KKU Res. J. 2013; 18(2): 200-211
http : //resjournal.kku.ac.th

Investigation of the Self-cleaning Properties of Cotton Fabrics Finished with Nano-TiO_2 and Nano-TiO_2 Mixed with Fumed Silica.

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Abstract

The aim of this work is to investigate the self-cleaning properties of woven cotton fabrics after coating with either nanoparticles of TiO_2 (Degussa, P-25) or mixtures of P-25 and fumed silica (Aerosil200). The TiO_2 and fumed silica were dispersed in toluene by exposure to ultrasound and then stirring prior to use. After drying, the particles were dispersed in water at 0, 0.5, 1.0 and 2.0 wt/wt% then applied to the cotton fabrics using a pad-dry-cure technique. The finished fabrics were stained with direct dye, coffee, tomato sauce, and soft drink, and then irradiated with artificial sunlight (xenon arc lamp) for 24 h. The K/S values at different time intervals were recorded to measure the self-cleaning ability of the finished fabrics. The results showed that every sample possessed self-cleaning abilities. The self-cleaning effect was stronger for samples coated with higher TiO_2 concentrations. The decomposition of a direct dye stain was most significant compared to other stains. Mostly, the finished samples appeared clean after one wash whereas the untreated fabrics required repeated washing. However, with the addition of fumed silica, a reduction in self-cleaning ability was observed.

Keywords: cotton, photocatalytic surface, self-cleaning textile, textile finishing, titanium dioxide

1. Introduction

It has been widely accepted that titanium dioxide (TiO_2) in the anatase form displays a good photocatalytic properties (1). This substance has a band gap of approximately 3.2 eV and thus can be excited by UV radiation whose wavelength is shorter than 388 nm. Upon UV exposure, an electron from the valence band becomes promoted to the conduction band resulting in the formation of a negative-electron (e^-) in the conduction band and a positive-hole (h^+) in the valence band. The positive-hole of TiO_2 can separate a water molecule into a hydroxyl radical (OH•) while the negative-electron reacts with an oxygen molecule to generate a superoxide radical anion (O_2^-). These radicals possess strong oxidation potential to decompose surrounding organic pollutants into CO_2 and H_2O, leading to the so-called self-cleaning effect. By coating TiO_2 (films or particles) on the surface of interest, the unwanted organic compounds, e.g. microorganisms, odor, and stains are expected to be removed upon illumination by UV light either from the sun or internal lighting (2). Main applications include air purification, water purification, and sterilization (3). It has been shown that although TiO_2 in the anatase form exhibits superior photocatalytic activity to the rutile form, mixing of these two crystal structures can result in an enhanced photocatalytic performance compared to either single form (4,5). The important feature of using nano-sized particulate TiO_2 is the larger surface-to-volume ratio that favors the production of active oxygen molecules and increases the available area for the photocatalytic action with organic compounds (6). Degussa P-25 is a widely used commercial nanoparticles of TiO_2 having the average crystallite size of 30-40 nm and an anatase-to-rutile mixed phase ratio of 4:1. Bozzi et al. reported that when cotton textiles were coated with these nanoparticles, red wine and coffee stains decomposed under daylight irradiation (3). In recent years, TiO_2 photocatalytic finishing of textiles for self-cleaning applications has become an active research area. Textile materials that have been investigated include cotton (3,7-9), wool (10,11), polyester (10-12), polyamide (11) etc.

Recently, an important work on the improvement of photocatalytic activity of TiO_2 by non in situ doping with fumed silica was carried out by Jafry, Liga, Li and Barron (13). The authors observed an improvement in the deactivation of viruses (bacteriophage MS2) by simply stirring TiO_2 (P-25) with fumed silica in toluene solvent when compared with TiO_2 alone. They ascribed this enhanced antiviral action to the increase in the photocatalyst band gap. This leads to a reduction in electron-hole recombination and thus the formation of more hydroxyl radicals produced from TiO_2-SiO_2 particles. They also suggested the possibility of increased absorption of MS2 onto the doped catalyst surface. Since the killing of virus relied on free radicals generated via photocatalytic action of TiO_2-SiO_2, it would be interesting to use a similar approach to find out whether TiO_2 decomposition of stains would be more effective by doping with silica as well. This investigation of the effect of silica-doped TiO_2 on the self-cleaning ability of textiles was therefore included within the present research. The outcome if successful will have industrial significance as it would be convenient and cost-saving to be able to derive a better textile finishing formula by simple mixing of two types of particles.

In the present study, cotton textiles were coated with nano-TiO_2 and four different mixtures of nano-TiO_2 and fumed silica. The photocatalytic performances under a solar simulator were evaluated by observing the fading of stains. The stains and the light source were chosen in order to simulate the normal using of garments and home textiles. Following illumination, the samples were washed in a washing machine to evaluate the effect of applying a photocatalyst coating.

2. Materials and Methods

A cotton plain weave grey fabric (mass per unit area of 123 g/m^2) was purchased from a local store (Phahurat market, Thailand). The fabric has 133 yarns/inch in the warp and 68 yarns/inch in the weft direction. The warp and weft yarn counts are Ne 42 and Ne 45, respectively. Nano titanium dioxide Degussa P-25 was purchased from Evonik (Thailand). Fumed silica, Aerosil200, was kindly supplied by Boontrakarn Chemicals Co.,Ltd., Thailand.

2.1 Dispersion of nano-TiO_2 and nano-TiO_2/ fumed silica particles

TiO_2 nanoparticles were dispersed in toluene using an ultrasonic bath (Transsonic digital, Elma) for 1 min at room temperature followed by stirring using a magnetic stirrer for 1 h, vacuum filtered, and then dried. Next, the nanoparticles were washed with copious acetone before being vacuum filtered and then dried again. For the mixture of TiO_2 and fumed silica, the same procedure was conducted, but both substances were dry-mixed prior to dispersing at predetermined weight percentages of fumed silica based on the amount of TiO_2: 0, 10, 30 and 60%.

2.2 Finishing of cotton fabrics

The TiO_2 nanoparticles were stirred in distilled water at a total solid weight of 2 g/100 ml of water whereas for the nano-TiO_2/fumed silica mixtures, the total solid weight was fixed at 1 g/100 ml of water. Cotton fabric was scoured and bleached before use. The fabric was cut into rectangular pieces of samples with dimensions of 5cm x 5cm. The fabric samples were dipped in the particle solution for 3 min and then padded by a laboratory padding mangle with various percentage wet pickups (Labtec, Newave Lab. Equipments, Co., Ltd.). Finally the fabrics were taken out and cured at 130°C for 5 minutes using a laboratory mini dryer (Labtec, Newave Lab. Equipments, Co., Ltd.).

2.3 Evaluation of the self-cleaning properties under artificial sunlight

Irradiation of all samples was carried out in the cavity of a Suntest solar simulator (Atlas Suntest CPS, Germany) with a 1500 watt air-cooled xenon arc lamp as a light source. Four types of stain were studied for TiO_2-finished samples: direct dye (Everdirect supra turquoise blue FBL or C.I. Direct Blue 199), coffee (Nescafé Latte), tomato sauce (Heinz), and soft drink (see details in Table 1). One stain was dropped on one piece of sample at a volume of 100 µl using a micropipette (Transferpette®). The top half of each stained area was covered with a piece of aluminium foil while the bottom half was left exposed to the simulated sunlight. This half covering was done to observe how the simulated sunlight changes the color intensity of the stained fabrics by comparing between the exposed and unexposed parts. The color intensity (K/S) was measured using a spectrophotometer (GretagMacbeth color i5) at different time intervals. For the TiO_2/fumed silica finished samples, only the direct dye stain was studied and the reduction in K/S values was recorded after 24-h exposure.

Table 1. Types of stain used and their corresponding coloring organic components.

Stain type	**Coloring organic component**
Direct dye	A complex of copper with phthalocyanine
Coffee	Caramelized sucrose products
Tomato sauce	Lycopene
Soft drink	Allura Red AC

2.4 Effects of washing cycles on the residual stains

After illumination in a Suntest chamber for 24 h, selected samples were washed in a washing machine (Gyrowash, James H. Heal Co., Ltd.) from 1 to 3 cycles according to ISO 105-C05:1989. The K/S values and photographic images were recorded.

3. Results and Discussion

3.1 Determination of the percentage of TiO_2 add-on

Table 2 showed the weights of the fabrics before and after padding, and also the concentrations of TiO_2 in the pad solutions. These parameters can be used to calculate the actual solid level, i.e. TiO_2 level, added to the cotton samples. Using the following equation yields the percentage of TiO_2 add-on:

$$\%\ TiO_2\ \text{add-on} = \frac{\%TiO_2\ \text{in solution} \times \%\ \text{wet pickup}}{100}$$

where

$$\%\ \text{wet pickup} = \frac{\text{weight of wet fabric after pad - weight of dry, untreated fabric} \times 100}{\text{weight of dry, untreated fabric}}$$

The higher percentage of TiO_2 add-on indicated greater amounts of TiO_2 coating on the fabrics with increasing TiO_2 concentrations.

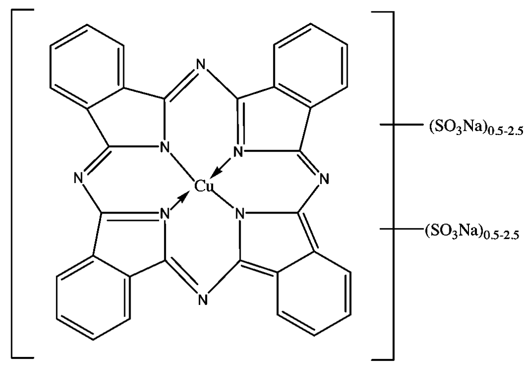
Table 2. Sample weights and the resulting percentage add-ons for pristine and TiO_2-coated samples.

TiO_2 concentration (% wt/wt)	Sample weight (g)		% wet pickup	% TiO_2 add-on
	Before pad	After pad		
0.0	3.53	5.85	65.72	0.00
0.5	3.50	5.85	67.14	0.34
1.0	3.51	6.15	75.21	0.75
2.0	3.51	6.02	71.51	1.43

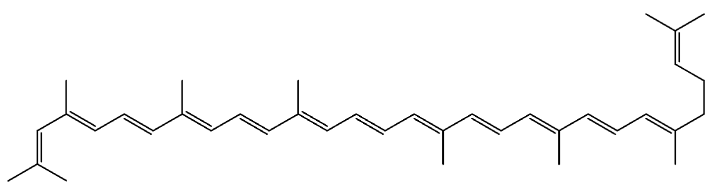
3.2 Evaluation of self-cleaning performance of TiO_2-finished samples via spectrophotometry

As shown in Table 1, each of the stains used in this study contained a major coloring component as follows: a direct dye (C.I. Direct Blue 199); Lycopene (in tomato sauce); caramelized sucrose (in coffee); and an acid dye, namely Allura Red AC (in soft drink).

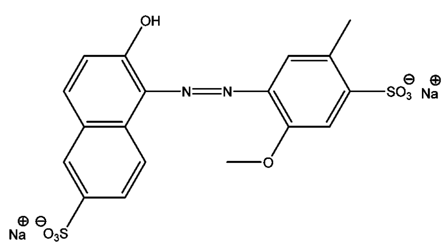
The chemical structures of these compounds are provided in Fig. 1 except for the caramelized sucrose products whose brown-colored components have not been individually identified. The direct dye used here was a complex of copper with phthalocyanine. Lycopene is an unsaturated hydrocarbon. Caramelized sucrose products were obtained by heating of sugar, in other words, roasting the coffee beans. The outcome is the formation of thousands of compounds which have not been investigated thoroughly. The compounds that give rise to the brown color could be minor aromatic compounds (dye-like molecules) as suggested by Golon et al. (14). The acid dye in soft drink was a sodium salt of an azobenzene derivative containing sulfonate groups. In the literature, coffee and red wine stains are probably the organic pollutants most commonly employed for the evaluation of self-cleaning textiles by the use of photocatalysts (6,8,9,11,15-17). This work, therefore, extended the study to other types of organic compounds.



a) C.I. Direct Blue 199



b) Lycopene



c) Allura Red AC

Figure 1. Chemical structures of the major coloring components found in a) direct dye, b) tomato sauce, and c) soft drink.

Figs. 2 are the photographic images of fabric samples after staining. The color intensities of the four types of stain were different at the starting point (0 h of illumination) as can be seen either by visual inspection or from the K/S values: C.I. Direct Blue 199 > coffee > tomato sauce > soft drink (see Figs 3a-d).

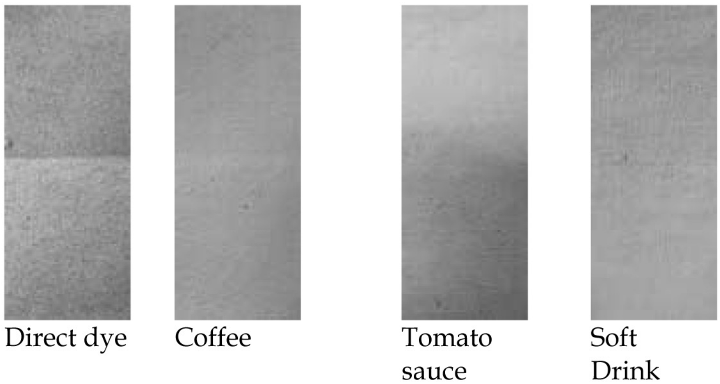


Figure 2. Photographic images of TiO_2-finished cotton fabrics after illumination by a solar simulator for 24 h. The upper half of each ample was covered with an aluminium foil and thus unexposed. The bottom half was subjected to direct exposure. Four types of stain were investigated: direct dye, coffee, tomato sauce, and soft drink.

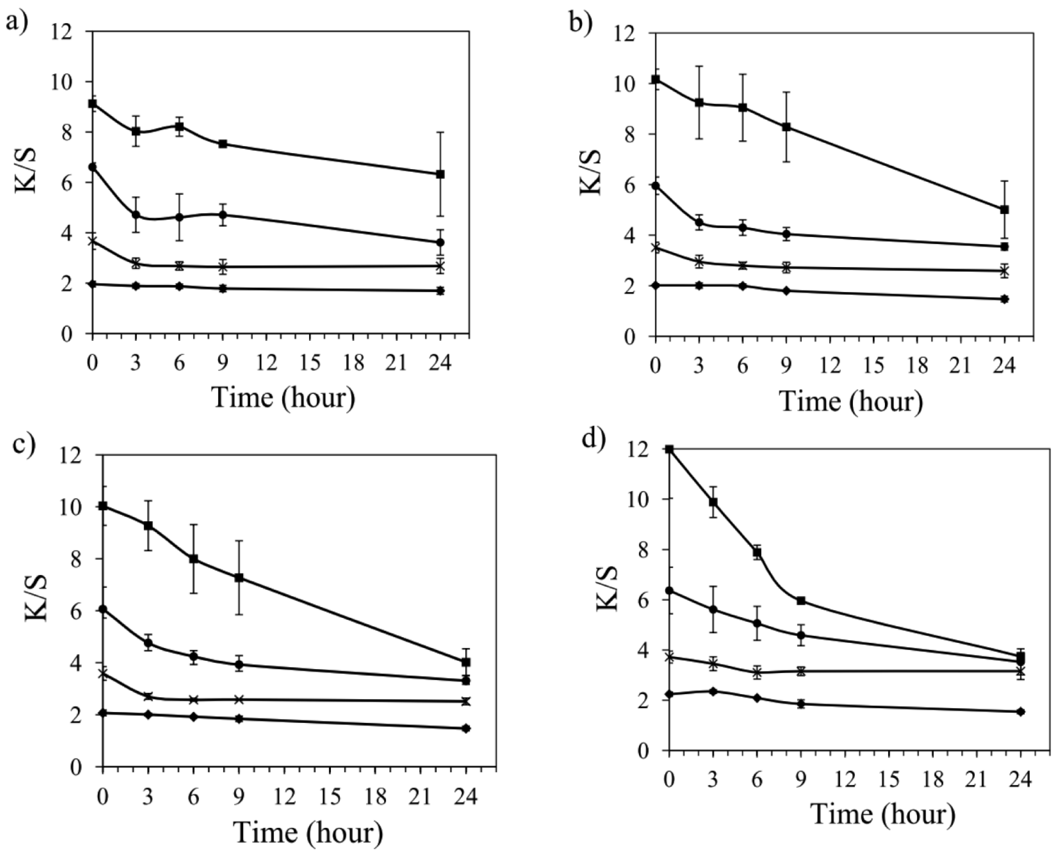


Figure 3. Plots of K/S values versus time for illuminated samples: a) pristine cotton, cotton coated with b) 0.5 wt/wt% TiO_2, c) 1.0 wt/wt% TiO_2, and d) 2.0 wt/wt% TiO_2. The Stains used were (■) C.I. Direct Blue 199, (●) coffee, (x) tomato sauce and (◆) soft drink.

A strong blue color was obtained for the sample stained with C.I. Direct Blue 199 while the soft drink stain was barely visible by visual inspection. Fabrics, both with and without nano-TiO_2 coating, showed decreasing K/S values with increasing illumination time. This reflects the effect of the UV spectrum in the artificial sunlight in fading organic stains. However, the reduction is staining was more pronounced with increasing TiO_2 concentration especially for the direct dye stained samples. The self-cleaning ability of these nano-TiO_2 finished samples arose from the photocatalytic properties of TiO_2 under artificial sunlight, which convert organic compounds into CO_2 and H_2O. After 24 h illumination, the colors of all the stains were much lighter than their initial colors. Incomplete color change of coffee and red wine after 24-hour illumination with simulated solar light was also reported by Meilert and coworkers (8). It should be noted that lycopene is responsible for the color in both the red wine and the tomato sauce. Although TiO_2 is a photocatalyst that utilizes UV radiation to decompose organic molecules, it has been proposed that the decomposition of lycopene under visible light by TiO_2 may occur due to a process called "dye sensitization", i.e. the lycopene molecule absorbs light in a range beyond the band gap of TiO_2 to promote an electron and inject it into the TiO_2 conduction band, initiating the oxidative process (18). Bozzi et al. suggested the same mechanism accounts for the decomposition of the colored organic components found in red wine and coffee (3). Taking into account the good self-cleaning activity of samples stained with synthetic organic dyes: C.I. Direct Blue 199 and Allura Red AC, these compounds probably underwent the same visible light-induced decomposition mechanism in addition to the classical UV-induced decomposition process by TiO_2. The chemical structures of all these compounds contain aromatic rings which are likely to be found in caramelized sugar as well.

It maybe thought that this color change is primarily a result of exposure of the stains to light. As controls, pristine cottons were also stained and illuminated in the same way as the TiO_2-coated samples. For the untreated fabrics, the change in color intensity of the stains after 24 h of illumination was barely visible. This indicates that the presence of TiO_2 was the major factor accounting for the decomposition of these stains. Without the use of these nanoparticles, the decomposition of stains was virtually non-existent under artificial sunlight (see Figs 4(a)-(d)).

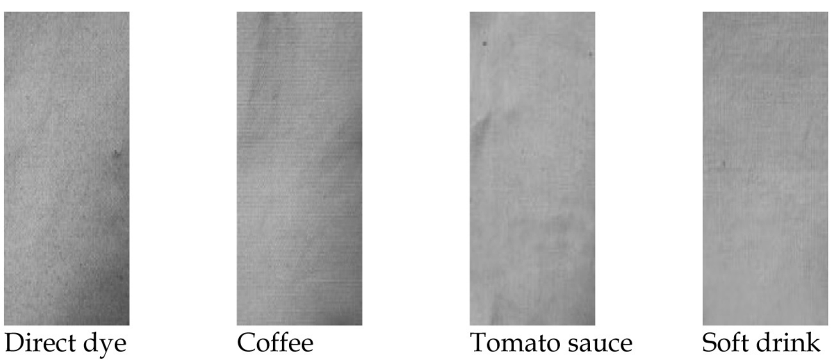


Figure 4. Photographic images of pristine cotton fabrics after illumination by a solar simulator for 24 h. Only the lower half area of the samples was exposed to artificial sunlight. Samples were stained with direct dye, coffee, tomato sauce, and soft drink.

3.3 Study the effects of fumed silica on the photocatalytic efficiency

As can be seen from Fig 5, before illumination with artificial sunlight, all samples having different TiO_2:SiO_2 ratios displayed similar K/S values (variations limited within error bars). After 24-h illumination, all the samples showed lowered K/S values as expected. However, with the addition of fumed SiO_2, the reduction in K/S after exposure was much smaller; the percentage reduction of K/S for pure TiO_2 coating was 40% while those of silica-containing TiO_2 coating were consistently lower, at approximately 18%. Therefore, it can be deduced that partly replacing TiO_2 with fumed silica, from 10 to 60 wt/wt%, reduced the photocatalytic performance. This can be viewed as either a positive or negative feature. According to the literature, the photocatalytic effect of the TiO_2 destroys the organic matrix in which the TiO_2 itself is embedded, e.g. an organic binder (19). Doping with silica is suggested as one approach that can suppress this photocatalytic destruction. From the literature, Jafry et al. reports an improvement in the antiviral properties of TiO_2 after mixing with fumed silica and exposure to ultrasound in toluene solution. The authors ascribe the enhanced photocataytic effects to two possible factors: first, an increase in the TiO_2 band gap or, secondly, an increase in the surface area by mixing together these particles. Since inactivation of microbes and decomposition of stains are based on the same photocatalytic mechanism, one would expect an improvement in stain removal via this approach. However, such improvement was not detected and the reduced efficiency was ascribed to the replacement of TiO_2 photocatalyst by the photocatalytically inactive fumed silica. It should be noted that the effects of silica on TiO_2 photocatalytic performance are controversial in the literature, e.g. both enhancement (13,20) and deterioration (19,21) have been reported.

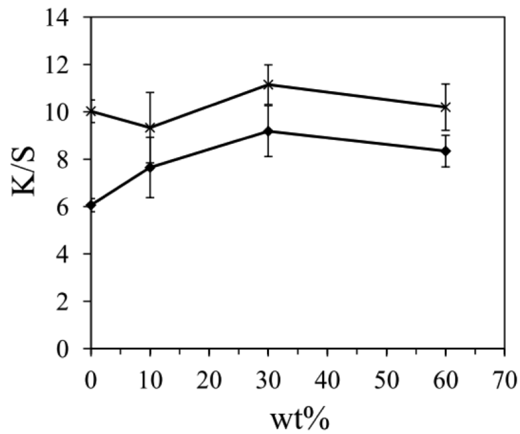


Figure 5. Plots of K/S values of cotton fabrics coated with TiO_2/fumed silica at various ratios before (x) and after (◆) 24-h artificial sunlight exposure.

3.4 Effects of washing cycles on the color change of stained fabrics coated with nano-TiO_2

The photographic images shown in Fig. 6 confirm the benefits of the TiO_2 photocatalyst for self-cleaning textile applications. Although the stains were not completely removed after exposure to simulated sunlight for 24 h, the color intensities of the residual stains were much weakened. We then tested the samples containing TiO_2 in terms of how easily they could be cleaned. After exposure, the color of the lower half of each sample appeared less intense compared to the upper, unexposed half. After one wash in a standard washing machine, the samples stained with C.I. Direct Blue 199 and Allura Red AC looked clean to the eyes while those stained with coffee and tomato sauce still appeared tainted. Table 3 displays the K/S value of the samples finished with 2 wt/wt% TiO_2 before and after washing one, two or three times. The results agree well with visual perception. Coffee and tomato-sauce spots were persistent that they needed three washing cycles before appearing nearly clean to the eyes. The exposed parts of the fabric were cleaned more easily because the stains had been partially decomposed by the TiO_2 photocatalyst. As expected, stain removal from the unexposed sample area required more washing cycles.

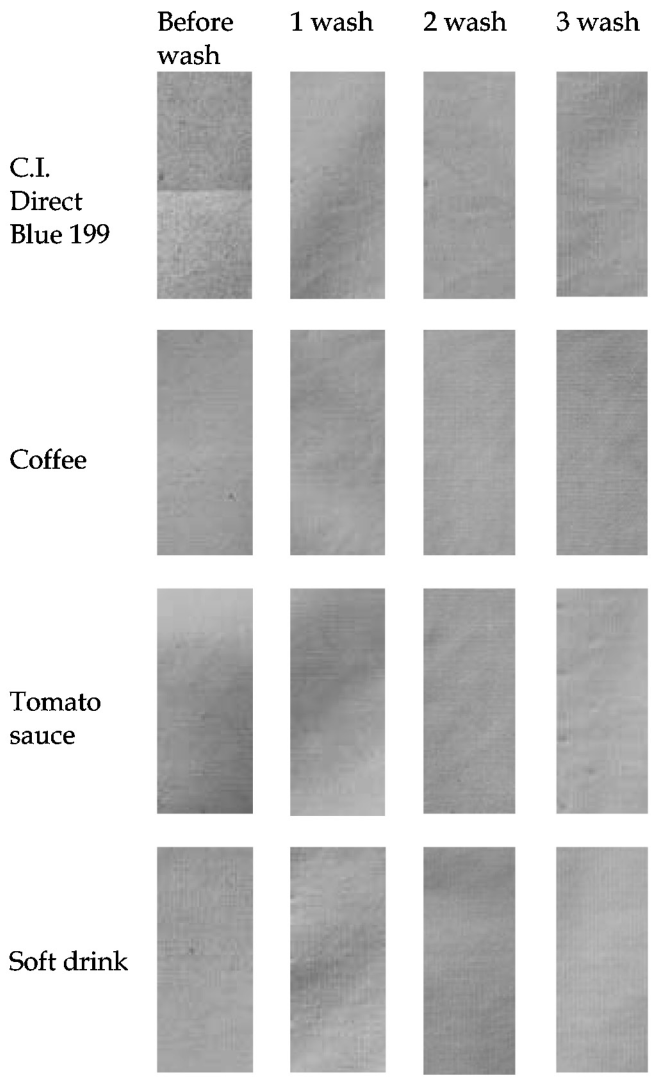


Figure 6. Photographic images of pristine cotton fabrics after illumination by a solar simulator for 24 h. The numbers on top indicate the number of washings the samples underwent. Types of stains are indicated on the left.

Table 3. K/S values of cotton samples finished with 2 wt/wt% TiO_2. Data were collected both from areas exposed and unexposed to 24-h artificial sunlight.

Stain	Number of washes	Area measured	
		Exposed	Unexposed
Direct dye	0	3.63	10.68
	1	1.91	2.96
	2	1.51	2.42
	3	1.52	2.44
Coffee	0	3.43	6.53
	1	2.43	3.66
	2	2.03	2.87
	3	2.15	2.83
Tomato	0	3.58	3.86
	1	3.01	3.26
	2	2.42	2.68
	3	2.47	2.56
Soft drink	0	1.68	2.38
	1	1.56	1.79
	2	1.32	1.95
	3	1.35	1.99

It could be argued that the removal of stains is due to the removal of TiO_2 particles during washing. This explanation does not hold in the present study since the stains on the unexposed area remained after three washes, as can be seen clearly for the coffee-stained sample. This implies the retention of TiO_2 on the fabric surface. Uddin et al. have shown that nanoparticles of TiO_2 can anchor onto cellulosic fibers to the extent that they can withstand up to 20 washing cycles (22).

4. Conclusion

This work reports the evaluation of photocatalytic activities of cotton coated with TiO_2 nanoparticles with the aim of obtaining self-cleaning textiles. A pad-dry-cure technique was used as a coating process. Results showed that the stains, i.e. direct dye, coffee, tomato sauce, and soft drink were partially decomposed after 24-h illumination with artificial sunlight. Complete removal of direct dye and soft drink in a single wash cycle confirmed the enhancement of self-cleaning efficiency by TiO_2 coating via two separate mechanisms: a dye-sensitization mechanism through exposure to visible light, and a classical UV-stimulated photocatalytic action. TiO_2 remained on the fabrics after three washes. Study of the photocatalytic performance of nano-TiO_2/fumed silica was also conducted, and it was found that the photocatalytically-inactive fumed silica showed an adverse effect on the self-cleaning properties.

5. Acknowledgement

The authors gratefully acknowledge the financial support provided by Thammasat University under the TU New Research Scholar, Contract No. 13 /2555. We would like to thank Dr. Punrattanasin (Department of Textile Science and Technology, Thammasat University) and Mr. Thongcharoen (Thailand Textile Institute) for their support. We are also grateful to the Department of Chemistry, Thammasat University, for providing access to their laboratory equipment.

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