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Photo induced silver on nano titanium dioxide as an enhanced antimicrobial agent for wool

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ABSTRACT

In this study an effective nanocomposite antimicrobial agent for wool fabric was introduced. The silver loaded nano TiO_2 as a nanocomposite was prepared through UV irradiation in an ultrasonic bath. The nanocomposite was stabilized on the wool fabric surface by using citric acid as a friendly cross-linking agent. The treated wool fabrics indicated an antimicrobial activity against both *Staphylococcus aureus* and *Escherichia coli* bacteria. Increasing the concentration of Ag/TiO_2 nanocomposite led to an improvement in antibacterial activities of the treated fabrics. Also increasing the amount of citric acid improved the adsorption of Ag/TiO_2 on the wool fabric surface leading to enhance antibacterial activity. The EDS spectrum, SEM images, and XRD patterns was studied to confirm the presence of existence of nanocomposite on the fabric surface. The role of both cross-linking agent and nanocomposite concentrations on the results was investigated using response surface methodology (RSM).

1. Introduction

Population explosion and environmental pollution encourage researchers to seek hygienic and secure production methods to facilitate human living conditions [1]. In recent decades, there have been a lot of developments using nanotechnology in the textile industry. For instance, different kinds of antimicrobial treatments have been utilized to protect garments against harmful microorganisms [2,3]. Among various nanoparticles, TiO_2 has attracted a great deal of scientists' attention because of its chemical stability, low cost, ease of availability, non-toxicity, and optical properties [4,5].

The photocatalytic features of TiO_2 under UV rays have been confirmed. When TiO_2 is irradiated by UV rays ($\lambda < 388$ nm), an electron from the valence band is promoted to the conduction band, producing pairs of negative electrons (e^-) and positive holes (h^+) [5–8]. These active species play an important role in initiating oxidation and reduction reactions [8]. Although there are numerous advantages in utilizing the TiO_2, there are some disadvantages for the pure one as follows. Firstly, nano TiO_2 shows the photocatalytic activities just under UV rays which is one of the major barriers in developing its usage and secondly the electron–hole recombination rate is too high resulting in low photocatalytic efficiency [9]. It has been suggested that through adding noble metals on the surface of TiO_2 its demerits can be reduced [10,11]. This phenomenon occurs through mitigating the rate of electrons and holes recombination by trapping the electrons, expanding the light efficiency into visible territory, and modifying the surface properties of photocatalysts [10]. Some noble metals such as Pt [12,13], Au [14,15], and Ag [10] have been used for this purpose. It has been confirmed that through modifying the TiO_2 nanoparticles by silver ions photoactivity and antimicrobial features are improved [10]. In addition, Ag/TiO_2 nanocomposite shows antibacterial activities even under visible rays [10,16].

Some pieces of research have been conducted regarding the application of nanoparticles on textiles. For instance, Daoud and Qi obtained self-cleaning keratins and cottons through the sol–gel method [17,18]. Along the same lines, Montazer and Pakdel reduced the photoyellowing of wool by TiO_2; they also obtained self-cleaning wool fabrics through applying the nano TiO_2 particles immobilized by carboxylic acids [19–21]. Moreover, Bozzi et al. produced the self-cleaning wool–polyamide fabric using nano TiO_2 stabilized by plasma pretreatment [22]. Some studies have focused on imparting the antimicrobial properties to textiles by

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employing various substances. For example, Wang obtained antimicrobial wool using nano SiO_2 [23]. Singh et al. assessed the antimicrobial property of some natural dyes on wool [23,24]. Additionally, other compounds such as quaternary ammonium salts [25], chitosan [26], and curcumin [27] have been employed to produce the antimicrobial fabrics.

In this study, the nanocomposites were anchored on the surface of wool using citric acid. It has been confirmed that nano TiO_2 particles in acidic solutions have positive charges leading to a great tendency towards carboxyl and hydroxyl groups with negative charges [17–21]. Also citric acid as a cross-linking agent introduces additional negative charged groups on the wool surface increasing the nanoparticles adsorption [19].

Lack of scientific reports on antibacterial activities of Ag/TiO_2 nanocomposites on textiles, encouraged the researchers of this study to assess the antibacterial activity of treated wool fabrics with Ag/TiO_2 against two common pathogenic bacteria: *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). The antibacterial studies were conducted through two diverse methods of biofilm and suspension. Bacterium biofilm was done on the fabric surface as a qualitative method and bacterium growth measurement was carried out by suspension as a quantitative method. In order to conduct an accurate investigation, response surface methodology (RSM) was used through which the impact of each independent variable on response surfaces was evaluated. RSM allows model adequacy including lack of fit, designs of higher order to be built up sequentially, and provides an internal estimate of error [20]. Furthermore, response surface designs neither require a large number of runs nor too many levels of independent variables [28,29].

2. Materials and methods

2.1. Materials

A 100% wool fabric with twill structure, and 159 g/m^2 fabric mass was used. Nano titanium dioxide powder (Degussa P-25) with average particle size of about 21 nm from Evonik (Germany) and silver nitrate with 99% purity from Merck (Germany) were employed to prepare the nanocomposite. Citric acid (CA) and sodium hypophosphite (SHP) with purity of more than 99% were purchased from Merck (Germany). The investigated microorganisms were *E. coli* (ATCC 11303) and *S. aureus* (ATCC 1112). Tryptic soy agar culture medium was bought from Merck (Germany).

2.2. Apparatus

A UV-A bulb (400 W, HPA, 320 nm < λ < 400 nm) from Philips (Belgium) was used as an artificial UV source. XRD patterns were obtained using Philips X' Pert MPD diffractometer with a Cu generator bulb (40 KV, 40 mA) (The Netherlands). SEM images and EDS spectra were obtained using XL30 scanning electron microscopy (Netherlands). An ultrasonic bath model DSA 100-XN1-2.5L, 100 W, 40 kHz (Taiwan) was used to mix the components of the impregnating bath. In addition, to create linkages between wool and carboxylic acid (CA) treated samples were cured in an oven.

2.3. Ag/TiO_2 nanocomposite preparation

To produce Ag/TiO_2 nanocomposite, first TiO_2 along with 100 mL distilled water was poured into a volumetric flask in the required amount. Next, in order to suspend the nano TiO_2 particles in water the solution was sonicated in the ultrasonic bath for 10 min. Subsequently, silver nitrate was added to the solution and then the finishing bath was illuminated by UV-A rays for 15 min. Finally, the nanocomposite can be obtained with turning the color solution into cream-brown.

Ag/TiO_2 nanocomposite is produced as a result of the reaction between silver nitrate and titanium dioxide in the ultrasonic bath under UV rays. The reactions between TiO_2 and $AgNO_3$ are summarized in [30–32].

$$AgNO_3 \xrightarrow{UV,US} Ag_2O + NO_2 + NO \quad (1)$$

$$Ag_2O \xrightarrow{UV,US} Ag + O_2 \quad (2)$$

$$Ag + TiO_2 \xrightarrow{UV,US} Ag/TiO_2 \quad (3)$$

2.4. Scouring

The wool samples were washed in a bath containing 2 g/L nonionic detergent with L:G = 50:1 (liquor to good ratio) at 50° C for 15 min. Then, it was rinsed with distilled water and dried at 110 °C for 5 min.

2.5. Ag/TiO_2 nanocomposite treatment

Diverse amounts of Silver/titanium dioxide nanocomposite, citric acid (CA), and sodium hypophosphite (SHP) were used in the finishing bath with 100 mL volume according to Table 1. The prepared solution was sonicated for 10 min and then the samples were put into the bath and maintained for 30 min. The treated samples were dried at 110 °C for 10 min and then cured at 160 °C for 4 min.

2.6. Antibacterial test using biofilm method (qualitative method)

In this method, through a sterile clip several pieces of fabric were placed in separate test tubes containing 0.5 mL Muller-Hinton broth and then 0.5 mL of bacteria culture was added to each tubes. After a slight shake, the tubes were put in an incubator at 37 °C for 18–24 h. Subsequently, using a sterile clip, a piece of fabric was taken out from each test tube and washed with distilled water. The washed samples were then put in the agar Muller-Hinton media for 1 min transferring the bacteria from the samples into the agar. Afterwards, the pieces of fabric were picked up using a sterile clip and then the culture medium was incubated at 37 °C for 18 h. After the incubation, the growth of bacteria colonies was compared visually [33,34].

2.7. Antibacterial test using suspension method (quantitative method)

Two pathogenic microorganisms including *E. coli* (gram negative) and *S. aureus* (gram positive), as two most evaluated species were tested by using AATCC 100-2004 test method. The number of viable bacteria colonies on the agar plate before and after a nanocomposite treatment was counted and the results reported as percentages of bacteria reduction according to

$$\text{Bacteria reduction } (R)\% = 100(A - B)/A \quad (4)$$

where (A) and (B) are the numbers of bacteria colonies recovered from the untreated and the treated wool samples respectively after inoculation and incubation and (R) is the reduction percentage of bacteria colonies [35].