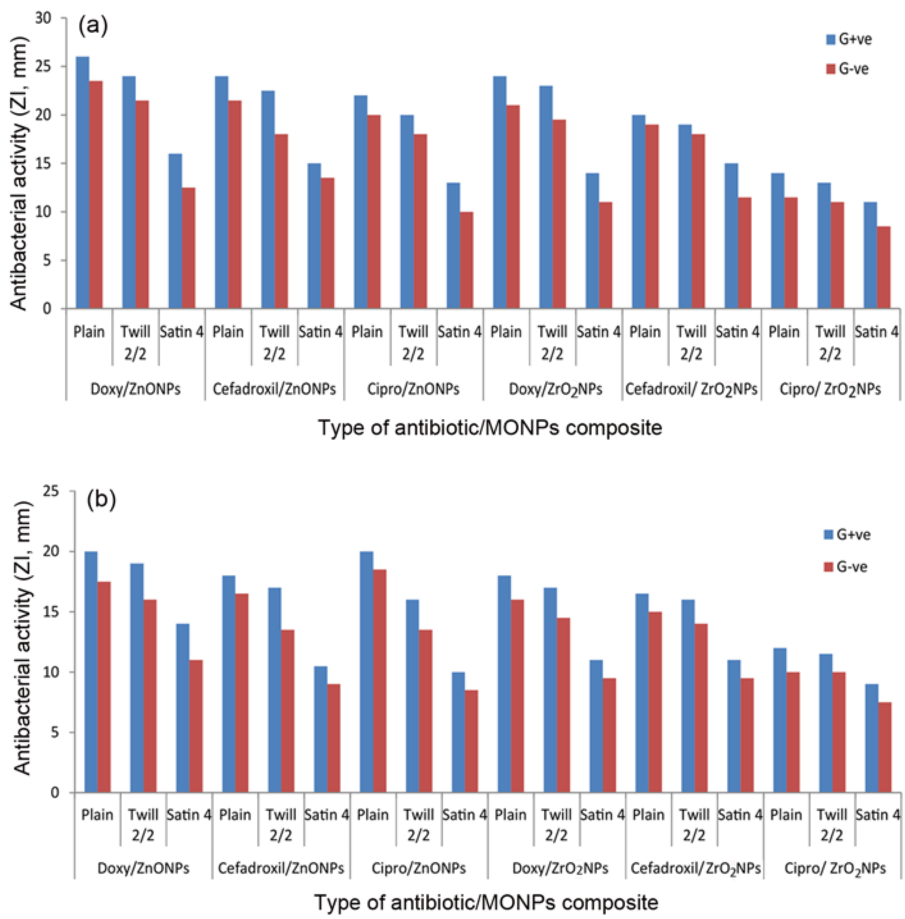


Figure 9. Effect of antibiotic/MONPs composites types on antibacterial activity of treated cotton fabric (a), and cotton/PET (b) at weft direction. *Footnote*: Finishing formulation: CA (25 g/*l*), SHP (12.5 g/*l*), antibiotic (1 % w/v), MONPs antibiotic (1 % w/v), wet pick-up (80 %), drying at 100 °C/3 min, thermofixation at 160 °C/2 min.

structure and blocking the pores between the fibers preventing the air from passing through fabric structure freely.

SEM and EDX of untreated and coated C/PET plain weave fabric by ZnONPs and ZrO_2NPs and their composites with the nominated antibiotics in presence CA/SHP are given in Figure 11, 12 respectively. The SEM images demonstrated the deposition of active ingredients, i.e MONPs and/or antibiotics onto the treated fabric surface. The EDX spectra of coated fabrics with MONPs, Figure 11, 12(b), confirmed the existence of elements Zn and Zr respectively. While, the EDX spectra of coated fabrics with antibiotic/MONPs, Figure 11, 12(d-h), confirmed the existence of nitrogen elements related to the used antibiotic along with Zn and Zr elements respectively. From all the EDX spectra, it can be concluded that the extent of loading MONPs onto the fabric surface improved according to the type of the used antibiotic as follow: doxymycin/MONPs > cefadroxil/MONPs > ciprofloxacin/MONPs > MONPs which reflected the positive role of antibiotics on loading and fixation of MONPs onto the coated fabric surfaces.

Effect of Type of Substrate

The data obtained in Tables 1 and Figures 2, 4, 5, 7-10 signified that the type of substrate and type of weave played an important role in antibacterial functionality, performance and physical properties of coated fabric samples. Regarding the type of substrate at the weft direction, coated fabric samples with cotton fibers at the weft direction showed higher %N and metal content in case of treating with antibiotics and MONPs respectively. This can be attributed to the enhancement in the extent of ester-crosslinking of CA/SHP onto the treated cotton fabric samples. Regarding the type of weave, plain 1/1 and twill 2/2 showed similarity in the nitrogen and metal content as well as antibacterial functionality, and they were much higher than satin 4. Coated twill fabric samples showed marginal increase in %N and metal content compared with plain fabric samples which may be due to lower the interlacement between the fibers in twill fabric samples enhanced the extent of penetration of active ingredients into the fabric construction. However, coated plain fabric samples showed better

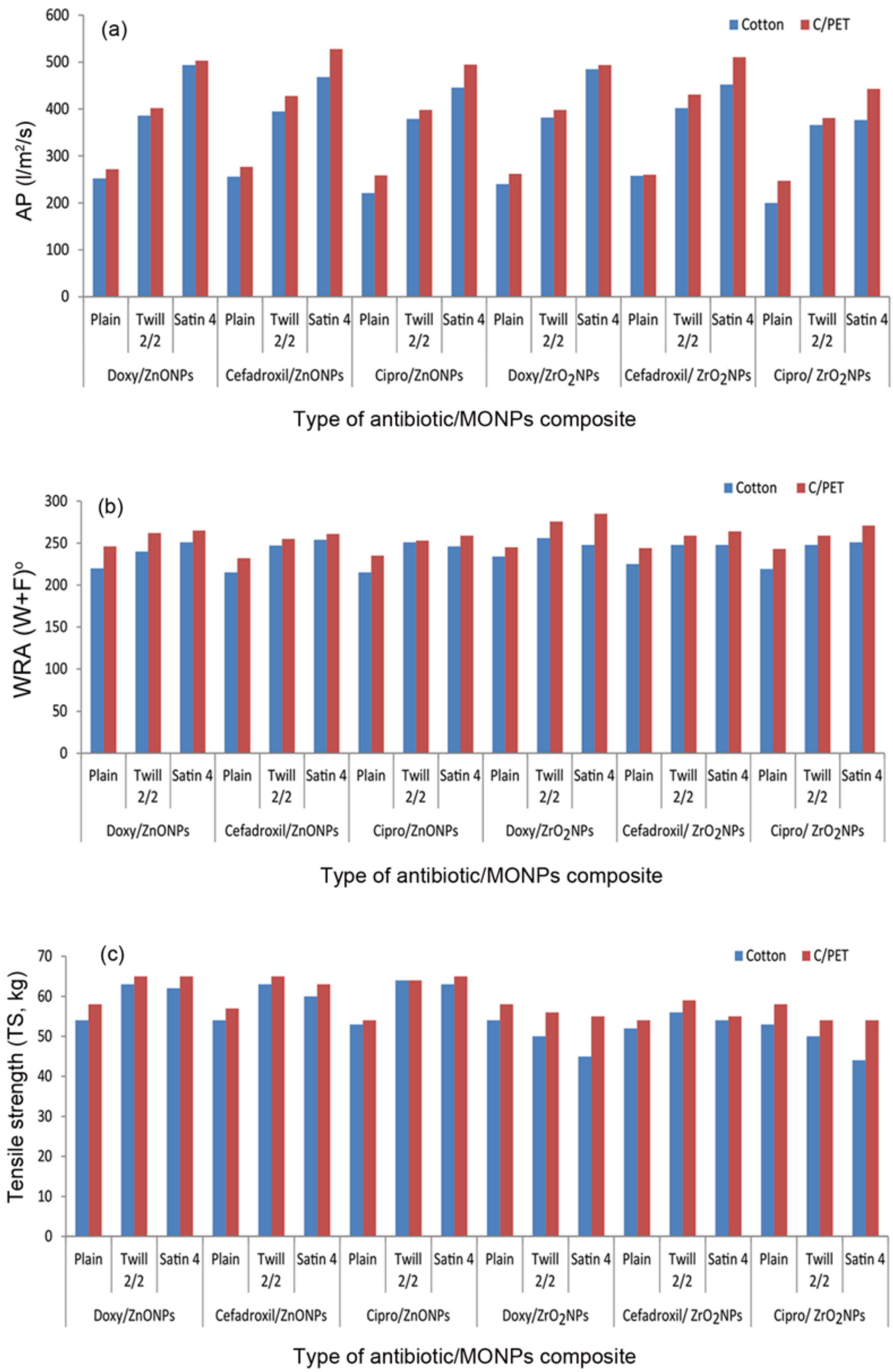


Figure 10. Effect of antibiotic/MONPs composites types on performance properties of treated fabric samples; (a) AP: air permeability, (b) WRA (W+F)^{o}: wrinkle recovery angle (warp+weft), and (c) TS: tensile strength. *Footnote*: Finishing formulation: CA (25 g/*l*), SHP (12.5 g/*l*), antibiotic (1 % w/v), MONPs antibiotic (1 % w/v), Wet pick-up (80 %), drying at 100 ^{o}C/3 min, thermofixation at 160 ºC/2 min.

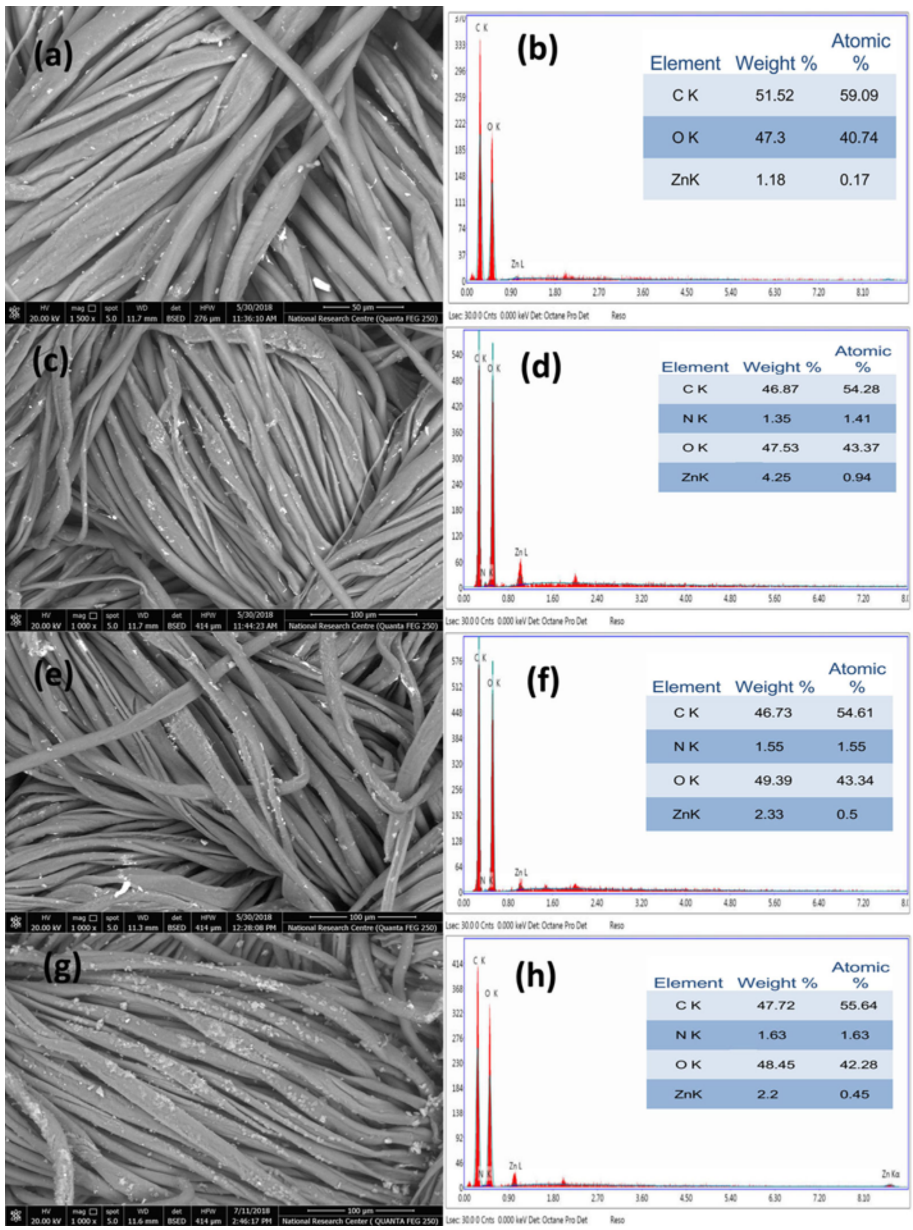


Figure 11. SEM images and EDX spectra of treated cotton/polyester fabric samples with ZnONPs (a, b), doxymycin/ZnONPs (c, d) cefadroxil/ZnONPs (e, f), and ciprofloxacin (g, h).

antibacterial functionality compared with the coated twill fabric samples. This can be attributed to that the surface area of plain coated fabric is higher which in turn enhanced their antibacterial functionality. On the other hand, satin 4 samples showed the lowest antibacterial activity which may be due to decrease in the extent of ester-crosslinking onto/into the fabric structure, therefore lowering the loading and fixation of active ingredients, i.e. antibiotic and MONPs onto/within the fabric structure.

Regarding performance and physical properties, the obtained results showed that the wrinkle recovery angle WRA improved while air permeability decreased according to the type of weave and followed the decreasing order: satin 4 > twill 2/2 > plain 1/1. On the other hand, the decrease in the tensile strength showed the following order: satin 4 > twill 2/2 > plain 1/1 > untreated, most probably due to the number of fibers interlacement points.

Durability to Wash

Table 2 presents the effect of repeated washing cycles on antibacterial activity and performance properties of selected coated plain weave fabric samples. The obtained results

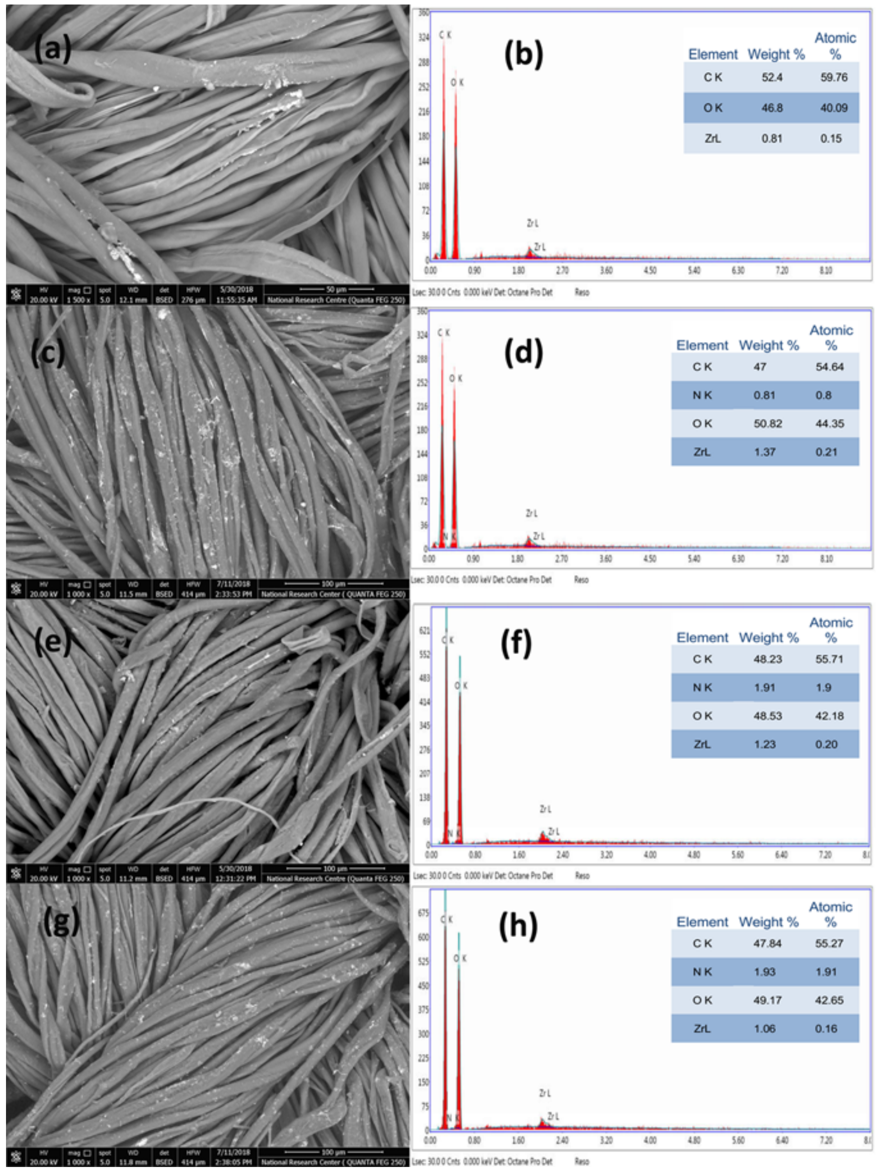


Figure 12. SEM images and EDX spectra of treated cotton/polyester fabric samples with ZrO_2NPs (a, b), doxymycin/ZrO_2NPs (c, d) cefadroxil/ZrO_2NPs (e, f), and ciprofloxacin (g, h).

Table 2. Effect of repeated washing cycles on antibacterial functionality and performance properties of selected coated fabric samples

Type of antibiotic/ MONPs composite	Type of substrate (at weft direction)	Washing cycles	Antibacterial activity (ZI, mm)		AP ($l/m^2/s$)	WRA $(W+F)^o$
			G+ve	G-ve		
Doxy/ZnONPs	Cotton	1	26.0	23.5	252	220
		15	24.5	21.5	260	210
	Cotton/PET	1	24.0	21.5	277	246
		15	18.0	15.5	286	238
Doxy/ZrO_2NPs	Cotton	1	24.0	21.0	240	234
		15	22.0	18.0	248	225
	Cotton/PET	1	18.0	16.0	262	245
		15	15.5	13.5	275	238

signified that the increment of washing cycles up to 15 showed a trivial decrease in antibacterial and anti-crease properties along with improve in air permeability which confirmed the durable fixation and binding of doxymycin/ZnONPs onto the coated substrates. The variation in the tested properties can be due to the partial removal of unfixed or entrapped of active ingredients, i.e. doxymycin and MONPs from the fabric surface. Moreover, the variation in the antibacterial functionality and performance properties from one wash cycle to 15 washing cycles is ruled by the type of substrate, the extent of distribution and fixation of antibiotic/MONPs composite onto the coated substrate.

Conclusion

In this work, durable antimicrobial functionalization of cotton polyester blended fabrics with proper performance and physical properties was successfully achieved by coating cotton/polyester fabrics having different type of weave namely plain, twill 2/2 and satin 4 by antibiotics and MONPs individually and combined in presence of CA as a crosslinking agent and SHP as a catalyst with the aid of sonication, followed by drying and curing at 100 ^{o}C/3 min and 160 ^{o}C/2 min respectively. The results obtained signified that the antibacterial activity improved significantly and followed the decreasing order: antibiotic/MONPs > antibiotic > MONPs > CA/SHP. Among the used composites, doxymycin/ZnONPs showed the highest antibacterial efficiency. The variation in the performance and physical properties was governed by the type of substrate, type of weave, and type of composites as well as the extent of fixation of the nominated active ingredients onto/into the fabric structure. Among the used substrate, plain weave Cotton/polyester with cotton fibers at the weft direction was the most proper candidate for this treatment.

References

1. M. Mahbubul Bashar and M. A. Khan, *J. Polym. Environ.*, **21**, 181 (2013).
2. N. A. Ibrahim in "Handbook of Textile and Industrial Dyeing" (M. Clark Ed.), p.148, Woodhead Publishing, UK, 2011.
3. N. A. Ibrahim, B. M. Eid, M. A. Youssef, H. M. Ibrahim, H. A. Ameen, and A. M. Salah, *Carbohydr. Polym.*, **97**, 783 (2013).
4. T. Harifi and M. Montazer, *Carbohydr. Polym.*, **88**, 1125 (2012).
5. Y. Gao and R. Cranston, *Text. Res. J.*, **78**, 60 (2008).
6. N. A. Ibrahim, B. Eid, E. A. El-Aziz, T. M. Abou Elmaaty, and S. M. Ramadan, *RSC Adv.*, **7**, 33219 (2017).
7. N. A. Ibrahim, N. M. Abdel Moneim, E. S. Abdel Halim, and M. M. Hosni, *J. Clean. Prod.*, **16**, 1321 (2008).
8. M.-S. Cao, W.-L. Song, Z.-L. Hou, B. Wen, and J. Yuan, *Carbon*, **48**, 788 (2010).
9. S. M. Abo El-Ola, *Polym.-Plast. Technol. Eng.*, **46**, 831 (2007).
10. N. A. Ibrahim, B. M. Eid, M. M. Hashem, R. Refai, and M. El-Hossamy, *J. Ind. Text.*, **39**, 233 (2010).
11. N. A. Ibrahim, B. M. Eid, and M. S. Abdel-Aziz, *Appl. Surf. Sci.*, **392**, 1126 (2017).
12. N. A. Ibrahim and B. M. Eid in "Handbook of Sustainable Polymers: Processing and Applications" (V. K. Thakur and M. K. Thakur Eds.), p.215, Pan Stanford, USA, 2016.
13. N. A. Ibrahim, A. A. Aly, and M. Gouda, *J. Ind. Text.*, **37**, 203 (2008).
14. N. A. Ibrahim, A. R. El-Gamal, M. Gouda, and F. Mahrous, *Carbohydr. Polym.*, **82**, 1205 (2010).
15. N. A. Ibrahim, N. A. Abd El-Ghany, B. M. Eid, and E. M. Mabrouk, *Int. J. Biol. Macromol.*, **111**, 526 (2018).
16. N. A. Ibrahim, E. M. R. El-Zairy, and B. M. Eid, *J. Text. Inst.*, **108**, 1406 (2017).
17. N. A. Ibrahim, M. H. Abo-Shosha, M. A. Gaffar, A. M. Elshafei, and O. M. Abdel-Fatah, *Polym.-Plast. Technol. Eng.*, **45**, 719 (2006).
18. N. A. Ibrahim and B. M. Eid in "Handbook of Composites from Renewable Materials, Volume 3: Physico-Chemical and Mechanical Characterization" (V. K. Thakur, M. K. Thakur, and M. R. Kessler Eds.), p.103, Wiley Scrivener, USA, 2017.
19. N. A. Ibrahim, B. M. Eid, E. A. El-Aziz, T. M. A. Elmaaty, and S. M. Ramadan, *Int. J. Biol. Macromol*., **105**, 769 (2017).
20. N. A. Ibrahim, B. M. Eid, and H. El-Batal, *Carbohydr. Polym.*, **87**, 744 (2012).
21. N. A. Ibrahim, B. M. Eid, M. S. Abdel Aziz, S. M. Hamdy, and S. E. Abd Allah, *Cellulose*, **25**, 6207 (2018).
22. N. A. Ibrahim, B. M. Eid, and M. S. Abdel-Aziz, *Appl. Surf. Sci.*, **389**, 118 (2016).
23. N. A. Ibrahim in "Nanotechnology in Diagnosis, Treatment and Prophylaxis of Infectious Diseases" (M. Rai and K. Kon Eds.), p.191, Elsevier Publisher, UK, 2015.
24. M. Shateri-Khalilabad and M. E. Yazdanshenas, *Text. Res. J.*, **83**, 993 (2013).
25. N. A. Ibrahim, A. A. Aly, B. M. Eid, and H. M. Fahmy, *Fiber. Polym.*, **19**, 2298 (2018).
26. Y.-Q. Kang, M.-S. Cao, J. Yuan, L. Zhang, B. Wen, and X.-Y. Fang, *J. Alloy Compd.*, **495**, 254 (2010).
27. A. I. Vogel, "Elementary Practical Inorganic Chemistry", Longman, London, 1975.
28. M. M. A. El-Hady, A. Farouk, and S. Sharaf, *Carbohydr. Polym.*, **92**, 400 (2013).
29. M. Umair, T. Hussain, K. Shaker, Y. Nawab, M. Maqsood, and M. Jabbar, *J. Text. Inst.*, **107**, 596 (2016).
30. E. Tastan, M. Akgun, A. Gurarda, and S. Omeroglu, *IOP Conf. Ser.: Mater. Sci. Eng.*, **254**, 182014 (2017).
31. Y. Wang and D. Zhao, *J. Ind. Text.*, **35**, 239 (2006).
32. R. Dastjerdi and M. Montazer, *Colloids Surf. B.*, **79**, 5

(2010).
33. W. He, H.-K. Kim, W. G. Wamer, D. Melka, J. H. Callahan, and J.-J. Yin, *J. Amer. Chem. Soc.*, **136**, 750 (2014).
34. G. Applerot, A. Lipovsky, R. Dror, N. Perkas, Y. Nitzan, R. Lubart, and A. Gedanken, *Adv. Funct. Mater.*, **19**, 842 (2009).
35. M. Hashem, S. Sharaf, M. M. Abd El-Hady, and A. Hebeish, *Carbohydr. Polym.*, **95**, 421 (2013).
36. G. Duan, C. Zhang, A. Li, X. Yang, L. Lu, and X. Wang, *Nanoscale Res. Lett.*, **3**, 118 (2008).
37. Y.-L. Lam, C.-W. Kan, and C.-W. M. Yuen, *Text. Progr.*, **44**, 175 (2012).
38. I. Chopra and M. Roberts, *Microbiology and Molecular Biology Reviews : MMBR*, **65**, 232 (2001).
39. H. F. O. Silva, K. M. G. Lima, M. B. Cardoso, J. F. A. Oliveira, M. C. N. Melo, C. Sant'Anna, M. Eugênio, and L. H. S. Gasparotto, *RSC Adv.*, **5**, 66886 (2015).
40. R. E. Buck and K. E. Price, *Antimicrob. Agents Chemother.,* **11**, 324 (1977).
41. B. A. de Marco and H. R. N. Salgado, *J. Phys. Chem.*, **6**, 67 (2016).
42. M. LeBel, *Pharmacother. J. Human Pharmacol. Drug Ther.*, **8**, 3 (1988).
43. K. Aithal, N. Udupa, B. Varma, and R. Kurian, *Indian J. Dent. Res.*, **6**, 123 (1995).
44. K. Muthu, K. Gunasekaran, A. Kala, P. Govindasamy, P. Rajesh, and P. Moorthi, *Int. J. Curr. Microbiol. Appl. Sci.*, **4**, 211 (2015).
45. S. Durgapal, S. Mukhopadhyay, and L. Goswami, *Int. J. Appl. Pharm.*, **9**, 1 (2017).
46. C. Gu and K. G. Karthikeyan, *Environ. Sci. Technol.*, **39**, 2660 (2005).