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Simultaneous Synthesis of Nano ZnO and Surface Modification of Polyester Fabric

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Abstract: In this study, synthesis of zinc oxide nanoparticles was carried out along with the hydrolysis of polyester fabric using sodium hydroxide to increase the surface activity and enhance the nanoparticles adsorption. The polyester fabrics were treated with zinc acetate and sodium hydroxide at different bath conditions, ultrasound and stirrer, resulting in formation of ZnO nanospheres and ZnO nanorods. The presence of zinc oxide with different shapes on the surface of the polyester fabrics was confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Also, the X-ray diffraction patterns established the composition of wurtzite structure of zinc oxide. The self-cleaning property of treated polyester fabrics was evaluated through discoloring dye stain under sunlight irradiation. The antibacterial activities of the samples against two common pathogenic bacteria including *Escherichia coli* and *Staphylococcus aureus* were also assessed. The results indicated that the photocatalytic and antibacterial activities of the ultrasound treated polyester fabrics were superior compared to the stirrer treated samples.

Keywords: Zinc oxide, Polyester, Hydrolysis, Ultrasound, Self-cleaning, Antibacterial

Introduction

The self-cleaning coating technology is an innovative strategy for functional finishing of textile [1-3]. Different semiconductors were used for preparation of textile with self-cleaning property. For instance, Karimi *et al*. produced self-cleaning cotton fabrics using nano-TiO_2 [4]. Along the same lines, Behzadnia and colleagues obtained photocatalytic fabrics based on zinc oxide coatings on wool fabrics [5]. Moreover, a chemical coating of cotton with zirconium dioxide nanoparticles with self-cleaning property was reported by Moazami *et al*. [6]. Also, textiles with multiple characteristics can be fabricated through applying the nano-semiconductors. Deposition of the semiconductors like TiO_2, ZnO and ZrO_2 on textiles provides multi-functional properties such as self-cleaning, UV-protection, superhydrophilic, antibacterial, flame retardancy, *etc.* [7-12]. The treated textiles with nano-semiconductors could be used in practical applications such as medical devices, healthcare, wound dressing, military, protective suits, personal care product, clothing and others [13].

Polyester is one of the most widely used versatile polymers owing to its high strength, high modulus, abrasion resistance, heat set stability, light fastness and chemical resistance [14]. However, due to its poor wettability and lack of functional groups, durable functional finishing of polyester fabrics have became concerns of the textile industry. Several studies have reported that surface modification of the polyester could be performed using different pretreatments and techniques such as plasma treatment, hydrolysis and aminolysis [15-17]. The alkaline treatment hydrolysis of the polyester fabric leads to enhance the hydrophilicity and surface reactivity [18]. In this study, synthesis of zinc oxide nanoparticles and alkaline hydrolysis of the polyester fabric were conducted in one step by ultrasound and conventional stirrer methods. The functional polyester fabrics were prepared by applying zinc acetate as a zinc oxide precursor and using sodium hydroxide as both a strong base for synthesis zinc oxide and an agent capable of hydrolysis of polyester surface. The role of the concentrations of zinc acetate and sodium hydroxide over the photocatalytic self-cleaning performance and antibacterial activities of treated fabrics was investigated.

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Experimental

Materials

Plain weave polyester fabric with the fabric weight of 188 g/m^2 was used. Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as a precursor to synthesis ZnO nanostructure and sodium hydroxide (NaOH) were utilized from Merck Co. (Germany). Direct green 6 (CI 30295) was purchased from Alvan Sabet Co. (Iran).

Instrument

An ultrasonic bath Euronda Eurosonic® 4D, 350 W, 50/60 Hz (Italy) was used for synthesis processing. SEM images and EDS patterns were established by Phenom ProX, scanning electron microscope (SEM) (The Netherlands). The standard procedure was followed, in which samples for SEM and EDS analyses were coated with a gold layer before tests to ensure sufficient electrical conductivity and to prevent charging effects. X-ray diffraction was performed on an INEL (model EQuinox 3000) X-ray diffractometer to study the presence and crystalline structure of the nano ZnO on the fabric surface. The patterns were recorded in the diffraction range of 2θ from angle of 10^{o} to 80^{o} with a scanning speed of 2^{o}/min at 2θ step of 0.040^{o}. Cu Kα radiation (λ=1.540 Å) with detector scan mode operating at 40 kV and 30 mA was used to investigate changes in crystalline. The Fourier transform infrared (FT-IR) spectrum was carried out by Bruker FT-IR (Germany) for analysis of the changes that appeared in functional groups on polyester fabrics surface through the alkaline treatment. The fabric bending length was tested on a Shirley Bending Length apparatus (Shirley Developments Limited, England).

Methods

(1) Synthesis of nano ZnO on polyester fabric through conventional stirrer bath:

Different amounts of zinc acetate (1, 2, 3, 4 and 5 % wt.) were dissolved in 100 m*l* distilled water at ambient temperature under vigorous stirring using magnetic stirrer. The sodium hydroxide (1, 2, 3 and 4 % wt.) was slowly added to the aqueous solution of zinc acetate under constant stirring. Next, the fabrics were immersed into the solutions, and the temperature was then increased. The solution was stirred at 85 °C for 60 min. The treated fabrics were dried at 60 °C for 30 min followed by curing at 130 °C for 4 min. Finally, the treated fabrics were washed with distilled water and dried at 70 °C for 24 h.

(2) Synthesis of nano ZnO on polyester fabric through ultrasound bath:

To synthesis of nano zinc oxide particles on the polyester fabric, diverse amount of zinc acetate (1, 2, 3, 4 and 5 % wt.) were used as precursor in 100 m*l* water in the ultrasound bath. The polyester fabrics were immersed into the solutions, and different amounts of sodium hydroxide (1, 2, 3 and 4 % wt.) were added to the bath under ultrasonic irradiation. The solution was irradiated at 65 °C for 45 min. The treated samples were dried at 60 °C for 30 min and then cured at 130 °C for 4 min. At the end, the sonotreated fabrics were washed with distilled water and dried at 70 °C for 24 h.

Test Methods

In order to investigate the self-cleaning properties of treated polyester fabrics, colorant stains were created on the fabrics. The treated polyester fabrics were stained by direct green 6 with concentration of 100 mg/*l* in distilled water. After being stained, the samples exposed to the sunlight (Yazd, Iran) irradiation for 7 consecutive days. The sample colors were measured before and after illumination, and based on their color difference (ΔE^*), their self-cleaning properties were compared. Color coordinates were determined by color measurement software using the CIE L^* a^* b^* color space at D65/10°. In the CIELAB system, color is expressed in terms of CIE L^*, a^* and b^* values, where L^* defines lightness, a^* denotes the red-green value and b^* indicates the yellow-blue value. The total color difference (ΔE^*) was calculated according to equation (1).

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{1}$$

The antibacterial properties of the treated fabrics were measured by AATCC 100-2004 test method against *Escherichia coli* (*E. coli*, ATCC 25922, Gram-negative bacterium) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923, Gram-positive bacterium) as common pathogenic bacterium. Antibacterial activity was expressed in terms of the percentage reduction of the microorganisms and calculated as:

$$\text{Percentage reduction of microorganisms (R)\%} = (A - B)/A \times 100 \tag{2}$$

where, A and B are the number of microorganisms colonies on untreated and treated fabrics, respectively.

There was 3.4×10^5 colony forming units (cfu) of bacteria in the primary inoculum. Saline solution 8.5 g/*l* sodium chloride to 1000 m*l* distilled water was used as the neutralizing solution. Serial dilution of 10-10,000 was made for incubation on agar plate. Tryptic soy agar (Merck, Germany) was applied as the agar.

Fabric stiffness as expressed in terms of bending length was measured according to ASTM D 1388-96 (2002) test method [19]. The bending rigidity of the fabrics was calculated using equation (3).

$$G = M \times (C)^3 \tag{3}$$

where, G is the bending rigidity (mg cm), M fabric weight (mg/cm^2) and C, average bending length (cm).

Also, hydrophilicity of the samples was conducted according to AATCC 79-2000 test method.

Results and Discussion

Characterization

In the preparation method, the ZnO nanostructures were formed after mixing the zinc salt with sodium hydroxide solution [20]. The following reaction may proceed resulting in the nanostructures formation:

$$(Zn(CH_3COO)_2 \cdot 2H_2O) + 2NaOH \rightarrow ZnO + 2NaCH_3COO + H_2O \tag{4}$$

Considering the alkalinity of the process, the alkaline hydrolysis of the polyester fabric occurred along with the ZnO nanostructures synthesis [21].

The surfaces of the treated and untreated polyester fabrics were observed with scanning electron microscopy (SEM). The SEM images of raw polyester (A), polyester treated with zinc oxide at conventional stirrer bath (B-D), and polyester treated with zinc oxide at ultrasound bath (E and F) are presented in Figure 1. While the surface of the raw polyester fabric is smooth, the synthesized ZnO nanoparticles are distributed on the surface of the treated fabrics. Through

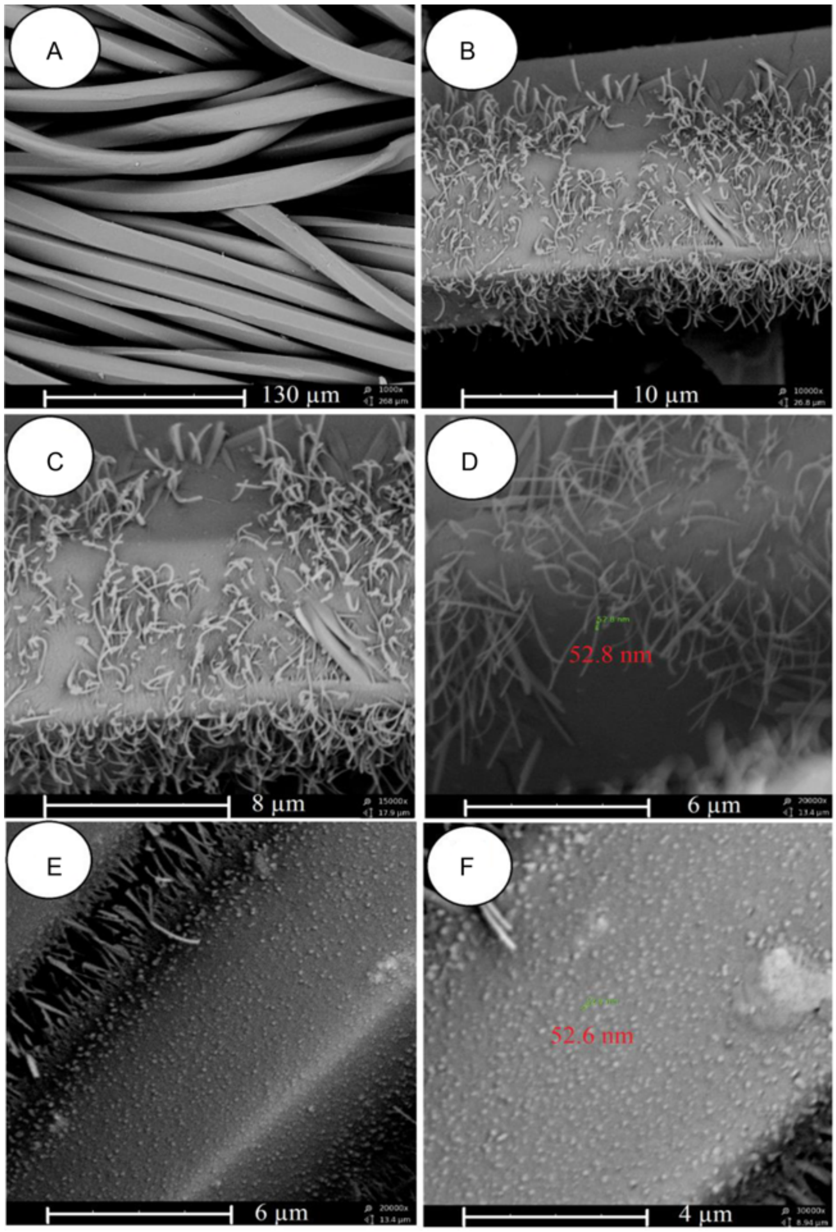

Figure 1. SEM images of various polyester fabrics; (A) raw, (B-D) treated with zinc oxide at conventional stirrer bath, and (E and F) treated with zinc oxide at ultrasound bath. Note the different magnifications for (A) 1 kX, (B) 10 kX, (C) 15 kX, (D) 20 kX, (E) 20 kX, and (F) 30 kX.

finishing treatment at conventional stirrer bath, vertically aligned ZnO nanorods were successfully achieved over the entire polyester surface with an average diameter of 52 nm (Figure 1(B-D)). Also, it is thoroughly possible to recognize the zinc oxide nanoparticles on the surface of polyester fabric treated at ultrasound bath (Figure 1(E)). The sonosynthesized zinc oxide nanoparticles are uniformly spread on the surface of the sample due to the ultrasound irradiation. The images at higher magnification indicate the presence of spherical-shaped particles, with an average size of 52.6 nm (Figure 1(F)).

The successful formation of the zinc oxide nanoparticles on the treated fabrics was verified by the chemical compositions analyzed by EDS. As shown in Figure 2(A) and (B), zinc and oxygen are two elements on the treated samples apart from the carbon that relates to the polyester fabric. As the fabrics were coated by gold layer before SEM observation, Au peaks are also included in the spectra.

XRD patterns were used to confirm the presence of zinc oxide on the fabric surface and to study crystalline status (Figure 3). The peaks at 2θ values of 17^{o}, 23.1^{o}, and 26.4^{o} are the diffraction peaks of the original polyester substrate.

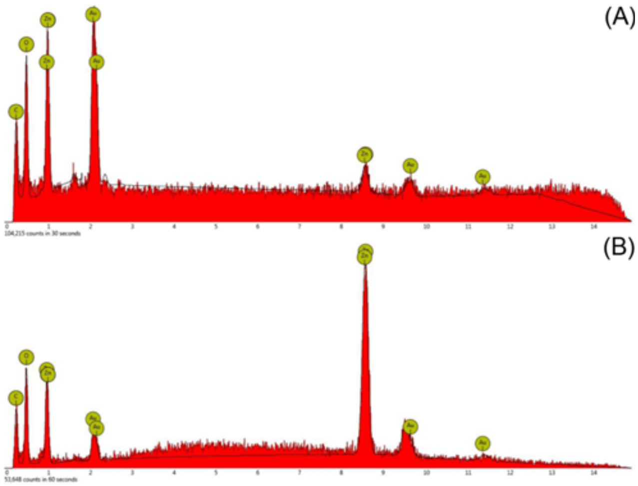

Figure 2. EDS spectra of treated polyester fabric with zinc oxide at (A) stirrer and (B) ultrasound baths.

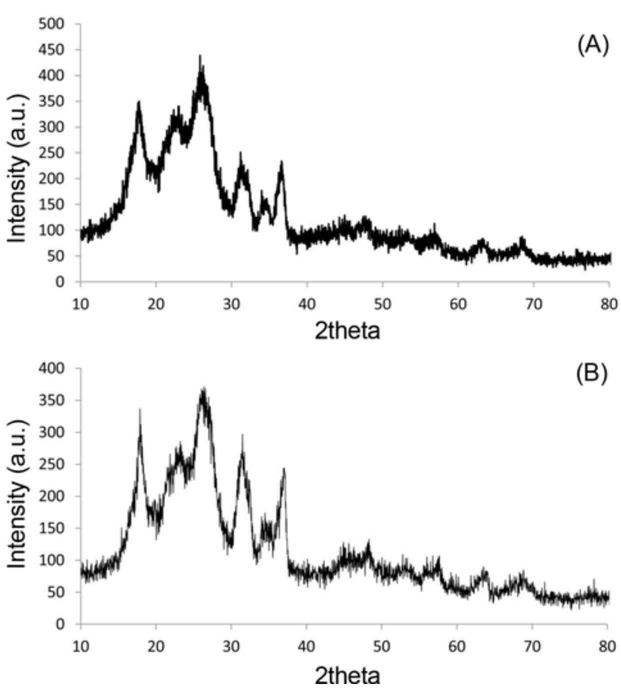

Figure 3. XRD patterns of treated polyester fabric at (A) stirrer and (B) ultrasound baths.

Seven reflection peaks appeared at 2θ values of 31.9 ° (100), 34.6 ° (002), 36.5 ° (101), 47.7 ° (102), 56.8 ° (110), 63.1 ° (103), and 67.1 ° (202) could be indexed as the hexagonal wurtzite structure of ZnO, which were consistent with the values in the standard card (JCPDS 36-1451). Both treated fabrics confirmed the formation of wurtzite zinc oxide phase in the XRD patterns. However, for the conventional treated sample lack of ultrasound irradiation led to appear sharper peaks around polyester crystals due to less loading of nanoparticles on the fabric surface. This may be recognized

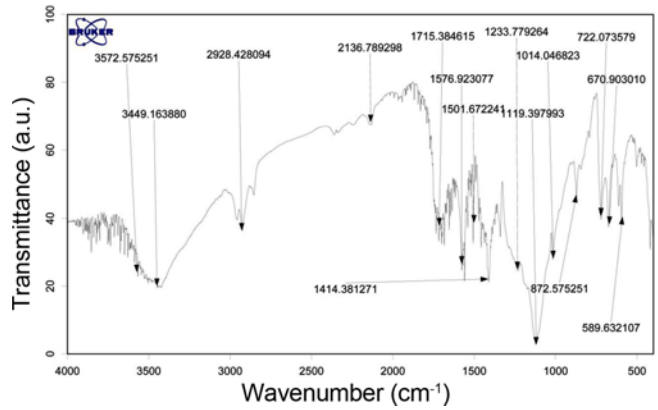

Figure 4. FT-IR spectrum of alkaline treated polyester fabric with sodium hydroxide (4 % wt.) at ultrasound bath.

as coating of polyester with nano ZnO shielding the X-ray beam.

The finishing of polyester fabric with sodium hydroxide is a versatile method for producing hydrophilic groups such as hydroxyl and carboxyl on the surface of the fabric. The effect of alkaline hydrolysis on the chemical properties of polyester fabric was studied by FT-IR spectroscopy (Figure 4). The FTIR spectrum of the treated sample with NaOH indicated the characteristic peaks attributed to C=O (carboxylic acid), C-O (ester acid), C-H (stretching vibration), and C-H (bending vibration) at 1715, 1000-1500, 2928 and 722 cm^{-1}, respectively. Also, the peak at approximately 3450 cm^{-1} confirmed the forming of terminal groups of -OH on the surface of polyester fabric after the alkaline process, which is derived from the interaction of the hydroxide ions with the electron-deficient carbonyl groups [21].

Self-cleaning Performance

The polyester fabrics were stained with direct green 6 dye solution and exposed to sunlight irradiation. The fabric color coordinates was calculated before and after sunlight irradiation, and the self-cleaning performance obtained based on the color difference (ΔE^*). The raw polyester fabrics were not photoactive (ΔE^* in the range of 1-3). As seen in Figure 5 and 6, all the zinc oxide treated fabrics showed higher ΔE^* values arising from photocatalytic activity of ZnO nanoparticles to degrade dye stain. Irradiation of photo-catalyst like ZnO by light with more energy, compared to its band gaps, generates electron-hole pairs that induce redox reactions at the surface of the photocatalyst. Thus, nano ZnO can decompose common organic matters, dye molecules, bacterial cell membranes, etc. [22].

Results show that the amount of self-cleaning for the treated samples is higher when treated at alkaline condition. Increasing the concentration of sodium hydroxide increases the photodegradation of direct green 6. This could be a result of the increase of polar groups such as carboxyl and

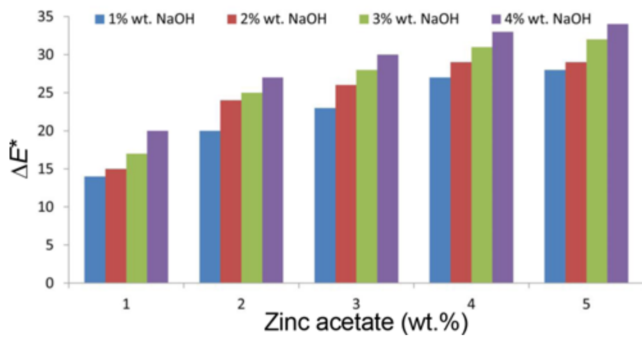

Figure 5. Comparative diagram of self-cleaning performance results of the polyester samples treated at stirrer bath.

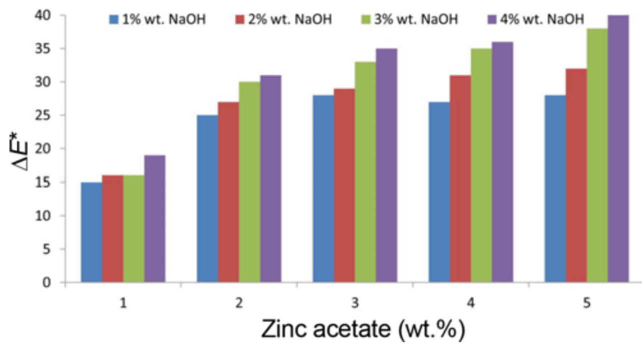

Figure 6. Comparative diagram of self-cleaning performance results of the polyester samples treated at ultrasound bath.

hydroxyl groups on the surface of the fibers, which may favor the adsorption of ZnO nanoparticles on the samples. Also, the increase in the zinc acetate concentration had a tangible effect on the self-cleaning performance of treated polyester fabrics, and the ΔE^* of treated samples increased progressively because of the higher zinc oxide content on the fabric surface. Moreover, the ultrasound treated fabrics confirmed more self-cleaning activity in comparison with stirrer treated samples. Ultrasound irradiation prevents particles from aggregation on the surface of polyester fibers. As seen in SEM images, the distribution of zinc oxide on ultrasound treated sample is more uniform due to using ultrasonic in comparing with conventional treated sample. This may lead to higher photocatalytic activity in terms of self-cleaning.

Antibacterial Assay

Zinc oxide nanoparticles possess unique characteristics such as photocatalytic, electrical, optical, dermatological and antibacterial, which can make it possible to produce a textile with self-cleaning and antibacterial properties. Moreover, zinc oxide is bio-safe and biocompatible for applications in medicine textile [23]. The ZnO treated textile can inhibit the growth of bacteria possibly by two mechanisms. The first important reason is the production and penetration of reactive oxygen species. The hydroxyl radical and hydrogen peroxide can penetrate into the cell membranes which lead to the death of bacteria [24-26]. The second reason is the presence

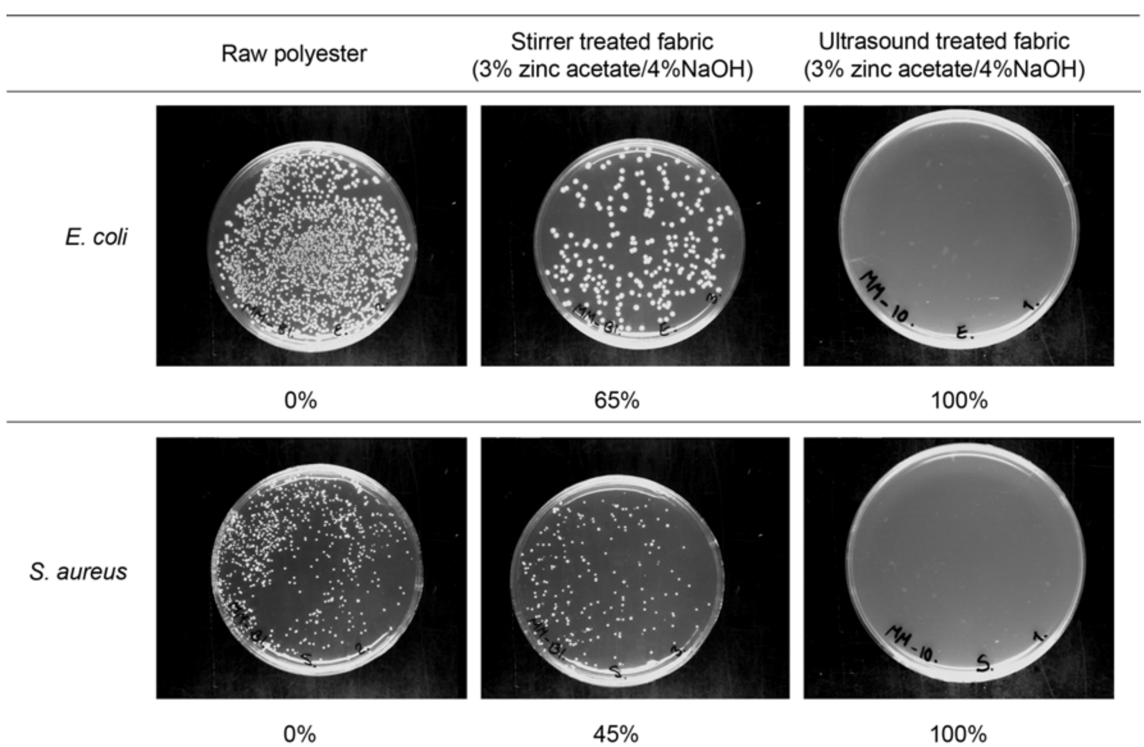

Figure 7. The antibacterial efficiency of the polyester samples.

Table 1. Flexibility and wettability of treated and untreated polyester fabrics

Sample	Bending length (cm)	Bending rigidity (mg·cm)	Water droplet adsorption time (s)
Raw polyester	2.4	259.89	84
Stirrer treated fabric (3 % zinc acetate/4 %NaOH)	1.8	109.64	9
Ultrasound treated fabric (3 % zinc acetate/4 %NaOH)	1.5	63.45	8

of Zn^{2+} ions in the bacterial culture. These positive ions react with negatively charged at the cell surface of microorganism causing a variation of cell permeability, transforming normal metabolism of microorganisms leading to microorganism death [27].

The antibacterial activities of the samples were evaluated quantitatively by suspension method against both *E. coli* and *S. aureus* bacteria. The percentage of the bacteria reduction by ultrasound/ZnO treated, stirrer/ZnO treated and raw polyester samples are reported in Figure 7.

The raw polyester fabrics provide a suitable media for growth of microorganisms. The antibacterial efficiencies of the ultrasound and stirrer treated fabrics against *E. coli* bacteria were 100 % and 65 %, respectively. Also, the ultrasound treated sample indicated higher antibacterial activities than stirrer treated sample against *S. aureus*, which is due to more and homogeneous loading of zinc oxide on the treated fabric surface under ultrasound irradiation. It is certificated that the transmission of finer size materials establishes more antibacterial activity comparing with the usual size [27].

Flexibility and Wettability

Bending length, bending rigidity and hydrophilicity properties of the polyester samples are summarized in Table 1. The bending lengths of the ultrasound treated and stirrer treated samples were reduced by 38 % and 31 % in comparison to the raw polyester fabric, indicating higher flexibility and softer handle. A similar result has been reported by Allahyarzadeh and co-workers, indicating that the alkaline hydrolysis resulted in producing lightweight polyester fabrics with silk like properties [28]. Also, the treated samples indicate the shorter time of the water droplet adsorption compared to that of the untreated fabrics, which further demonstrated the alkaline hydrolysis of polyester fabric. Alkaline hydrolysis introduces more hydrophilic groups on the fabric surface which led to higher wettability [29].

Conclusion

As showed, simultaneous synthesis of zinc oxide nanoparticles and alkaline hydrolysis of polyester fabric surface was developed. Polyester fabrics with self-cleaning property, antibacterial efficiency, improved hydrophilicity and flexibility were obtained by finishing process at ultrasound and stirrer baths. Through SEM, XRD and EDS patterns the presence of zinc oxide nanoparticles on the surface of the treated polyester fabrics was confirmed. It was found that zinc oxide nanospheres and nanorods were synthesized on the fabrics treated at ultrasound and stirrer, respectively. All properties of the treated polyester fabric at ultrasound bath were superior compared to the treated sample at stirrer bath. Applying ultrasound irradiation in finishing process led to synthesized zinc oxide with finer size and homogenous distribution on the fiber surface.

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