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Eco-friendly Dual-Functional Textiles: Green Water-Repellent & Anti-Bacterial

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Abstract: Water repellent and antibacterial property of Carnauba wax nanoparticles (CWNs) and Zinc oxide (ZnO) nanoparticles has been assessed on the Cotton, Cotton/nylon6 and Nylon6 fabrics using layer by layer (LBL) self-assembly method. Carnauba wax is synthesized into nanoparticle by solvent-free emulsion and melt-dispersion techniques. The prepared particles are cubical in shape, the particle size is less than 150 nm and ζ-potential of -16.6 mV is measured. Plasma treatment was used in order to functionalization of fabric's surface. ZnO was chosen as a positive charge component to create carnauba/ZnO bilayers on fabrics. The results clearly show that the plasma treatment improves the function ability of fabrics and make the suitable substrate to absorb CWNs/ZnO bilayers. The significant water-repellent property was obtained via depositing of four bilayers on fabrics. Antibacterial activities toward Gram-positive as well as Gram-negative bacterial strains were confirmed because of the presence of ZnO on fabrics.

Keywords: Carnauba wax, Zinc oxide, Water-repellent, Anti-bacterial, Layer-by-layer self-assembly method

Introduction

Protection against environmental factors such as water and microorganism is some of the purposes of multifunctional textiles. Water maintain in spherical shape without spreading onto the water-repellent textiles, but after a long time of contact or with a high-pressure, water can be absorb by textiles [1]. The main approach to obtain these textiles is the use of finishing agents with low superficial tension in relation to water. Low-surface-energy materials such as fatty acids, fluorinated compounds, silicon based compound or higher alkanes is the conventional finishing agents to prepare water-repellent textiles [2]. Among the mentioned materials, fluorinated compounds (Fluorocarbons, FCs) are exciting technology to produce commercially textiles [3]. However, they have a huge environmentally concern. Fluorinated hydrocarbon compounds can degrade into shorter fluoroalkanes that bio-accumulate in living organisms [4].

On the other hand, according to the Wenzel and Cassie-Baxter theories, super hydrophobic surfaces require low surface tensions and sufficiently rough surfaces [5,6]. Natural surfaces like the lotus or carnauba palm leaves show water-repellent properties have obtained from the rough structure of a surface combined with a low surface energy. These leaves are chemically made of wax and structurally have micro and nano-scale roughness that enables the trapping of air underneath water droplets and so super hydrophobic surface were produced [7].

Although lotus as a natural water-repellent surface is well known but there is not considerable research about textile inspired by carnauba palm effect.

Carnauba wax, produced from Brazilian palm tree Copernicia cerifera, is a substance commonly used as coating in food, confectionery and cosmetic industries [8]. In hot weather, the plant with broad fan-like leaves secretes wax to protect the leaves from damage. People, who want to collect the wax, dry the leaves and then beat them to dislodge the yellowish to brown coating. The wax is refined and bleached before it is used. It contains mainly esters of fatty acids (80-85 %), fatty alcohols (10-15 %), acids (3-6 %) and hydrocarbons (1-3 %). Carnauba wax is insoluble in water and soluble in organic solvents like ethyl acetate and chloroform. This means that it is highly durable. It can make something waterproof and wear resistant. Its melting point is between 78-88 ^{o}C and the relative density is about 0.97 [9].

Plasma treatment was used in order to functionalization of fiber's surface. The oxidation of the fiber's surface and the generation of free radicals and edging of the surface are the most probable reactions to be achieved by plasma treatments [10]. In this regard, plasma pretreatment is a possible method to enhance the fiber affinity to accept chemicals. If the surface of fibers are free from contamination, the polymer can react with oxygen atoms which will from carbonyl, carboxyl or hydroxyl functional groups of substrate and so the polymer surface has been chemically functionalized [11]. Plasma treatment changes the outer layer of material without interfering with the bulk properties. Therefore, the inherent physical properties of fibers do not change during plasma pretreatment.

In the present research, to achieve a water repellent textile, natural based nanometer-sized particles were used to prepare the roughness with low-surface energy on fabric. The novelty of our investigation was to develop the natural-based double-purpose fabrics, which would water-repellent and protect the skin from the bacteria at the same time. In summary, the research includes following steps:

1. Carnauba wax nanoparticles (CWN) were prepared by an organic solvent free emulsion/melt dispersion method.
2. Characterization of CWNs via scanning electron

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microscopy (SEM) and dynamic light scattering (DLS) methods.
3. Pretreatment of cotton, cotton/PA6 and PA6 fabrics via low temperature plasma (LTP) method.
4. Finishing of fabrics via layer-by-layer (LBL) method.
5. Assessment of different properties of treated fabrics.

Experimental

Materials

Carnauba wax (Carnuabawachs, Kremer Pigmente, Germany) and Tween 80 (DAEJUNG, Korea) were used as the main ingredient and water-soluble surfactant, respectively. Zinc oxide nano powder (98 % purity, particle size 20-30 nm, VCN materials, Iran), sodium hydroxide (Merck, Germany) were used in LBL finishing process. All chemicals and materials were used as received.

Cotton, Nylon 6/Cotton (50:50) and Nylon 6 fabrics were purchased from Yazdbaf and Tehran Zarnakh companies (IRAN), respectively. Adrasil HP (P-836, ADRASA, Spain) was used as a nonionic detergent for pretreatment process of fabrics.

Experimental

Preparation of Carnauba Wax Nanoparticles (CWNs)

CWNs were prepared by an organic solvent free method [9]. In a typical experiment, 0.3 g of Carnauba wax was heated above its melting temperature (90 °C) in a water bath. Tween 80 with high hydrophilic-lipophilic balance (HLB=15) was introduced into 10 m*l* water (90 °C) under magnetic stirring for 2 min. Surfactant mixture was added to the molten Carnauba under magnetic stirring at 90 °C until the white mixture was obtained. The mixture was sonicated in a sonication bath (SIGMA SONIC C5-100-28, Behin Tamin Ahura Co., Iran) for 4 min at 30 KHz frequency and 100 W power to form the emulsion. The prepared emulsion was poured into 100 m*l* of cooled water (2-5 °C) under mild magnetic stirring at ambient temperature for 3 min to promote the solidification of lipid nanoparticles and the mixture was homogenized by Ultrasonic Homogenizer (FAPAN Co. Ltd., Iran), at 45 % amplitude (20 W) in a pulse regime (10 s on-5 s off) during 60 s. A centrifuge (PROLABO, France) was used to separate extra water to achieve a more concentrated CWN suspension (at 6000 rpm, 4 times during 15 min).

Pretreatment of Fabrics

Washing Process

Before any further treatment, all kinds of fabrics were washed in an aqueous solution containing 2 g/*l* of nonionic surfactant, Adrasil HP, with liquor to goods ratio of 1:25 for 45 min at 60 °C. After washing, the samples were rinsed twice in distilled water and dried at room temperature for 24 h.

Low Temperature Plasma (LTP) Pretreatment of Fabrics

In this research, Cotton, Cotton/Nylon 6 and Nylon 6 were plasma treated with O_2 gas. In this regard, fabrics were cut to the require dimensions for each experiment. The Plasma-Tex (atmospheric plasma machine, Adeeco Company, Iran) at frequency 25 kHz, Power 2.5 kW and speed 1 m/min was used for six-repeated treatment. After treatment, the specimens were sealed in bag at ambient temperature before any subsequent operation.

Layer-by-layer (LBL) Self-assembly Finishing of Fabrics

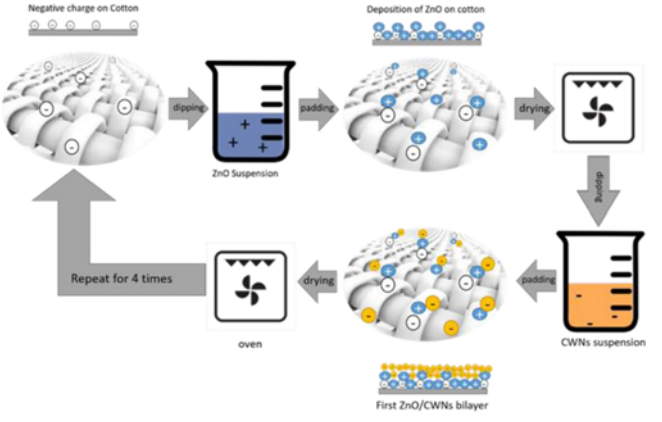
The fibers with positive charge can attract negative charge compound such as CWNs. So the ZnO nanoparticles were used as positive charge material.

The suspension of ZnO was prepared freshly before each experiment by directly adding ZnO nano powder into pure water and then was dispersed by ultra-sonication (at 45 % amplitude (20 W) in a pulse regime (10 s on-5 s off) for 10 minutes. ZnO nanoparticles have positive zeta potential when the pH of suspension is between 6.4 to 9.4 and have the most positive charge around pH 8.3 [12]. In this regard, the pH of suspension was adjusted by NaOH solution to achieve to pH 8.

LBL procedure was carried out according to the Scheme 1.

The plasma treated cotton fabrics were alternately dipped into a 4 % OWF (on weight of fabric) ZnO suspension and 4 % (OWF) CWNs solution for 5 min at room temperature. The samples were padded (100 % pick up) after each dipping procedure and dried in an oven (70 °C, 15 min). Then samples were immersed in the oppositely charged solution to make one bilayer of ZnO/CWNs on fabric every time. This process sequence was repeated for the deposition of five ZnO/CWNs bilayers on each fabric.

Activation of functional groups of polyamide on Nylon 6 and Cotton/Nylon 6 fabrics was done by decreasing the pH under the isoelectric point of polyamide [13]. In this regard, Nylon 6 and Cotton/Nylon 6 fabrics were immersed in HCl



Schematic 1. LBL method for finishing of CWNs/ZnO bilayers on fabrics.

(0.1 N, pH=3.5) for 5 minutes and then dried in 60 °C for 15 min and after that, LBL process was continued by immersing the fabric in CWNs and ZnO solutions according to Schematic 1.

Characterization

Characterization of CWNs

Dynamic light scattering (DLS, VASCO2, CORDOUAN, France) was used for evaluation of the average of particle size, polydispersity index (PI) and Zeta potential of CWNs. Morphology of CWNs was evaluated by scanning electron microscopy (SEM) technique (AIS2100, SERONTECH-NOLOGIES, Korea). One drop of 20-fold-diluted CWNs suspension was placed on a coverslip and dried at room temperature and was used for SEM analysis.

Characterization of the Treated Fabrics

The morphology of the fabric samples (untreated, plasma treated and CWNs/ZnO treated fabrics) were determined by SEM.

Contact angles were measured with the sessile drop technique. Droplets of deionized water were dropped from a height of 6 mm above the sample and it was video recorded for 30 seconds. The contact angles at the beginning and after 30 seconds were evaluated. For each sample, three fabrics were tested with two drops on each fabric; 6 drops in total were evaluated. The volume of the droplets was set to 11 μl [14].

To measure the efficacy of antibacterial textiles, AATCC 100-2004 standard was used. *E.coli* and *A.aureus* as gram-negative and gram-positive bacteria were grown in liquid culture. The concentration of the microorganism was standardized and the microbial culture was diluted in a sterile nutritive solution. The control and test fabric swatches were inoculated with microorganisms. The inoculation was performed such that the microbial suspension touches only the fabric. Bacteria levels on both control and test fabrics were determined at "time zero" by elution in a large volume of neutralizing broth, followed by dilution and plating. A control was run to verify that the neutralization/elution method effectively neutralizes the antimicrobial agent in the fabric. Additional inoculated control and test fabrics were allowed to incubate, undisturbed in sealed jars, for 24 hours. After incubation, microbial concentrations were determined. Reduction of microorganisms relative to initial concentrations and the control fabric was calculated (equation (1)).

$$R(\%) = \frac{B-A}{B} \times 100 \quad (1)$$

where, R is percentage of reduction, A is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over desired contact period. B is the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation (at 0 contact time) [15].

Results and Discussion

Characterization of CWNs

Due to the lipophilic characteristic, higher melting point (87 °C) than other natural waxes and lower surface tension (32 dynes/cm) of Carnauba wax than water, solid nanoparticles of Carnauba are well suitable compound for preparation of water repellent surface [9]. In this research, for the first time, this property of Carnauba wax was used to create water-repellent textiles.

The solvent free emulsion/melt dispersion method has been modified in this study in order to access submicron size Carnauba wax particles. The ultra-sonication, surfactant and cold-water volume are the effective parameters in the synthesis of CWNs. Using of high shear stress during the sonication in both emulsification steps; the possibility of making small droplets by surfactants is increased.

Introducing of the warm emulsion into the cold water with temperature about 2 °C is promoted the lipid recrystallization and precipitation of solidified CWNs. When the warm emulsion is added to the cold water at once, the cooling process accelerate and the smaller nanoparticles are obtained and because of the presence of surfactant, newly formed particles have no enough time to accumulate and form the large particles [16].

Figure 1 depicts the SEM image of CWNs. It can be seen that, the prepared particles are cubical in shape and the mean diameter of particles calculated by Microstructure Distance Measurement Software is less than 150 nm. The prepared CWNs dispersion tested by DLS method had a PDI value less than 0.2 indications a relatively homogeneous distribution of particles and the Z-average of 139.22 nm which confirmed the results obtained from SEM.

Zeta potential is the potential difference between the mobile dispersion medium and the stationary layer of the dispersion medium attached to the dispersed particle [17]. A dispersion of CWNs was produces from pure wax and water in presence of Tween 80 as emulsifier. The initial pH of the

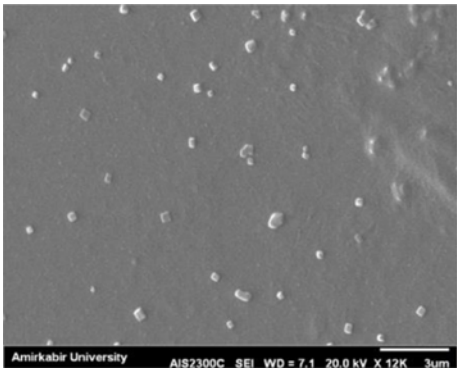


Figure 1. SEM micrograph of CWNs after 10 times dilution with distilled water.

dispersion was in the acidic range (pH=4.5) at which a ζ-potential of -16.6 mV was measured. This negative charge of CWNs provided electrostatic repulsion and stabilized the dispersion. Dissociation of acidic groups on the surface of CWNs will give rise to negatively charged surface.

Characterization of the Plasma Treated Fabrics

Modification of fabric surface is a way to acceleration the concentration of functional groups [10]. Use of oxygen in plasma treatment is proven to enhance wettability of textile materials [18]. Under the plasma condition, the oxygen plasma species can be produced as follows:

· Ion and electron formation

$$e^- + O_2 \rightarrow O_2^+ + 2e^- \quad (2)$$

· Atom and radical formation

$$e^- + O_2 \rightarrow O + O \quad (3)$$

· Generation of heat and light

$$e^- + O_2 \rightarrow O_2^{\cdot} + 2e^-$$

$$O_2^{\cdot} \rightarrow hv$$

$$e^- + O \rightarrow O^{\cdot} \quad (4)$$

· Generation of oxygen radical [19].

$$O^{\cdot} \rightarrow hv \quad (5)$$

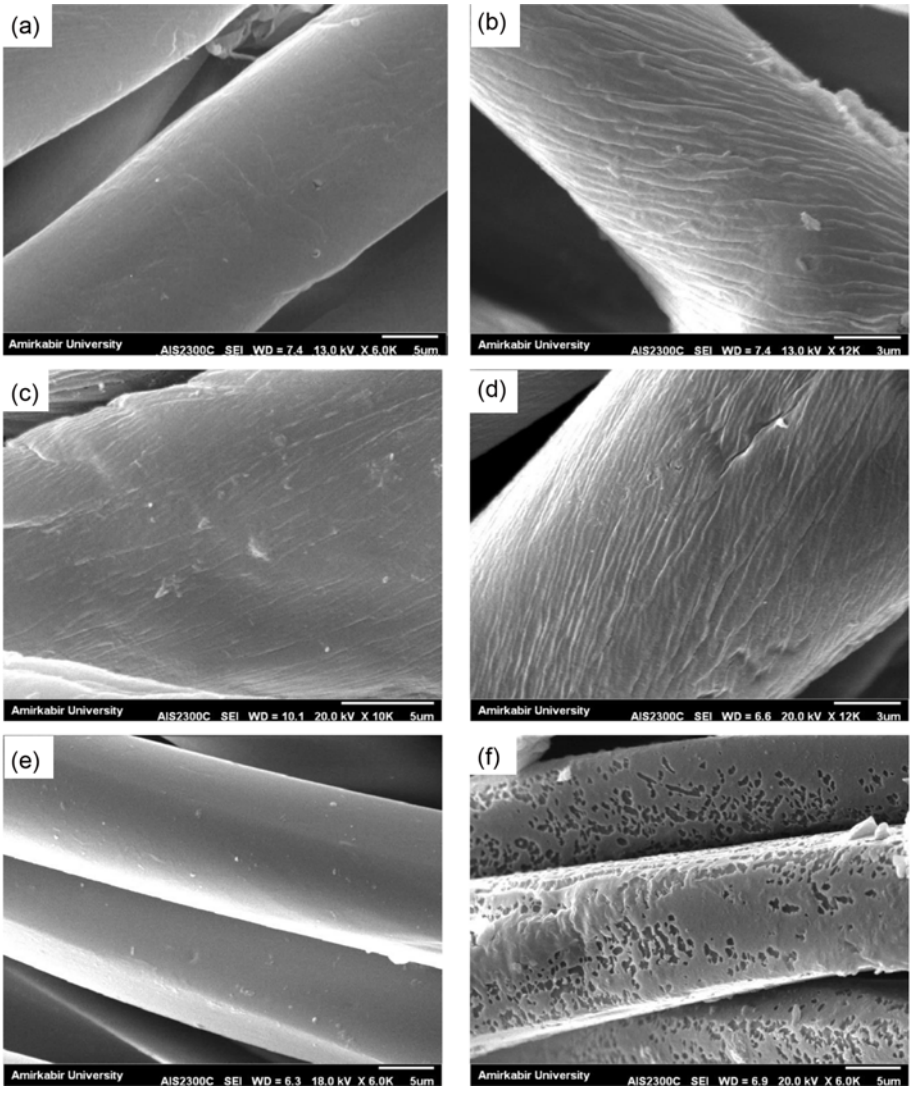


Figure 2. Untreated Cotton (a), plasma treated Cotton (b), untreated Cotton/Nylon 6 (c), plasma treated Cotton/Nylon 6 (d), untreated Nylon 6 (e) and plasma treated Nylon 6 (f) fabrics.

$O_2^{\cdot}, O^{\cdot}$ are excited states of O_2 and O and they are active plasma species in the atmospheric plasma treatment. The interaction of the active plasma species with Cotton and Nylon 6 surfaces, involves several electron-mediated processes and etching the surface. Some of these reactions can promote homolytic bond cleavages and lead to the formation of free-radical sites and a variety of functionalization mechanisms. Free radical sites contain unpaired electrons, which are not involved in chemical bonding, so they are extremely unstable and reactive [11].

The morphological change on the surface of Cotton, Cotton/Nylon 6 and Nylon 6 fabrics was assessed by SEM images before and after plasma treatment (Figure 2). It can be seen that plasma affects the degree of etching. The untreated fabrics are smoother and the plasma treated fabric show a dense population of grooves and slits.

Characterization LBL Treated Fabrics with CWNs

The plasma treated Cotton, Cotton/Nylon 6 and Nylon 6 fabrics were treated by LBL method according to the Schematic 1. In order to assessment, SEM images were obtained from the treated fabrics. As can be shown in Figure 3, grooves and slits, which are created during plasma pretreatment, were filled by CWNs and ZnO nanoparticles and the coating is remain even after washing procedure.

In order to assess water repellent properties of the treated fabrics, water contact angle were measured with the sessile drop technique and is reported in Table 1. As expected, due to low surface energy of carnauba wax (32 dynes/cm) [20], water droplets placed on the fabric surface with the large contact angle, which indicates the hydrophobic nature of fabrics after finishing during 30 sec and even after washing procedure. For all three types of the treated samples, the

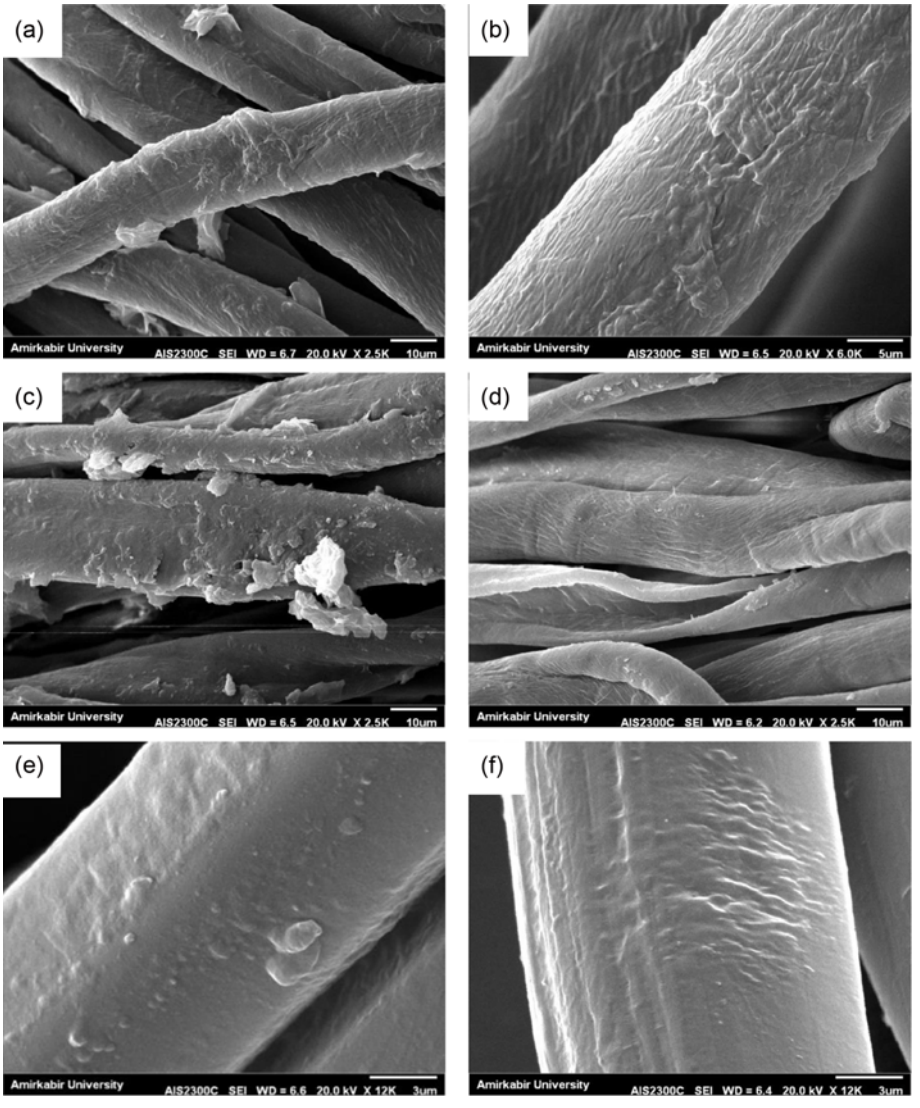


Figure 3. Treated Cotton (a), Cotton/Nylon 6 (b) and Nylon 6 (c) fabrics via LBL method and treated Cotton (d), Cotton/Nylon 6 (e) and Nylon 6 (f) fabrics after washing.

Table 1. Contact angles of different fabric sample against water as the wetting medium

Sample		Averaged contact angle (°)	
		0 sec	30 sec
Cotton	Untreated	45.36	0
	Treated with CWNs	128.3	131.2
	After washing	108.5	103.2
Cotton/ Nylon 6	Untreated	141.6	48.7
	Treated with CWNs	136.1	133.5
	After washing	125.7	124.8
Nylon 6	Untreated	128.6	77.3
	Treated with CWNs	113.63	111.6
	After washing	107.9	105.1

drop of water stayed on the surface of the fabric for more than three minutes without spreading.

The treated fabrics with CWNs/ZnO bilayers were investigated according to AATCC 100-2004 standard for antibacterial activity against *S. aureus* and *E. coli* as gram-positive and gram-negative bacteria, respectively. ZnO nanoparticles were used as bonding agent and a positive charge carrier in bilayer formation in LBL method. As can be seen in Table 2, Zinc oxide in addition to participate in development of CWNs/ZnO bilayers on fabrics, has been effective in creation of antibacterial effect as well.

Surface negative charges on the bacterial cells are due to the ionized carboxylic, phosphate and amino groups and play an effective role in the association of the ZnO nanoparticles to the bacterial surface. The negative charge of bacteria cell wall are trapped by ZnO nanoparticles with a positively charged hole (h+). The trapped ZnO nanoparticles produce reactive oxygenated species (ROS) that cause to the damage to bacterial cell structure [21].

Conclusion

In the present study, the Cotton, Cotton/Nylon 6 and Nylon 6 fabrics are treated after atmospheric plasma with Carnauba wax nanoparticles/ZnO via LBL method. The method used to produce Carnauba wax nanoparticles is solvent-free and completely environmentally friendly. The water repellent and antibacterial properties of fabrics increase, which are attributed to attach Carnauba wax nanoparticles and ZnO on the surface and due to formation of CWNs/ZnO bilayers. The significant change in surface morphology of fabrics after plasma and LBL treatments are observed in SEM, which clearly reveals the dense population of grooves and slits on fabrics and the deposition of bilayers in outer layer of fabrics, respectively. Thus, the study clearly indicates that the Carnauba wax has a great potential to make the water-repellent fabrics in environmental-friendly manner and the good antibacterial effect can be obtained as a positive side effect in this novel finishing method.

Acknowledgment

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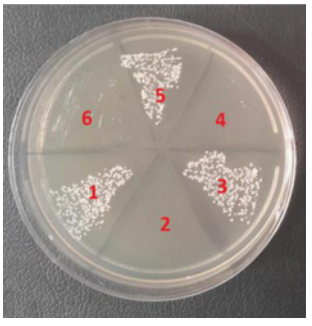
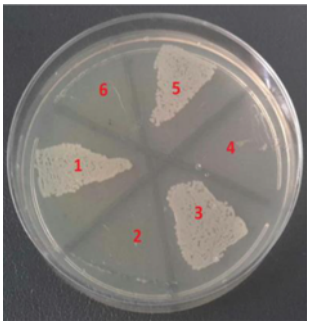
Table 2. Antibacterial activity of the untreated and treated samples with CWNs/ZnO bilayers

	Sample	*S. aureus*		*E. coli*	
		CFU after 24 h	Antibacterial effect (%)	CFU after 24 h	Antibacterial effect (%)
1	Untreated Cotton	5.3×10^5	-	5×10^5	-
2	Treated Cotton	0	100	0	100
3	Untreated Cotton/Nylon 6	5.1×10^5	-	4.8×10^5	-
4	Treated Cotton/Nylon 6	0	100	0	100
5	Untreated Nylon 6	5×10^5	-	4.5×10^5	-
6	Treated Nylon 6	2.3×10^2	99.95	0	100
	Figure				

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