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Self-cleaning properties of bleached and cationized cotton using nanoTiO_2: A statistical approach

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ABSTRACT

Cationization is a novel treatment on cotton to produce fabric with new characteristics. Bleached cotton fabric has already been treated with nanoTiO_2 (NTO) to create fabric with self-cleaning properties. However treatment of cationized cotton with NTO has not been reported. In this research, the self-cleaning properties of bleached and cationized cotton treated by NTO were compared and optimized using a statistical model. The bleached cotton was first cationized with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat-188). The NTO particles were stabilized on the cotton surface using butane tetra carboxylic acid (BTCA) in the presence of sodium hypophosphite (SHP) under different curing conditions including UV irradiation (UV), high temperature (High temp) and a combination of UV and high temperature (UV–Temp). The central composite design (CCD) was used for different variables based on Design of Expert software. The appropriate model was obtained for each condition to create optimum color difference. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) were also employed to indicate the NTO particles on the fabric surface including the size of nanoparticles and their crystallinity.

1. Introduction

In recent years, NTO attracts much attention because of their photo catalytic activity and ability to absorb ultra-violet irradiation (Cassaignon, Koelsch, & Jolivet, 2007; Dastjerdi & Montazer, 2010; Jung & Park, 1999; Montazer & Pakdel, 2010; Uddin et al., 2007; Watson, Beydoun, Scott, & Amal, 2003). In addition, the deposition of NTO particles on fabrics used to obtain different characteristics such as: self-cleaning (Bozzi, Yuranova, & Kiwi, 2005; Carneiro et al., 2007; Huang, Huang, Nguyen, & Hsu, 2007; Mihailovicǐ et al., 2010; Uddin et al., 2008; Yang, Han, & Choy, 2006; Yuranova, Mosteo, Bandara, Laubb, & Kiwi, 2006), waste material and pollutants decomposition (Klaus et al., 2003; Pal, Pehkonene, Yu, & Ray, 2007; Yao, Ho, Yan, & Tzeng, 2007; Zhang, Su, Zhao, & Tan, 2008), harmful bacteria growth prevention (Sunada, Watanabe, & Hashimoto, 2003; Liu & Yang, 2003; Zhao, Krishna, Hua, Moudgil, & Koopman, 2009; Rincon & Pulgarin, 2003), crease recovery angle improvement (Chen & Wang, 2006; Nazari, Montazer, & Rahimi, 2009; Nazari, Montazer, Rashidi, Yazdanshenas, & Anary-Abbasinejad, 2009; Nazari, Montazer, Rashidi, Yazdanshenas, & Moghadam, 2010; Wang & Chen, 2005a) and UV-protection (Gouda & Keshk, 2010).

The property of photo catalysis contributes to the decomposition of the organic substances existed on the surfaces of nanoparticles. Self-cleaning of modified cotton by NTO at low temperature shows that bleached and mercerized cottons can be activated by RF-plasma, MW-plasma and UV-irradiation incorporating negatively charged groups to anchor NTO on the fabric surface. This process is promising for the total removal of stains containing persistent color pigments on the cotton fabrics (Bozzi, Yuranova, Guasaquillo, Laub, & Kiwi, 2005; Meilert, Laub, & Kiwi, 2005; Yuranova, Laub, & Kiwi, 2007).

Also, cationization of cotton fabric has been considered in the recent studies and dyeing of treated fabric with anionic dye without salt reported (Kamel, El-Shishtawy, Youssef, & Mashaly, 2007; Kamel, El Zawahry, Ahmed, & Abdelghaffar, 2009; Montazer, Malek, & Rahimi, 2007; Wang, Ma, Zhang, Teng, & Yang, 2009a; Wang, Ma, Zhang, Teng, & Yang, 2009b). It was shown that the exhaustion method has the lowest reaction efficiency and pad-steam or pad-batch have the highest one for cationization of cellulose with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHTAC) (Hashem, Hauser, & Smith, 2003).

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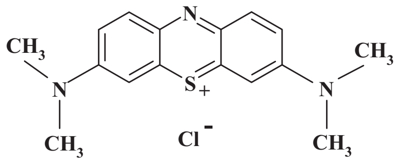


Scheme 1. Structure of methylene blue.

Over the past decade, multifunctional carboxylic acids have been used as non-formaldehyde durable press and cross linking agents for cotton (Mao & Yang, 2001; Sricharussin, Ryo-Aree, Intasen, & Poungraksakirt, 2004; Welch, 1997). Among the different investigated poly carboxylic acids, BTCA is the most effective cross linking agent for cotton (Hebeish, Hashem, Abdel-Rahman, & El-Hilw, 2006). Several studies have been conducted to use the NTO and BTCA in order to improve crease recovery angle (Nazari, Montazer, Rahimi, 2009; Nazari, Montazer, Rashidi, et al., 2009; Nazari et al., 2010; Wang & Chen, 2005b; Yuen et al., 2008).

Recently, response surface methodology (RSM) includes factorial design and regression analysis has been used to evaluate the effective parameters and create models for selecting optimum conditions of variables for a desirable response such as optimized enzyme production from microorganisms (Dutta, Dutta, & Banerjee, 2004), optimization of extraction process of polysaccharides (Yongjiang, Zhong, Jianwei, Minger, & Xueqian, 2009), the rates of dye removal (Cho & Zoh, 2007; Körbahti, 2007; Secula, Suditu, Poulios, Cojocaru, & Cretescu, 2008) and the dyeing condition (Wang, Lin, Wang, Hsiung, & Liu, 2007). Also, we reported the using response surfaces methodology (RSM) for modification of wool surface by liposomes for dyeing with weld (Montazer, Zolfaghari, Toliat, & Moghadam, 2009) and optimization of wool dyeing with madder and liposome (Montazer, Taghavi, Toliyat, & Moghadam, 2007).

We have already investigated and reported the influences of NTO particles on bleached cotton and cationized cotton to improve the crease recovery angle (Nazari, Montazer, Rahimi, 2009; Nazari, Montazer, Rashidi, et al., 2009; Nazari et al., 2010). In this paper, we compared the self-cleaning properties of bleached cotton (B) and cationized cotton (C) treated with NTO and BTCA under different curing conditions (UV, High temp and UV–Temp). The influence of NTO photo catalyst on the degradation of methylene blue (MB) was quantified. The present study focused on implementing the central composite design (CCD) to optimize the self-cleaning properties of these fabrics. The best treatment conditions to obtain self-cleaning properties on the treated cottons will be subsequently discussed.

2. Experimental

2.1. Material

BTCA, sodium hydroxide, sodium hypophosphite (SHP) and methylene blue (C.I. Basic Blue 9, Scheme 1) were supplied by Merck Chemical Co., Germany. 3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (Quat-188), were purchased from Fluka Company, Switzerland. Non-ionic detergent (Rucogen DEN) composed of fatty alcohol ethoxylate from Rudolf Chemie Co., (Tehran, Iran). Nanotitanium dioxide was employed as the photo catalyst with characteristic of our previous study including full width at half maximum (FWHM) of the peak at 25.2° (0.3971) and using Scherrer's equation, the average crystal diameter of about 38.55 nm was calculated and reported (Nazari et al., 2010). These particles were prepared from Degussa Chemie Co., Duisburg, Germany. The desized, scoured and bleached plain weave 100% cotton fabric was used with wrap density 32 yarn/cm, weft density 30 yarn/cm and fabric weight of 118 g/m^2.

2.2. Instrument

Finishing compounds were prepared and dispersed using an ultrasonic bath (200 V, 50 W, 40 kHz). A heating oven was used to dry and cure the samples. Some of the treated samples were exposed to the UVA (320–400 nm) irradiation of an HPA 400S lamp (400 W, Philips, Belgium). The microspopic oictures was taken by a scanning electron microscopic (SEM) using an LEO 440i (UK). Color coordinates (CIE L*, a*, b*) were determined with reflectance spectrophotometer (color-guide sphere, D/8° spin, Germany). An X-ray diffractometer type 3003 PTS, SEIFERT, Germany ($\lambda = 1.54060$ Å, at 40 kV and 30 mA) with Cu Kα irradiation was used to identify the crystalline phase and also crystal size using Scherrer's equation (Wang, Wu, & Xu, 2005).

2.3. Method

The cotton fabric samples were prepared in 15 cm × 6 cm swatches. These samples were of bleached (B) and bleached-cationized (C) fabrics in order to perform experiments. The cotton fabric was cationized based on pad-batch method, using 20 g/L 3-chloro2-hydroxypropyl trimethyl ammonium chloride (Quat-188) and 8 g/L sodium hydroxide with 100% wet pick up. These samples were placed in closed bags for 24 h in ambient temperature.

The aqueous finishing dispersion was prepared by the mixtures of cross-linking agent BTCA and SHP with the amount of 60% of BTCA and NTO (based on weight of bath: O.W.B) and required percentage of distilled water in ultrasonic bath for 10 min.

The cotton fabrics were padded with 80% wet pick up by freshly prepared aqueous solutions. The padded fabrics were dried at 110 °C for 3 min and then cured with different conditions: UV (15 min UVA irradiation), High temp (180 °C, 2 min) and UV-Temp (UVA irradiation and high temperature). Finally, the finished samples were washed at 70 °C for 30 min using a solution containing 2 g/L Na_2CO_3 and 1 g/L non-ionic detergent (Rucogen DEN), and dried at ambient conditions.

MB photo degradation was conducted through discoloration analysis of dye stains after exposing to UV-A radiation for 30 min.

The treated samples were placed on the flat surface and then one drop of Basic Blue 9 (1%) was dripped vertically on the surface using burette (50 mL), form 1 cm above the fabric. The color stains on the sample surface were created with approximate diameter of 2.25 cm. The dye stained samples were them dried in ambient temperature.

The Δa^*, Δb^*, ΔL^*, and ΔE^* of stained samples were measured before and after UV-A irradiation using reflectance spectrophotometer. On the basis of measured CIE color coordinates, total color difference (ΔE^*) was determined by Eq. (1):

$$\Delta E^* = \sqrt{(\Delta a*)^2 + (\Delta b*)^2 + (\Delta L*)^2}\ 129 \tag{1}$$

where ΔL^* is the color lightness difference; Δa^* is red/green difference and Δb^* is yellow/blue difference.

Hence, ΔE^* of treated cottons under UV-A irradiation were calculated and the degree of self-cleaning for different samples were compared. The water drop absorption time of blank and treated cottons were also examined. This experiment was evaluated based on AATCC 79-2000 standard test method.

2.4. The experimental design

The central composite design used for experimental plan with three variables. These variables were including the amounts of BTCA, NTO and different curing conditions. The ranges of these variables are: BTCA (50.96–99.04 g/L), NTO (0.12–5.02%) and curing method (UV, High temp, UV–Temp). Details of the design for

Table 1
Central composite design for color difference (ΔE^*) samples B and C with BTCA and NTO cured with different methods.

Run numbers	Factors			Δa^* (B)	Δb^* (B)	ΔL^* (B)	Response	Δa^* (C)	Δb^* (C)	ΔL^* (C)	Response
	A: BTCA (g/L)	B: NTO (%)	Curing method				ΔE^* (B)				ΔE^* (C)
Blank 1	0	2.57	UV[a]	−4.96	2.83	0.49	5.73	−4.38	2.62	0.44	5.12
Blank 2	0	2.57	High Temp[b]	−6.08	3.25	0.57	6.92	−5.68	3.08	0.52	6.48
Blank 3	0	2.57	UV–Temp[c]	−6.94	3.88	0.68	7.98	−6.41	3.49	0.61	7.32
1	58.00	4.30	UV[a]	−13.89	8.92	1.24	16.55	−15.40	10.51	1.44	18.70
2	75.00	2.57	UV[a]	−14.30	9.56	1.29	17.25	−16.01	10.99	1.52	19.48
3	99.04	2.57	UV[a]	−14.98	9.98	1.33	18.05	−16.81	11.85	1.64	20.63
4	75.00	2.57	UV[a]	−14.36	9.43	1.28	17.23	−16.04	10.92	1.49	19.46
5	75.00	5.02	UV[a]	−14.01	8.69	1.23	16.53	−15.39	10.46	1.42	18.66
6	75.00	0.12	UV[a]	−11.32	6.38	1.11	13.04	−12.86	8.11	1.16	15.25
7	92.00	0.84	UV[a]	−14.18	9.82	1.32	17.30	−15.92	11.16	1.54	19.50
8	75.00	2.57	UV[a]	−14.28	9.62	1.30	17.27	−15.90	11.19	1.54	19.50
9	75.00	2.57	UV[a]	−14.39	9.35	1.27	17.21	−16.15	10.72	1.47	19.44
10	75.00	2.57	UV[a]	−14.21	9.76	1.31	17.29	−15.83	11.32	1.56	19.52
11	50.96	2.57	UV[a]	−13.84	8.52	1.22	16.30	−14.97	10.11	1.36	18.12
12	58.00	0.84	UV[a]	−11.17	6.66	1.12	13.05	−12.83	8.26	1.17	15.30
13	92.00	4.30	UV[a]	−14.97	10.08	1.34	18.10	−16.82	11.86	1.65	20.65
14	58.00	0.84	High temp[b]	−12.37	7.86	1.15	14.70	−13.99	9.21	1.26	16.80
15	58.00	4.30	High temp[b]	−15.28	10.34	1.39	18.50	−16.55	11.73	1.61	20.35
16	99.04	2.57	High temp[b]	−17.23	12.10	1.70	21.12	−18.57	13.16	2.13	22.86
17	75.00	2.57	High temp[b]	−16.00	11.04	1.53	19.50	−17.48	12.38	1.82	21.50
18	75.00	0.12	High temp[b]	−12.76	7.12	1.14	14.66	−14.01	9.12	1.25	16.76
19	75.00	2.57	High temp[b]	−16.04	10.95	1.50	19.48	−17.51	12.31	1.80	21.48
20	92.00	0.84	High temp[b]	−15.72	11.51	1.58	19.55	−17.48	12.47	1.86	21.55
21	75.00	2.57	High temp[b]	−15.90	11.21	1.55	19.52	−17.48	12.41	1.84	21.52
22	50.96	2.57	High temp[b]	−15.77	10.67	1.46	19.10	−17.22	11.95	1.68	21.03
23	75.00	5.02	High temp[b]	−15.29	10.29	1.38	18.48	−16.58	11.64	1.60	20.32
24	75.00	2.57	High temp[b]	−16.11	10.81	1.48	19.46	−17.50	12.29	1.76	21.46
25	92.00	4.30	High temp[b]	−17.21	12.18	1.72	21.15	−18.54	13.27	2.15	22.90
26	75.00	2.57	High temp[b]	−15.76	11.45	1.57	19.54	−16.78	11.92	1.66	20.65
27	75.00	2.57	UV–Temp[c]	−18.02	12.63	1.92	22.09	−19.29	14.28	2.27	24.11
28	75.00	2.57	UV–Temp[c]	−18.05	12.56	1.90	22.07	−19.39	14.12	2.25	24.09
29	75.00	0.12	UV–Temp[c]	−13.75	8.33	1.19	16.12	−15.34	10.22	1.37	18.48
30	92.00	4.30	UV–Temp[c]	−19.05	13.50	2.21	23.45	−19.93	15.49	2.38	25.35
31	58.00	4.30	UV–Temp[c]	−16.68	11.81	1.63	20.50	−18.40	13.04	2.11	22.65
32	92.00	0.84	UV–Temp[c]	−18.02	12.65	1.94	22.10	−19.00	14.73	2.31	24.15
33	58.00	0.84	UV–Temp[c]	−13.69	8.49	1.20	16.15	−15.24	10.39	1.40	18.50
34	75.00	2.57	UV–Temp[c]	−17.95	12.76	1.96	22.11	−19.14	14.52	2.29	24.13
35	75.00	2.57	UV–Temp[c]	−18.05	12.52	1.88	22.05	−19.62	13.76	2.23	24.07
36	75.00	5.02	UV–Temp[c]	−16.66	11.80	1.62	20.48	−18.45	12.91	2.01	22.61
37	50.96	2.57	UV–Temp[c]	−17.43	12.22	1.74	21.36	−18.67	13.38	2.17	23.07
38	75.00	2.57	UV–Temp[c]	−17.96	12.78	1.98	22.13	−18.81	14.96	2.33	24.15
39	99.04	2.57	UV–Temp[c]	−19.02	13.46	2.19	23.40	−20.10	15.23	2.35	25.33

[a] UVA irradiation for 15 min.
[b] Heating (at 180 °C for 2 min).
[c] UVA irradiation for 15 min and then heating (at 180 °C, 2 min).

samples B and C with BTCA in the presence of NTO presented in Table 1 (Run 1–39). Also, the influence of the variable on the results Y (ΔE^*) was adjusted using the following second order polynominal function:

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum c_i X_i^2 i \geq j \quad i, j = 1, 2, 3 \qquad (2)$$

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i are regression coefficients that explain the influence of the variables in their linear form, b_{ij} are regression coefficients of the interaction terms between variables, and c_i are the coefficients of quadratic form of variables.

3. Results and discussion

3.1. Water and MB drop absorption time

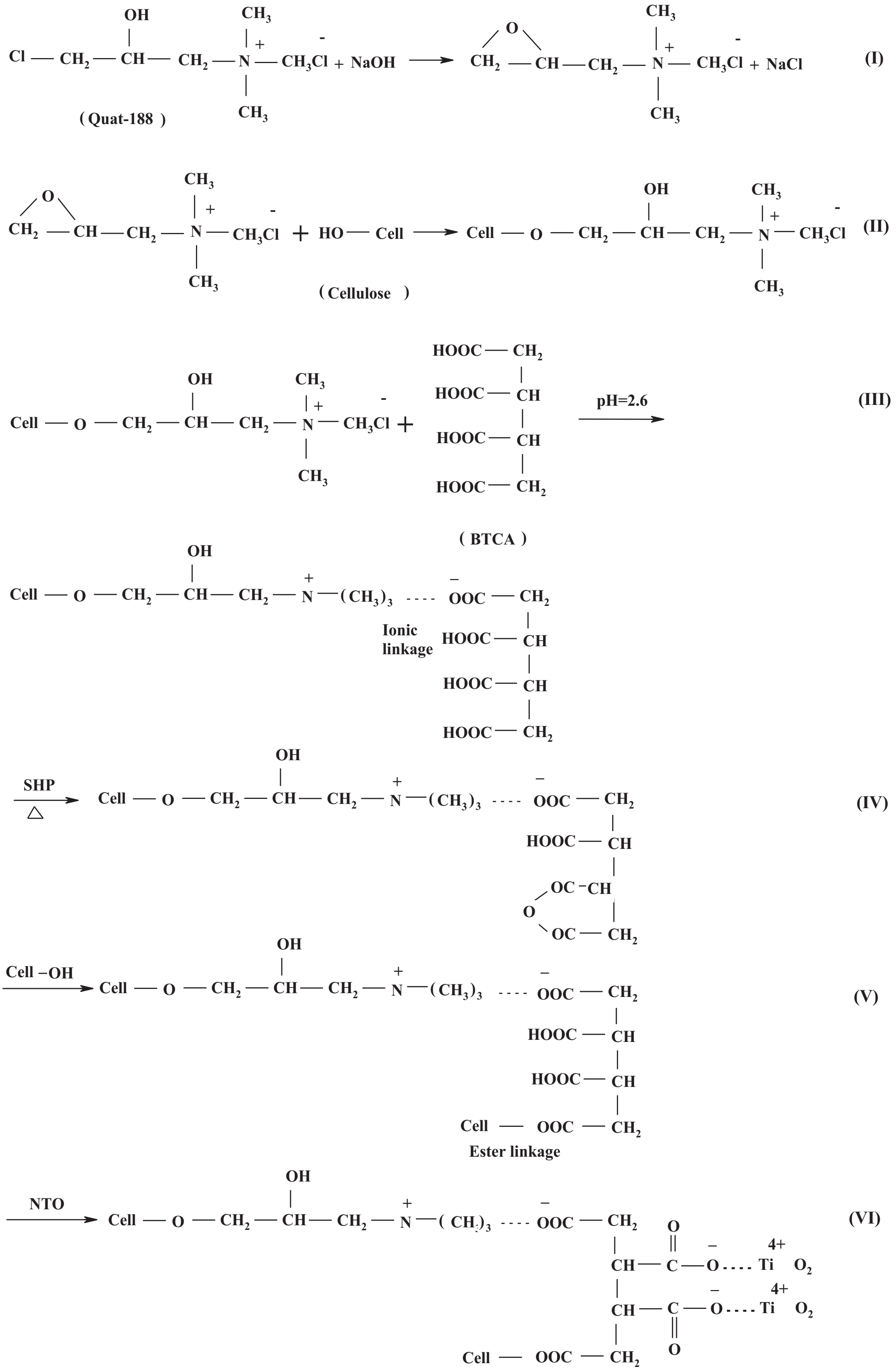
The results indicate the water drop absorption time for the cationized samples decreased as compared with bleached ones (Table 2). This can be attributed to the cationization process in alkali media leads to the removal of some impurities from the cotton fabric and ease of water molecules to access to the hydrophilic groups, and also to high hydrophilicity of cationic groups on cellulosic chains. The treatment of samples B and C with BTCA in the presence of NTO and SHP is the reason for increasing of water drop absorption time. This is because of the reaction of cotton hydroxyl groups

Table 2
The mean values of water and MB drop absorption time on the different cotton samples.

Sample	Mean of water drop absorption time (s)	Mean of MB drop absorption time (s)
Bleached blank sample (B)	11	16
Bleached-cationized blank sample (C)	6	25
Bleached sample 39 (99.04 g/L BTCA, 2.57% NTO, UV–Temp)	14	12
Cationized Sample 39 (99.04 g/L BTCA, 2.57% NTO, UV–Temp)	9	21

with the BTCA carboxyl groups and cross-linking of cellulosic chains leading to a decrease in the available hydroxyl groups in cross-linked cotton. The lowering of cotton hydrophilicity can help to decrease the adsorption of liquid soil and self-cleaning properties.

The results in Table 2 illustrated that the sample C needs longer time to adsorb MB drop as compared to the sample B. This can be related to the repulsion between positive charges on cationic cotton surfaces and MB dye molecules. Also, the treatment of cotton



Scheme 2. Suggested linkage mechanism of bleached and cationized cotton with BTCA and NTO.

Table 3
ANOVA for response surface quadratic model for samples B.

Source	Sum of squares	Df	Mean square	*F* value	*p*-Value Prob > *F*
Model	269.32	11	24.48	59.48	<0.0001 significant
A [BTCA]	38.55	1	38.55	93.66	<0.0001
B [NTO]	42.41	1	42.41	103.04	<0.0001
C [Curing]	133.16	2	66.58	161.76	<0.0001
AB	5.20	1	5.20	12.64	0.0014
AC	0.78	2	0.39	0.95	0.4007
BC	0.44	2	0.22	0.53	0.5936
A^2	0.74	1	0.74	1.81	0.1901
B^2	45.69	1	45.69	111.00	<0.0001
Residual	11.11	27	0.41		
Lack of fit	11.10	15	0.74	740.08	<0.0001 significant
Pure error	0.012	12	1.000E−003		
Cor total	280.43	38			

with BTCA in the presence of NTO and SHP cause a decrease in the MB drop absorption time on samples 39 (Table 2). This can be considered as a result of carboxylate anionic groups creation on the cotton surfaces. The BTCA-treated samples tend to absorb MB cationic molecules quicker than that of the blank samples. Although the water absorption of the cross-linked cotton with BTCA is slower but the presence of some carboxylate anion groups on the cross-linked cotton surfaces makes the fabric surface more attractive for cationic dye (MB). Therefore, the cationized cross-linked cotton has a higher absorbency for MB based on the results of the experiments. According to these findings, it can be concluded that the presence of NTO particles on the cotton fabric can be considered as the most important factor in creating the self-cleaning property and the main source for degradation of MB dye molecules.

3.1.1. *Self-cleaning properties*

The reaction mechanism of Quat-188 and BTCA with cotton is proposed in Scheme 2. First, intermediate anhydride cycles were formed as shown in reaction I. The cotton was cationized through reaction II. The BTCA was bonded to cotton by Quat-188 via ionic linkage by reaction III. The binding of cotton with BTCA was continued via ester linkage through reactions IV and V. On the other hand, two other free carboxylic groups of BTCA could bond to NTO via strong electrostatic interactions through reaction VI (Yuranova et al., 2007).

The Δa^*, Δb^*, ΔL^*, and ΔE^* of bleached (B) and bleached-cationized (C) cotton fabrics treated with BTCA under different conditions were reported in Table 1. As shown in Table 1 the values of color lightness differences (ΔL^*) are proportional with the values of total color differences (ΔE^*), namely, with the increase of ΔL^*, the ΔE^* increases. The results in Table 1 confirm the increase of ΔE^* with increasing of BTCA concentration. Also, increase of NTO concentration leads to increase of ΔE^*. Further increase of NTO decreases the ΔE^* due to the agglomeration of NTO particles in the finishing bath or on the fabric and/or inhibiting the action of the cross-linking agent on cotton at higher concentrations of NTO. Lin et al confirmed the photo catalytic activity enhancement by increasing the effective reactive surface area of the dispersed NTO particles (Lin et al., 2007). Also, the results in Table 1 show that at the given concentration of BTCA, NTO, SHP and the same curing conditions, the values of ΔE^* for samples C are higher than for samples B. This can be attributed to the higher amount of BTCA on the samples C that help more attraction of NTO particles on the fabric surface.

Three curing methods including UV irradiation (UV), high temperature (Temp) and the combination of these two methods (UV–Temp) have been studied. As shown in Table 1, the order of ΔE^*decrease for the three methods is:

$$\text{UV–Temp} > \text{High temp} > \text{UV}.$$

It appears that with the UV–Temp curing method, both cross-linking mechanisms of cotton fabric based on UV–Temp method was occurred. The details of the mentioned mechanisms have been reported in our previous study (Nazari, Montazer, Rahimi, 2009; Nazari, Montazer, Rashidi, et al., 2009). Therefore, the treated fabrics cured with UV or High temp methods show lower ΔE^* comparing with UV–Temp. However, these results revealed that some chemical species generated on the NTO surface can transfer to the methylene blue and cause dye photo degradation.

No comprehensive mechanism of methylene blue photo degradation is still established, however, Tatsuma et al suggested two possible mechanisms for the discoloration of MB; namely, reversible reduction of MB to the leuco form and irreversible oxygenation or decomposition of MB (Tatsuma, Tachibana, Miwa, Tryk, & Fujishima, 1999). Meanwhile, O° and OH°, that are liberated from the surface of oxides including TiO_2 by the photon-stimulated des-

Table 4
ANOVA for response surface quadratic model with BTCA for samples C.

Source	Sum of squares	Df	Mean square	*F* value	*p*-Value Prob > *F*
Model	252.72	11	22.97	70.26	<0.0001 significant
A [BTCA]	40.39	1	40.39	123.51	<0.0001
B [NTO]	38.75	1	38.75	118.51	<0.0001
C [Curing]	122.98	2	61.49	188.04	<0.0001
AB	4.56	1	4.56	13.95	0.0009
AC	0.26	2	0.13	0.39	0.6778
BC	0.22	2	0.11	0.33	0.7209
A^2	0.41	1	0.41	1.25	0.2732
B^2	43.28	1	43.28	132.34	<0.0001
Residual	8.83	27	0.33		
Lack of fit	8.82	15	0.59	587.81	<0.0001 significant
Pure error	0.012	12	1.000E−003		
Cor total	261.55	38			

orption, could also be responsible for the bleaching, as a result of oxidation of methylene blue (Knotek, Jones, & Rehn, 1979).

Based on Table 1, in similar conditions, samples C treated with BTCA have higher ΔE^* as compared to the samples B. The cationized cotton containing Quat-188 can form ionic and covalent bonds with BTCA (Scheme 2), while these bonds appear to be only covalent in the bleached cotton. At one hand, BTCA with four carboxylic acid groups is able to form bonds with hydroxyl groups in cellulose polymer chains, and in other hand is able to make electrostatic bonds with NTO (Yuranova et al., 2007). Hence, regarding the greater presence of BTCA on the cationized cotton as compared to the bleached cotton, this compound can act as NTO stabilizer and maintains more NTO on the surface of the cationized cotton. Consequently, the use of cationized cotton enhances the photo degradation efficiency as compared to the bleached cotton.

3.2. Statistical analysis

For treated samples B, the analysis of variance (ANOVA) is given in Table 3. According to the ANOVA results, the fitted models of self-cleaning (ΔE^*) by using Design-Expert software are given in Eqs. (3)–(5), respectively.

$$\begin{aligned}\Delta E^*(\mathrm{B})_{\mathrm{UV}} = {} & +7.16145 + 0.020406 \times \mathrm{BTCA} + 4.88720 \times \mathrm{NTO} \\ & - 0.022385 \times \mathrm{BTCA} \times \mathrm{NTO} + 6.53114\mathrm{E} - 004 \\ & \times \mathrm{BTCA}^2 - 0.49436 \times \mathrm{NTO} \end{aligned} \tag{3}$$

$$\begin{aligned}\Delta E^*(\mathrm{B})_{\mathrm{High\ temp}} = {} & +7.99861 + 0.035714 \times \mathrm{BTCA} + 5.00040 \\ & \times \mathrm{NTO} - 0.022385 \times \mathrm{BTCA} \times \mathrm{NTO} + 6.53114\mathrm{E} \\ & - 004 \times \mathrm{BTCA}^2 - 0.49436 \times \mathrm{NTO}^2 \end{aligned} \tag{4}$$

$$\begin{aligned}\Delta E^*(\mathrm{B})_{\mathrm{UV-Temp}} = {} & +9.26343 - 0.046216 \times \mathrm{BTCA} + 5.07725 \\ & \times \mathrm{NTO} - 0.022385 \times \mathrm{BTCA} \times \mathrm{NTO} + 6.53114\mathrm{E} \\ & - 004 \times \mathrm{BTCA}^2 - 0.49436 \times \mathrm{NTO}^2 \end{aligned} \tag{5}$$

The analysis of variance (ANOVA) for samples C with BTCA is given in Table 4. According to the experimental design, the result was analyzed and approximating functions of self-cleaning were obtained in Eqs. (6)–(8), respectively.

$$\begin{aligned}\Delta E^*(\mathrm{C})_{\mathrm{UV}} = {} & +8.00136 + 0.052544 \times \mathrm{BTCA} + 4.72285 \times \mathrm{NTO} \\ & - 0.020968 \times \mathrm{BTCA} \times \mathrm{NTO} + 4.84429\mathrm{E} - 004 \\ & \times \mathrm{BTCA}^2 - 0.48114 \times \mathrm{NTO}^2 \end{aligned} \tag{6}$$

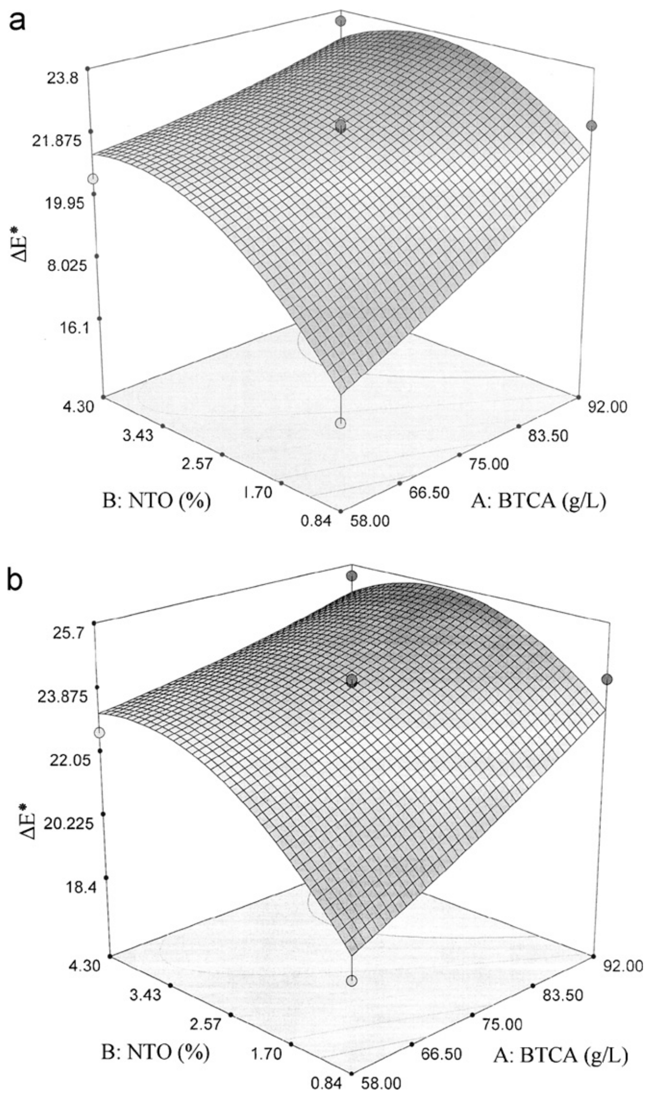


Fig. 1. Design of expert plot for samples B (a) and C (b) with NTO and BTCA under curing UV–Temp.

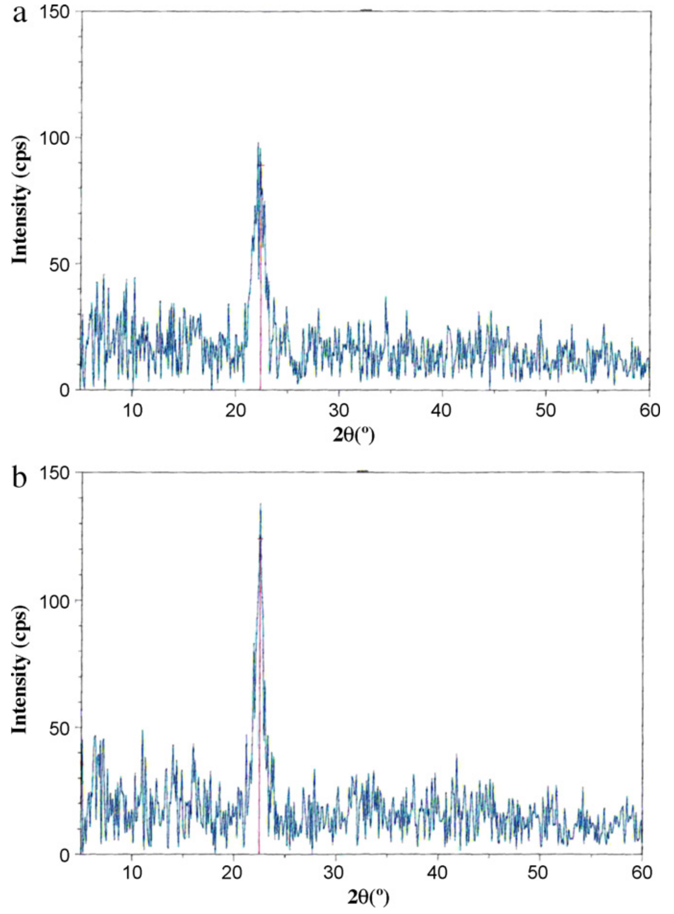


Fig. 2. XRD pattern of samples B (a) and C (b) treated with 99.04 g/L BTCA, 2.57% NTO under curing UV–Temp.

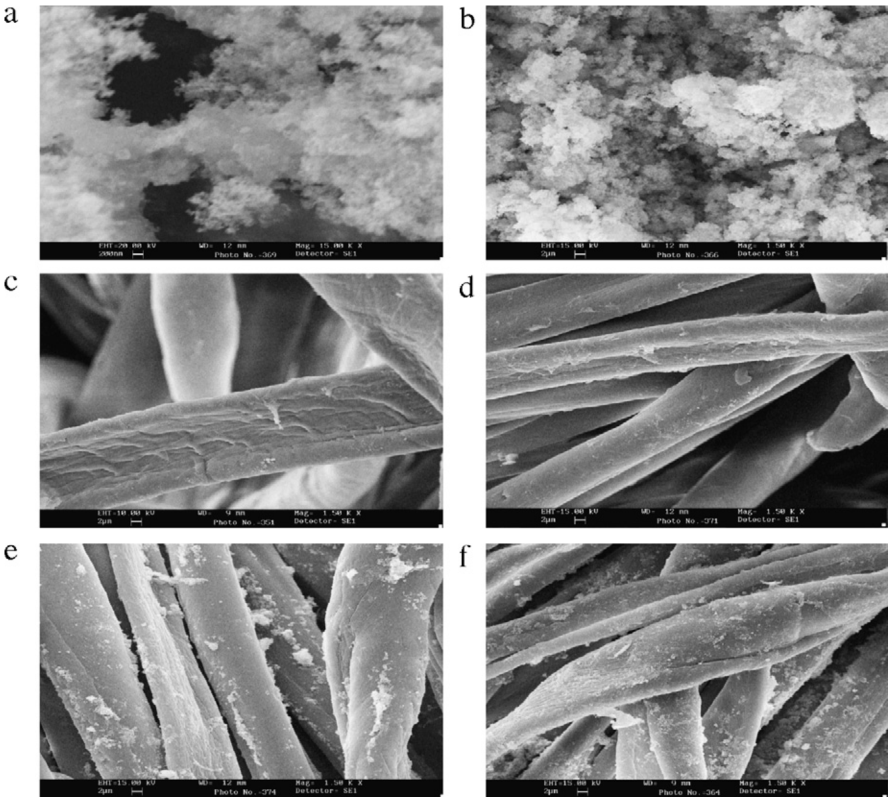


Fig. 3. SEM images of the (a) nanoTiO$_2$ powder (magnification = 15,000×), (b) nanoTiO$_2$ powder (magnification = 1500×), and (c) bleached cotton, (d) bleached-cationized cotton, (e) 50.96 g/L BTCA and 2.57(%) NTO for sample B, (f) 50.96 g/L BTCA and 2.57 (%) NTO for sample C (magnification = 1500×) and UV–Temp curing method.

$$\Delta E^*(\mathrm{C})_{\mathrm{High\,temp}} = +9.78235 + 0.053929 \times \mathrm{BTCA} + 4.76347 \times \mathrm{NTO} - 0.020968 \times \mathrm{BTCA} \times \mathrm{NTO} + 4.84429\mathrm{E}-004 \times \mathrm{BTCA}^2 - 0.48114 \times \mathrm{NTO}^2 \quad (7)$$

$$\Delta E^*(\mathrm{C})_{\mathrm{UV-Temp}} = +10.99008 + 0.066121 \times \mathrm{BTCA} + 4.85422 \times \mathrm{NTO} - 0.020968 \times \mathrm{BTCA} \times \mathrm{NTO} + 4.84429\mathrm{E}-004 \times \mathrm{BTCA}^2 - 0.48114 \times \mathrm{NTO}^2 \quad (8)$$

Fig. 1a and b shows the response surface of the model for treated samples. By using the Design of Expert software the optimum condition (ΔE^* = 23.61) with desirability of 1.000 belongs to sample B (Fig. 1a) containing 91.75 (g/L) BTCA and 3.24 (%) NTO cured in UV–Temp. Besides, Fig. 1b shows the optimum design point (ΔE^* = 25.45) with desirability of 1.000 for sample C including the BTCA concentration of 91.42 (g/L), the NTO concentration of 3.54(%), and the curing method of UV–Temp.

3.3. X-ray diffraction (XRD) analysis

The XRD patterns of the sample B (Fig. 2a) and the sample C (Fig. 2b) cured under UV–Temp method with 99.04 g/L BTCA and 2.57% NTO are reported. It can be observed that the major peak of all spectrums is anatase ($2\theta = 22.4^\circ$), whereas the peak related to rutile phase ($2\theta = 27.5^\circ$) cannot be observed in XRD spectrums (Jung & Park, 1999). Arbuj et al. (2009) reports that the rutile phase of NTO is photo catalytically less active than its anatase counterpart. Therefore, the coated fabrics with NTO have anatase crystallite phase and can effectively operate under UV irradiation.

3.4. SEM

Fig. 3(a–f) illustrates the SEM of NTO powder (a) (magnification = 15,000×) and NTO powder (b) (magnification = 1500×), and control sample B (c), control sample C (d), sample B treated with BTCA (e), sample C treated with BTCA (f) (magnification = 1500×). Fig. 3c shows the morphology of bleached cotton fibre. Fig. 3d shows the cationization pre-treatment on cotton surface. The surface changes of cotton fibres treated with BTCA in the presence of NTO are shown after padding and UV–Temp curing (Fig. 3(e and f)). These pictures show the higher amount of NTO loading on the surface of sample C than sample B when they were treated in the same conditions. This can be attributed to the presence of more carboxylic acid groups on the surfaces of the bleached-cationized cotton (C) than the bleached cotton (B) after BTCA treatment. This can maintain more particles of NTO on the fibre surface. However, these pictures confirm the loading of NTO particles on cotton fabric by the simple padding process, but their distribution on the fiber surface was not quite uniform, possibly because of the aggregation of some NTO particles on the cotton surfaces.

4. Conclusions

The purpose of this study was to investigate the self-cleaning properties of bleached (B) and bleached-cationized (C) cotton with NTO and BTCA as an eco-friendly cross-linking agent which was then optimized using a statistical model. Also three different curing methods (UV, High temp, UV–Temp) were applied to investigate the effect of curing conditions on the self-cleaning behaviour of various cottons. It can be concluded that at a given concentration of NTO, cross-linking agent and catalyst, and curing method, the color difference (ΔE^*) values of cationized cotton are higher than bleached cotton. The statistical analysis by Design of Expert indicated that the treated bleached cotton with 91.75 g/L BTCA, 3.24% NTO and 55.05 g/L SHP and cured with UV–Temp show the optimum self-cleaning ($\Delta E^* = 23.61$) with a desirability of 1.000. The optimum conditions for cationized cotton with a desirability of 1.000 gave self-cleaning ($\Delta E^* = 25.45$) with 91.42 g/L BTCA, 3.54% nanoTiO$_2$ and 54.85 g/L SHP cured with UV–Temp. According to the statistical analysis, the treated fabrics with NTO particles and BTCA easily enable photo degradation of the MB dye molecules. However, cationization pre-treatment of cotton fabric leads to improve the self-cleaning property.

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