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Abstract

In the study, sol-gel based TiO_2 nanoparticles (NPs) were doped by Cu(II), and the surface of cotton fabric was coated with Cu-doped TiO_2 NPs to develop self-cleaning and antibacterial properties. Coffee stains were introduced on the modified cotton fabric and under suntest illumination; a decrease in the color of coffee stain was followed over time via K/S value to determine self-cleaning performance. The photocurrent in a photoelectrocatalytic reactor was measured to evaluate the photocatalytic effect of Cu(II) doping. TiO_2 NPs showed self-cleaning and antibacterial effects under UV-illuminated conditions. However, no effects were observed under dark (non-illuminated) conditions. The modified textiles with Cu(II) doped TiO_2 NPs showed antibacterial activity against E. coli under light and dark conditions. Under the 2 hr illumination period, fluctuating color changes were observed on the raw cotton fabric, and stains remained on the fabric while 78% and 100% color removals were achieved in the cotton fabrics coated by Cu doped TiO_2 NPs in one hr and two hrs, respectively.

Keywords: Cotton fabric, copper doping, Titanium dioxide NPs, self-cleaning, antibacterial activity, photocatalytic effect

1. Introduction

The textile industry has focused on nano-technological materials and production systems because of their environmentally friendly and harmless properties. The development of self-cleaning (Liang et al., 2018), antibacterial (Mishra and Butola, 2017), and UV-blocking (Pakdel et al., 2020) ecological nano-textiles with no adverse effects on the environment and human health during production and consumption have gained importance in recent years. Pakdel et al. (2020) have coated cotton fabric by using TiO_2 and hollow glass microspheres to impart thermal insulation, flame retardancy, acoustic performance, UV protection, and mechanical properties. El-Naggar et al. (2016) have studied the antibacterial properties of TiO_2 NPs coated on the cotton fabrics, and they achieved 95% bacterial reduction even after 20 washing cycles. Semiconductor NPs are frequently used to impart these properties to materials.

TiO2 is one of the most studied materials due to its low cost, non-toxic nature, chemical and physical stability, and the oxidation/reduction potential to remove organics (Saad et al., 2016; Zhang et al., 2019). Also, TiO_2 has a bandgap energy of 3.2 eV, and the quantum efficiency of TiO_2 is relatively low under sunlight. The photocatalytic performance of TiO_2 depends on the optical, morphological, and structural properties of TiO_2 (Daghrir et al., 2013; Khaki et al., 2017; Unwiset et al., 2018). The anatase phase of the TiO_2 is known for its high photoactivity, among other phases (Saad et al., 2016). However, high-temperature calcination (300-1000°C) is required to obtain highly photoreactive crystalline phases, which is unsuitable for textile applications (Mathew et al., 2018). Alternative coating methods to calcination have been investigated to overcome this problem, and promising results have been gathered (Doganli et al., 2016; Li et al., 2018).

To improve the photocatalytic efficiency of TiO_2, it is necessary to decrease the recombination rate of the photoexcited electron-hole pair. In recent years, many different methods have been progressed to overcome these challenges, such as optimizing powders morphology, doping TiO_2 with metals, and preparing TiO_2 composites (Etacheri et al., 2015). Adding metals or metal oxides into the bulk of a photocatalyst prevents the recombination of excited electron-hole pair, may reduce the bandgap energy, and enhances the photocatalyst's performance (Etacheri et al., 2015; Pelaez et al., 2012). Furthermore, the modification of TiO_2 by doping transition metals like Cr, Zn, Ag, and Cu can extend the UV absorption threshold of TiO_2 towards the visible region (Khaki et al., 2017; Mathew et al., 2018; Yoong et al., 2009). The sol-gel method is a facile, reproducible, low-cost, and low-temperature chemical process to prepare doped and nondoped TiO_2 NPs (Casagrande et al., 2018). Particle size distribution, surface area, morphology and the crystallinity of the product powder, the thickness of the film, and phase content can be controlled by solution variables such as precursor's nature, water-to-titanium molar ratio, pH of the prepared solution, dipping time, etc. (Sayilkan et al., 2005; Shan et al., 2010).

In addition to TiO_2 NPs, various metal oxide NPs have also been used to impart antibacterial and self-cleaning properties to fabrics. Kumbhakar et al. (2018) have synthesized reduced graphene oxide, and ZnO nanocomposites to impart self-cleaning properties to the cotton fabric and had achieved 91% methylene blue removal from fabric in 60 min under UV–vis light irradiation. Another study reported by Ahmad et al. (2019) coated cotton fabric with Reactive Blue-25 (RB-25)/TiO_2 using the sol-gel method, and 91% degradation of Rhodamine B dye was achieved. Tahmasebizad et al. (2020) have investigated the antibacterial behavior of TiO_2 co-doped with copper and nitrogen via the sol-gel method and reported that co-doping of TiO_2 enhanced the photocatalytic activity and antibacterial characteristics of the samples. Also, Komaraiah et al. (2019) have synthesized Fe-doped and

non-doped TiO_2 NPs using the sol-gel method. They reported that the Fe-doped TiO_2 NPs showed more catalytic activity compared to non-doped TiO_2. Another study investigated the antibacterial and self-cleaning properties of Mn-doped TiO_2 NPs that were deposited on the cotton fabric (Zahid et al., 2018). It has been reported that 100% reduction of Staphylococcus aureus (Gram-positive) and Klebsiella pneumoniae (Gram-negative) populations were achieved within 120 min under sunlight. Also, complete degradation of a methylene blue (MB) dye adsorbed on the fabric's surface was accomplished.

Altering the structural properties of TiO_2 by metal doping may modify its biocompatibility. Several studies have been published previously on the effect of different metal dopants on the bioactivity of TiO_2 (Aich et al., 2016; Mathew et al., 2018; Rao et al., 2018). Among many metals mentioned above, copper-based compounds exhibit superior effects on the photocatalytic and antibacterial performance of TiO_2 (Estekhraji and Amiri, 2017; Leyland et al., 2016; Unwiset et al., 2018). Furthermore, copper-modified TiO_2 exhibits antibacterial properties in the dark without UV. However, there is limited information about the effect of Cu doping on antibacterial and self-cleaning textile products. To our knowledge, there is only one work about copper modified textile surface done by Ibrahim et al. (2019), who worked on self-cleaning, UV protection, and the antibacterial effect with Cu_2O/TiO_2.

In this study, TiO_2 was doped with Cu(II) by the sol-gel method, and for the first time, photoelectrocatalytic (PEC) properties have been associated with self-cleaning and antibacterial properties. A cotton textile fabric was coated to provide self-cleaning and antibacterial properties. The performance of the modified cotton textile fabric was presented under both dark and UV-illuminated conditions.

2. Experimental methods and materials

2.1. Synthesis of Cu-doped TiO_2 and coating of cotton fabric

The sol-gel method was used to synthesize TiO_2 NPs, as described in the previous study (Chehade et al., 2018). To prepare the sol-gel solution, 25 ml of TTIP (Aldrich; 97%) and 5 ml of acetic acid were added to 500 ml of distilled water. Then, 3.5 ml of HNO_3 was added, and the resulting mixture was heated at 80 °C for 30 minutes. The formed TiO_2 colloid was mixed with a magnetic stirrer for 2 hours. The prepared solution was dialyzed against a pH of 2.5 aqueous HCl by using Spectra/PorDialysis membrane tubing (MWCO: 6−8 kD) to increase the pH of the sol-gel solution above 2 to prevent recombination of TiO_2 NPs. The dialyzing solution was replaced frequently (Foorginezhad and Zerafat, 2019). Then, the copper solution was prepared by adding Copper(II) sulfate pentahydrate (Sigma-Aldrich ReagentPlus®, ≥99% CAS #: 7758-98-7) into sol-gel solution dropwise as a Cu precursor, and an appropriate amount of solution that gives Cu(II)/solution ratio of 0.2%, 0.5%, 1%, 3%, and 5.5% by mass was mixed with the prepared TiO_2 solution.

Commercial cotton gray fabric (100%) was supplied from the manufacturer, and the fabric was scoured with non-ionic detergent to get rid of any possible wax, grease, simple stains, and other compounds from the fabric surface before the coating process. After pretreatment, the cotton fabric was cut into small pieces (5 cm×5 cm). TiO_2 NPs were deposited on the prepared cotton fabrics by using the dip-coating process. The dip-coating device set to the 2.5 mm/sec withdrawal rate, 5-999 mm/min varied movement speed, 430 mm of working range. The number of moves was adjusted to 100. Then, the cotton fabrics were rinsed and dried at room temperature. Finally, textile fabrics were subjected to heat treatment at 100 °C to activate the films.

2.2. Characterization of TiO_2 nanoparticles

Concentrated sulfuric acid was used to decompose 10 mg of coated cotton fabric samples. After the decomposition process, the solution was neutralized to analyze the presence and amount of TiO_2 NPs. The particle size distribution of TiO_2 NPs was measured using a Zetasizer (Malvern Nano ZS90, at room temperature, water refraction index of 1.33; viscosity of 0.8872; and pH 4–8). FEI-Philips XL30 Environmental Scanning Electron Microscope (SEM) was used to take images of the coated NPs on the fabric.

2.3 Antimicrobial activity test

The antibacterial properties of the coated textile materials were tested by using Staphylococcus aureus ATCC 29213 and Escherichia coli ATCC 25922 following the AATCC Test Method (Adi B. Chehna, Ann Laidlaw, Leander B. Ricard, 2015). Stock cultures of the bacteria were kept in a Nutrient Agar (NA). Before each activity test, bacteria were incubated at 37 ± 0.1°C for 24 h in the nutrient broth. The concentration of culture suspensions was adjusted to 106 CFU/mL (colony-forming units per milliliter) via 0.5 McFarland turbidity standard tubes. Cotton fabric samples having a size of 8 ± 0.1 cm^2 (2 cm x 4 cm) were utilized in all experiments. After adding the inoculum (100 mL), both coated and uncoated fabric samples were illuminated with 500 W at 35°C and in the solar simulator equipment (ATLAS SUNTEST). Then, the cotton fabrics were shaken in nutrient broth (25 mL) for three minutes. Parallel seeding was made by drip method from 4 consecutive dilutions into Nutrient Agar medium, and after incubation of petri dishes at 37±0.2 °C for 24–48 hours, all growing colonies were counted. All experiments were conducted in duplicate. The number of bacteria in each sample (CFU/cm^2 per fabric) was monitored to assess the antibacterial activity in cotton fabrics. Uncoated and coated samples were subjected to an antibacterial activity test under UV light exposure.

153 *2.4 Assessment of coffee stain degradation for self-cleaning activity*

154 Since coffee stains are the leading stains that occur in real life, the fabrics are stained
155 with coffee. The coffee stains were photocatalytically degraded to evaluate the self-cleaning
156 activity of cotton fabrics (coffee bag, 2 g/200 mL brewed at 80°C distilled water for 2 min).
157 Uncoated (control) and TiO_2-coated white fabric samples were disintegrated into small pieces
158 (5 cm × 5 cm). The samples were immersed in the hot coffee until the coffee was fully
159 absorbed throughout the fabric. Afterward, the samples were rinsed with clean water and then
160 exposed to light in the SUNTEST solar simulator. The color of coated and uncoated fabric
161 samples was then measured using the color-measuring device (Data Color 600 Dual-Beam
162 Spectrophotometer), and the color differences between uncoated and coated samples were
163 calculated. The self-cleaning activity test of cotton fabric was performed, as described in our
164 previous study (Doganli et al., 2016). The color difference values for each fabric sample were
165 accepted as self-cleaning efficiency of the samples, and it was quantified with the terms of
166 delta E (dE) and K/S. The dE and K/S values of measured samples were obtained directly
167 from the color measurement device. Components of the dE color measurement system are
168 positioned in a three-dimensional space. Those components are lightness of color (L* = 0
169 yielded black and L* = 100 indicated diffuse white), the position of color in color space
170 between green and red/magenta (a*, negative values indicated green color, while positive
171 values indicated red/magenta), and position of color in color space between blue and yellow
172 (b*, negative values indicated blue and positive values indicated yellow). Color value
173 differences between sample fabric and reference fabric for L*, a*, and b* parameters are
174 calculated using equations (1)–(4);

175 $$dL^* = L^*_{sample} - L^*_{reference} \quad (1)$$

176 $$da^* = a^*_{sample} - a^*_{reference} \quad (2)$$

$$db^* = b^*_{sample} - b^*_{reference} \quad (3)$$

Total color difference, (dE), is calculated from dL*, da*, and db* as follows:

$$\mathrm{dE} = [(\mathrm{dL}^*)^2 + (\mathrm{da}^*)^2 + (\mathrm{db}^*)^2]^{1/2} \quad (4)$$

K/S value is a ratio of light absorption (K) and light scattering (S) characteristics of color, and it is calculated depending on spectral reflectance (R in %) of the sample as it is given in equation (5):

$$K/S = (1 - 0.01R)^2/2(0.01R) \quad (5)$$

3. Results

3.1 The effect of Cu(II) adding on the particle size distribution of TiO_2 NPs

Film thickness, morphology, size, porosity, optical and electronic structure of the NPs depend on production technique and further coating processing. These parameters determine surface conditions for the formation of products and light conversion for treatment technologies. The advantages of the sol-gel method are good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost, and excellent photocatalytic properties (Akpan and Hameed, 2010; Sayilkan et al., 2005). (Jonidi Jafari and Moslemzadeh, 2020) have reviewed the literature to monitor the effect of synthesis methods of Fe-doped TiO_2 NPs for photocatalytic processes under UV-visible light, and it has been reported that the crystal sizes range from 5 to 25 nm in many studies. On the other hand, (Komaraiah et al., 2019) reported that the crystallite size of TiO_2 reduced from 9.64 nm to 7 nm with Fe doping. In the present study, the sol-gel method was applied to prepare TiO_2 and Cu-doped TiO_2 NPs. Figure 1 shows the size distribution of 0-10% Cu(II) doped TiO_2 NPs. Without doping, the average size distribution of the TiO_2 NPs was found to

be 28 nm. No significant change was observed in particle size with Cu(II) doping, and the average size distribution was found in the range of 18-32 nm.

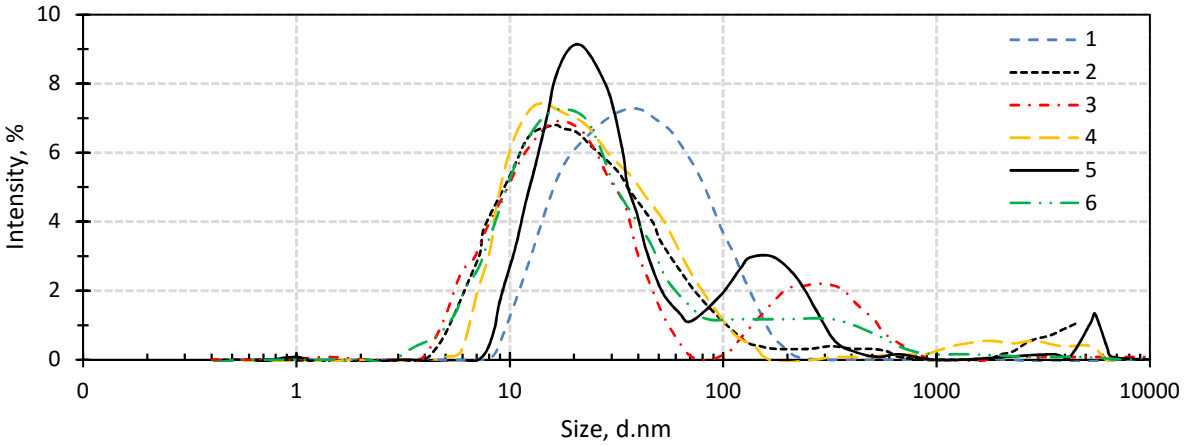
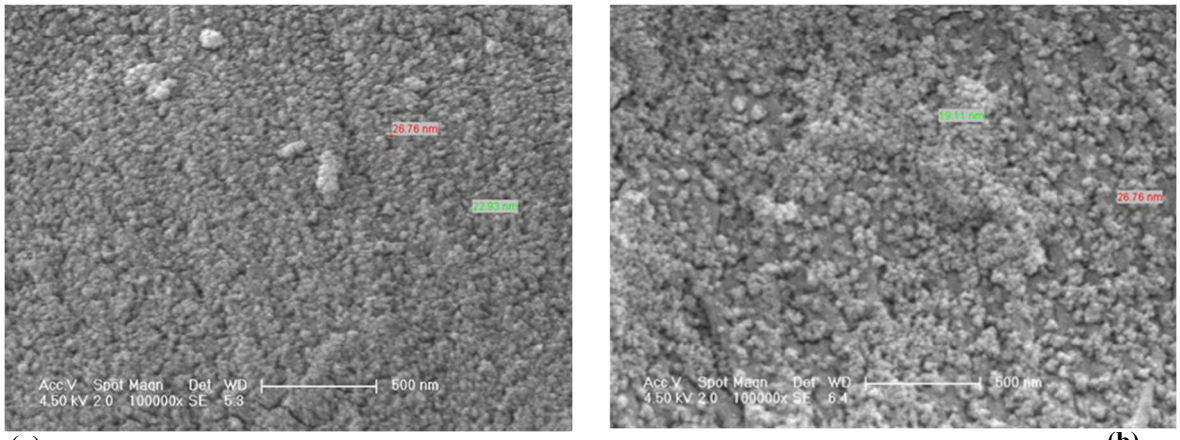


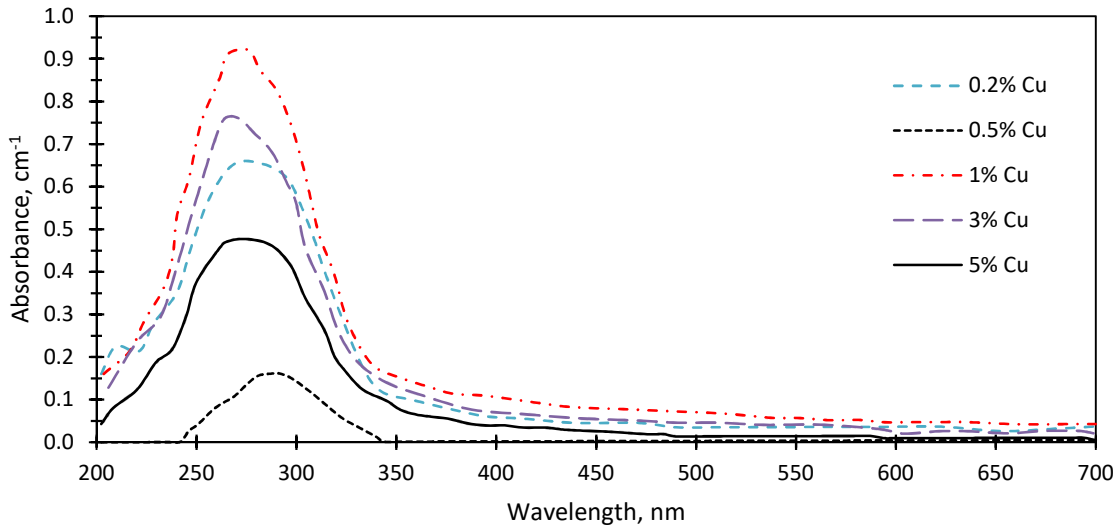
Figure 1. The particle size distribution of Cu-doped sol-gel (Cu ratio in sol-gel; 1: 0.2%, 2: 0.5%, 3: 1%, 4: 3%, 5: 5%, 6: nondoped)

Increasing the zeta potential by metal doping is important for the adsorption and then the deactivation of negatively charged bacteria on the surface of textile fabrics (Slavin et al., 2017). The zeta potential of TiO_2 NPs was measured after each doping and was observed to increase with Cu(II) doping. The zeta potential of non-doped TiO_2 was 6.0, and it reached 6.62 with 10% Cu(II) doping. It is reported that Cu(II) may shift the UV absorbance range of TiO_2 to the visible range (Mathew et al., 2018; Yoong et al., 2009). The images of immobilized Cu-doped and non-doped NPs on the cotton fabric are given in Figure 2. The Cu-doped TiO_2 NPs are clearly seen in Figure 2 (a), and the size of the doped NPs was measured as 22.9 – 26.7 nm.



213 **Figure 2.** The SEM images for (a) 5% Cu-doped TiO_2 and (b) non-doped TiO_2 NPs.

214 UV-Vis absorbance spectra show that Cu(II) does not change the max absorbance range of
215 TiO_2, but it allows TiO_2 to absorb visible light (Fig. 3).



216
217 **Figure 3.** The absorbance values for different doping ratios of Cu-doped TiO_2 NPs in the sol-
218 gel solution prepared at 100 °C.

219 Powdered TiO_2 NPs obtained at 100 ºC before and after Cu(II) doping are shown in Figure 4.
220 The color of commercially available TiO_2 powder is white. Thus, it is just suitable for white
221 textile fabric. However, in this study, yellowish TiO_2 powder was achieved by Cu(II) doping.
222 Therefore, this may be an advantage for using TiO_2 for the colored textile fabric.

Figure 4. The images for (a) 5% Cu-doped TiO_2 and (b) non-doped TiO_2 NPs.

3.2. The effect of Cu(II) doping on the photoelectrocatalytic performance of TiO_2 NPs

The photocatalytic chemistry of TiO_2 has been extensively studied over the few decades to understand the fundamentals of photochemical processes. The mechanism of the TiO_2 photocatalytic process is based on the formation of photo-excited electrons and holes. As electrons and holes are generated, many different chain reactions may be initiated, resulting in the formation of strong hydroxyl radicals (OH•) (Fig. 5).

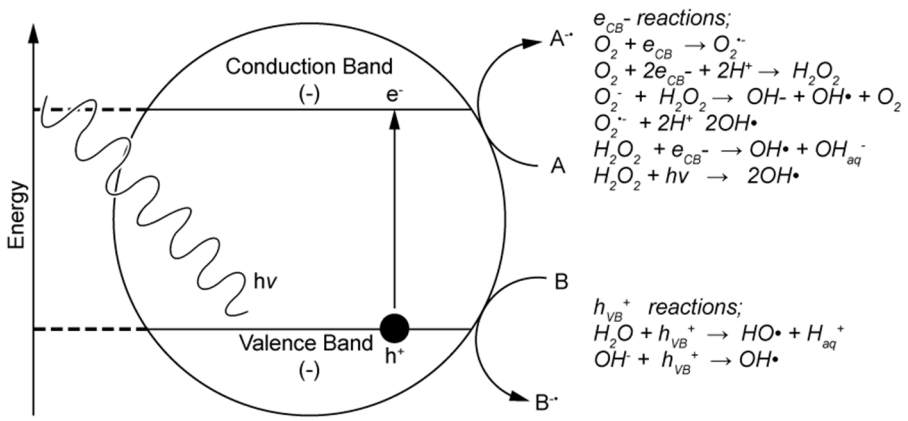


Figure 5. Principles of the photocatalytic process.

OH• radicals play an important role in removing bacteria, organic and inorganic contaminants (Doganli et al., 2016; Mahmoodi et al., 2006; Moongraksathum et al., 2018). However, in the absence of electron donors or acceptors, electron-hole pairs (e_{CB}^{-}/h_{VB}^{+}), have a life span of a few nanoseconds. Recombination of electron-hole pairs must be slowed to enhance photoactivity. One of the current strategies to enhance the photoactivity of TiO_2 is

doping TiO_2 with metal and non-metal ions to shift photo-response to the visible spectrum (Cong et al., 2011; Singh et al., 2019). A decrease in photocatalytic activity of TiO_2 is still a disadvantage regarding metal doping methods. The immobilization method determines photocatalytic activity of TiO_2.

In recent years, photoelectrochemical (PEC) methods have been widely adopted to measure the photocatalytic performance of novel TiO_2 NPs (Shan et al., 2010; Zhu et al., 2007). In this study, the photocurrent generated in a PEC reactor was used to evaluate the effects of calcination temperature and Cu(II) doping rate on the photocatalytic performance of TiO_2 nanofilms. It is well known that the photoactive phase of TiO_2 can be obtained over 300°C. However, in this study, the results showed that the TiO_2 film is active even at 25°C. A 1% Cu doping was found to be optimum doping rate at the temperatures of both 400°C and 25°C to get max photocurrent (Fig. 6 and Fig. 7).

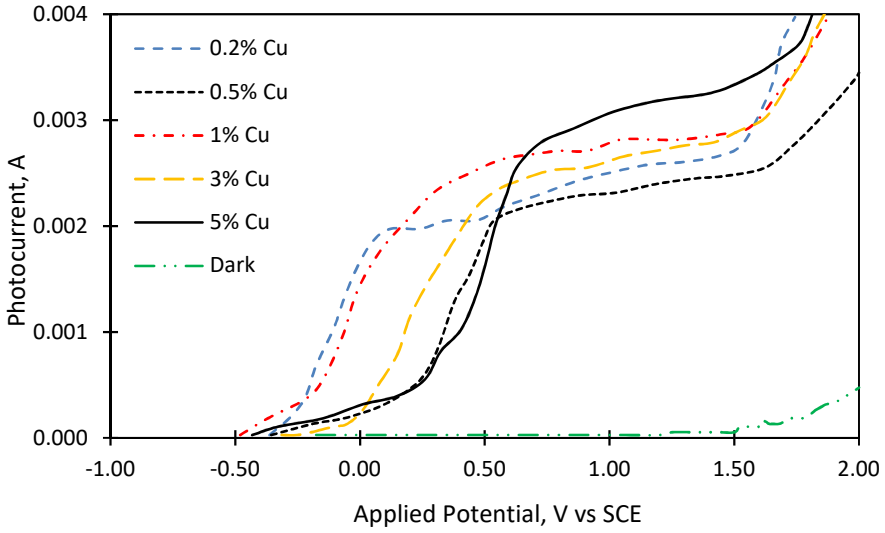
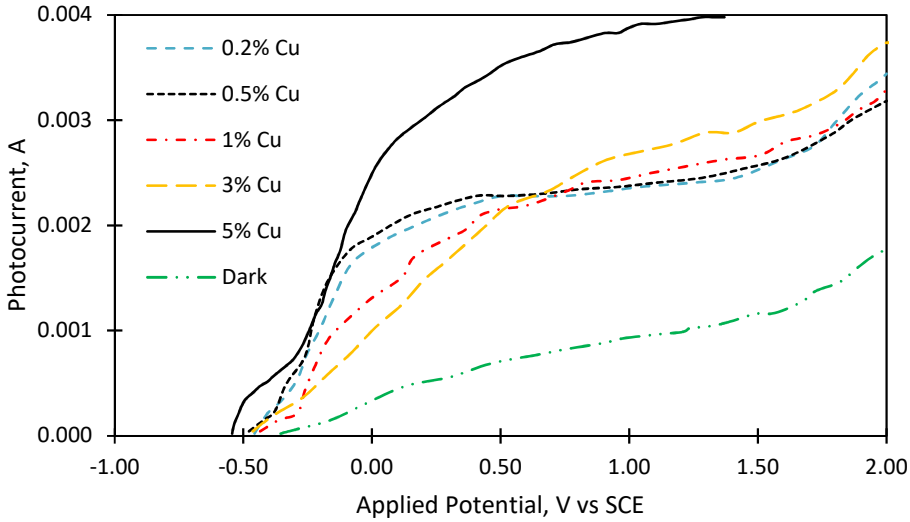


Figure 6. The photocurrent values for different doping ratios of Cu-doped TiO_2 NPs in the sol-gel solution prepared at 25 °C.



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254 **Figure 7.** The photocurrent values for different doping ratios of Cu-doped TiO_2 NPs in the
255 sol-gel solution prepared at 400 °C.

256 A small number of studies show that TiO_2 calcined at low temperature values may
257 show photocatalytic property (Saad et al., 2016). There are still many gaps to be clarified
258 about the measurement of anatase and rutile phase in the amorphous phase achieved at low
259 temperatures. Also, commercially available Degussa P25 consisting of anatase and rutile
260 mixture is still the best performing photocatalyst (El-Sheikh et al., 2014). Results show that
261 calcination at a higher temperature just decreased the activation energy of TiO_2 films, but
262 TiO_2 powder calcined at low-temperature values may be photoactive at higher illumination or
263 external potential values (Fig. 8).

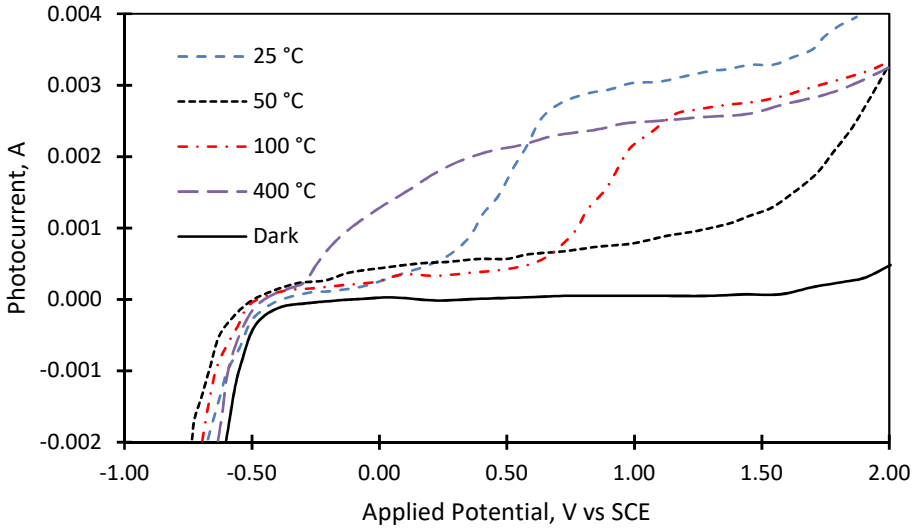
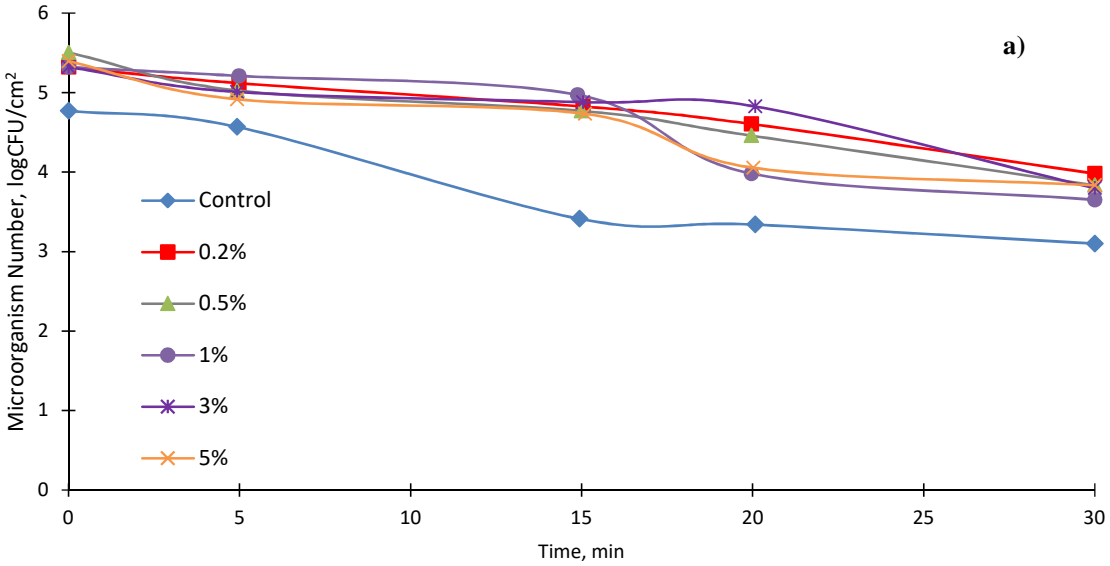


Figure 8. The Effect of sol-gel temperature on photocurrent (1% Cu-doping).

3.3. Antibacterial properties of Cu doped TiO_2

Results show that TiO_2 and Cu(II)-doped TiO_2 NPs increased the E. coli number on the textile surface. These results were attributed to the hydrophilic effect of TiO_2 on the cotton surface. However, the deactivation of E. coli on the raw and modified textiles is almost the same as initial log CFU decreased from 5.5 to 4 on the modified textile fabrics, while the initial E. coli number decreased from log 4.8 to log 3.4.



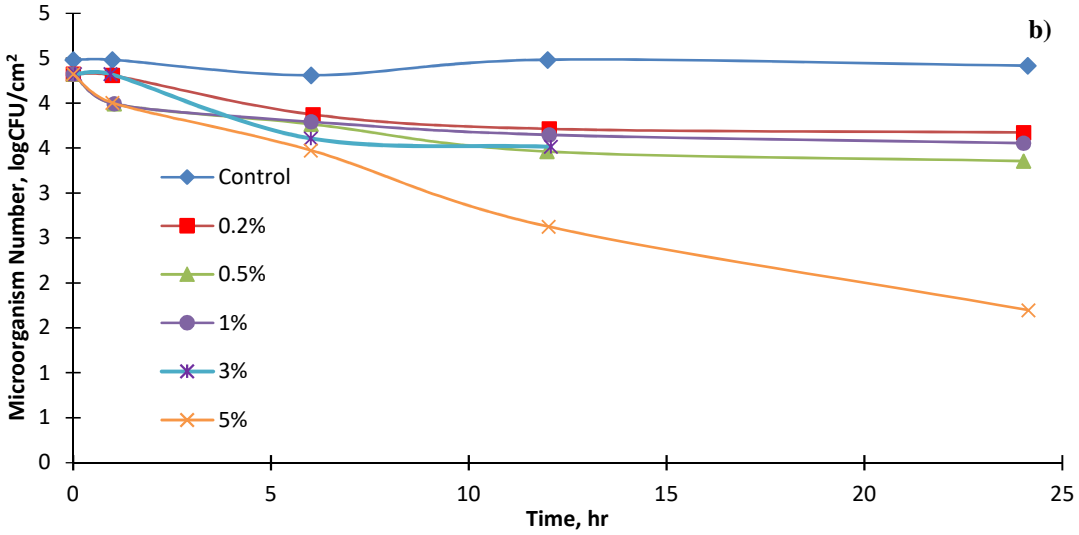


Figure 9. Antibacterial properties of the doped-TiO2 NPs: (a) change in the number of microorganisms by minute and (b) change in the number of microorganisms by the hour.

The antibacterial experiments were also performed in the dark. As shown in Figure 9, even after 25 hours of incubation time under dark conditions, no antibacterial effect was observed on the non-doped TiO_2 coated cotton fabric while Cu(II) doping clearly exhibits an antibacterial effect, and a significant antibacterial effect was achieved in the dark at 5% Cu(II) doping rate.

3.4. Self-cleaning Effect

Most of the studies in the literature used dye solutions to determine the self-cleaning performance of the TiO_2 NPs (Shaban et al., 2016; Zahid et al., 2018). However, in this study, coffee stains were used on the fabrics to represent real-life stains on the clothes. Even stronger initial color was observed on the 1% Cu(II) doped cotton fabric. However, 78% color removal was achieved under illumination in one hour, and color disappeared in two hours. Similar studies were conducted with methylene blue solution. (Zahid et al., 2018) reached 97% methylene blue removal efficiency in ten hours by using Mn-doped TiO_2 NPs, while (Komaraiah et al., 2019) have reached 96.7 methylene blue removal in four hours with Fe-doped TiO_2 NPs. The initial color was light on the raw cotton textile. However, some darker

color was observed even after a two-hour illumination period. Results reflect that Cu(II) doping may provide TiO_2 NPs not only antibacterial property but also self-cleaning function (Fig. 10).

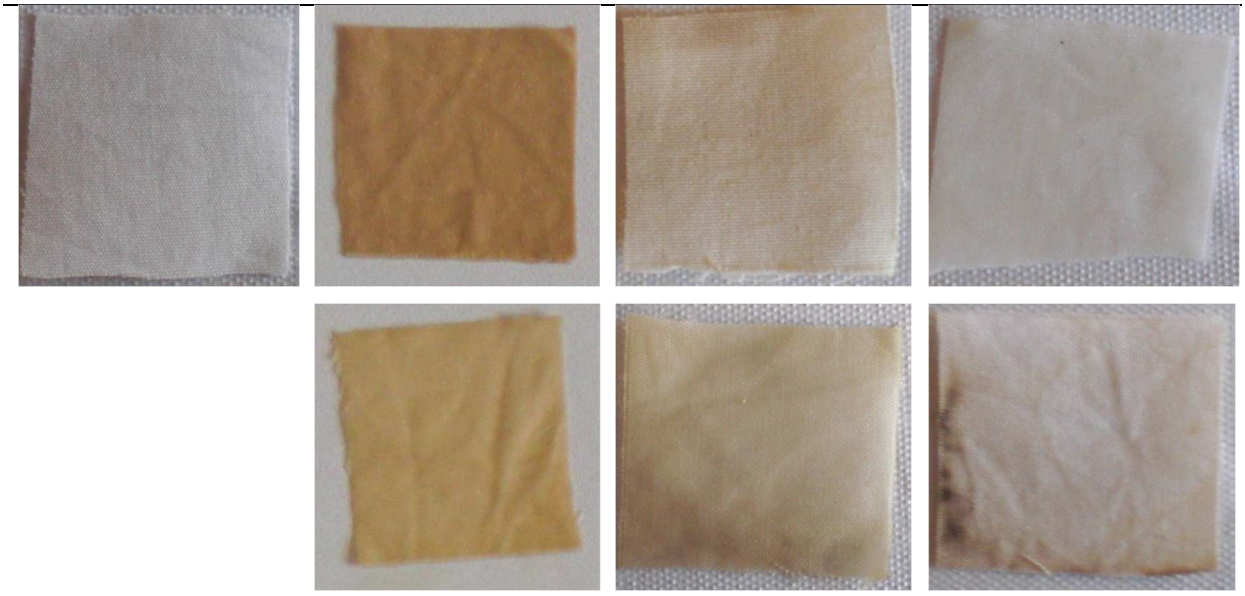


Figure 10. Self-cleaning performance of 1% Cu(II) doped TiO_2 calcined at 25 °C.

4. Conclusion

Under UV illumination, TiO_2 NPs provide textile fabric self-cleaning and antibacterial properties. However, under dark conditions, the TiO_2 coated textile surface may not be antibacterial. Thus, in this study, Cu(II) doping was applied to provide cotton fabric antibacterial function in the dark. The sol-gel based Cu(II) doped TiO_2 NPs were dip-coated on the Ti foil at different temperatures. The photocatalytic performance of the modified films was measured in a PEC reactor by photocurrent measurement. Coffee was used to stain the cotton fabric, and the K/S ratio was observed to determine the self-cleaning performance. Even at 25 °C, photocurrent was achieved at 0.5 V external potential. This means that the film achieved at low temperature values may be active at higher illumination intensities. As expected, a significant antibacterial function was achieved in the dark at the high Cu(II)

303 loading of 5%. Coffee stain removals measured as K/S value improves that even at low-
304 temperature values, sol-gel based Cu(II) doped TiO_2 NPs may exhibit a self-cleaning effect
305 under sunshine illumination provided by solar simulator equipment.

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309 **Declaration of competing interest**

310 The authors declare that they have no known competing financial interests or personal
311 relationships that could have appeared to influence the work reported in this paper

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Raw cotton fabric

Stained cotton fabric

After 1hour illumination

After 2 hours Illumination