Research article

Multi Self-cleaning Properties of Zinc Oxide Nanoparticles/ Polydimethylsiloxane (ZnO/PDMS) Composite on Polyester Textile

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textile;
composite

Abstract

Self-cleaning textiles can be divided into three categories, which are the physical, chemical, and biological self-cleaning types. Physical self-cleaning refers to the lotus effect, which relates to the hydrophobic properties of the textile. Chemical self-cleaning is the degradation of color stains, discolored solutions and other organic species that come into contact with textiles. The last is biological self-cleaning, which is the ability to kill bacteria that become attached to the textiles. In this research, the development of all three self-cleaning properties of polyester textile coated with zinc oxide nanoparticles/ polydimethylsiloxane (ZnO/ PDMS) composite was focused. The ZnO nanoparticles were synthesized by a hydrothermal process, which involved blending PDMS with various concentrations of ZnO nanoparticles. The polyester textile was coated with ZnO/ PDMS composite solution via a dip coating technique done with various dipping times. The lotus effect, which depends on hydrophobic properties, was analyzed by water contact angle measurement. The chemical self-cleaning of the polyester textile was examined by photocatalytic methylene blue dye degradation with UV-Vis spectrometry. The inhibition zone of antibacterial activity was tested via disc diffusion technique. From these results, it was found that the polyester textile coated with ZnO/PDMS composite demonstrated all self-cleaning properties, physical, chemical and biological, in a significantly way.

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1. Introduction

At present, there is a large amount of research concerned with the preparation of self-cleaning fibers or textiles [1-4]. Textiles with self-cleaning properties can be divided into three categories, and they are the physical self-cleaning, chemical self-cleaning and biological self-cleaning types [5]. Physical self-cleaning takes place via the Lotus effect, which is the result of superhydrophobic properties. Chemical self-cleaning is the deterioration of paint and organic matter when such substances come into contact with textiles via photocatalytic effects. Finally, biological self-cleaning is an antibacterial process involving the killing of bacteria that become attached to textiles [6-9].

Zinc oxide nanoparticles are a type of nanomaterial with many outstanding properties. They are widely used in polymers, textiles, and cosmetic materials because of their UV protective properties [10, 11]. The band gap of zinc oxide nanoparticles is about 3.37 eVs and can absorb radiation in a wavelength of about 376 nm, which is in the range of ultraviolet light. In addition, zinc oxide nanoparticles are antibacterial and self-cleaning under UV light due to the photocatalytic effect [12]. In the past research, zinc oxide nanoparticles were synthesized into a chitosan/zinc oxide nanoparticle composite and then coated onto cotton fibers to provide effective antibacterial and UV protection. It was found that increasing the concentration of zinc oxide/chitosan nanoparticles effectively improved the anti-UV and antibacterial properties of cotton textile [13]. In addition, studies were conducted on the synthesis of composites of soluble starch and zinc oxide nanoparticles, which were then coated onto paper. It was found that the coated paper was antibacterial and had increased surface strength and smoothness [14]. There are also a lot of research articles related to the self-cleaning and antibacterial properties of zinc oxide nanoparticles [15-17].

PDMS polymers are hydrophobic polymers with excellent waterproofing properties. Moreover, they are chemically inert and resistant to thermal degradation, and oxidizing agents. They are well capable of being applied as films. Therefore, PDMS polymers have been used as film coatings due to the Si-O-Si structure and the -CH3 groups in the PDMS polymer. PDMS is a hydrophobic and nonpolar polymer that demonstrates low surface energy and good hydrophobicity [18].

In this research, the development of all three self-cleaning properties of polyester textile by coating with zinc oxide nanoparticle/polydimethylsiloxane (ZnO/PDMS) composite was focused. The ZnO nanoparticles were synthesized by a hydrothermal process that involved the blending of PDMS with ZnO nanoparticles at various concentrations (0.3, 0.5 and 0.7 mg/mL). The polyester textile was coated with the ZnO/PDMS composite solution via a dip coating technique with the different dipping times of 15, 30, 45, 60, 75 and 90 min, respectively. The lotus effect, which depends on hydrophobic properties, was analyzed by water contact angle measurement. The biological self-cleaning properties were investigated by measuring antibacterial efficacy using a disc diffusion technique and the gram-negative and gram-positive bacteria, *Escherichia coli* and *Staphylococcus aureus*, respectively. The chemical self-cleaning properties of the coated polyester textile were examined by photocatalytic methylene blue dye degradation on a UV-Vis spectrometer.

2. Materials and Methods

2.1 Synthesis of zinc oxide nanoparticles

Zinc oxide nanoparticles were synthesis by the hydrothermal process. High-purity zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$; 99.5%) and ammonium hydroxide solution (NH_4OH; ≥99.9%) were purchased from Sigma – Aldrich Reagents Co., LTd. and used without further purification. In a typical procedure, 0.05 mole of $Zn(CH_3COO)_2.2H_2O$ was dissolved in 50 ml of deionized water (DI water) by stirring continuously until the solution was clear, and then using as the starting solution of $Zn(CH_3COO)_2.2H_2O$. In order to obtain the NH_4OH precipitating agent, NH_4OH solution was diluted with DI water to get 0.4 M concentrated NH_4OH. After that, the 0.4 M NH_4OH was dripped very slowly into the starting solution of $Zn(CH_3COO)_2.2H_2O$, and stirred continuously until the pH value of the solution is 7.5. Then, it was stirred continuously for 1 h. Next, the mixed solution was autoclaved at 120°C for 4 h to allow the hydrothermal reaction to proceed. After completion of the reaction, the white precipitate was separated centrifugally and washed several times with DI water. Finally, the washed pricipitate was dried at 80°C in an oven overnight in order to obtain the zinc oxide nanoparticles.

The phase formation and crystal structure of the synthesized powders were studied using X-ray diffraction (XRD, Rigaku company model Smart Lab, CuKα, 2θ = 25-75°, and the phases were identified using the JCPDS (ICDD) index).

2.2 Preparation of ZnO/PDMS composite solutions

In this research, the sylgard 184 silicone elastomer kit as a PDMS precursor was used. In order to obtain the stock PDMS solution, PDMS precursor was mixed with isopropanol at a ratio 1:10 and ultrasonicated for 10 min. Then, stoichiometric amounts of zinc oxide were dissolved into DI water in order to obtain the ZnO concentrations of 0.3, 0.5 and 0.7 mg/mL. After that, the two solutions were mixed together at a ratio 1:1, with continuous stirring inorder to obtain the homogeneous composite solutions, which were specified as ZnO 0.3 mg/mL, ZnO 0.5 mg/mL and ZnO 0.7 mg/mL, respectively.

2.3 Deposition of ZnO/PDMS composites on polyester textiles

The polyester textile was cut into pieces of size 2.5 x 2.5 cm^2. The pieces were cleaned with detergent, followed by DI water and ethanol ultrasonic (30 min in each), and dried at 60°C in an oven for 10 min. After that, the polyester textile pieces were coated with the ZnO/PDMS composite solution (ZnO 0.3 mg/mL, ZnO 0.5 mg/mL and ZnO 0.7 mg/mL) by dip coating technique with different dipping time (15, 30, 45, 60, 75 and 90 min) and dried at 60°C in an oven for 1 h.

Then, all sof the coated amples of polyester textiles were characterized by X-ray diffraction (XRD, Rigaku Company, model Smart Lab, CuKα, 2θ = 15 – 60°, and the phases were identified using the JCPDS (ICDD) index). The physical self-cleaning properties of the samples were analyzed by water contact angle measurement. The biological self-cleaning properties (antibacterial efficacy) were tested using a disc diffusion technique with the gram-negative and gram-positive bacteria, *E. coli* and *S. aureus*, respectively. The last property to be investigated, which was the chemical self-cleaning property, was studied by observing the degradation of organic matter with methylene blue dye under photocatalytic reaction.

3. Results and Discussion

3.1 Phase formation and crystal structure of zinc oxide nanoparticles

Figure 1 shows the X-ray diffraction pattern of zinc oxide nanoparticles synthesized via hydrothermal process with zinc acetate as a precursor and ammonium hydroxide as a precipitator. It was found that the X-ray diffraction pattern of synthesized zinc oxide nanoparticles was of a pure phase because the X-ray diffraction pattern was consistent with zinc oxide compound data in JCPDF file No. 36-1451. The diffraction pattern corresponds to a Wurtzite structure and has peak intensities at the planes (101), (100) and (002), respectively.

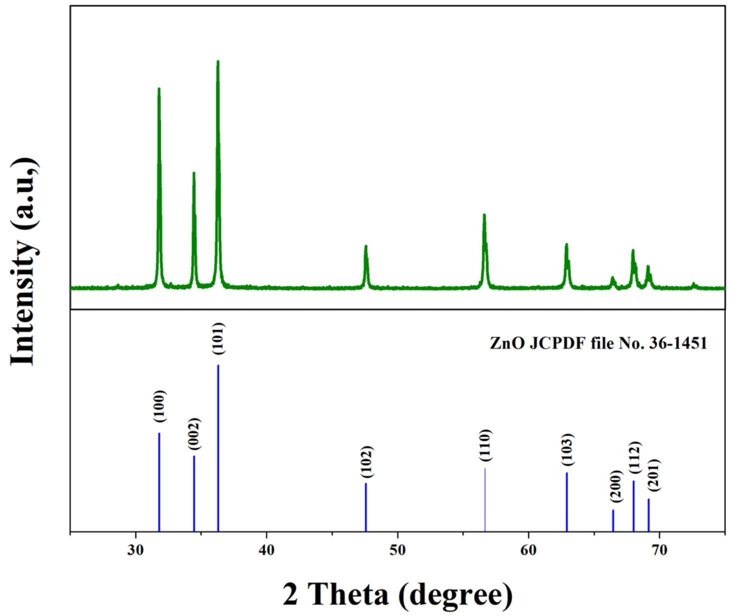

Figure 1. X-ray diffraction pattern of zinc oxide nanoparticles

3.2 Deposition of ZnO/PDMS composites on polyester textiles

After the synthesis, pure zinc oxide nanoparticles were mixed with PDMS at different concentrations of zinc oxide nanoparticles, which were 0.3, 0.5 and 0.7 mg/mL, to obtain the ZnO/PDMS mixtures. The prepared composites were then coated onto polyester textiles using a dipping process. In the experiment, the dipping times were 15, 30, 45, 60, 75 and 90 min, respectively.

Figure 2a shows the X-ray diffraction patterns of polyester textiles coated with ZnO/PDMS composite with a zinc oxide concentration of 0.3 mg/mL using different dipping times of 15, 30, 45, 60, 75 and 90 min. It was found that at 15 min, the composited ZnO/PDMS had been coated onto the polyester textiles. This can be seen from the positions of 2θ = 36.24, 31.75 and 34.42°, which characterize the X-ray diffraction of zinc oxide nanoparticles at the plane positions of (101), (100) and (002), respectively. Moreover, it was also found that when the dipping time was longer, the peak intensity at the plane positions (101), (100) and (002) of zinc oxide nanoparticles increased. This was also observed for zinc oxide concentrations of 0.5 and 0.7 mg/mL, as shown in Figures 2b and 2c.

3.3 Physical self-cleaning properties of polyester textiles

The wetting properties of the polyester textiles were assessed by measuring contact angle with water. Figure 3 shows the physical self-cleaning ability of polyester textiles coated with ZnO/PDMS composites at ZnO concentrations of 0.3, 0.5, 0.7 mg/mL and different dipping times of 15, 30, 45, 60, 75 and 90 min.

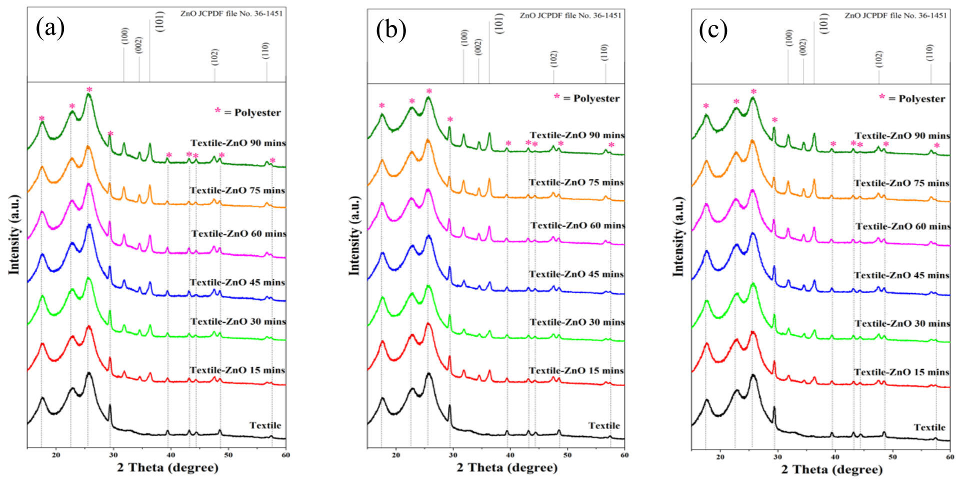

Figure 2. X-ray diffraction patterns of polyester textiles coated with ZnO/PDMS composites with different zinc oxide concentrations: (a) 0.3 mg/mL (b) 0.5 mg/mL (c) 0.7 mg/mL

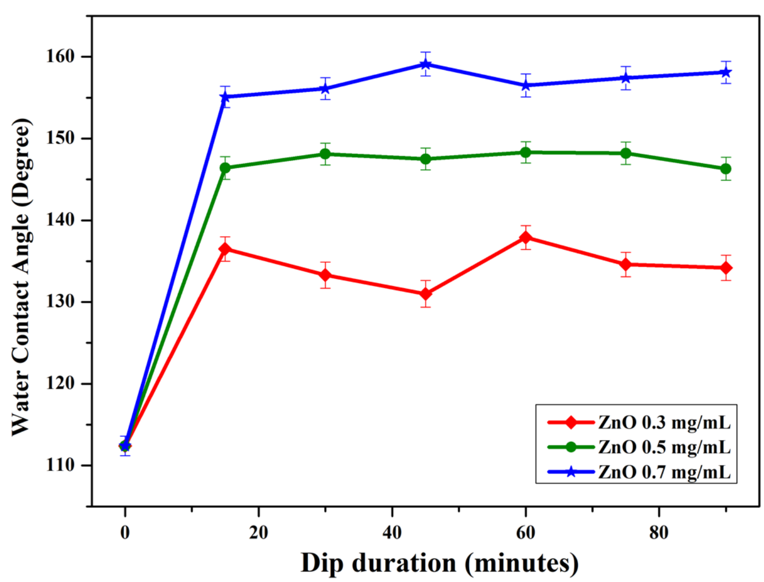

Figure 3. Water contact angle of polyester textiles coated with ZnO/PDMS composites at different ZnO concentrations and dipping times

Figure 3 shows that the polyester textiles coated with ZnO/PDMS with higher ZnO concentrations had increased contact angles. From the water contact angle of untreated polyester textiles at 112°, the contact angles increased to 133.24°, 145.87°, and 158.38° with ZnO concentrations of 0.3, 0.5 and 0.7 mg/mL, respectively. This indicates that the concentration of 0.7 mg/mL had a superhydrophobic property that was most suitable for physical self-cleaning of the polyester textiles.

3.4 Biological self-cleaning properties of polyester textiles

Biological self-cleaning properties of polyester textiles treated with ZnO/PDMS composites with the different ZnO concentrations of 0.3, 0.5, 0.7 mg/mL and different dipping times of 15, 30, 45, 60, 75 and 90 min, respectively were analyzed. The antibacterial efficacy determined by the disc diffusion technique with the representative gram-negative and gram-positive bacteria, *E. coli* and *S. aureus*, are shown in Figure 4.

Antibacterial efficacy is directly proportional to the size of the clear zone in which the larger the clear zone, the higher the efficacy of bacteria inhibition. In Figure 4, polyester textiles treated with ZnO/PDMS composites with higher ZnO concentrations and dipping times produced larger clear zones for both *E. coli* and *S. aureus*.

Zinc oxide nanoparticles can inhibit bacteria under the influence of UV irradiation via a photocatalytic reaction. The superoxide molecules involved are hydrogen peroxide and hydroxide ion. These molecules permeate the bacterial cell membrane, causing damage to components such as lipids, DNA, and bacterial proteins. In addition, nano-ZnO can inhibit bacteria in the dark. The electrons and proton holes of the ZnO interact with water molecules to form hydroxide and hydrogen ions. The oxygen molecules inside the bacterial cells are activated to form superoxide anions which react with hydrogen ions and electrons to become hydrogen peroxide, which can kill bacterial cells.

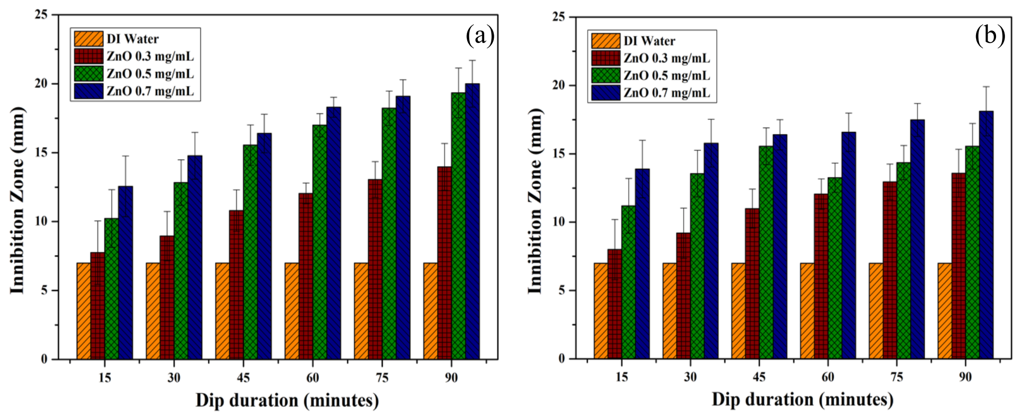

Figure 4. Inhibition zones of antibacterial activity of polyester textiles coated with ZnO/PDMS composite at different ZnO concentrations and dipping times
(a) *E. coli* (b) *S. aureus*

3.5 Chemical self-cleaning properties of polyester textiles

From the physical and biological self-cleaning results, it was found that the optimum concentration of ZnO was 0.7 mg/mL because it was the only concentration that gave superhydrophobic properties. It can also inhibit both gram-negative and positive bacteria. Polyester textiles coated with ZnO/PDMS composites under the condition of ZnO at 0.7 mg/mL were tested for their chemical self-cleaning ability by photocatalytic methylene blue dye degradation. Polyester textiles that had been coated with ZnO at 0.7 mg/mL concentration and at different dipping times of 15, 30, 45, 60, 75 and 90 min were immersed in methylene blue solution and UV irradiated for a total of 120 min. Samples were collected every 30 min, the results are presented in Figure 5 and Figure 6.

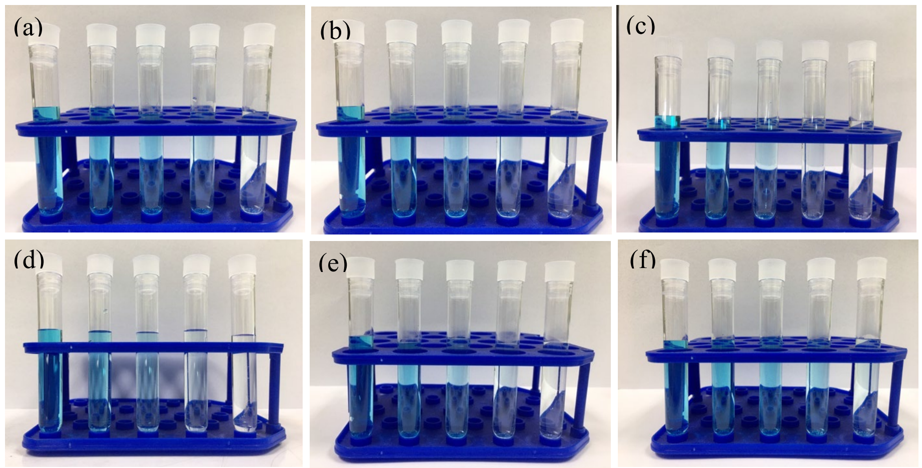

Figure 5. Transparent methylene blue dye from the photocatalytic treatment of polyester textile coated with ZnO/PDMS composites under conditions of ZnO at 0.7 mg/mL with different dipping times (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min (f) 90 min

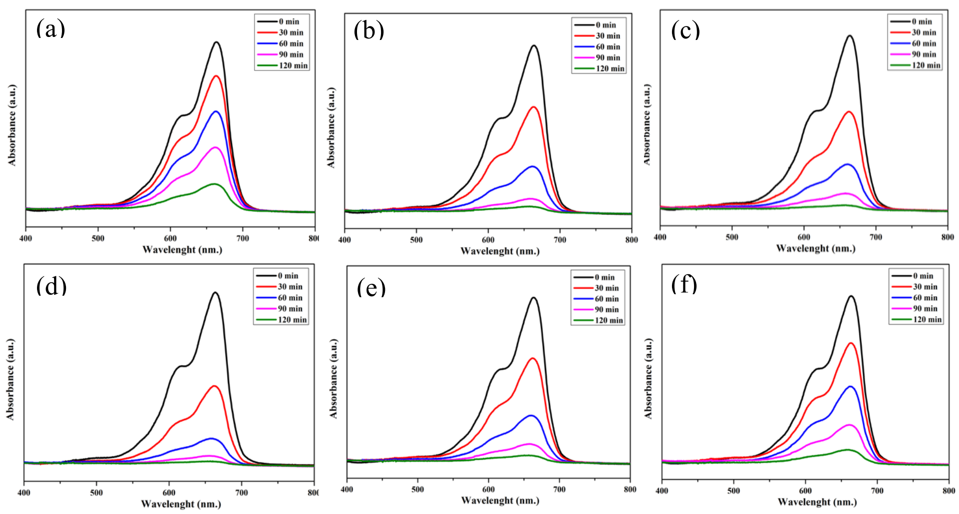

Figure 6. Absorbance of the methylene blue dye following photocatalytic treatment of polyester textile coated with ZnO/PDMS composites under conditions of ZnO at 0.7 mg/mL with different dipping times (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 75 min (f) 90 min

Figure 5 illustrates the degradation ability of the coated textiles on methylene blue dye via a photocatalytic reaction, which was observed via the transparent solutions. At 60 min dipping time, the solution is relatively transparent compared to other dipping times, a result that corresponds to the absorbance results in Figure 6. Figure 6 shows the influence of dipping time on the ability of polyester textile coated with ZnO/PDMS composite at a concentration of ZnO at 0.7 mg/mL to degrade methylene blue dye by photocatalytic reaction. It was found that methylene blue dye had the highest absorbance at the wavelength of 664 nm [19, 20]. During the first 30 min dipping time first and without UV irradiation, the surface area of the polyester textile had a balance between the absorbent and the adsorbed material. Without UV light irradiation, methylene blue was not degraded. However, with UV irradiation, the absorbance intensity of methylene blue was reduced as shown in Figure 6 (a)-(d), which shows the ability to degrade methylene blue dye through photocatalytic reaction of polyester textiles treated with ZnO/PDMS composites. When the dipping time increased to 15, 30, 45 and 60 min, the absorbance intensity of methylene blue decreased with time. This was probably due to the amount of deposited ZnO nanoparticles increasing with time of dipping. However, when the dipping time was longer than 60 min (Figure 6 (e)-(f)), the sample ability to degrade methylene blue dye decreased, probably due to the coating layer of ZnO/PDMS composite material on polyester textiles being too thick. Therefore, increasing the amount of ZnO nanoparticles deposited beyond a certain point did not lead to greater active surface area. Some ZnO nanoparticles were submerged under the thicker layers, so the degradation ability of the coating on methylene blue dye by photocatalytic reaction was reduced.

From the absorbance in Figure 6, the degradation efficiency on methylene blue can be calculated using equation 1.

$$\%\ \text{degradation efficiency} = = \frac{Ao-At}{Ao} \times 100 \ \ldots\ldots\ldots\ldots\ldots \qquad \ldots\ldots\ldots(1)$$

where A_0 is the maximum absorbance at 0 min.
A_t is the maximum absorbance at various time intervals.

From Figure 7, it was found that polyester textiles coated with ZnO/PDMS composites under the different dipping times (15, 30, 45, 60, 75 and 90 min) were able to decompose methylene blue solution when the duration of UV irradiation was increased accordingly. Considering the methylene blue degradation efficiency after 120 min of UV irradiation under all conditions, it was found that the polyester textiles coated with ZnO/PDMS composite material with a dipping time of 60 min gave the highest methylene blue degradation efficiency, which was 97.40%, as shown in Figure 8.

Polyester fabric coated with ZnO/PDMS composite materials can degrade methylene blue solution due to the photocatalytic process of the UV-activated zinc oxide nanoparticles. When an electron receives an excitation energy, it jumps from the valence band to the conduction band. This results in the formation of holes in the valence band. The electron and the hole can react with H_2O and O_2 forming superoxide anion, $\cdot O_2^-$, and a hydroxyl radical, $\cdot OH$, which can degrade dye molecules into small molecules such as H_2O and CO_2, as shown in Figure 9 and equations (2)-(6) [21].

$$ZnO + h\nu \longrightarrow h^+_{VB} + e^-_{CB} \qquad (2)$$

$$h^+_{VB} + H_2O \longrightarrow \cdot OH + H^+ \qquad (3)$$

$$e^-_{CB} + O_2 \longrightarrow \cdot O_2^- \qquad (4)$$

$$\cdot O_2^- + \text{MB dye} \longrightarrow \text{dye}_{re} \qquad (5)$$

$$\cdot OH + \text{MB dye} \longrightarrow \text{dye}_{OX} \qquad (6)$$

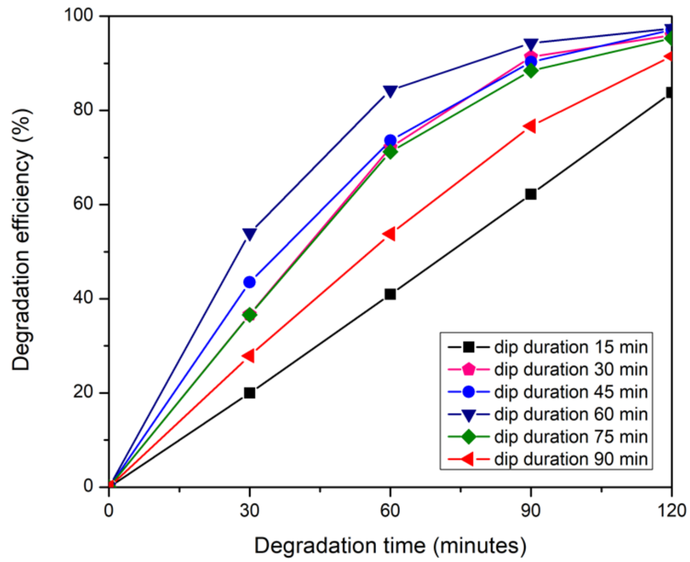

Figure 7. The methylene blue degradation efficiency during 0-120 min of polyester textiles coated with zinc oxide/PDMS nanoparticle composite materials with a concentration of zinc oxide nanoparticles of 0.7 mg/mL

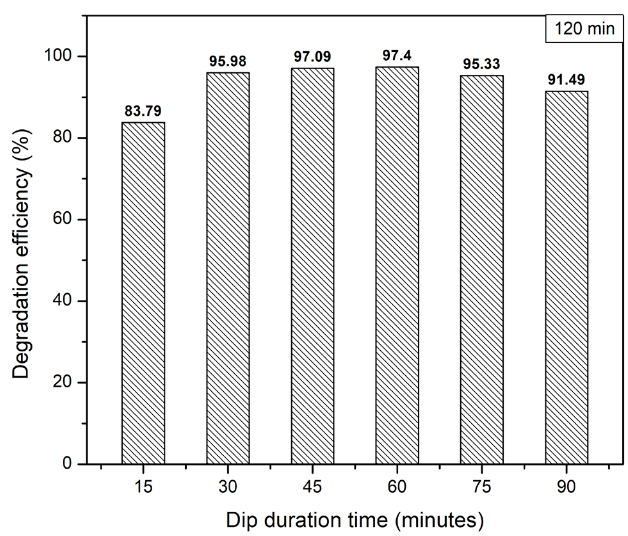

Figure 8. The 120 min methylene blue degradation efficiency of polyester textiles coated with zinc oxide/PDMS nanoparticle composite materials with a concentration of zinc oxide nanoparticles of 0.7 mg/mL

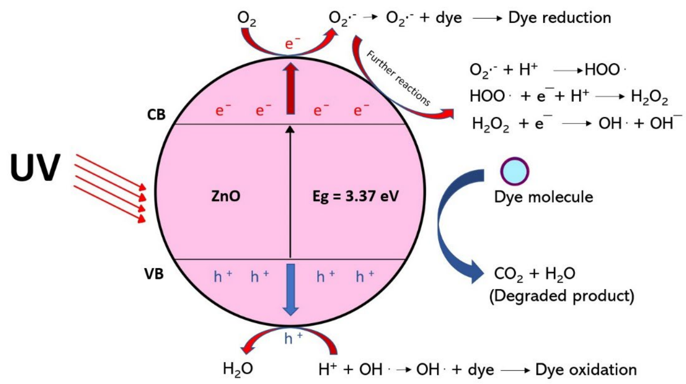

Figure 9. The dye degradation mechanism of ZnO nanoparticles via photocatalytic reaction

Further reaction,

$$\cdot O_2^- + H^+ \longrightarrow HOO\cdot$$

$$HOO\cdot + e^- \longrightarrow H_2O_2$$

$$H_2O_2 + e^- \longrightarrow 2\cdot OH$$

4. Conclusions

From the experimental results, it can be concluded that polyester textiles coated with ZnO/PDMS composites with a concentration of ZnO = 0.7 mg/mL applied by dipping technique exhibit a wide range of self-cleaning properties. Physically, the coating is superhydrophobic. Biologically, it is capable of inhibiting both *S. aureus* (gram-positive) and *E. coli* (gram-negative) bacteria, and chemically, it can degrade organic matter as measured by the ability to photo-catalytically degrade methylene blue dye. The optimum dipping time was 60 min because ii was at this time that the coated polyester textiles decomposed the most organic matter; this dipping time gave the highest methylene blue degradation efficiency of 97.40%.

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