Statistical Optimization of Durable Multifunctional Properties of Cellulase Cotton Using Nano-TiO_2 Sonoloading

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Abstract- **Preparation of durable cotton fabrics with multifunctional properties has been lately the center of researchers' attention and also utilizing nanoparticles is an effective strategy to gain this target. Here, acid cellulase enzyme in ultrasonic bath and nano-TiO_2 sonoloading were utilized on cotton fabric to obtain self-cleaning, antifungal, protection against ultra-violet and x-linking features on fabric. Also, statistical design of D-optimal was applied for variables of time, temperature, acid cellulase, and TiO_2 nanoparticles concentrations in ultrasonic bath. Laundering durability was measured for prepared cotton samples and discussed in optimized conditions using response surface methodology. Also, reflectance spectra analyses (200-400 nm), scanning electron microscopy, and energy-dispersive X-ray (EDX) were employed to confirm TiO_2 nanoparticles presence on treated cotton surfaces. The research results reveal that durable multifunctional properties including color difference amounts (24.09), antifungal activity against** *Candida albicans* **(98.51%), ultra-violet protection factor (45.13), and dry crease recovery angle (256.3°) are significantly high at optimized condition (cellulase enzyme: 1.32%, Temperature: 60 °C, Time: 31.1 min, TiO_2 nanoparticles: 1.07%) as compared with blank sample.**

Keywords: **cellulase, durability, TiO_2 nanoparticles, response surface methodology**

I. INTRODUCTION

Among all natural fibers, cotton is one of the most significant fibers in textile industry due to its properties such as softness, high absorption, and convenience in wear [1]. Cotton is a cellulosic fiber [2]. One of the most well-known methods of improving cellulose surface is applying cellulase treatment utilized for functions such as bio-scouring [3], bio-finishing [4], air permeability, and improvement of brightness and softness [5] of cellulosic fabrics through wet-processing and environmental-friendly [6].

Using ultrasonic energy operation is considered as one of the most conventional methods used in textile industry. The reason is related to positive and worthwhile results gained in bleaching, dyeing, and finishing treatments [7-9]. For instance, utilizing ultrasonic waves could be referred in order to promote leather efficiency and time treatment decrease [10]. Ultrasonic energy along with ozonation as green processing leads to remarkable hydrophilic and brightness characteristics of cotton fabrics [11]. Also, this potential is used in synthesis process of nanoparticles colloidal solution in textile finishing [12]. Besides, synergistic effect of ultrasound irradiation on enzyme treatment has been also widely reported [13-17]. Efficiency of pre-treatment and bio-polishing was significantly enhanced using ultrasonic treatment during enzymatic processing [18,19]. Also, Tissera *et al.* [20] reported reactive dye uptake through accelerating of dye-fiber interaction applying ultrasonic energy. In 2017, El-Nahhal *et al.* [21] used successfully ultrasonic irradiation accompany with different surfactants to stabilize nano-structured ZnO particles on cotton fiber surfaces and attempted to control their shape and size as encapsulated species. Creating novel properties in textiles beside particular ones such as self-cleaning, x-linking, antifungal, and ultra-violet protection were evaluated by many researchers [22-24]. TiO_2 nanoparticles (NTp) are able to be activated by solar energy and produce multi-functional properties in textiles. Therefore, there is extensive interest in extending NTp utilization since they are harmless, inexpensive and easy to use [25]. Fabrics treated with NTp illustrated excellent anti-bacterial characteristics against *E. coli* and *S. aureus* [26], mothproofing [27], and self-cleaning [28]. Nevertheless, one of the main limitations of generalizing NTp usage especially in industry scale could be attributed to low laundering durability of these particles. Although several studies were accomplished related to increase durability of NTp and promoting binding efficiency such as using cross-linking agents [29], graft polymerization under γ-ray irradiation [30], and surface modification

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[31,32]; but, no comprehensive study was reported related to statistical optimizing of surface hydrolyze treatment via acidic cellulase enzyme in ultrasonic bath and in continue, effect of mentioned process accompany with cross-linking agent on NTp efficiency using ultrasonic energy and enhancing laundering durability of NTp on cotton fabrics. Therefore; in this research, enzymatic treatment variables including temperature, time, cellulase enzyme, and NTp concentrations were firstly attended; then, laundering durability of important properties such as self-cleaning, antifungal, protection against ultra-violet and x-linking was enhanced and maximized by applying response surface methodology (RSM) statistical analysis.

II. EXPERIMENTAL

A. Materials and Instruments

Desized, scoured, and bleached plain weave 100% cotton fabric (15×10 cm^2) was used with wrap density 32 yarn/cm, weft density 30 yarn/cm, and fabric weight of 118 $g.m^{-2}$. Acid cellulase enzyme (Rucolase ZEL) and non-ionic detergent (Rucogen DEN) composed of fatty alcohol ethoxylate were purchased from Rudolf Chemie Co. (Tehran, Iran). NTp was employed as photo catalyst with anatase crystalline structure and average particle size of 21 nm from Degussa Chemie Co. (Duisburg, Germany) and butane tetra carboxylic acid (BTCA), sodium hypophosphite (SHP), sodium carbonate and methylene blue were prepared from Merck Chemical Co. (Germany). Enzymatic and NTp compounds were dispersed and sonicated using an ultrasonic bath (200 V, 50 W, and 40 kHz). Reflectance spectra were recorded at UV region (200-400 nm) using an UV/VIS spectrophotometer (CARRY 500 scan, Varian, Australia). Energy-dispersive spectroscopy (EDX) was used to characterize elemental composition of treated cotton fabrics. Scanning electron microscopic (SEM) observations were carried out on treated fabrics samples using a KYKY-EM3200 electron microscope (China).

B. Methods

B.1. Scouring

Fabric samples (15×10 cm^2) were scoured with 1% on weight of fabric (owf) nonionic detergent and 1% owf sodium carbonate for 20 min at 60 °C and L:G (liquor-to-goods ratio) = 40:1. Scoured samples were rinsed several times and then dried at room temperature.

B.2. Enzymatic Treatment

Enzymatic treatments were carried out with different enzyme concentrations, temperatures, and times at pH 5 and L:G equals to 20:1 in ultrasound bath. Next, fabrics were maintained for 15 min at temperature of 70 °C and pH 9.5, in order to denature the enzyme. Finally, cotton samples were rinsed to eliminate any remained enzyme.

B.3. NTp Treatment

Modified and blank 1 cotton samples were treated with different concentrations of NTp, 100 g/L BTCA, and 60 g/L SHP, for 25 min in an ultrasonic bath through an exhaustion method and then padded with foulard with 100% wet pick-up. NTp treated fabrics dried at 90 °C for 4 min followed by curing at 170 °C for 4 min in an oven. Finished samples were washed at 65 °C for 15 min with 2 g/L Na_2CO_3 and 1 g/L nonionic detergent (Rucogen DEN), and finally dried at room temperature.

B.4. Measurement

Color stains self-cleaning characteristics of methylene blue (MB) solution was accomplished as a widely known model compound through discoloration analysis of color stains after exposing to daylight irradiation for 12 h. Treated samples were placed on flat surface and one drop of MB (1%) was vertically dripped on surface using a burette (50 mL), form 1 cm above the fabric. Color changes were studied with a reflectance spectrophotometer (color-guide sphere, D/8° spin, Germany) and color difference (ΔE*) was calculated by Eq. (1) [33]:

$$\Delta E^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta l^*)^2} \quad (1)$$

Quantitative antifungal efficiency of treated cotton fabric was determined against *C. albicans* according to AATCC100 guideline. After preparing fresh culture of fungus strain on nutrient agar (18 h at 37 °C), fungus were cultured, washed, and suspended in normal saline to an optical density (OD) 620 of 0.1 which is equal to 1.5×10^8 CFU/mL. A dilution of 1:10 from each fungus suspension was subsequently prepared. Blank and treated fabrics were placed in sterile 50 mL polystyrene conical tubes and sterilized in an autoclave (15 min at 121 °C). Fabrics were separately inoculated with fungus suspension (10^6 CFU/mL) and incubated for 48 h at room temperature. Four samples (dilution of 1:10) were serially prepared and 0.1 mL from each dilution was inoculated on Mueller–Hinton agar and spread on the surface thoroughly. Plates were incubated for 18 h at 37 °C, the fungus colonies were then counted and total CFU/mL was determined for each experiment. The antifungal efficiency was calculated according to Eq. (2) [34,35]:

$$R = \frac{(A - B)}{A} \times 100 \quad (2)$$

Where, A and B are the number of fungus colonies recovered from blank and treated fabrics, respectively, after inoculation and R is the reduction percentage of fungus colonies [36]. The ultra-violet protection factor (UPF) was calculated using mean percentage transmission in UV-B (290–320 nm) and UV-A (320–400 nm) regions. UPF was measured in accordance with following Eq. (3) [37]:

$$UPF = \frac{\sum_{290\ nm}^{400\ nm} E_\lambda \times s_\lambda \times d_\lambda}{\sum_{290\ nm}^{400\ nm} E_\lambda \times s_\lambda \times T_\lambda \times d_\lambda} \quad (3)$$

Where, λ is the wavelength (nm); E_λ is the relative erythemal effectiveness; S_λ corresponds to the solar UV spectral irradiance (W m^{-2} nm^{-1}), T_λ is the spectral transmittance of the fabric, and d_λ refers to the wavelength increment (nm). Dry crease recovery angle (DCRA) of warp (w) plus weft (f) of treated cotton fabrics were evaluated using AATCC test method 66-2003. Specimens were prepared in 40×15 mm swatches and 500±5 g of weight loaded on folded specimens for 5 min±5 s. Recorded vertical angle guidelines were aligned and recovery angles were measured [38]. Laundering durability of self-cleaning, antifungal, UPF and x-linking features of treated samples was evaluated according to AATCC 61(2A)-2003. In this approach, each cycle of laundering process is equivalent to five home laundries in ambient conditions at 38 ± 3 °C.

B.5. Design of Experiments

Findings were completely investigated by Design Expert software using analysis of variance (ANOVA). Quality of fit polynomial model was presented by coefficient of determination R^2, and its statistical significance was checked with adequate precision ratio and by F-test. D-optimal design was used with four variables for experimental plan. Corresponding codes are listed in Table I besides lower and higher values for each variable.

Trial version of Design Expert 8.0.1.0 was utilized from Stat-Ease, Inc., USA. Details of treatment design using D-optimal are presented in Table II. Also influence of variables on the results Y_1 (ΔE^*), Y_2 (% reduction of fungus), Y_3 (UPF), and Y_4 (DCRA) was adjusted using polynomial function. Model terms were selected or rejected based on the P-value with a 95% confidence level.

III. RESULTS AND DISCUSSION

A. Self-Cleaning, Antifungal, UPF and X-Linking Properties

Effect of the cotton surface hydrolyzed with acid cellulase enzyme and sonoloading NTp on self-cleaning (ΔE^*) of treated cotton sample under daylight irradiation for 12 h is illustrated in Table II. Low photo degradation of MB is emerged under daylight for blank sample (ΔE^*_{Blank}= 5.23, Table II). The results of Table II show that ΔE^* amounts significantly increased through sonoloading of NTp on modified cotton. This relates to the photo catalyst property of NTp which more discoloration of modified cotton samples with NTp compared with blank sample confirms that. The highest amount of ΔE^* (24.46) is related to sample Run: 2 that is treated with acid cellulase enzyme concentration of 1.06% at 60 °C and for 30.62 min and also concentration of 1.10% NTp. Cotton enzyme treatment causes crack and void formation on the cotton chains surface (SEM images, Fig. 3) and it probably seems that this factor could absorb more NTp via physical imprisonment; and in this case, NTp illustrates more photocatalyst characteristic. Meanwhile, cotton surface hydrolyzed with cellulase enzyme leads to produce more functional groups and enhance surface functionality [39] to possibly absorb more and better NTp. On the other hand, ultrasound energy is capable of breaking down NTp aggregates and micelles [18]. Therefore, NTp mono-molecules [18] increase leads to promote efficiency and connection capability of NTp to modified cotton cellulose chains. Consequently, by increasing mono-molecules of NTp on modified cotton cellulose surface, self-cleaning of all treated samples was significantly increased as compared with blank sample for discoloring MB molecules. *C. albicans* is the most common fungus species isolated from biofilms either formed on (permanent) implanted medical devices or on human tissue

TABLE I
EXPERIMENTAL RANGES OF CODED FACTORS

			Real values of the coded levels	
Name	Units	Code	-1	+1
Acid cellulase concentration	%	A	0.50	2.00
Time	min	B	20.0	40.0
Temperature	°C	C	30.0	60.0
NTp concentration	%	D	0.10	1.10

TABLE II
D-OPTIMAL DESIGN FOR ΔE*, PERCENT OF REDUCTION OF FUNGUS, UPF, AND DCRA VALUES OF SONO-CELLULASE HYDROLYZED COTTON AND TREATED WITH NT_p SONOLOADING

Run	Enzyme conc. (%)	Temperature (°C)	Time (min)	NT_p (%)	*ΔE	Reduction of fungus (%)	UPF	DCRA (°)
Blank	0.00	0.00	0.00	0.00	5.23	0.00	7.26	10.09
Blank 1	0.00	0.00	0.00	1.00	14.13	48.32	15.56	46.5
1	0.50	30.00	28.86	0.10	17.37	75.05	35.12	240.2
2	1.06	60.00	30.62	1.10	24.46	98.77	44.36	218.3
3	2.00	60.00	40.00	0.10	16.66	52.98	40.12	203.9
4	1.06	46.99	26.91	0.35	21.66	96.11	42.13	208.7
5	2.00	60.00	20.00	1.10	23.54	57.34	39.78	204.8
6	0.50	44.96	20.00	1.10	22.86	84.32	35.33	245.7
7	2.00	34.75	20.00	0.10	18.71	50.36	38.17	198.7
8	0.50	60.00	20.00	0.10	16.42	75.09	35.63	226.8
9	2.00	30.00	20.00	1.10	22.37	58.46	35.14	205.6
10	2.00	60.00	40.00	0.10	17.11	52.78	33.14	188.7
11	2.00	60.00	20.00	1.10	23.97	57.49	35.56	199.8
12	0.99	44.99	40.00	0.10	18.56	94.1	38.53	220.5
13	1.81	30.00	40.00	1.10	24.11	95.32	40.37	214.7
14	1.07	30.00	20.00	0.57	21.17	96.33	40.13	236.7
15	1.81	60.00	20.94	0.10	17.43	97.42	41.56	216.3
16	2.00	55.67	40.00	1.10	23.56	63.11	35.78	196.5
17	1.25	37.50	28.20	1.10	24.37	98.36	46.78	226.1
18	0.50	30.00	40.00	1.10	22.17	84.76	39.44	250.3
19	2.00	44.95	30.06	0.60	20.36	54.36	34.12	205.8
20	0.50	60.00	40.00	0.66	19.49	77.14	37.63	257.3
21	0.50	60.00	40.00	0.66	19.48	77.17	37.93	258.6
22	1.22	30.00	34.92	0.55	21.56	97.17	42.12	234.8
23	2.00	30.00	40.00	0.10	16.37	50.11	29.18	187.9
24	0.50	30.00	28.86	0.10	17.71	75.11	35.43	240.8
25	0.99	44.99	40.00	0.10	18.78	94.15	38.74	219.6

[40,41]. *C. albicans* could generate infections that range from skin superficial infections to life-threatening systemic infections. Although there are several ambiguities related to this important human pathogen considering pathogenicity mechanisms [42-44]. The designed experiments results in Table II demonstrate *C. albicans* fungus reduction amounts of sono-cellulase cotton samples with different amounts of NTp sonoloading. It shows that NTp sonoloading on sono-cellulase cotton samples could effectively cause *C. albicans* fungus decrease [45]. The least decrease of *C. albicans* fungus related to sample Run:7 is resulted with acid cellulase concentration of 2.00% at 34.75 °C for 20.00 min and also 0.10% NTp. The reason might be related to more enzyme concentration, more decomposition of cellulose polymer chains, and more hydrophilicity of cellulose and also cellulase itself which is likely a desired environment for other microorganism growth. So that, modified cotton with more hydrophilicity produces more accommodating environment for fungus growth. Also by increasing enzyme concentration and more increasing NTp concentration (Run:2), more and significant decrease in *C. albicans* fungus (98.77%) is obtained. In this research, the use of ultrasound energy could play an important role in creating optimal antifungal property as a beneficial assistant factor in both of two treatments: a) effective hydrolyze of cotton surface with acid cellulase enzyme, and b) more dispersion of NTp as mono-molecules form [18]. In this research, efficiency of textiles UV blocking was elaborated using ultra violet protection factor (UPF). UPF is defined as ratio of average effective irradiance calculated for skin to average UV irradiance calculated for skin protected by the test fabric. It has been initially established by Australian/ New Zealand standard AS/NZS 4399. UPF is determined by measuring direct and diffuse transmission of fabric across wavelength range 290–400 nm which include UVB (290–315 nm) and UVA (315–380 nm) regions (Eq. (3)).

TABLE III
UPF RATING FOR TEXTILE FABRICS [46]

UPF values	UPF ratings	UV protection category
<15	-	Not labeled
15-24	15 and 20	Good protection
25-39	25, 39, and 35	Very good protection
40-50	40, 45, 50, and 50+	Excellent protection

Table III shows fabrics protected against UV which are divided into 4 groups [46].

UPF amounts of sono-cellulase cotton samples treated with NTp sonoloading along with BTCA cross-linking agent are exhibited in Table III. The least UPF amount (29.18) is related to sample Run: 23 and the highest UPF amount (46.78) is related to sample Run: 17. UPF ranges of treated samples considering dividing in Table III illustrate that all modified cotton samples have obtained UV protection with exquisite and optimal degrees. So that even in sample Run: 7 with the least amount of NTp (0.10%), an UPF amount with good degree was obtained. The reason could be more dispersion of NTp in mono-molecules particles standing forms and homogenous and appropriate distribution of NTp on sono-cellulase cotton fabrics which were able to efficiently block day irradiation. In this reserch, DCAR amounts of sono-cellulase cotton samples treated with NTp sonoloading accompany with BTCA were presented. BTCA compounds as cross-linking agents are able to make cross-linkages between polymeric chains in modified cellulose and as a result enhance DCRA property. Since, BTCA compound is known as a free formaldehyde environment friendly cross-linking agent, it could create x-linking property and more adherence among polymeric chains of modified cotton. In previous research, NTp presence was analyzed as a co-catalyst and cross-linking mechanism was suggested using NTp [47]. Also in other study, increase of DCRA efficiency was announced with BTCA compared with CA [48]. The highest amount of DCRA (258.6°) is related to sample Run: 21. The reason might be cotton sono-enzyme treatment, creating cracks and voids on cotton surface, more presence of NTp via absorption, and enhancing their efficiency as co-catalyst. Consequently, more presence of NTp in mono-molecules form makes more cross-linkages via BTCA among modified cotton polymeric chains and increase of DCRA amounts. Blank sample 1 containing NTP 1%, without enzyme pretreatment, is illustrated in Table II. Reason is related to clarifying and highlighting role of enzymatic modifying treatment of cotton fabrics and attending its impressibility on NTP efficiency. By comparing blank sample 1 with other treated Runs in Table II, role of enzymatic treatment with ultrasound energy could be obviously and significantly observed on efficiency of properties such as self-cleaning degree, % reduction of fungus, UPF and DCRA.

B. Statistical Analysis

This study was conducted according to RSM and D-optimal. In total, 25 designed experiments were conducted according to Table II. In this model, impacts of independent variables including acid cellulase concentration, time, temperature, and NTp on response surfaces were assessed. Average values of 6, 4, 3, and 5 replicates for self-cleaning degree, percentage of reduction of fungus, UPF and DCRA are reported in Table II, respectively. Mathematical equations in terms of coded factors via reduced quadratic models related to self-cleaning degree, % reduction of fungus, UPF and DCRA of sono-cellulase hydrolyzed cotton treated with NTp using Design-Expert software are presented in Eqs. (4 -7):

$$\Delta E^{*} = +10.36 + 8.37\times A + 0.19\times B - 0.02\times C + 3.5\times D + 0.05\times B\times D - 3.20\times A^{2} - 0.002\times B^{2} \quad (4)$$

$$\text{Reduction}_{(C.\ albicans)}(\%) = +36.83 + 130.27\times A + 0.04\times B - 0.54\times C - 21.79\times D + 0.92\times C\times D - 56.80\times A^{2} \quad (5)$$

$$\text{UPF} = +25.78 + 30.02\times A + 0.07\times B - 0.19\times C - 5.78\times D + 0.26\times C\times D - 12.07\times A^{2} \quad (6)$$

$$\text{DCRA} = +248.04 - 27.70\times A - 0.09\times B + 0.02\times C + 56.69\times D - 40.11\times D^{2} \quad (7)$$

A, B, C, and D terms are described in Table I. Therefore; response surfaces of ΔE*, reduction of fungus, UPF and DCRA of sono-cellulase hydrolyzed cotton samples are illustrated in Fig. 1.

Figs. 1a to 1d illustrates response surfaces for ΔE* model, reduction of fungus, UPF and DCRA of modified cotton samples.

The effect of changes in NTp concentration and temperature variables on self-cleaning amounts considering fixing other two variables of time and enzyme concentration are presented in Fig. 1a. Based on Fig. 1a, there is a sharp increase in self-cleaning properties with increase in NTp concentration. In comparison, higher temperature only resulted in a slight change in ΔE* values. The effect of changes in NTp concentration and time variables on *C. albicans* reduction amount considering fixing other two variables of temperature and enzyme concentration is illustrated in Fig. 1b. Based on Fig. 1b, by increasing NTp concentration, tangible changes are not observed

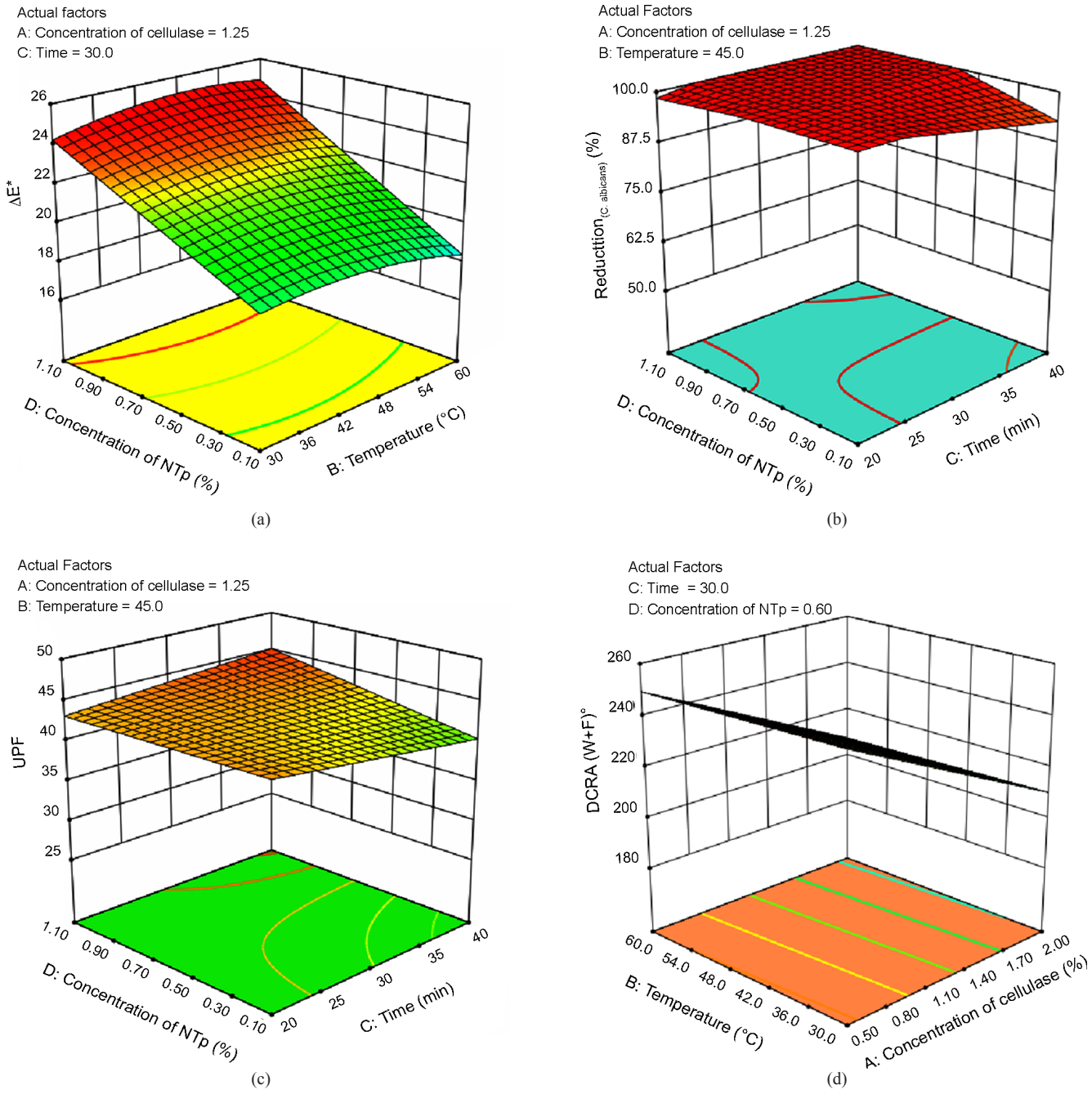

Fig. 1. Response surfaces for: (a) ΔE*, (b) reduction of *C. albican*s, (c) UPF, and (d) DCRA (W+F)° as a function of NTp (%), cellulase enzyme (%), time (min), and temperature (°C) for modified cotton samples.

in reduction amount of *C. albicans*; while, by increasing time, a little reduction is shown in reduction amount of *C. albicans*. Impressibility of UPF dependent variable from changes of NTp concentration and time variables is exhibited in Fig. 1c. Based on Fig. 1c, by increasing NTp concentration, a little increase is demonstrated in UPF amounts, while, by increasing time, tangible changes are not observed in UPF amounts. Also DCRA amount impressed by changes of temperature and enzyme concentration variables is demonstrated in Fig. 1d. Based on Fig. 1d, there is a sharp decrease in DCRA values with increase in enzyme concentration. In comparison, higher time only resulted in slight change in DCRA values. Also, the recommended treatment was achieved accordingly as it is reported in Table IV.

Analysis of variance (ANOVA) was used for reduced quadratic model to analyze data in order to obtain interaction between process of independent variables and

TABLE IV
ΔE*, REDUCTION OF *C. ALBICANS*, UPF AND DCRA OF MODIFIED COTTON FABRICS TREATED IN BLANK AND OPTIMIZED CONDITION AND AFTER LAUNDERING DURABILITY TEST

Run	Enzyme conc. (%)	Temperature (°C)	Treatment time (min)	NTp (%)	ΔE*	Reduction of fungus (%)	UPF	DCRA (°)
Blank	0.00	0.00	0.00	0.00	5.23	0.00	7.26	10.09
Blank 1	0.00	0.00	0.00	1.00	14.13	48.32	15.56	46.5
Optimized condition	1.32	60.00	31.10	1.07	24.63	98.77	45.94	258.6
After laundering durability test	1.32	60.00	31.10	1.07	24.09	98.51	45.13	256.3

TABLE V
ANOVA RESULTS FOR REDUCED QUADRATIC MODEL OF ΔE* OF THE TREATED COTTON FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	182.14	7	26.02	77.36	<0.0001 Significant
A [cellulase]	1.36	1	1.36	4.04	0.0605
B [temp]	0.0587	1	0.0587	0.1746	0.6813
C [time]	0.6158	1	0.6158	1.83	0.1937
D [NTp]	152.74	1	152.74	454.13	<0.0001
BD	1.89	1	1.89	5.61	0.0300
A^2	11.91	1	11.91	35.42	<0.0001
B^2	1.17	1	1.17	3.49	0.0791
Residual	5.72	17	0.3363		
Lack of fit	5.44	12	0.4535	8.22	0.0151
Pure error	0.2757	5	0.0551		
Cor total	187.86	24			

R^2: 0.9696, Adjusted R^2: 0.9570, Predicted R^2: 0.9328, Adeq precision: 25.406, C.V.%: 2.84
The predicted R^2 of 0.9328 is in reasonable agreement with the adjusted R^2 of 0.9570; i.e. the difference is less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 25.406 indicates an adequate signal. This model can be used to navigate the design space.

TABLE VI
ANOVA RESULTS FOR REDUCED QUADRATIC MODEL OF REDUCTION OF C. ALBICANS OF THE TREATED COTTON FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	7057.35	6	1176.22	23.79	<0.0001 Significant
A [cellulase]	1241.88	1	1241.88	25.12	<0.0001
B [temp]	7.82	1	7.82	0.1582	0.6955
C [time]	0.3531	1	0.3531	0.0071	0.9336
D [NTp]	159.20	1	159.20	3.22	0.0895
CD	293.74	1	293.74	5.94	0.0254
A^2	4206.73	1	4206.73	85.10	<0.0001
Residual	889.81	18	49.43		
Lack of fit	889.77	13	68.44	9848.06	<0.0001 Significant
Pure error	0.0347	5	0.0069		
Cor total	7947.15	24			

R^2: 0.8880, Adjusted R^2: 0.8507, Predicted R^2: 0.7369, Adeq precision: 14.218, C.V.%: 9.19
The predicted R^2 of 0.7369 is in reasonable agreement with the adjusted R^2 of 0.8507; i.e. the difference is less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 14.218 indicates an adequate signal. This model can be used to navigate the design space.

TABLE VII
ANOVA RESULTS FOR REDUCED QUADRATIC MODEL OF UPF OF THE TREATED COTTON FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	245.54	6	40.92	7.18	0.0005 Significant
A [cellulase]	0.2131	1	0.2131	0.0374	0.8488
B [temp]	17.41	1	17.41	3.06	0.0975
C [time]	1.67	1	1.67	0.2923	0.5954
D [NTp]	22.37	1	22.37	3.93	0.0630
CD	24.46	1	24.46	4.29	0.0529
A^2	189.90	1	189.90	33.33	<0.0001
Residual	102.57	18	5.70		
Lack of fit	69.19	13	5.32	0.7972	0.6598 Not significant
Pure error	33.38	5	6.68		
Cor total	348.11	24			

R^2: 0.7054, Adjusted R^2: 0.6071, Predicted R^2: 0.4114, Adeq precision: 9.817, C.V.%: 6.27
The predicted R^2 of 0.4114 is in reasonable agreement with the adjusted R^2 of 0.6071; i.e. the difference is less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 9.817 indicates an adequate signal. This model can be used to navigate the design space.

responses [49]. The results were then analyzed by ANOVA to assess ‘‘goodness of fit’’ (Table V-VIII). For each model, P-value less than 0.05 imply that model is significant at 95% confidence level, whereas models with P-values greater than 0.1 are usually considered insignificant [50].

Software examines all variables and their interactions to be included in proposed model. Sometimes it is necessary to exclude unimportant interactions from final model. In this study, responses did not fit well in a proposed quadratic model, and therefore, some insignificant interactions among variables (AB, AC, and A2) were eliminated from model [51]. According to analysis of variance (ANOVA), reduced quadratic model for ΔE*, reduction of *C. albicans*, UPF and DCRA of modified cotton samples was statistically significant at F-values of 77.36 (Table V), 23.79 (Table VI), 7.18 (Table VII), and 23.89 (Table VIII) and P-values of <0.0001, <0.0001, 0.0005, and <0.0001, respectively.

A desirable precision and reliability were proven for each experiment by low value of coefficient of variation (CV%) of each developed model (2.84, 9.19, 6.27, and 3.93% for ΔE*, reduction of *C. albicans*, UPF and DCRA,

TABLE VIII
ANOVA RESULTS FOR REDUCED QUADRATIC MODEL OF DCRA OF THE TREATED COTTON FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	8952.07	5	1790.41	23.89	<0.0001 Significant
A [cellulase]	6978.30	1	6978.30	93.12	<0.0001
B [temp]	28.66	1	28.66	0.3825	0.5436
C [time]	1.09	1	1.09	0.0146	0.9051
D [NTp]	343.95	1	343.95	4.59	0.0453
D^2	395.97	1	395.97	5.28	0.0330
Residual	1423.90	19	74.94		
Lack of fit	1294.45	14	92.46	3.57	0.0836 Not significant
Pure error	129.45	5	25.89		
Cor total	10375.97	24			

R^2: 0.8628, Adjusted R^2: 0.8267, Predicted R^2: 0.7755, Adeq precision: 13.258, C.V.%: 3.93
The predicted R^2 of 0.7755 is in reasonable agreement with the adjusted R^2 of 0.8267; i.e. the difference is less than 0.2. Adeq precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratio of 13.258 indicates an adequate signal. This model can be used to navigate the design space.

respectively). Also, results expressed good agreement between experimental and model predictions with high correlation coefficients [52]. Adequate precision compares range of predicted values at design points to average prediction error, in other words, a signal-to-noise ratio. Its desired value is 4 or greater [53]. Adequate precision values greater than 4 for all responses devoted that all of the predicted models could be used to examine experimental domain. P-values related to concentration of cellulase enzyme variable are the least amount among other independent variables for each responses of reduction of *C. albicans* and DCRA. In other words, concentration of cellulase enzyme has the highest significant effect among other independent variables on mentioned responses. The reason could be related to an effective and synergism role of acidic cellulase enzyme because of creating modifications on cotton fabric surface and also increasing efficiency of NTp. Also P-value of NTp concentration variable for ΔE* and UPF responses are the least among other independent variables. In a way that the highest effectiveness on ΔE* and UPF dependent variables is accomplished by NTp concentration factor. The reason could be likely related to effective role of utilizing appropriate concentration of NTp in increase of enzyme treatment efficiency and consequently higher and more effective absorption NTp on cotton fabrics.

C. Laundering Durability of Sono-Cellulase Cotton Treated with Optimized Condition

Reflection curves of blank and treated cotton sono-cellulase fabrics in the optimized conditions before and after laundering durability analysis in UV region (200-400 nm) are presented in Fig. 2.

Reflectance amounts of blank cotton sample are more than those of other treated cotton samples. In a way that, sono-cellulase cotton sample has the lowest reflection amount in the optimized condition. This confirms that the highest absorption amount of prepared samples in optimized condition exist in UV region; that is in accordance with UPF amounts mentioned in Table III. Meanwhile it shows that in one hand, ultrasound energy leads to more dispersion of NTp and on the other hand, applying this energy in enzyme treatment causes cracks and voids on the cotton surface which could well imprison NTp in it. Also reflectance amounts of treated sono-cellulase cotton after laundering durability and in optimal conditions demonstrated that reflectance amounts have a little more than optimized sample before laundering durability analysis. This approves high laundering durability of sono-cellulase cotton sample prepared in the optimized condition. This might be related to applying ultrasound energy as an assistant factor which could be able to, in one hand, produce appropriate position as NTp locations on cotton fabrics and on the other hand, hinder aggregating NTp in integrated forms and micelles. Also, other reason of high laundering durability of treated cotton in optimized condition could be presence of BTCA cross-linking and stabilizer agent which is capable of making more and stronger connections of NTp with cotton polymeric chains via electrostatic interaction between NTp cationic centers and anionic carboxyl groups.

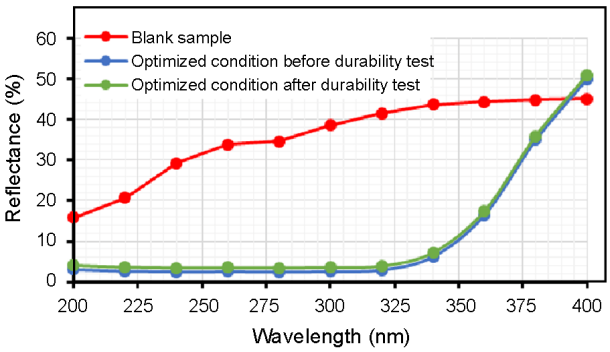

Fig. 2. Reflection curves of blank and treated cotton sono-cellulase fabrics at optimized condition before and after durability test.

Figs. 3a-c exhibit SEM images of blank and treated sono-cellulase cotton samples (cellulase enzyme: 1.30%, Temp: 60 °C, Time: 31.1 min, NTp: 1.07%) before, and after laundering durability analysis in optimized condition.

Cracks and voids in blank sono-cellulase cotton are clearly observable in Fig. 3a. Also treated cotton sample in the optimized conditions is illustrated in Fig. 3b. Almost the presence of homogenous NTp is observable. Tracks created on the cotton samples could imprison more NTp via physical imprisonment. The SEM images related to cotton sample treated in optimized conditions are presented in Fig. 3c after laundering durability. These images imply that howbeit several laundering cycles, the highest number of NTp was connected to sono-cellulase samples via strong connections. Besides utilizing ultrasound energy and BTCA cross-linking agent which enhance laundering durability, it could be referred to definite amounts of NTp and BTCA and also the most excellent and selected conditions of cotton fabric treated with acid cellulase enzyme. So that experiments statistical design based on D-optimal method and statistical analysis with RSM technique lead to not only remarkable decrease of experiments number, costs and consumptive energies but also the most appropriate condition is recommended with the highest efficiency. In a way that, considering optimized condition resulted through reduced quadratic models in all experiments, optimistic perspective to economic costs and benefits and vast production of sono-cellulase cotton fabric treated with NTp compound could be achieved. Also EDX

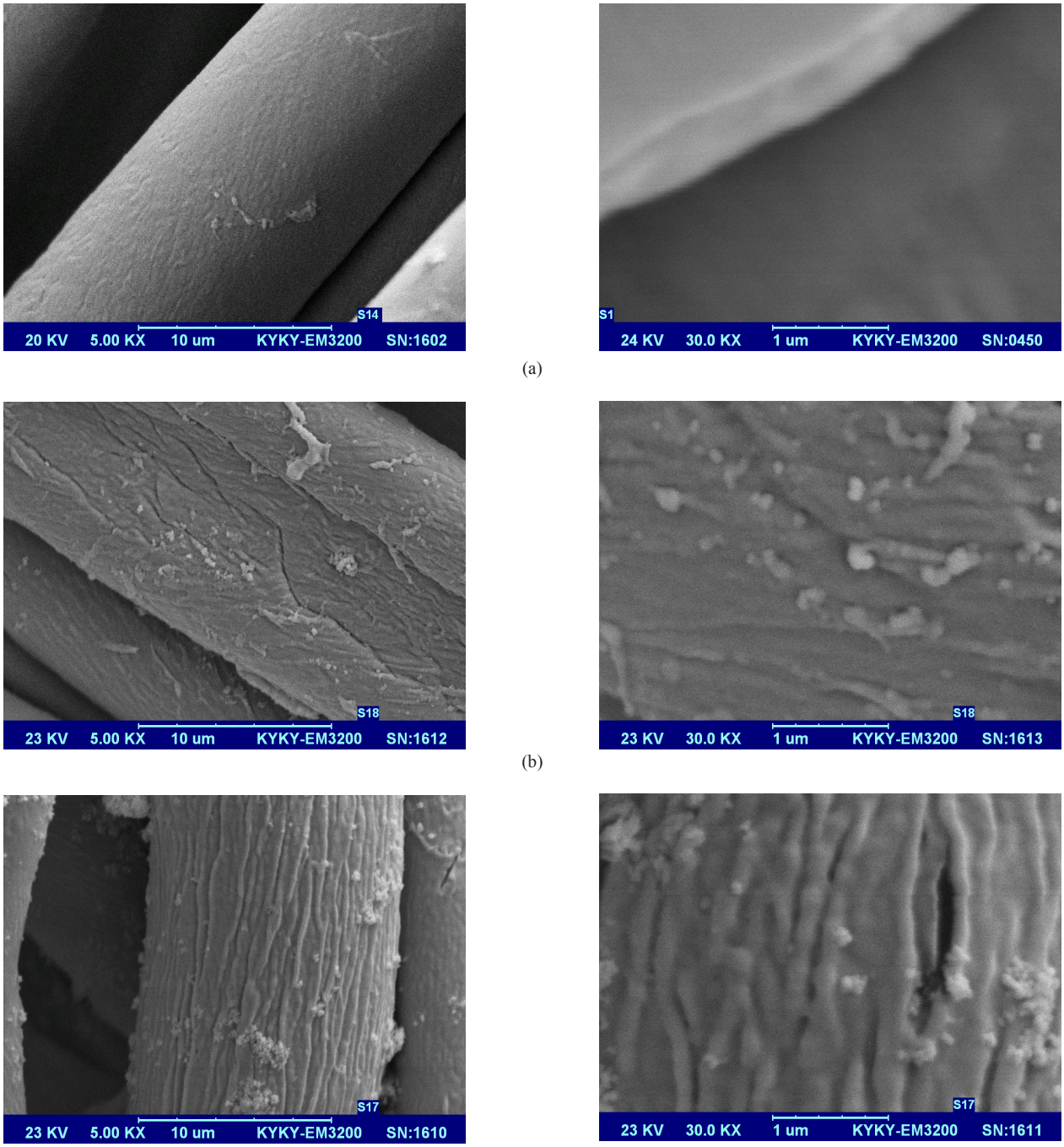

Fig. 3. Response surfaces for: (a) ΔE*, (b) reduction of *C. albica*ns, (c) UPF, and (d) DCRA (W+F)° as a function of NTp (%), cellulase enzyme (%), time (min), and temperature (°C) for modified cotton samples.

analysis was performed in order to confirm NTp presence on sample treated in optimized conditions before and after laundering durability test (Fig. 4). Observed small peak of titanium about 4.5 keV approves NTp presence on sono-cellulase sample in optimized condition and confirms SEM and reflectance spectrographs results obtained. However, observed small peak about 2.1 keV is related to Au which was made as a result of coating conditions. As it is perceived, bulk amounts of Ti atoms were preserved on modified cotton surfaces after laundering durability analysis. It seems that presence of strong bonds could result in durable and strong connection of NTp compound with modified cotton polymeric chains and consequently lead to increase laundering durability.

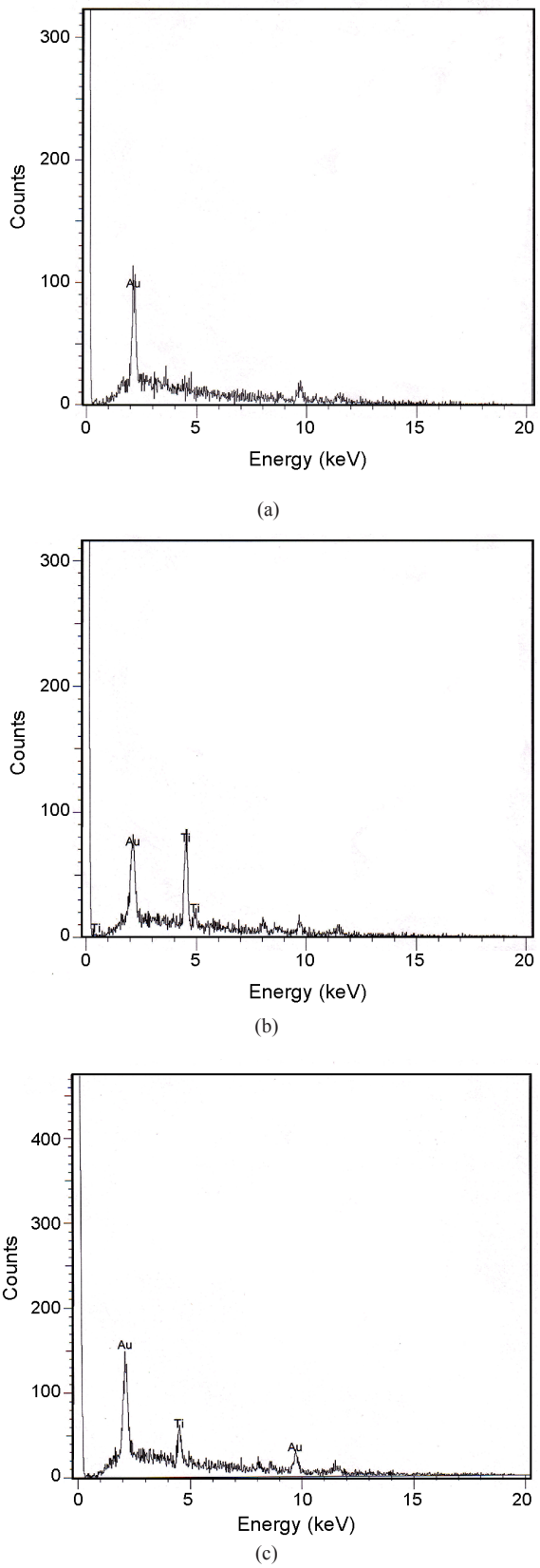

Fig. 4. EDX analysis of: (a) blank and treated sono-cellulase cotton samples at optimized condition (cellulase enzyme: 1.30%, Temp: 60 °C, Time: 31.1 min, NTp: 1.07%) (b) before and (c) after laundering durability test.

IV. CONCLUSION

In this research, sono-cellulase cotton treated with NTp and BTCA was prepared to create multi-functional properties such as self-cleaning, antifungal, UV protection and x-linking based on impregnating conventional technique via increasing absorption and consequently enhancing laundering durability. Therefore, the results obtained from reflectance spectrographs and SEM and EDX images confirmed high laundering durability of modified cotton samples. Meanwhile, other resulted findings are elaborated as follows: a) Applying ultrasound energy as a dispersing agent could produce more proper dispersion of NTp into mono-molecules forms. b) Using ultrasonic energy during enzymatic treatment cause making more cracks and voids on modified cotton fabrics and finally lead to more and stronger deposition and loading of NTp via physical absorption enhancement. c) D-optimal statistical design and RSM analysis with reduced quadratic models lead to decrease experiments, consumptive time, required energy, and high costs of preparing enzyme material and NTp. d) It seems that presence of both physical imprisonment and electrostatic interaction plays an efficient role in increasing laundering durability of modified cotton samples. e) It appears that considering optimizing process in accomplished research and attending economic costs and benefits, positive perspective was achieved to widely produce durable modified cotton fabrics with multi-functional properties.

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