

Modeling and Optimization of Colloidal Nanosilver Pretreatment on Acid-Free Dyeing, Antibacterial, and Hydrophilicity of Polyamide-6,6 Using Response Surface Methodology

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Received: 18 January 2020, accepted: 29 July 2020

Abstract- Enhancement of dyeability, antibacterial, and hydrophilicity of polyamide-6,6 was introduced with colloidal silver nanoparticles (CSNs) and butane tetra carboxylic acid (BTCA) using cubic statistical models. Different concentrations of CSNs and BTCA were investigated to evaluate their influences on dyeability, antibacterial, hydrophilicity, and color change properties of polyamide-6,6 fabric by applying statistical design of D-optimal method. Antibacterial property of treated sample was tested by Gram-negative bacterium *Escherichia coli* and Gram-positive bacterium *Staphylococcus aureus*. To achieve optimum conditions for polyamide-6,6, response surface methodology was also utilized. Here, CSNs were stabilized on polyamide-6,6 surface using BTCA as crosslinking agent in order to enhance washing durability. Scanning electron microscopy and energy-dispersive spectroscopy were employed to characterize presence of CSNs on surface of polyamide-6,6 and elemental composition of treated polyamide-6,6 fabrics. Treatment optimization led to considerably absorption enhancement of C.I. Acid Red 81 dye through cubic statistical models on polyamide-6,6 surfaces as well as antibacterial and hydrophilicity characteristics and minimized color change caused due to CSNs influence. The principal result is synergetic effect utilizing BTCA accompany with CSNs on enhancing and durability of mentioned properties quantitatively in optimized conditions. Overall, the suggested method could be introduced as a new route, disclosing various desirable multifunctional characteristics to polyamide-6,6 fabric.

Keywords: cubic statistical models, optimization, polyamide-6,6, silver nanoparticles

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I. INTRODUCTION

Polyamides also known as nylons have excellent properties. Polyamides characteristics have been extensively investigated and utilized. Some of these properties include: *in situ* synthesis of CSNs and its dyeing simultaneously [1], ultraviolet protection [2], isotherms, kinetics, thermodynamics of acid dye [3], ultrafine nanofibers [4], enhanced mechanical [5], thermal stability, yellowing properties [6], and micro-fibril morphology development through nanoclay [7].

Polymer technology was widely applied in the textile industry by polymer science development [8]. In dyeing and finishing processes, polymer was also utilized as auxiliary besides textile materials. As size in warp sizing, polyacrylic acid, polyacrylate, polyacrylamide, and polyvinyl alcohol are used [9]. Polymers such as polyurethane [10], polysiloxane [11], polyphosphate [12], polyurethane/polyaniline, and poly(ethylene oxide) [13] are used as auxiliaries in finishing process of textile to enhance quality or performance of fabric. Among new different investigated reagents, polycarboxylic acids are known as the most promising formaldehyde-free cross-linking agents of textile fibers. Butane tetra carboxylic acid (BTCA) is one of the most beneficial and expensive cross-linking agents [14]. BTCA is also applied as formaldehyde-free cross-linking agent [15] for flame retardancy treatment [16] with sodium hypophosphate (SHP) as catalyst. It is suggested to include cyclic anhydrides as reactive intermediates reacted through cross-linking mechanism by hydroxyl groups of fabrics. Esterification may happen just through heating or in presence of SHP catalyst [17,18].

Recently, emerging of modern garment productions was developed significantly based on loading of nanomaterials on textiles. Silver nanoparticles could be applied in many

applications, such as electro-conductivity, UV protection, and antimicrobial applications [19]. Several methods were developed to improve durability of CSNs on fibers because textiles finishing with nanoparticles are not stable against washing. For example, a single step green synthesis of silver nanoparticles from silver nitrate (AgNO_3) using *Cassia tora* leaves extract as reducing agent on cotton surface which increases stability of CSNs in laundering processes. Synthesis process was taken place in boiling temperature and led to swelling of fabrics. Therefore, Ag particles are supposed to penetrate into fabric structure and are entrapped within fabric [20]. Also, sonochemical irradiation is utilized for permanent finish of the CSNs on textile materials [21].

Dyeing levelness and fastness of polyamide-6,6 with acid dyes are very essential. Fairly weak physical binding of dyes on fibers caused poor wash and wet fastness of conventional acid dyed polyamide textiles [22]. In the present research, polyamide-6,6 fabric production with multifunctional properties, such as antibacterial and high dyeability was investigated through conventional exhaustion method. To the best of our knowledge, there is no report regarding statistical optimization of dyeability enhancement, antibacterial, and hydrophilicity with minimal color change of polyamides fabrics using colloidal silver nanoparticles (CSNs) and BTCA cross-linking agents. This is the reason why polyamide-6,6 fabrics were pretreated with various concentrations of CSNs and BTCA and dyed with C.I. Acid Red 81 dye. The influence of BTCA and CSNs concentration on the exhaustion of C.I. Acid Red 81 dye, antibacterial, and hydrophilicity properties was reinforced with minimized color change of polyamide-6,6 fabrics using cubic statistical models. Consequently to

optimize dyeability, antibacterial, and color change of polyamide-6,6 fabrics, the best treatment conditions were illustrated through response surface methodology (RSM) analysis.

II. EXPERIMENTAL

A. Materials

Polyamide-6,6 fabric plain knitted, 70 den and a weight of 85 g/m^2 and C.I. Acid Red 81 dye were procured from Sigma–Aldrich. Information of utilized acid dye is illustrated in Table I. A colloid solution of nanosilver was employed with 65 nm average of particle size from Europe Nano Group Company (Germany). 1,2,3,4-Butanetetracarboxylic acid ($\text{C}_8\text{H}_{10}\text{O}_8$) with a purity of 98% and a molecular mass of 234.16 g/mol, sodium phosphate monohydrate ($\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$) with a purity of 99% and a molecular mass of 105.99 g/mol, sodium carbonate (Na_2CO_3) with a purity of 99% and a molecular mass of 105.99 g/mol, tryptic soy agar (TSA) culture medium and sodium chloride with a purity of 99.9% were supplied from Merck Co. (Germany). Materials were used without any further purification. Non-ionic detergent (Rucogen DEN) was prepared from Rudolf Chemie Co., (Germany).

Finishing baths contents were prepared using an ultrasonic bath (200 V, 50 W, 40 kHz). Surface morphology of treated samples were carried out using a scanning electron microscope (VEGA\\TESCAN-XMU, Czech), equipped with an energy dispersive X-ray diffractometer (EDX). Thermal oven was used to dry and cure samples. The overall color differences through CIE color coordinates between control and pretreated polyamide-6,6 samples were measured using a reflectance spectrophotometer (color-guide sphere, D/10° spin, Germany) with CIE standard

TABLE I
INFORMATION AND CHEMICAL STRUCTURE OF C.I. ACID RED 81 DYE

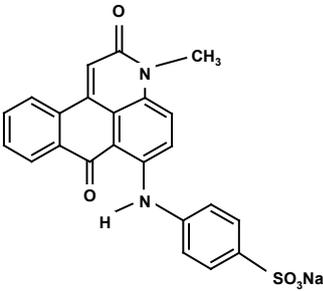
Name	C.I. Acid Red 81
Chemical structure	
Molecular structure	Anthraquinones
Molecular formula	$\text{C}_{23}\text{H}_{15}\text{N}_2\text{NaO}_3\text{S}$
Molecular weight	454.43 g/mol
CAS registry number	6846-33-9

TABLE II
D-OPTIMAL DESIGN FOR EXHAUSTION OF C.I. ACID RED 81 DYE, COLOR CHANGE, REDUCTION OF *S. AUREUS* AND *E. COLI*, AND WATER ABSORPTION EFFICIENCY OF THE CONTROL AND POLYAMIDE-6,6 SAMPLES PRETREATED WITH BTCA CROSS-LINKING AGENT AND CSNS

Run	Factor		Responses				
	CSNs (ppm)	BTCA (%)	Exhaustion (%)	Color change (ΔE)	Reduction of <i>S. aureus</i> (%)	Reduction of <i>E. coli</i> (%)	Water absorption (s)
Control	0.00	0.00	68.13	0.00	0.00	0.00	9.2
Control 1	30.00	0.00	73.11	1.69	76.23	75.12	12.36
Control 2	0.00	6.00	60.68	0.11	62.12	60.56	4.0
1	35.00	5.25	89.14	0.95	90.11	89.15	7.6
2	10.00	3.00	87.11	0.57	81.37	75.47	7.6
3	10.00	9.00	88.32	0.20	84.15	93.15	6.9
4	10.00	6.00	88.61	0.26	83.11	94.11	7.3
5	50.00	4.59	90.09	1.50	99.45	97.59	4.1
6	23.13	3.75	87.11	0.72	85.18	92.15	6.1
7	10.00	9.00	88.34	0.15	84.17	93.11	6.8
8	36.55	3.00	89.07	1.21	92.14	88.36	4.8
9	50.00	9.00	92.13	1.22	99.34	97.36	4.4
10	36.55	3.00	89.09	1.21	92.18	88.33	4.8
11	50.00	4.59	90.11	1.51	99.48	97.56	4.2
12	26.96	6.34	89.76	0.42	86.19	91.14	5.7
13	41.49	6.75	93.57	1.12	95.14	87.15	4.6
14	30.00	9.00	89.54	0.27	89.14	90.81	7.4
15	10.00	3.00	87.13	0.57	81.34	75.44	7.5
16	50.00	9.00	92.11	1.22	99.31	97.32	4.5

illuminant D65. Reflectance and absorbance spectra of control and pretreated polyamide-6,6 samples were measured using a Perkin-Elmer Lambda 35 UV-visible spectrophotometer.

B. Analyses and Tests

B.1. Scouring

Polyamide-6,6 samples (10×5 cm²) were washed in a bath containing 1 g/L of nonionic detergent with L:G=40:1 (liquor to good ratio) at 65 °C for 15 min, then rinsed with water and dried at room temperature.

B.2. Polyamide-6,6 Fabric Impregnation with BTCA and CSNs

Finishing bath was prepared with combination of BTCA, SHP with the amount of 60% of BTCA as catalyst, CSNs (based on weight of bath: O.W.B) and required percentage of distilled water in an ultrasonic bath for 10 min (Table II). The scoured polyamide-6,6 fabrics were impregnated with freshly predispersed solutions at 80 °C for 30 min. The impregnated polyamide-6,6 fabrics were dried at 80 °C for 3 min. The pretreated samples were cured at 170 °C for 3 min. Afterwards, the finished samples were washed at 60 °C

for 20 min using a solution containing 1 g/L Na₂CO₃ and 1 g/L nonionic detergent (Rucogen DEN), and finally dried at ambient conditions.

B.3. Dyeing

Dyeing of control and CSNs/BTCA pretreated polyamide-6,6 samples was performed with C.I. Acid Red 81 dye (1% OWF). Polyamide-6,6 samples were added to a dye-bath at 40 °C and left for 5 min. Then C.I. Acid Red 81 dye was added to the dye-bath and temperature was increased to 80 °C within 20 min and maintained for 45 min at pH 7 and L:G=45:1 [23]. Samples were finally washed and dried at room temperature. Influence of CSNs/BTCA pretreatment on the percentage of dye-bath exhaustion was calculated according to Eq. (1):

$$E(\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

Where, C_0 and C_f are, respectively, the concentrations of dye before and after dyeing based on absorption at the maximum wavelength for the acid dye in water (λ_{\max} C.I. Acid Red 81=508 nm).

B.4. Color Change

Color change in this research means “the overall color differences between control and pretreated polyamide-6,6 samples with CSNs/BTCA”. This measurement was performed before dyeing treatment using the reflectance spectrophotometer (color-guide sphere, D/10° spin, Germany) with CIE standard illuminant D65 and calculated according to Eq. (2) [24]:

$$\Delta E = \left[(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2 \right]^{0.5} \quad (2)$$

Where, ΔE is the color change between control and CSNs/BTCA-pretreated polyamide-6,6 fabrics. Here, L^* , a^* , and b^* are the values of lightness, redness–greenness, yellowness–blueness, respectively, and calculated using a computer color comparison system.

B.5. Wash Fastness

Wash fastness of CSNs/BTCA-pretreated polyamide-6,6 samples was evaluated according to AATCC 61(2A)-1996. Basically, 2 g/L solution was prepared from a standard soap at pH 8.5-9. Washing was performed at 50 °C for 45 min at 42 rpm rotation. Each stage of washing equals to 5 times washing at 38±3 °C through this method [24]. Polyamide-6,6 fabrics that contain different CSNs and BTCA were washed for 10 times and whose properties including dyeability, antibacterial, hydrophilicity, and color change were measured.

B.6. Water Drop Absorption Time

Water drop absorption time of pretreated and dyed polyamide-6,6 fabrics was determined based on AATCC 79-2000. A sample was closed and leveled in a frame to a diameter of 15 cm in this test. A burette was placed with a standard tip above horizontal level of sample with 6 mm interval. Light source was hold at 45° angle and vision angle was placed at 45° angle opposite to light source. The chronometer was stopped when no drop was seen on the polyamide-6,6 surface.

B.7. Antibacterial Test

Two pathogenic micro-organisms including *Staphylococcus aureus* (*S. aureus*) ATCC 65380 as gram-positive bacteria and *Escherichia coli* (*E. coli*) ATCC 11303 as Gram-negative were tested using AATCC 100-2004 test method. The colonies on agar plate were the number of viable bacteria which were counted before and after treatment with the different concentrations of CSNs and BTCA. Results were reported as percentage of bacteria reduction according to Eq. (3):

$$R(\%) = \left(\frac{A_1 - A_2}{A_2} \right) \times 100 \quad (3)$$

Here, A_1 and A_2 are the numbers of bacteria colonies recovered from control and pretreated polyamide-6,6 samples with CSNs and BTCA, respectively, after incubating for 24 h at 37 °C and 65% relative humidity. R is the reduction percentage of bacteria colonies.

B.8. Design of Experiments (DOE)

Central composite design was applied in order to conduct an experimental plan with two variables. The limits of the variables based on actual factors were: BTCA (3.00-9.00%) and CSNs (10.00-50.00 ppm). Details of pretreatment using D-optimal design with CSNs and BTCA concentrations are presented in Table II (run 1-16). Trial version of Design Expert 8.0.1.0 was utilized from Stat-Ease, Inc. (USA). Also, the influence of variables on exhaustion (%) of C.I. Acid Red 81 dye, color change, antibacterial activity against *E. coli* and *S. aureus*, and absorption time of water drop was adopted using cubic polynomial function (Eq. (4)):

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum c_i X_i^2 \quad i \geq j \quad i, j = 1, 2, 3 \quad (4)$$

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

III. RESULTS AND DISCUSSION

A. Dyebath Exhaustions

Based on initial studies, independent variables of BTCA (3.00-9.00%) and CSNs (10.00-50.00 ppm) and dependent variables including exhaustion of C.I. Acid Red 81 dye, color change, reduction of *S. aureus* and *E. coli*, and water absorption time were selected for more investigation during optimization. Table II illustrates the exhaustion values of control and pretreated polyamide-6,6 fabric dyed with C.I. Acid Red 81 dye. Dye exhaustion was improved by nanotechnology pretreatment due to stabilizing of CSNs with cationic charge on the surface of polyamide-6,6 fabric. It increases electrostatic absorption of C.I. Acid Red 81 dye with sulphonyl groups on the pretreated polyamide-6,6 fabrics (Scheme 1). Further, durability of CSNs was indicated on polyamide-6,6 fabric with desirable washing durability because of BTCA presence as a cross-linking agent. Mechanism of covalent bond formation between polycarboxylic acid and polyamide-6,6 and its effect



Scheme 1. Suggested linkage mechanism of polyamide-6,6 with BTCA, CSNs, and C.I. Acid Red 81.

on the durability of CSNs were also presented by Montazer *et al.* [24].

However, exhaustion of pretreated samples was increased with high CSNs and BTCA concentration (run: 9 and 16) as compared with control samples. It could result more electrostatic linkage of C.I. Acid Red 81 with cationic groups of CSNs. The reason could be related to desaturation of functional groups existing in cross-linking BTCA agent in a way that has tendency to react with CSNs. As a result, design to find out effects of each variable and their interactions using experimental and also obtaining optimum dyeing conditions on CSNs/BTCA pretreated polyamide-6,6 fabrics were very beneficial. Statistical models supplied treatment conditions with optimized C.I. Acid Red 81 exhaustion. However, results revealed that pretreatment with CSNs and BTCA on polyamide-6,6 fabric significantly improved absorption of anthraquinonoid acid dye of C.I. Acid Red 81 compared to control samples. The conventional dyeing process causes special limitations close to boiling-point [25,26]. Therefore, it was attempted to decrease polyamide-6,6 vulnerability via applying methods, such as using special auxiliary agents during dyeing process. To develop different dyeing qualities, more investigations were progressed in recent years, and new technologies are being attempted to reduce fiber damage, decrease energy consumption, and increase productivity [27]. In last decade new methods were required to be applied in increasing laws related to competitive market and environment conditions in area of dyeing. This statement led to emergence of tendency for utilizing new technologies such as ultrasound [28], ultraviolet [29], ozone [30], plasma [31], gamma irradiation [32], laser [33], microwave [34], e-beam irradiation [35], ion implantation [36], and supercritical carbon dioxide [37] in textile industry. These new technologies not only cause decrease in time, energy, and chemical consumption, but also decrease in wastewater load. Despite a lot of searching, unfortunately

there was no report related to pretreating with CSNs and its optimization via cubic models of RSM to enhance dyeability of polyamide-6,6 fabric with acid dye. In the present study, possibility of reduction in dyeing temperature has further investigated without using acid auxiliary agent. In fact, using acidic agent in usual dyeing bath causes creation of cationic sites on polyamide-6,6 molecular chains and increases tendency to absorb anionic-acid dye. But in this research, CSNs stabilized by BTCA cross-linking agent are capable of acting as acidic replacement and creating more cationic groups on polyamide-6,6 molecular chains (Scheme 1). However, CSNs are fixed with high temperature on polyamide-6,6 fabric and acted as an adhesive agent between C.I. Acid Red 81 and polyamide-6,6 fiber. Hence, great amount of C.I. Acid Red 81 dye molecules may react with polyamide-6,6 fabric. Thus, CSNs pretreatment on polyamide-6,6 fabrics suggests remarkable effect on polyamide-6,6 fabric dyeability. In this manner, polyamide-6,6 dyeing with C.I. Acid Red 81 dye was accomplished without the presence of acid auxiliary agent and this method was introduced as a novel effective approach in order to improve dyeability of polyamide-6,6 fabric through nanotechnology.

B. Color Change

Color change values (ΔE) of control and pretreated fabrics were measured at room temperature using a reflectance spectrophotometer (color-guide sphere, D/10° spin, Germany) with CIE standard illuminant D65. Effect of BTCA cross-linking agent that was applied to stabilize CSNs on polyamide-6,6 fabric surface on color change is illustrated in Table II. Color change of pretreated polyamide-6,6 fabrics increases by increasing CSNs concentration at constant concentration of BTCA as it could be observed for the set of each following runs (run: 2, 8, 10, and 15). Therefore, samples with lowest BTCA and CSNs (BTCA: 3.00 %, CSNs: 10.00 ppm) (run: 2 and 15) illustrate higher color change than control sample. The highest color change of pretreated samples is related to samples run: 5 and 11 that is due to their nature and agglomeration of CSNs on polyamide-6,6 fabric surface. Because of high surface energy of nanoparticles, most of them tend to aggregate and form large particles. When nanoparticles are placed adjacent to each other, interaction forces including van der Waals attraction form to aggregate. In addition, CSNs properties demonstrate that these particles could easily aggregate [38]. This could be considered as a preventive effect of CSNs which were utilized in polyamide-6,6 polymeric chains. Different values of color change could be obtained by controlling ratio of CSNs and BTCA concentration which could be

adjusted to textile end-use. Color change of the samples decreases by increasing BTCA concentration at constant CSNs as it could be presented for the set of each following runs (run: 2, 3, 4, 7, and 15, run: 5, 9, 11, and 16). This can be attributed to the performance conditions and existence of SHP and BTCA which possibly preventing from agglomeration of CSNs. On the other hand, BTCA is the most effective among polycarboxylic acids with retention of fabric whiteness [39]. BTCA is a strong cross-linking agent that could improve both adsorption and retention of more CSNs on polyamide-6,6 surface, since it contains four functional groups. Esterification mechanism was suggested to include cyclic anhydrides as reactive intermediates which are reacted by hydroxyl groups of fabrics [24,40].

C. Antibacterial Properties

The experiments designed in Table II revealed reduction percentages of *E. coli* and *S. aureus* bacteria by pretreated polyamide-6,6 fabrics with various concentrations of BTCA and CSNs as compared with control samples. It is possible that BTCA separately has intermediate antibacterial effects (sample control 2). Increasing BTCA concentration caused decreasing of bacteria growth considerably on both types of bacteria. It could be attributed to the presence of more carboxylic groups of BTCA which led to more absorption of CSNs on polyamide-6,6 fabric surface through electrostatic attractions. Also increasing CSNs caused increase of antibacterial property. The

highest value of bacteria reduction was 97.59% for *E. coli* and 99.48% for *S. aureus* for samples run 5 and 11 (BTCA 4.59% and CSNs 50.00 ppm), respectively (Fig. 1). Thus, *E. coli* exhibited a little more resistance than *S. aureus*. Killing bacteria by antibacterial agents can be resulted from the demolition of bacteria membrane, the spatial deformation, deformation of bacteria enzyme, and the chromosome damage. Consequently, synergetic effect of CSNs/BTCA combination is noticeable on the antibacterial properties obtained. BTCA accompanying with CSNs on polyamide-6,6 fabric which have a complementary effect showed a noticeable reduction in *E. coli* Gram-negative and *S. aureus* Gram-positive bacteria.

D. Hydrophilicity/Hydrophobicity

Influence of CSNs and BTCA pretreatment on absorption time of water of control and pretreated polyamide-6,6 surfaces is reported in Table II. Nanotechnology treatment led to decrease of water drop absorption time. Water absorption time of the samples decreased by increasing BTCA and CSNs concentrations as it is exhibited in the Table II. It could be related to (a) considering high surface energy of CSNs [41] and (b) remaining hydrophilic carboxylic groups of BTCA [42]. The lowest water absorption was 4.1 s for sample run 5 (BTCA 4.59% and CSNs: 50.00 ppm). As a result, considerable changes have been occurred in hydrophilicity of BTCA/CSNs-pretreated polyamide-6,6 fabrics as compared to control and control 1 samples. The other important factor which led to improve C.I. Acid Red 81 dye absorption is higher hydrophilicity of polyamide-6,6 fabric pretreated with CSNs. Hydrophilicity was more important in fabrics dyed with C.I. Acid Red 81 due to the presence of more hydrophilic groups in the acid dye structure (Table I). Moreover, improved hydrophilicity of pretreated polyamide-6,6 might be clearly suggested as an effective factor in higher acid dye exhaustion. This reason could allow water and dye molecules to penetrate more easily into polyamide-6,6 fabrics [43].

E. Statistical Analysis

Optimization of pretreatment process plays an important role in improving polyamide-6,6 performance. RSM provides sufficient information of variables effects and overall experimental error with minimum number of experiments [44]. This technique has been extensively utilized in textile processing optimization, such as natural dyeing with henna [45] and cumin [46] dyes improved with plasma treatment and durable multifunctional properties of cellulose cotton using nano-TiO₂ sonolading [47] to analyze effect of independent variables and optimize process responses using factors proper values. The present

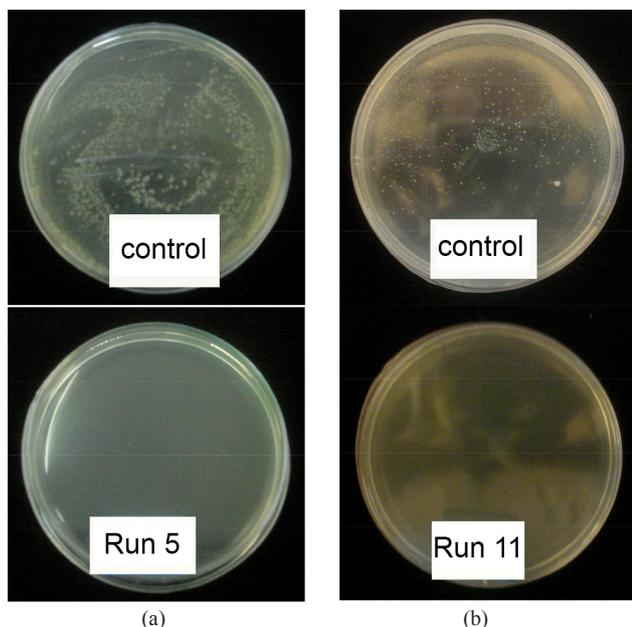


Fig. 1. Antibacterial activity of the pretreated polyamide-6,6 fabrics against: *E. coli* (left) (a) control and run: 5, and *S. aureus* (right) (b) control and run: 11 (run 5 and 11 pretreated with BTCA 4.59% and CSNs 50.00 ppm)

study has been conducted based on D-optimal design and response surface methodology (RSM). There have been no literature references related to simultaneous optimization of significant properties such as exhaustion, color change, reduction of *S. aureus* and *E. coli*, and water absorption efficiency of polyamide-6,6 samples pretreated with CSNs and BTCA through cubic models. In total, 16 designed experiments were conducted according to Table II. The influences of independent variables including BTCA and CSNs concentrations were assessed in this model on response surfaces. These responses include dyeability, color change, reduction of *S. aureus* and *E. coli*, and water absorption time of pretreated polyamide-6,6 samples. Final equations could be presented in terms of coded or actual factors by software. The equations introduced in this research are based on actual one. Statistical equations in terms of actual factors by cubic models related to exhaustion of C.I. Acid Red 81, color change, reduction of *S. aureus* and *E. coli*, and water absorption time of polyamide-6,6 samples pretreated with CSNs and BTCA using Design-Expert software are suggested in Eqs. (5) to (9):

$$\begin{aligned} \%Exhaustion_{(C.I. Acid Red 81)} = & +115.11-0.27 \times (CSNs)-16.71 \times \\ & (BTCA)+0.02 \times (CSNs \times BTCA)+0.01 \times (CSNs^2) \\ & +3.14 \times (BTCA^2)+2.90 \times 10^{-4} \times (CSNs^2 \times BTCA)-3.00 \times 10^{-3} \\ & \times (CSNs \times BTCA^2)-1.17 \times 10^{-4} \times (CSNs^3)-0.18 \times (BTCA^3) \end{aligned} \quad (5)$$

$$\begin{aligned} Color\ change = & +0.90-0.06 \times (CSNs)+0.11 \times (BTCA)-6.89 \times \\ & 10^{-4} \times (CSNs \times BTCA)+2.84 \times 10^{-3} \times (CSNs^2)-0.04 \times \\ & (BTCA^2)+1.87 \times 10^{-4} \times (CSNs^2 \times BTCA)-7.95 \times 10^{-4} \end{aligned}$$

$$\begin{aligned} & \times (CSNs \times BTCA^2)-0.38 \times 10^{-4} \times (CSNs^3)+3.6 \times 10^{-3} \times (BTCA^3) \end{aligned} \quad (6)$$

$$\begin{aligned} Reduction_{(S.aureus)} = & +83.70-0.36 \times (CSNs)-0.66 \times (BTCA)- \\ & 0.05 \times (CSNs \times BTCA)+0.03 \times (CSNs^2)+0.27 \times (BTCA^2)- \\ & 4.08 \times 10^{-5} \times (CSNs^2 \times BTCA)+2.96 \times 10^{-3} \times (CSNs \times BTCA^2)- \\ & 2.27 \times 10^{-4} \times (CSNs^3)+0.02 \times (BTCA^3) \end{aligned} \quad (7)$$

$$\begin{aligned} Reduction_{(E.coli)} = & -40.14+5.17 \times (CSNs)+45.22 \times (BTCA)- \\ & 0.68 \times (CSNs \times BTCA)-0.12 \times (CSNs^2)-5.66 \times (BTCA^2)+ \\ & 1.73 \times 10^{-3} \times (CSNs^2 \times BTCA)+0.04 \times (CSNs \times BTCA^2)+ \\ & 1.29 \times 10^{-3} \times (CSNs^3)+0.23 \times (BTCA^3) \end{aligned} \quad (8)$$

$$\begin{aligned} Water\ absorption\ time = & -16.73-1.44 \times (CSNs)+20.62 \times (BTCA) \\ & +0.41 \times (CSNs \times BTCA)+0.05 \times (CSNs^2)-3.81 \times (BTCA^2)- \\ & 7.76 \times 10^{-4} \times (CSNs^2 \times BTCA)+1.62 \times 10^{-3} \times (CSNs \times BTCA^2)- \\ & 5.06 \times 10^{-4} \times (CSNs^3)+0.21 \times (BTCA^3) \end{aligned} \quad (9)$$

Response surfaces were drawn through achieved statistical models (Eqs. (5) to (9)), and the relation was obtained between each independent variable and also exhaustion of C.I. Acid Red 81, color change, reduction of *S. aureus* and *E. coli*, and water absorption time of polyamide-6,6 samples. Therefore, response surfaces of polyamide-6,6 samples are presented in Figs. 2a–2e, respectively.

Optimum conditions of characteristics including exhaustion of C.I. Acid Red 81, color change, reduction of *S. aureus* and *E. coli*, and water absorption time of polyamide-6,6 samples were found by means of Design-Expert software which were illustrated as 8.70% BTCA,

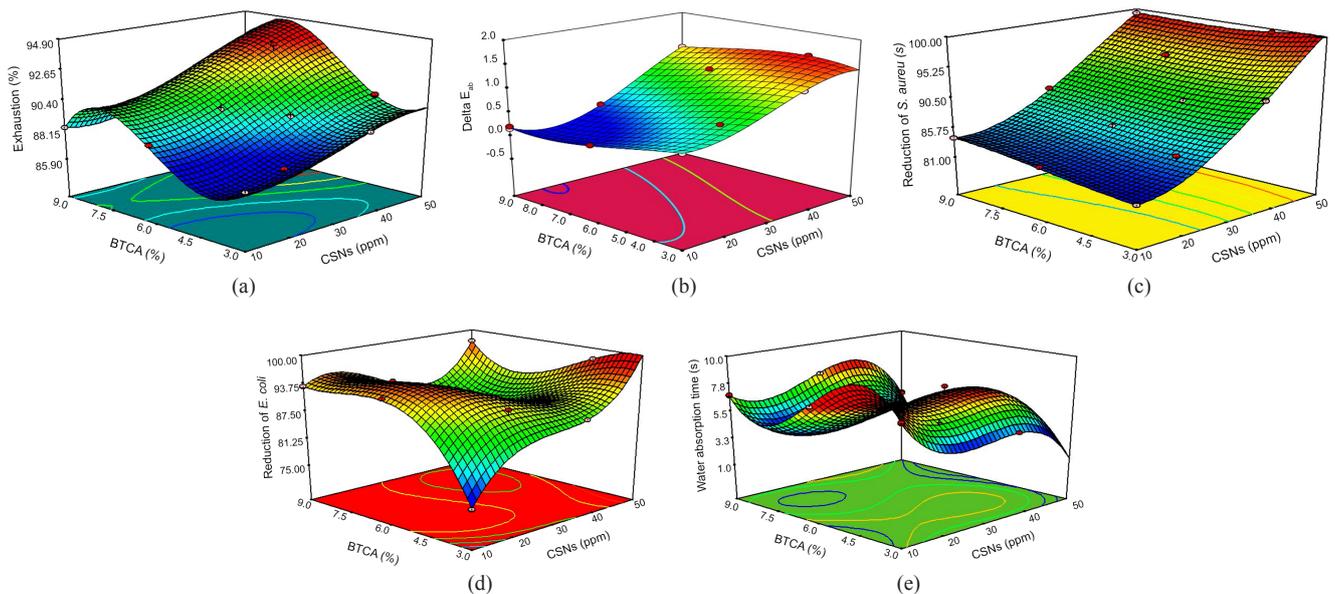


Fig. 2. Response surfaces for: (a) the exhaustion of C.I. Acid Red 81 dye, (b) color change, reduction of (c) *S. aureus* and (d) *E. coli*, and (e) absorption time of water as a function of BTCA and CSNs for polyamide-6,6 samples.

TABLE III
ANOVA RESULTS OF EXHAUSTION OF C.I. ACID RED 81 DYE FOR THE PRETREATED POLYAMIDE-6,6 FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	51.23	9	5.69	39.26	0.0001 Significant
A [CSNs]	2.26	1	2.26	15.62	0.0075
B [BTCA]	4.68	1	4.68	32.27	0.0013
AB	0.23	1	0.23	1.60	0.2526
A ²	0.62	1	0.62	4.30	0.0835
B ²	3.09	1	3.09	21.32	0.0036
A ² B	0.13	1	0.13	0.92	0.3750
AB ²	0.26	1	0.26	1.77	0.2318
A ³	0.16	1	0.16	1.11	0.3335
B ³	3.24	1	3.24	22.33	0.0032
Residual	0.87	6	0.14		
Lack of fit	0.87	1	0.87	4344.43	<0.0001
Pure error	1.000E-003	5	2.000E-004		
Cor total	52.10	15			

R²: 0.9833, adjusted R²: 0.9583, CV%: 0.43

5.22% SHP, 48.58 ppm CSNs, 93.08% exhaustion of C.I. Red Acid 81, 1.19 ΔE, reduction of 98.66% *S. aureus* and 93.46% *E. coli*, 4.1 s drop absorption time. Thus by controlling two key factors including CSNs and BTCA, crosslinking agent is capable of enhancing influence on dyeability and antibacterial properties of pretreated polyamide-6,6 fabrics. Analysis of variance (ANOVA) was applied to

analyze data to obtain interaction between independent variables and responses. Results were then analyzed by ANOVA to assess “goodness of fit” (Tables III–VII). It was observed that designed cubic models of polyamide-6,6 samples were statistically significant for exhaustion, color change, reduction of *S. aureus* and *E. coli*, and water absorption time characteristics at F-value of 39.26 and

TABLE IV
ANOVA RESULTS OF COLOR CHANGE (ΔE) FOR THE PRETREATED POLYAMIDE-6,6 FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	3.41	9	0.3786	357.54	< 0.0001 Significant
A [CSNs]	0.1962	1	0.1962	185.31	< 0.0001
B [BTCA]	0.0358	1	0.0358	33.84	0.0011
AB	0.0097	1	0.0097	9.12	0.0234
A ²	0.1111	1	0.1111	104.91	< 0.0001
B ²	0.0004	1	0.0004	0.3903	0.5551
A ² B	0.0550	1	0.0550	51.96	0.0004
AB ²	0.0180	1	0.0180	17.02	0.0062
A ³	0.0170	1	0.0170	16.05	0.0071
B ³	0.0014	1	0.0014	1.28	0.3006
Residual	0.0064	6	0.0011		
Lack of fit	0.0051	1	0.0051	19.44	0.0070
Pure error	0.0013	5	0.0003		
Cor total	3.41	15			

R²: 0.9981, adjusted R²: 0.9953, CV%: 3.97

TABLE V
ANOVA RESULTS OF REDUCTION OF *S. AUREUS* FOR THE PRETREATED POLYAMIDE-6,6 FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	690.77	9	76.75	302.36	<0.0001 Significant
A [CSNs]	23.19	1	23.19	91.36	<0.0001
B [BTCA]	0.12	1	0.12	0.48	0.5148
AB	2.98	1	2.98	11.72	0.0141
A ²	19.66	1	19.66	77.44	0.0001
B ²	0.47	1	0.47	1.84	0.2232
A ² B	2.631E-003	1	2.631E-003	0.010	0.9222
AB ²	0.25	1	0.25	0.98	0.3595
A ³	0.61	1	0.61	2.41	0.1717
B ³	0.031	1	0.031	0.12	0.7405
Residual	1.52	6	0.25		
Lack of fit	1.52	1	1.52	3235.54	<0.0001
Pure error	2.350E-003	5	4.700E-004		
Cor total	692.29	15			

R²: 0.9978, adjusted R²: 0.9945, CV%: 0.56

values of prob>F (0.0001) (Table III), F-value of 357.54 and values of prob>F (<0.0001) (Table IV), F-value of 302.36 and values of prob>F (<0.0001) (Table V), F-value of 133.48 and values of prob>F (<0.0001) (Table VI), and F-value of 27.04 and values of prob>F (<0.0004) (Table VII), respectively. Fit of model could be evaluated based on R² coefficients. Therefore, R² of models of exhaustion, color change, reduction of *S. aureus* and

E. coli, and water absorption time could not explain 1.67, 0.19, 0.22, 0.50, and 2.41% of total variables of polyamide-6,6 samples models, respectively (Tables III–VII).

F. Washing Durability

Washing durability of exhaustion of C.I. Acid Red 81, color change, reduction of *S. aureus* and *E. coli*, and water absorption time of CSNs/BTCA-pretreated polyamide-6,6

TABLE VI
ANOVA RESULTS OF REDUCTION OF *E. COLI* FOR THE PRETREATED POLYAMIDE-6,6 FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	695.34	9	77.26	133.48	<0.0001 Significant
A [CSNs]	26.03	1	26.03	77.97	0.0005
B [BTCA]	3.68	1	3.68	6.35	0.0453
AB	73.43	1	73.43	126.86	<0.0001
A ²	17.23	1	17.23	29.76	0.0016
B ²	8.11	1	8.11	14.01	0.0096
A ² B	4.73	1	4.73	8.17	0.0289
AB ²	48.52	1	48.52	83.83	<0.0001
A ³	19.56	1	19.56	33.80	0.0011
B ³	5.64	1	5.64	9.74	0.0206
Residual	3.47	6	0.58		
Lack of fit	3.47	1	3.47	5881.33	<0.0001
Pure error	2.950E-003	5	5.900E-004		
Cor total	698.81	15			

R²: 0.9950, adjusted R²: 0.9876, CV%: 0.84

TABLE VII
ANOVA RESULTS OF WATER ABSORPTION TIME FOR THE PRETREATED POLYAMIDE-6,6 FABRICS

Source	Sum of squares	Df	Mean square	F-value	P-value prob>F
Model	28.19	9	3.13	27.04	<0.0004 Significant
A [CSNs]	0.66	1	0.66	5.68	0.0545
B [BTCA]	2.89	1	2.89	24.96	0.0025
AB	2.15	1	2.15	18.55	0.0051
A ²	2.24	1	2.24	19.37	0.0046
B ²	1.554E-008	1	1.554E-008	1.341E-007	0.9997
A ² B	0.95	1	0.95	8.20	0.0287
AB ²	0.075	1	0.075	0.65	0.4508
A ³	3.02	1	3.02	26.05	0.0022
B ³	4.51	1	4.51	38.89	0.0008
Residual	0.70	6	0.12		
Lack of fit	0.68	1	0.68	168.76	<0.0001
Pure error	0.020	5	4.000E-003		
Cor total	28.89	15			

R²: 0.9759, adjusted R²: 0.9399, CV%: 5.77

TABLE VIII
EXHAUSTION OF C.I. ACID RED 81 DYE, COLOR CHANGE, REDUCTION OF *S. AUREUS* AND *E. COLI*, AND WATER ABSORPTION TIME OF POLYAMIDE-6,6 FABRICS PRETREATED IN CONTROL AND OPTIMIZED CONDITION AND AFTER WASHING DURABILITY TEST

Run	Factor		Responses					
	CSNs (ppm)	BTCA (%)	Exhaustion (%)	Color change (ΔE)	Reduction of <i>S. aureus</i> (%)	Reduction of <i>E. coli</i> (%)	Water absorption (s)	Wash fastness
Control	0.00	0.00	68.13	0.00	0.00	0.00	9.2	4
Optimized (before durability test)	48.58	8.70	93.08	1.19	98.66	93.46	4.1	4-5
Optimized (after durability test)	48.58	8.70	91.15	1.09	98.35	93.11	4.8	5

sample in optimized condition was measured after washing durability test. Obtained data are summarized in Table VIII. Results of Table VIII confirmed that BTCA crosslinking agent can be durably linked to polyamide-6,6 polymeric chains. Positively loaded Ag⁺ might be attracted by negative charges of carboxylates anions of BTCA attached on polyamide-6,6. Therefore, there exist strong electrostatic forces of attraction between groups of carboxylate anionic related to polycarboxylic acid and CSNs cations. Polycarboxylic acids are strong crosslinking agents that could improve absorption of more CSNs on polyamide-6,6 surface since they contain several functional groups. Also this fact exhibited perseverance of balanced ratio of CSNs and BTCA concentration on polyamide-6,6 fabric. Possibly BTCA crosslinks create a lattice void with carboxyl and amino groups that is related to polyamide-6,6 and trapped CSNs that leads to producing nanorough on polyamide-6,6

fabrics [38]. Reason of slight decrease after durability test in exhaustion of C.I. Red Acid 81 and antibacterial characteristics could be attributed to removal of few CSNs available on polyamide-6,6 surface as a result of evaluating durability evaluation. Therefore, pretreated polyamide-6,6 contains great durability of characteristics in optimized condition including exhaustion of C.I. Red Acid 81, antibacterial, and hydrophilicity characteristics with minimal color change. Wash fastness of polyamide-6,6 fabrics pretreated in control and optimized conditions was evaluated according to AATCC 61(1A)-2007 [1]. However, wash fastness of pretreated dyed fabrics was increased due to strong electrostatic interaction between anionic sophonyl group of dyes and CSNs cation attached to BTCA bonded polyamide-6,6 fabric. BTCA is able to act as a stabilizer of CSNs on polyamide-6,6 surfaces and had a synergistic effect on pretreated polyamide-6,6 samples

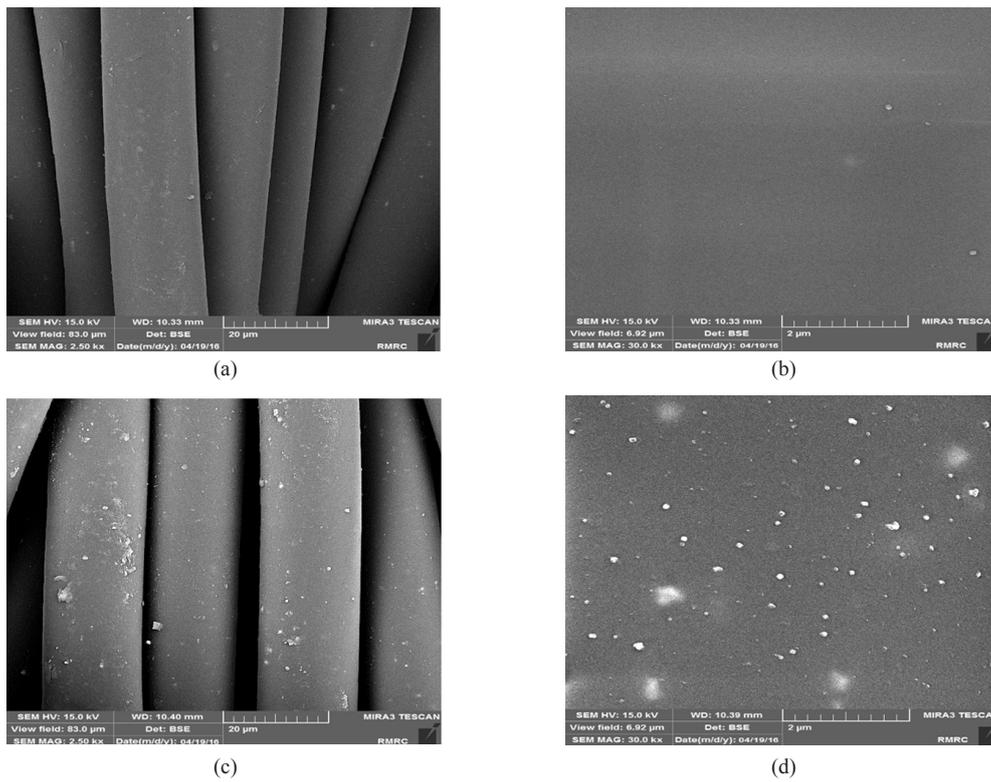
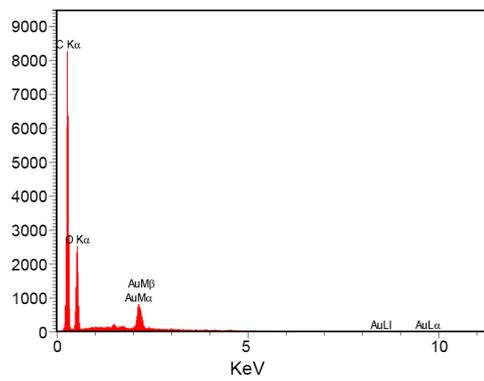
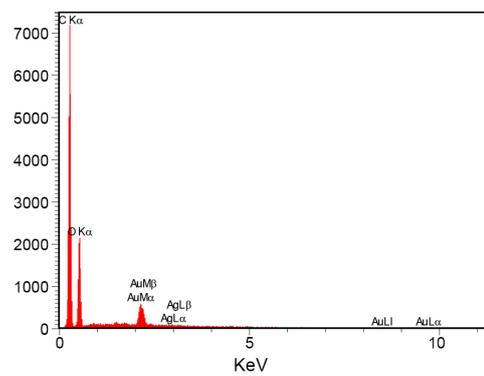


Fig. 3. SEM images of polyamide-6,6 samples (a,b) control and (c,d) optimized condition (48.58 ppm CSNs, 5.22% SHP, and 8.70% BTCA) (a, c: 2500× and b, d: 30000×).



Elements	wt (%)	A (%)
C	62.74	70.16
O	35.42	29.71
Ag	0.00	0.00
Au	1.84	0.13
Total	100.00	100.00

(a)



Elements	wt (%)	A (%)
C	66.71	74.56
O	30.05	25.19
Ag	0.37	0.05
Au	2.87	0.20
Total	100.00	100.00

(b)

Fig. 4. EDX images of polyamide-6,6 samples: (a) control and (b) optimized condition with 48.58 ppm CSNs, 5.22% SHP, and 8.70% BTCA.

which demonstrated a significance increase in washing fastness and dyeability of C.I. Red Acid 81 dye.

G. Scanning Electron Microscopy (SEM)

SEM images of control (Figs. 3a and 3b) and pretreated (Figs. 3c and 3d) polyamide-6,6 samples surface (48.58 ppm CSNs, 5.22% SHP, and 8.70% BTCA) in optimized condition are illustrated in Fig. 3 with two different magnifications (2500x and 30000x). The images imply that CSNs were utilized on polyamide-6,6 fabric surfaces by conventional impregnation process but their distribution on fiber surface was not quite even due to aggregating CSNs. Figs. 3c and 3d approved the appropriate treatment of polyamide-6,6 pretreated with BTCA and CSNs as efficient nanocomposite which caused enhancing dyeability of C.I. Red Acid 81 dye, antibacterial, and hydrophilicity characteristics with minimal color change. BTCA not only crosslinked polymeric chains of polyamide-6,6 as a polycarboxylic acid but also stabilized CSNs on the surface of polyamide-6,6 fabric [38].

H. EDX Analyses

Successful stabilization of CSNs on polyamide-6,6 samples was further confirmed by chemical compositions analyzed by EDX spectra and atomic percentage (Fig. 4); considering that coating conditions with Au are the same for each control (Fig. 4a) and pretreated (Fig. 4b) polyamide-6,6 samples. As shown in Fig. 4b, silver is one element on pretreated polyamide-6,6 fabric apart from carbon and oxygen that relates to polyamide-6,6 polymeric substrate. CSNs being placed on fabric surface were stabilized by BTCA and SHP crosslinking agents. Fig. 4b confirmed the presence of CSNs on pretreated polyamide-6,6 fabric surface in optimized conditions.

I. Reflectance and Absorbance Spectra

Reflectance and absorbance spectra of control and pretreated polyamide-6,6 samples in optimized conditions (48.58 ppm CSNs, 5.22% SHP, and 8.70% BTCA) in the

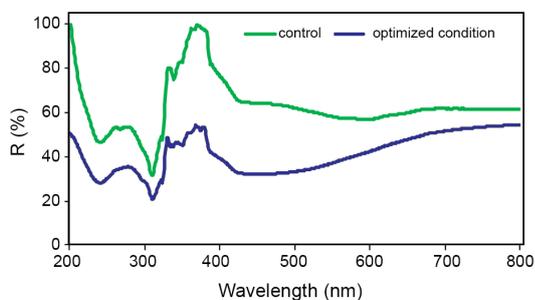


Fig. 5. The reflectance spectra of polyamide-6,6 samples: (a) control and (b) optimized condition with 48.58 ppm CSNs, 5.22% SHP, and 8.70% BTCA.

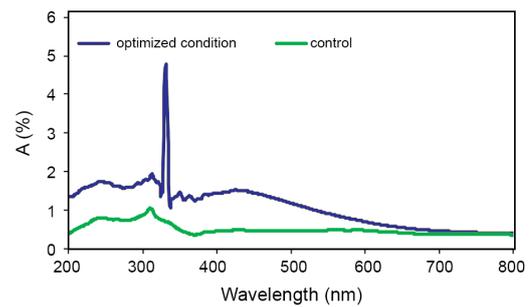


Fig. 6. The absorbance spectra of polyamide-6,6 samples: (a) control and (b) optimized condition with 48.58 ppm CSNs, 5.22% SHP, and 8.70% BTCA.

region 200–800 nm, which were obtained using a Perkin-Elmer Lambda 35 UV–visible spectrophotometer, are presented in Figs. 5 and 6, respectively. There was reflection increase in control sample and lower reflectance was related to pretreated polyamide-6,6 at optimized conditions (Fig. 5). Thus it is proposed that CSNs on polyamide-6,6 fabric acts as an absorber in wavelengths ranging from UV-visible 200 nm to 800 nm. These results are consistent with previous findings [24]. Therefore, the extent of absorbance of optimized polyamide-6,6 sample (Fig. 6) is more than that of control sample and the results are consistent with previous findings. UV absorbance features of CSNs-pretreated polyamide-6,6 sample are due to appearance of surface plasmon absorption band [48].

IV. CONCLUSION

In this research, scoured polyamide-6,6 fabrics were pretreated using BTCA and CSNs to enhance their dyeability, antibacterial, and hydrophilicity characteristics with minimal color change. RSM was utilized to model C.I. Red Acid 81 dye exhaustion, antibacterial, hydrophilicity, and color change characteristics of pretreated polyamide-6,6 fabric. Statistical analysis by Design of Expert indicated that modified polyamide-6,6 sample exhibits optimum exhaustion (93.08%) for C.I. Red Acid 81 dye, reduction of *S. aureus* (98.66%) and *E. coli* (93.46%), drop absorption time (4.1 s), and minimized color change ($\Delta E=1.19$) significantly. Durability of imparted characteristics including dyeability, antibacterial, and hydrophilicity was also being approved. Consequently, BTCA crosslinking agent with CSNs had a complementary effect on polyamide-6,6 samples which demonstrated noticeable increase in durable dyeability, antibacterial, and hydrophilicity properties. Meanwhile, some of benefits of this research could include environmental improvements by reduced consumption of auxiliary chemicals and energy savings with dyeing at lower temperatures.

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