A Novel Green Stabilization of TiO$_2$ Nanoparticles onto Cotton

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Abstract: Facile embedding of TiO$_2$ nanoparticles onto cotton fabric has been successfully attained by ultraviolet light irradiations. The adhesion of nanoparticles with fibre surface, tensile behaviour and physicochemical changes before and after ultraviolet treatment were investigated by scanning electron microscopy, energy dispersive X-ray and inductive couple plasma-atomic emission spectroscopy. Experimental variables i.e. dosage of TiO$_2$ nanoparticles, temperature of the system and time of ultraviolet irradiations were optimised by central composite design and response surface methodology. Moreover, two different mathematical models were developed for incorporated TiO$_2$ onto cotton and tensile strength of cotton after ultraviolet treatment and used further to testify the obtained results. Self-clean fabric through a synergistic combination of cotton with highly photo active TiO$_2$ nanoparticles was produced. Stability against ultraviolet irradiations and self-cleaning properties of the produced fabric were evaluated.

Keywords: UV fixation, Self-stabilization, TiO$_2$, Self-cleaning, Nanoparticles

Introduction

Nanotechnology has achieved much attention in recent years due to its fundamentals. Researchers have admitted that nanomaterials (NMs) play a prominent role in producing products with novel properties [1-6]. Scientists have inspected different types of NMs and TiO$_2$, CuO and ZnO are most common of them used in textile industry [7-9]. TiO$_2$ is the most significant and effective material which has been extensively employed in this field. The significant reasons for its use in multiple applications are its high photocatalytic activity, non-toxicity and chemical stability. The most intrinsic feature of TiO$_2$ NMs is its photocatalytic performance under ultraviolet (UV) light irradiations which trigger a series of oxidation and reduction reactions. Many researchers have confirmed that TiO$_2$ nanoparticles (NPs) are very effective in the purification of waste water, air and also keep the surfaces clean and sterile due to its photocatalytic effect [10-13]. Photocatalysis is a dynamic mechanism used in waste water treatment as well as self-cleaning and antimicrobial applications. In photocatalysis, materials absorb light energy and break down the molecules into their fragments i.e. atoms, ions and radicals. The principle behind photocatalysis is the conversion of light energy into chemical energy to produce radicals and other unstable chemical compounds. The primary oxidizing species formed during photocatalysis are hydroxyl radicals and superoxide anions [14,15].

In textiles, the incorporation of nanomaterials has been introduced during the last decade. Cheng *et al*. reported that there is almost no attraction between textile substrates (polymeric materials) and metal oxides particles (inorganic materials). This happens due to the difference in surface

energy of the two above mentioned materials that produces repellence on their interfaces [16]. So, the stabilization of NPs on textiles is not permanent particularly against washing. Different methods need different steps for the stabilization of inorganic nanomaterials on textile surfaces that are very time consuming and costly for large scale production. Regardless of the above-mentioned dilemma, researchers continued their efforts and used different approaches to embed or stabilize TiO$_2$ NPs on the surface of textiles. Abidi *et al*. reported sol-gel stabilization of TiO$_2$ on cotton fabric that improves UV scattering properties of cotton. They further used curing process to stabilize the developed nanosol on cotton [17]. Perelshtein *et al*. reported an ultrasonic assisted stabilization of TiO$_2$ NPs on cotton fabric to impart antimicrobial properties. Their results revealed that TiO$_2$ in its anatase and rutile form provides significant antimicrobial effects against microorganisms [18]. El-Rafie *et al*. and Hebeish *et al*. incorporated green synthesized silver NPs on cotton fabric in the presence of a binder by using a simple pad-dry-cure process. Their results revealed that cotton fabrics incorporated with silver NPs synthesized by green materials exhibit significant antimicrobial effects against *Staphylococcus aureus* and *Escherichia coli* [19,20]. Karimi *et al*. reported the fixation of nano TiO$_2$ and graphene oxide onto cotton fabric through oven heating and explained the synergetic effects of TiO$_2$/graphene nanocomposites on the photocatalytic efficiency of cotton fabric [21]. Long *et al*. developed fabrics with self-cleaning properties by stabilizing platinum modified TiO$_2$ NPs on cotton through dip-coating method that displayed significantly higher photocatalytic performance for methyl orange and coffee stain [22]. Gashti and Almasian reported the stabilization of carbon nanotubes on cotton fabric by UV radiations in order to develop flame retardant carbon/cellulose composites coatings [23]. In

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another study, Gashti *et al*. reported the incorporation of silica/kaolinite network on cotton surface through UV irradiations using succinic acid as a cross-linking agent to create a thermal resistant hydrophobic surface for cellulose based textiles [24].

Present study explains the stabilization of TiO$_2$ NPs on cotton by UV light. The work described here represents the unique demonstration of embedding TiO$_2$ NPs on textiles via UV light for optimised conditions. In addition, it is believed that this approach is a generic one and can also be extendable for other type of nanomaterials and fabrics.

Experimental

Materials

100 % pure cotton fabric (plain weave with fabric mass 115 gm^{-2}) was used as received from Department of Material Engineering, Technical University of Liberec, Czech Republic. The fabric was first washed with 1 gl^{-1} non-ionic detergent in a washing bath with fabric-liquor ratio 1:40. The fabric was then cut into (12.5×12.5 cm) uniform samples. TiO$_2$ NPs with average particle size 4 nm and specific surface area 150 m^{2}g^{-1} were used in this study as synthesized and reported in our previous investigation [25]. Distilled water was used throughout the study.

Design of Experiment

A central composite design (CCD) is a set of experimental design with three different design points i.e. factorial points (±1), centre point (0) and star/axial points (±α) which is beneficial in response surface methodology (RSM) to fit a quadratic model in order to estimate the effect of curvature. In CCD, the centre point is replicated for getting more precision of the experiment. The general form of a CCD with three input variables/factors (A, B, C) and their coded values (±1), centre point (0) and axial/star points (±α) is illustrated in Figure 1. For 3 factors CCD, the value of α is 1.68.

Table 1 shows the input variables (factors) with their coded values (minimum, maximum) and their central points whereas Table 2 illustrates the factors level setting in their coded form based on CCD.

The experimental design with different dosage of TiO$_2$ NPs under varying temperature and UV irradiations time for all samples for actual values based on CCD is shown in Table 3. To optimize the effects of independent variables, Design-Expert version 10 by Stat-Ease corporation was
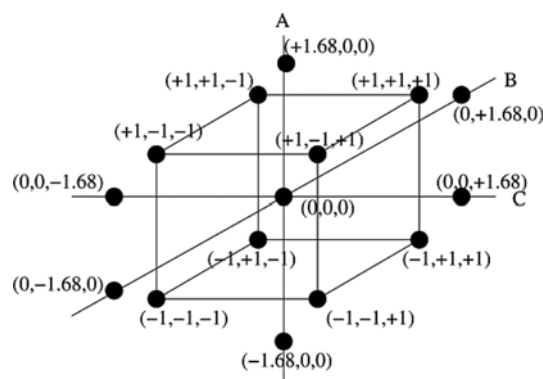

Figure 1. General form of a 3 factors central composite design.

Table 2. 3 factors general CCD matrix for experimental variables with coded values and factors level setting

Experimental trial	Factors level setting		
	A: TiO$_2$ dosage	B: Temperature	C: UV irradiations time
1	-1	-1	-1
2	1	-1	-1
3	-1	1	-1
4	1	1	-1
5	-1	-1	1
6	1	-1	1
7	-1	1	1
8	1	1	1
9	-α	0	0
10	α	0	0
11	0	-α	0
12	0	α	0
13	0	0	-α
14	0	0	α
15	0	0	0
16	0	0	0
17	0	0	0
18	0	0	0
19	0	0	0
20	0	0	0

used. The results include: Y$_1$: incorporated amount of TiO$_2$ NPs onto cotton after UV irradiations and Y$_2$: tensile strength of cotton after UV irradiations were adjusted by

Table 1. 3 factors CCD matric for experimental variables with their coded values

Factor	Name	Unit	Coded value		Central point	Mean	Std. dev.
A	TiO$_2$ dosage	gl^{-1}	-1=4	1=8	6	6	1.8
B	Temperature	^{o}C	-1=30	1=60	45	45	12.6
C	UV irradiations time	min	-1=40	1=120	80	80	33.9

using equation (1).

$$Y = b_0 + \sum b_i X_i + \sum b_{i,j} X_i X_j + \sum b_{i,i} X_i^2 \quad i \geq j$$
$$i, j = 1, 2, 3 \tag{1}$$

where b_0 is the coefficient of constant term, b_i represents the coefficient of linear term, b_{ii} is the coefficient of quadratic term and b_{ij} represents the coefficient of two factors interaction [26].

Suspension and Deposition of TiO$_2$ NPs

A suspension of TiO$_2$ NPs with water through ultrasonic homogeniser (Sonoplus HD 3200, Bandelin Electronics, Germany) was developed with concentration of TiO$_2$ NPs varying from 2 to 10 gl^{-1} according to CCD. Pad-dry
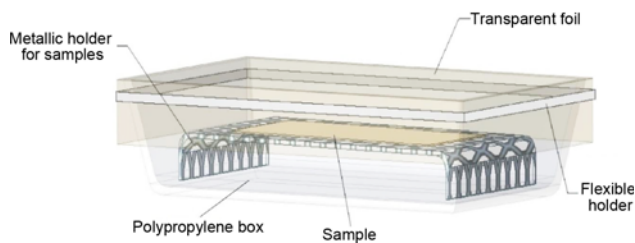

Figure 2. Schematic illustration of the experimental setup.

technique was used to deposit TiO$_2$ NPs on the surface of cotton. All samples were immersed in suspension for 2 min, squeezed on padder (Mathis, Switzerland) under pressure 3 kN with velocity 1 mmin^{-1} and finally dried in an oven at 60 °C for 30 minutes. These samples were named as TiO$_2$ treated samples whereas pristine samples were called untreated samples.

Embedding through UV Light

To investigate the adhesion, incorporation and surface changes, all TiO$_2$ treated and untreated samples were irradiated under UV light for different time intervals ranging from 15 to 150 min according to CCD. Intensities of UV-B and UV-A light were 4.1 mW·cm^{-2} and 40.4 mW·cm^{-2} respectively, sustained by fixing the distance between samples and UV lamp. An open system was developed consisting a polypropylene box and a special holder for samples enclosed in it as shown in Figure 2. To find out the crucial role to UV light, TiO$_2$ treated samples without UV irradiations were also used in leaching and self-cleaning processes for comparison.

Characterization

The morphological changes on the surface of treated and untreated samples were observed by UHR-SEM Zeiss Ultra

Table 3. 3 factors CCD design for experimental variables with actual values and responsive results

Sample name	TiO$_2$ dosage (g·l^{-1})	Temperature (°C)	UV irradiations time (min)	Y_1 (ppm)	Predicted results for Y_1 (ppm)	Y_2 (N)	Predicted results for Y_2 (N)
Untreated sample	0	0	0	0	0	504	0
1	6	70	80	2123	21	482	474
2	4	30	120	1590	1578	474	474
3	6	45	80	1383	1386	434	426
4	6	45	80	1386	1386	426	426
5	6	45	15	793	803	465	459
6	8	30	40	1590	1579	463	460
7	6	45	80	1380	1386	424	426
8	4	60	40	898	861	432	435
9	6	45	80	1389	1386	427	426
10	4	30	40	856	855	498	505
11	8	60	40	1781	1785	496	502
12	6	20	80	1763	1767	476	473
13	2	45	80	759	768	489	482
14	8	60	120	3319	3312	490	488
15	6	45	80	1398	1386	428	426
16	8	30	120	2895	2904	414	417
17	10	45	80	2999	2997	492	492
18	6	45	150	2756	2755	428	424
19	4	60	120	1805	1808	425	433
20	6	45	80	1381	1386	420	426

Y_1: incorporated amount of TiO$_2$ NPs after UV irradiations, Y_2: tensile strength after UV irradiations.

Plus with an accelerating voltage 2 kV equipped with an Energy Dispersive X-ray (EDX) spectrometer Oxford X-max 20. The charging effect was eliminated by the use of charge compensator (local N$_2$ injection). EDX analysis of the samples was performed at 10 kV accelerating voltage to confirm the elemental configuration of the embedded materials on the surface of cotton. The incorporated amount of TiO$_2$ NPs on cotton surface after UV irradiations was estimated by Inductive Couple Plasma-Atomic Emission Spectroscopy (ICP-AES) elemental analysis (Perkin Elmer optima 2100 DV). Tensile strength of all samples was measured on TIRA test 2300 with constant rate of extension (CRE) according to standard test method ISO 13934-1.

Durability against Washing and Leaching

The durability of embed TiO$_2$ NPs onto cotton fabric against washing was evaluated according to ISO 105 C06 (B1M) standard test method. 4 gl^{-1} detergent was used for each washing cycle at 50 ^{o}C for 45 min time interval. The washed specimens were then rinsed and dried at 60 ^{o}C for 15 min after each washing cycle. A Varian Cary 500 UV-vis-NIR spectrophotometer was used to evaluate absorption spectra of washing effluents. For leaching, the amount of Ti^{+4} ions present in the leaching solution was investigated to evaluate the adhesion and stability of the developed samples. For this purpose, different samples were treated with 1M NaCl solution at laboratory conditions for 6 h. Later, the samples were removed from leaching solution and the amount of Ti^{+4} was estimated by ICP-AES analysis.

Self-cleaning Assessment

Self-cleaning efficiency was evaluated on the basis of degradation activity of coffee stain under daylight irradiations for 12 h. The study was conducted by taking swatches (4×4 cm) from all samples and a coffee stain was dropped on them. After that, all samples were dried and exposed to daylight irradiations for different time intervals and colour difference was estimated according to equation (2):

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

where, *L* refers to lightness of the fabric, *a* and *b* stand for red-green colour and yellow-blue colour respectively.
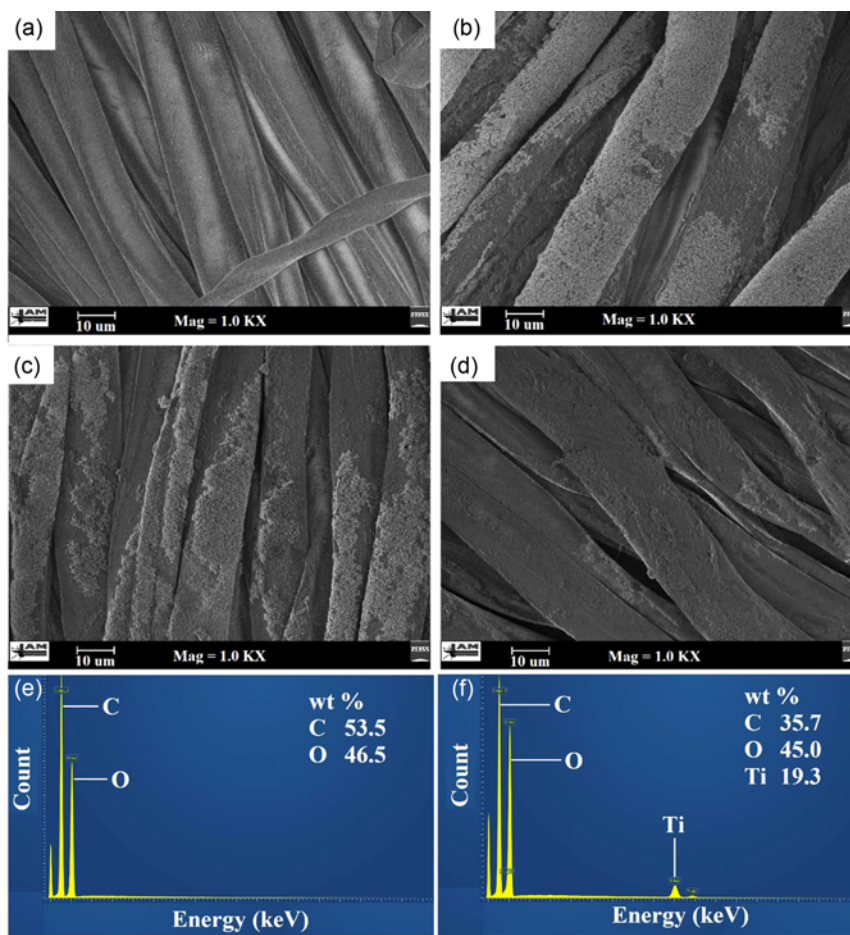

Figure 3. SEM analysis of (a) untreated sample, (b) sample 14 before UV treatment, (c) sample 14 after UV treatment, (d) UV treated sample after washing; and EDX spectra of (e) untreated sample, (f) sample 14.

Results and Discussion

SEM Analysis and EDX Spectra

The morphology of developed samples was investigated by Scanning Electron Microscopy (SEM) and EDX analysis. In Figure 3, a comparison of pristine cotton (untreated sample) with sample 14 is presented as we obtained highest incorporated amount of TiO_2 NPs for this sample (Table 3). In Figure 3(a), a clean and smooth surface of pristine cotton can be observed as no treatment was applied on it whereas a huge cluster of TiO_2 NPs deposited as a homogeneous thick layer on the surface of cotton fabric after padding can be seen in Figure 3(b). We also observed that the particles are evenly distributed on the surface of cotton Figure 3(b). In Figure 3(c), it can be seen that after UV irradiations, most of the NPs penetrated inside the cotton fibre structure and the remaining covered the surface as a condense layer and strongly aggregated while a completely rough surface of cotton with sufficient amount of TiO_2 NPs was observed after washing the sample as illustrated in Figure 3(d).

Elemental analysis and detection of existing elements were characterized by EDX spectroscopy. The EDX spectrum of untreated sample and sample 14 are presented in Figure 3(e-f) respectively. EDX spectra confirm the existence of TiO_2 NPs on cotton surface. Moreover, higher weight percentage of Ti element in sample 14 indicates higher loading of TiO_2 NPs. These results are in good agreement with SEM results.

ICP-AES Analysis

ICP-AES analysis of samples 1-20 confirmed the presence of TiO_2 NPs on cotton. However, Ti element was not found in untreated sample. In order to estimate the incorporated amount, the characteristic peak of titanium observed in emission spectra was counted and the results were reported in Table 3. The incorporated amount of TiO_2 NPs for samples 1, 11, 16, 17, 18 were 2123 ppm, 1781 ppm, 2895 ppm, 2999 ppm, 2756 ppm respectively, whereas the highest incorporated amount 3319 ppm was found in sample 14. The results are quite obvious as more dosage of TiO_2 NPs during padding results in more loading on cotton. These results are in good agreement with SEM and EDX results.

Washing Durability

Washing effluent analysis was used to evaluate the embedding of TiO_2 NPs on cotton fabric that provides an excellent evaluation of washing durability. The existing amount of TiO_2 NPs in the effluent is considered as durability against washing. More amount indicates lower durability. The effluent was evaluated by spectrophotometer during 6 washing cycles. During initial washing cycle, an absorption peak at 289 nm indicates the presence of TiO_2 NPs as illustrated in Figure 4. It happened because some of the physically attached and unstable NPs were migrated into
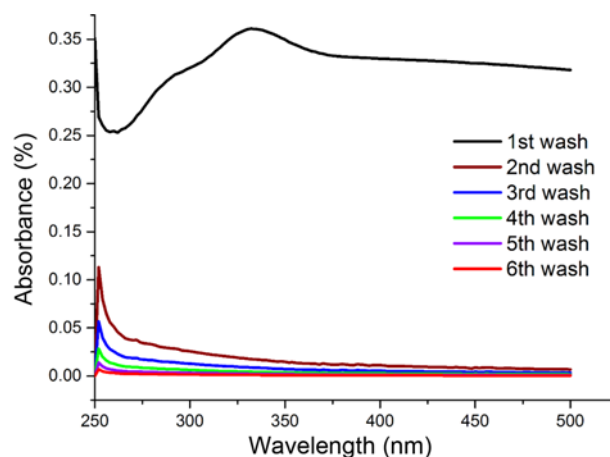

Figure 4. Washing effluent absorbance spectra of sample 14 during different washing cycles.

effluent during initial washing. The results confirmed that no absorption peak was observed during subsequent washing cycles showing the absence of TiO_2 NPs in washing effluent. Furthermore, the results reveal that TiO_2 NPs were strongly attached to cotton indicating the formation of covalent bond between TiO_2 NPs and cotton fibre. TiO_2 NPs have strong affinity towards carboxyl and hydroxyl groups. The bonding between TiO_2 NPs and hydroxyl groups present in cotton play a significant role in washing durability. These results are in good agreement with the findings of Daoud *et al*., Montazer *et al*., Pakdel and Daoud [27-29].

Leaching Durability

The contents of Ti^{+4} ions present in the leaching solution were 82 ppm, 107 ppm, 102 ppm, 48 ppm and 39 ppm for sample 3, sample 5, sample 10, sample 14 and sample 18 respectively. These results reveal that only 5 % TiO_2 was removed from the fabric surface by leaching in case of sample 5 whereas this percentage was decreased to 1.4 % for sample 14 and sample 18. On the other side, 63 % TiO_2 was removed for TiO_2 treated sample (without UV treatment). These results indicate that TiO_2 NPs incorporated on cotton surface by UV light irradiations were strongly anchored to the textile substrate as their minimal quantity was withdrawn from the fabric even after 6 h of leaching process.

Self-cleaning Efficiency

Figure 5 illustrates that coffee stains were decomposed completely after 12 h of sunlight irradiations through photocatalytic action of TiO_2. The colour difference was calculated and the results were reported in Table 4. Significant colour change was observed for samples 1 to 20 as presented in Figure 5. However, slight colour change was observed for TiO_2 treated sample (without UV treatment) and almost no change in untreated sample even after 12 h of continuous sunlight irradiations. In addition, the colour
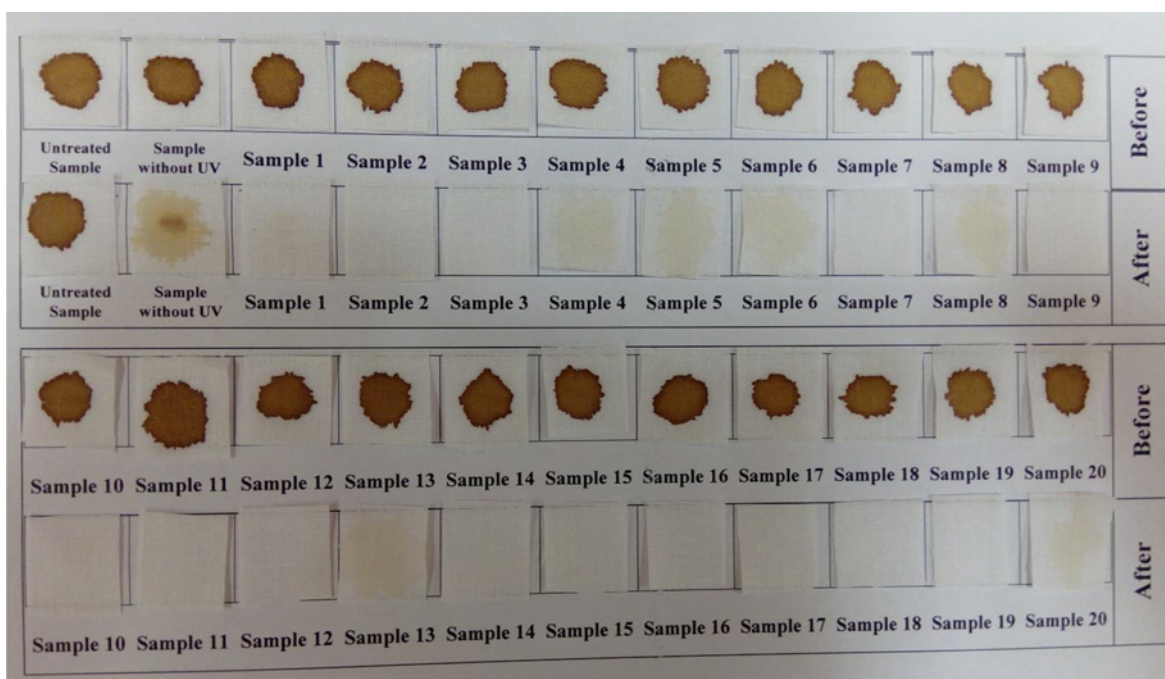
Figure 5. Self-cleaning efficiency of untreated, TiO$_2$ treated and treated samples after 12 h sunlight irradiations.

Table 4. Self-cleaning efficiency (ΔE) results

Sample	ΔE	Sample	ΔE
Untreated sample	5	Sample 10	84
TiO$_2$ treated sample (without UV)	48	Sample 11	83
Sample 1	82	Sample 12	83
Sample 2	80	Sample 13	80
Sample 3	81	Sample 14	90
Sample 4	82	Sample 15	84
Sample 5	78	Sample 16	82
Sample 6	79	Sample 17	83
Sample 7	82	Sample 18	83
Sample 8	83	Sample 19	83
Sample 9	81	Sample 20	82

values were higher for samples 1 to 20 as compared to TiO$_2$ treated sample and untreated sample respectively. These results indicate the self-cleaning efficiency of UV treated samples (samples 1 to 20) was significantly higher than TiO$_2$ treated sample (without UV treatment). This happens because of embedded TiO$_2$ NPs on cotton fabric as UV irradiations produce a covalent linkage between the OH group of TiO$_2$ and the OH group of cellulose that increases the durability of the treatment to impart functional properties. Experiments. These results are in good agreement with the findings of Abidi *et al*. [17]. Moreover, the results reveal that more amount of TiO$_2$ NPs incorporated on the surface of cotton fabric enhances the self-cleaning properties. Higher

colour difference leads to better self-cleaning efficiency obtained by sample 14 with optimal conditions as illustrated in Table 3.

Statistical Analysis

CCD and Response Surface Methodology (RSM) were used to optimize the experimental variables i.e. TiO$_2$ dosage, temperature and UV irradiations time. In total, 20 samples based on CCD were developed as described in Table 3. The resulted responses include Y_1: Incorporated amount of TiO$_2$ on cotton after UV treatment and Y_2: Tensile strength of cotton after UV treatment, were evaluated and discussed on the basis of RSM. For the evaluation of obtained results and the relationship between independent variables and response surfaces, different mathematical models (equation (3)-(4)) were established. In order to predict the responses for a given value of variables, the developed models are useful for further utilization. In Figures 6, 7, response surfaces were drawn based on the developed mathematical models.

ANOVA (analysis of variance) was conducted to evaluate the interaction between the variables and the responses of the designed samples and the results are presented in Tables 5, 6. Goodness of fit was evaluated on the basis of responses analysed by ANOVA. The lack of fit explains the data variations close to the fitted model and will be significant if the proposed model unable to fit the data well. The results indicate that the designed model for incorporated amount of TiO$_2$ NPs on cotton after UV irradiations is statistically significant at F-value 10592.9 and p-value <0.0001 as illustrated in Table 5. Furthermore, the developed model for

Table 5. ANOVA results for incorporated amount of TiO$_2$ NPs on cotton after UV irradiations

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	Remark
Model	10727146	9	1191905	10592.9	< 0.0001	Significant
A (dosage)	125761	1	496873	44156.6	< 0.0001	Significant
B (temperature)	416801	1	159863	1420.6	< 0.0001	Significant
C (UV irradiation time)	84894	1	431854	38376.8	< 0.0001	Significant
AB	16020.50	1	16020.50	142.3	< 0.0001	Significant
AC	180600	1	180600	1605.0	< 0.0001	Significant
BC	20604.50	1	20604.50	183.1	< 0.0001	Significant
A^2	3992212	1	3992212	3547.9	< 0.0001	Significant
B^2	563423	1	563423	5007.3	< 0.0001	Significant
C^2	227397	1	227397	2020.6	< 0.0001	Significant
Residual	1125.19	10	112.52			
Lack of fit	902.35	5	180.47	4.0	0.0755	Not significant
Pure error	222.83	5	44.57			
Cor total	10728271	19				

R-squared: 0.9999, adjusted R-squared: 0.9998, CV%: 0.62.

Table 6. ANOVA results for tensile strength of cotton after UV irradiations

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	Remark
Model	17334.20	9	1926.02	43.1	< 0.0001	Significant
A (dosage)	100.00	1	100.00	2.2	0.1653	Not significant
B (temperature)	1.18	1	1.18	0.02	0.8741	Not significant
C (UV irradiation time)	1678.88	1	1678.88	37.6	0.0001	Significant
AB	6272.00	1	6272.00	140.5	< 0.0001	Significant
AC	72.00	1	72.00	1.6	0.2328	Not significant
BC	450.00	1	450.00	10.08	0.0099	Significant
A^2	6028.78	1	6028.78	135.07	< 0.0001	Significant
B^2	4129.87	1	4129.87	92.5	< 0.0001	Significant
C^2	472.46	1	472.46	10.5	0.0087	Significant
Residual	446.35	10	44.63			
Lack of fit	338.85	5	67.77	3.1	0.1167	Not significant
Pure error	107.50	5	21.50			
Cor total	17780.55	19				

R-squared: 0.9749, adjusted R-squared: 0.9523, CV%: 1.47.

tensile strength is significant at F-value 43.1 and p-value <0.0001 as described in Table 6.

R-squared coefficient was used to evaluate the fit of the developed models. The results presented in Table 5 indicate that only 0.01 % of the total variables cannot be explained through this model for incorporated amount of TiO$_2$ NPs on cotton after UV irradiations. Furthermore, the results of R-squared for tensile strength indicate that only 2.51 % of the total variables cannot be explained by the model (Table 6).

The incorporated amount of TiO$_2$ NPs on cotton after UV

irradiations according to the developed model is calculated by equation (3):

$$Y_1 = 3311 - 310 \times (\text{Dosage}) - 89 \times (\text{Temperature}) - 14 \times (\text{UV time}) + 1.4 \times (\text{Dosage} \times \text{Temperature}) + 1.8 \times (\text{Dosage} \times \text{UV time}) + 0.08 \times (\text{Temperature} \times \text{UV time}) + 31 \times (\text{Dosage})^2 + 0.9 \times (\text{Temperature})^2 + 0.07 \times (\text{UV time})^2 \quad (3)$$

The tensile strength after UV irradiations according to the developed model is calculated by equation (4):
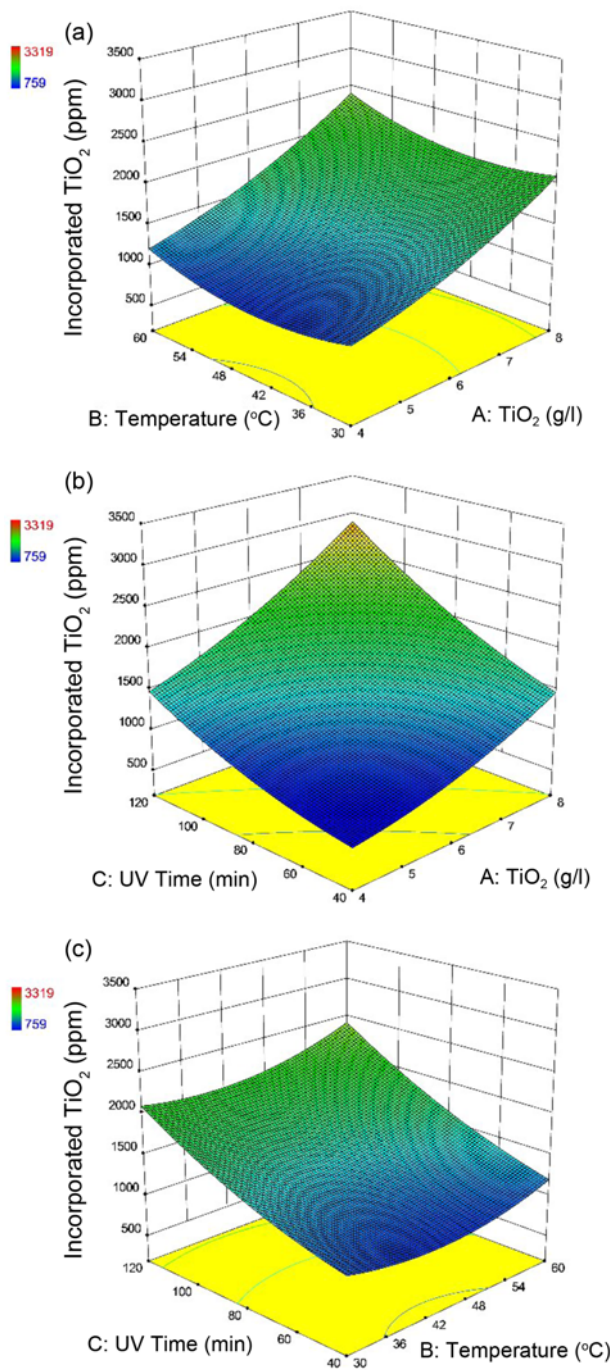
Figure 6. Response surfaces for incorporated amount of TiO₂ NPs on cotton after UV irradiations.

Figure 7. Response surfaces for tensile strength of cotton after UV irradiations.

$$Y_2 = 1035 - 83 \times (\text{Dosage}) - 13 \times (\text{Temperature}) - 1.2$$
$$\times (\text{UV time}) + 0.9 \times (\text{Dosage} \times \text{Temperature})$$
$$- 0.03 \times (\text{Dosage} \times \text{UV time}) + 0.01 \times (\text{Temperature}$$
$$\times \text{UV time}) + 3.8 \times (\text{Dosage})^2 + .07 \times (\text{Temperature})^2$$
$$+ 3.5 \times (\text{UV time})^2 \qquad (4)$$
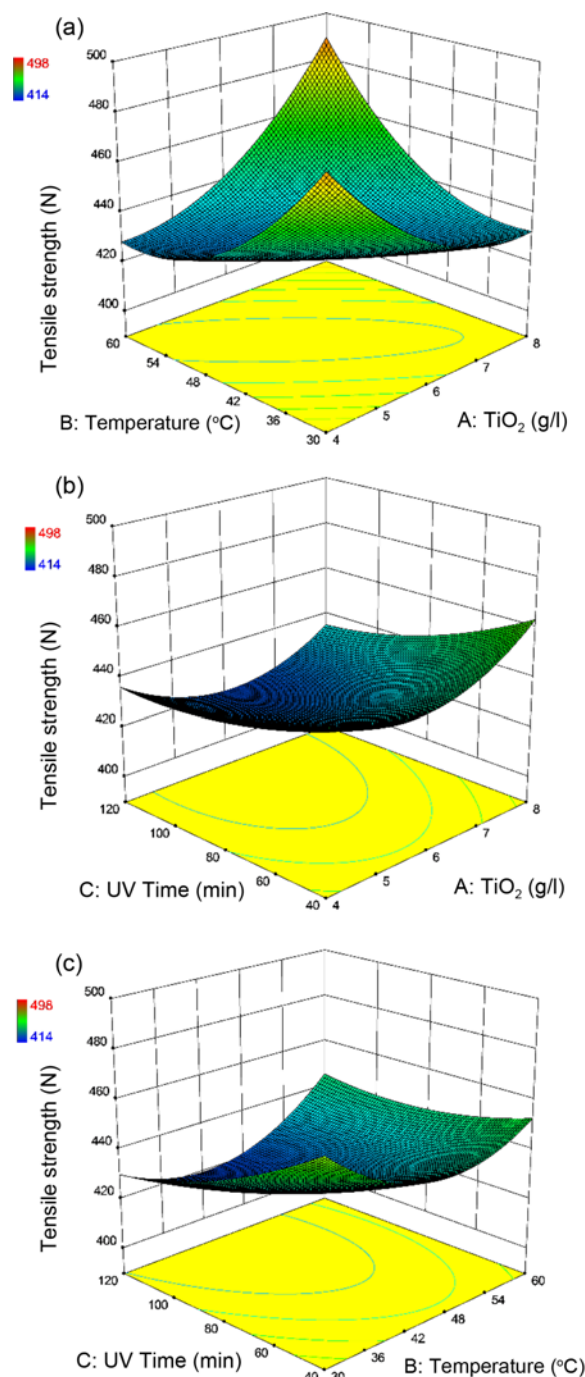
According to the above regression equations and obtained

results (Table 3), the optimal points for best possible results are 8 gl^{-1} TiO₂ dosage, 60 °C temperature and 120 min UV irradiations time. The predicted response values for Y_1 and Y_2 under optimal conditions (Sample 14) are 3312 ppm and 488 N respectively.

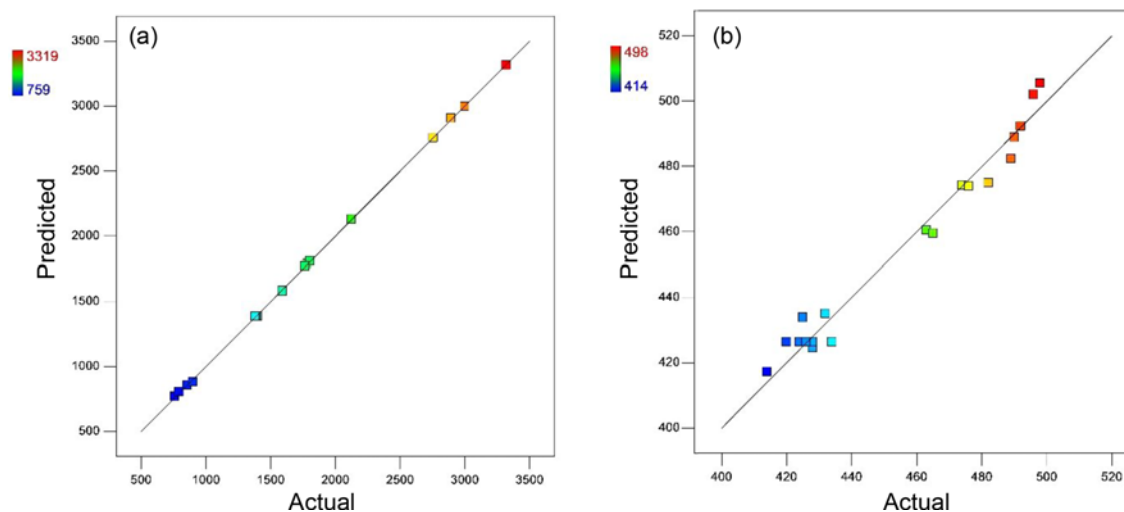The response surfaces are presented in Figures 6, 7 for incorporated amount of TiO₂ NPs on cotton after UV irradia-

Figure 8. A plot of actual vs predicted responses; (a) incorporated amount of TiO$_2$ and (b) tensile strength.

tions and tensile strength after UV irradiations respectively. It can be seen in Figures 6, 7 that increasing TiO$_2$ NPs dosage in the suspension results in more incorporated amount of TiO$_2$ NPs on the surface of cotton. Moreover, prolonged UV irradiations time leads to a higher fixation of TiO$_2$ NPs on cotton. This happened because UV irradiations provide most of the NPs a path to penetrate deep inside the fibre structure and strongly attached to them. The results revealed that the incorporated amount of TiO$_2$ NPs on cotton strongly depends on dosage of TiO$_2$ and UV irradiations time.

Actual vs predicted values plot is presented in Figure 8. This plot statistically explains the effects of the fitted model and compares it with the null model. It can be observed that all the values are very close to the fitted line indicating a good fit of the model.

Conclusion

TiO$_2$ NPs were successfully embedded on cotton fabric by UV light. SEM, EDX and ICP-AES analysis confirmed the deposition of TiO$_2$ NPs on cotton. Higher incorporated amount of TiO$_2$ NPs onto cotton led to higher self-cleaning efficiency. Washing and leaching durability of UV treated samples (samples 1 to 20) confirmed the role UV light irradiations for the stabilization of TiO$_2$ NPs onto cotton through covalent bonding. Moreover, almost similar tensile strength of untreated samples and samples 1 to 20 verified the fitting of the used method.

Statistical analysis confirmed that the obtained results solely rely on TiO$_2$ dosage, temperature and UV irradiations time. Optimal conditions for obtaining best possible results were attained by using 8 gl^{-1} TiO$_2$, 60 ^{o}C temperature and 120 min UV irradiations time.

References

1. P. Cai, W. R. Leow, X. Wang, Y. L. Wu, and X. Chen, *Adv. Mater.*, **29**, 1605529 (2017).
2. M. Ates, *J. Solid State Electrochem.*, **20**, 1509 (2016).
3. L. K. Bogart, G. Pourroy, C. J. Murphy, V. Puntes, T. Pellegrino, D. Rosenblum, D. Peer, and R. Lévy, *ACS Nano*, **8**, 3107 (2014).
4. L. Wang, Q. Xiong, F. Xiao, and H. Duan, *Biosens. Bioelectron.*, **89**, 136 (2017).
5. J. Xu, Y. Chen, L. Deng, J. Liu, Y. Cao, P. Li, H. Ran, Y. Zheng, and Z. Wang, *Biomaterials*, **106**, 264 (2016).
6. J. Yin and B. Deng, *J. Membr. Sci.*, **479**, 256 (2015).
7. I. Perelshtein, G. Applerot, N. Perkas, E. Wehrschuetz-Sigl, A. Hasmann, G. Gübitz, and A. Gedanken, *Surf. Coat. Technol.*, **204**, 54 (2009).
8. M. T. Noman, J. Wiener, J. Saskova, M. A. Ashraf, M. Vikova, H. Jamshaid, and P. Kejzlar, *Ultrason. Sonochem.*, **40**, 41 (2018).
9. R. Saravanan, S. Karthikeyan, V. Gupta, G. Sekaran, V. Narayanan, and A. Stephen, *Mater. Sci. Eng., C*, **33**, 91 (2013).
10. D. Caschera, F. Federici, T. de Caro, B. Cortese, P. Calandra, A. Mezzi, R. L. Nigro, and R. G. Toro, *Appl. Surf. Sci.*, **427**, 81 (2018).
11. S. Landi, J. Carneiro, S. Ferdov, A. M. Fonseca, I. C. Neves, M. Ferreira, P. Parpot, O. S. Soares, and M. F. Pereira, *J. Photochem. Photobiol. A: Chem.*, **346**, 60 (2017).
12. E. Pakdel, J. Wang, B. J. Allardyce, R. Rajkhowa, and X. Wang, *Sep. Purif. Technol.*, **170**, 92 (2016).
13. Y. Xu, J. Sheng, X. Yin, J. Yu, and B. Ding, *J. Colloid Interface Sci.*, **508**, 508 (2017).
14. A. Fujishima, T. N. Rao, and D. A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.*, **1**, 1 (2000).

15. J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, and D. W. Bahnemann, *Chem. Rev.*, **114**, 9919 (2014).

16. Q. Cheng, C. Li, V. Pavlinek, P. Saha, and H. Wang, *Appl. Surf. Sci.*, **252**, 4154 (2006).

17. N. Abidi, E. Hequet, S. Tarimala, and L. L. Dai, *J. Appl. Polym. Sci.*, **104**, 111 (2007).

18. I. Perelshtein, G. Applerot, N. Perkas, J. Grinblat, and A. Gedanken, *Chem. Eur. J.*, **18**, 4575 (2012).

19. M. El-Rafie, A. Mohamed, T. I. Shaheen, and A. Hebeish, *Carbohydr. Polym.*, **80**, 779 (2010).

20. A. Hebeish, M. El-Naggar, M. M. Fouda, M. Ramadan, S. S. Al-Deyab, and M. El-Rafie, *Carbohydr. Polym.*, **86**, 936 (2011).

21. L. Karimi, M. E. Yazdanshenas, R. Khajavi, A. Rashidi, and M. Mirjalili, *Appl. Surf. Sci.*, **332**, 665 (2015).

22. M. Long, L. Zheng, B. Tan, and H. Shu, *Appl. Surf. Sci.*, **386**, 434 (2016).

23. M. P. Gashti and A. Almasian, *Compos. Pt. B-Eng.*, **45**, 282 (2013).

24. M. P. Gashti, A. Elahi, and M. P. Gashti, *Compos. Pt. B-Eng.*, **48**, 158 (2013).

25. M. T. Noman, J. Militky, J. Wiener, J. Saskova, M. A. Ashraf, H. Jamshaid, and M. Azeem, *Ultrasonics*, **83**, 203 (2018).

26. F. Lessan, M. Montazer, and M. Moghadam, *Thermochim. Acta*, **520**, 48 (2011).

27. W. A. Daoud, S. Leung, W. Tung, J. Xin, K. Cheuk, and K. Qi, *Chem. Mater.*, **20**, 1242 (2008).

28. M. Montazer, F. Alimohammadi, A. Shamei, and M. K. Rahimi, *Colloids. Surf. B: Biointerface.*, **89**, 196 (2012).

29. E. Pakdel and W. A. Daoud, *J. Colloid Interf. Sci.*, **401**, 1 (2013).