

Statistical optimization of self-cleaning technology and color reduction in wool fabric by nano zinc oxide and eco-friendly cross-linker

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Abstract The stain resistance and intrinsic hydrophobic features of wool are the most important problems which have negative impacts on various aspects of wool and prompt scientists to find a solution over the past decades. Zinc oxide nanoparticles (ZnO-np) were successfully synthesized and stabilized on natural protein wool using the impregnation process with butane tetra carboxylic acid (BTCA) as eco-friendly cross-linker. In this research, these particles were linked to wool surface by BTCA and also sodium hypophosphite was used as a catalyst. The self-cleaning technology of ZnO-np deposited on the wool fabrics was followed by degrading of Direct Blue 71 and Disperse Red 1 as synthetic stains and also determined by degrading rate of food stains such as coffee and black mulberry under the ultraviolet irradiation. The hydrophilicity was monitored by water drop absorption time. The central composite design was used for different variables based on Design of Expert software. The analysis of variance was utilized to obtain the optimum models for wool with maximum color reductions and minimum absorption time. The presence of ZnO-np on the wool surface was confirmed with scanning electron microscopy. Further transmission and absorbance spectra validated the UV protection properties of ZnO-np-treated wool. The results showed that increasing the amount of ZnO-np leads to enhanced reduction of synthetic color stains than food

color stains on the treated wool fabric, while the fabric became more hydrophilic.

Keywords Butane tetra carboxylic acid · Eco-friendly · Zinc oxide nanoparticles · Central composite design (CCD) · Self-cleaning technology · Wool

Introduction

Animal wool is well known for its outstanding breathability, bio-degradability, dyeability, and resilience which have made it a superior fiber (Chen et al. 2009). Increasing the photo-stability and antishrinkage of natural wool and imparting new features such as self-cleaning (Tung and Daoud 2011) and hydrophilicity to wool has attracted a great deal of attention (Mansour 2010). The shrinkage in wool is due to the scales on its surface which results in fiber entanglement (Shao and Fan 2012). In order to overcome such shrinkages in wool fabric, some formaldehyde-based cross-linkers have been reported, which enhance both felt proofing (Allam et al. 2009) and binding (Reddie and Nicholls 1971). The formaldehyde, however, has now been informed as a toxin, skin irritant (De Groot et al. 2010), and confirmed human carcinogen (World Health Organization and International Agency for Research on Cancer, World Health Organization, International Agency for Research on Cancer 2006). Unfortunately, toxic compounds are required to create the protection characteristics on wool. However, due to the increasingly stringent provisions and more awareness among the customers, some researchers have started focusing on the development of novel protection finishes, and bio-friendly treatments for wool. Recently, eco-scouring (Bahtiyari and Duran 2013), waterless dyeing (Long et al. 2013), reusing (Shams-Nateri

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2011), recycling (Sikdar 2007), and sustainable treatment of wastewater (Visa et al. 2011), dyeing with ultrasonic energy (Mansour and Heffernan 2011), environmental management (Sikdar and Jain 2002), and optimization of proteases pre-treatment on natural dyeing of wool (Nazari et al. 2013a) have been investigated.

Self-cleaning technology (Peplow 2004) and hydrophilicity treatment (Montazer et al. 2011) of fibers by incorporating nanoparticles is a new concept that has been introduced in recent years. Nano-sized particles illustrate high photo-activity because of their large surface area per unit mass and also due to the diffusion of electrons/holes before recombination (Bozzi et al. 2005). Although intensive research has been conducted on self-cleaning technologies of cellulosic fabric for exploring the potential utilization of nanoparticles, little research has been informed on protein materials (Tung and Daoud 2009). Probably the utilization and development of such fibers had largely been impeded due to their limited chemical, thermal, and photo-stability (Arivithamani et al. 2014). To the best of our knowledge, there is no report related to stabilizing of ZnO-np with zero formaldehyde cross-linkers and its optimization via statistical approach of response surface methodology (RSM) in order to enhance self-cleaning technology and hydrophilicity of wool natural fabric.

The photo-catalytic characteristics of semi-conductors such as ZnO and TiO₂ initiate decomposition of organic pollutants (Morris et al. 2004) such as acetaldehyde (Khalilzadeh and Fatemi 2014) and textile dyes (Meenatchisundaram et al. 2014) that come into contact with the surface and thus prevent them from building up. Zinc oxide is an important alternative oxide semiconductor photo-catalyst whose mechanism of photo-catalysis has been proven to be similar to that of TiO₂ (Li et al. 2009). The most remarkable advantage of ZnO in comparison with TiO₂ is its absorption of a greater fraction of UV spectrum with related threshold of 425 nm. Electron mobility in ZnO is higher than that in TiO₂ making the former suitable for dye-sensitized solar cells. Recently, it has become possible to form vertical nanowires of ZnO (Greene et al. 2005). ZnO as a semiconductor with a large band gap (3.3 eV), big excitation binding energy (60 meV), and n-type conductivity, is abundant in nature and environmentally friendly (Nair et al. 2011). Zinc oxide is widely utilized in various fields such as surface acoustic wave filters, UV-blocking, gas sensors, photo-detectors, self-cleaning technology, purification of either wastewater or drinking water for human use due to its distinguished photo-catalytic, optical, electrical, electronic, dermatological, and antibacterial properties (Lin 2013), the photo-degradation of organic dyes, and mothproofing (Nazari et al. 2013b).

The multifunctional properties of poly carboxylic acids (PCA)-based zero formaldehyde cross-linkers such as

environment friendly and high accessibility lead to their utilization on the textile surfaces (Kim et al. 2003). The cross-linking, antibacterial activity, and the simultaneous antimicrobial and cross-linking finish are among these uses (Nazari et al. 2009). Carboxylic groups of PCA bio-friendly cross-linkers are potential sites for binding of TiO₂-np (Lugovskoy et al. 2008). The surfaces of wool fabrics should undergo an enrichment process that causes the introduction of these extra groups. Subsequently TiO₂-np was increasingly attached to modified fabric surface by an electrostatic bond more than before. The results reported by Daoud confirmed that the introduction of additional carboxylic groups to natural wool surface allowed for efficient binding of TiO₂ on the fabric surface which resulted in an enhancement of self-cleaning technologies (Tung and Daoud 2011). Bio-friendly cross-linker, BTCA, exhibited excellent multifunctional characteristics such as enhancing the adsorption, stability (Montazer and Seifollahzadeh 2011), and hydrophilicity (Montazer et al. 2011) of TiO₂-np treated surface. This caused the effective increase of the efficiency of TiO₂-np on characteristics such as self-cleaning technology, hydrophilicity, and UV protection. However, little valid researches have been published about the stabilization of ZnO-np on the textile surfaces through BTCA bio-cross-linker. Montazer et al. presented that by applying TiO₂-np on wool fabrics, the rate of photo-yellowing decreased (Montazer and Pakdel 2010). In other words, because of the presence of TiO₂ on the fabric surface, wool stability against UV irradiation increases (Cao et al. 2013). Semi-conductors such ZnO and TiO₂-np are powerful UV absorbers that are able to protect fabrics against adverse effects of UV irradiation.

In a previous study (Nazari et al. 2013a), we described the natural wool fabrics pre-treated with protease enzyme at different concentrations during various times. The dyeing process is carried out on the treated fabrics with madder and cochineal natural dyes. This could significantly enhance madder and cochineal natural uptake. Therefore, the enhanced mothproofing activity of bio-degradable wool fabric was optimized with madder as a natural dye through one factor statistical analysis (Nazari et al. 2014). Lack of scientific reports on statistical modeling of ZnO-np along with environmentally friendly cross-linkers without formaldehyde on natural wool self-cleaning technology motivated the researchers of this research toward optimizing and stabilizing of ZnO-np on wool fabric through surface modification using BTCA bio-cross-linker. The purpose of this study was to optimize and enhance the influences of both ZnO-np and bio-cross-linker (BTCA) concentration on durable self-cleaning technologies and hydrophilicity of natural wool fabrics through evaluating color reduction and drop absorption time. RSM was used in order to conduct an exact analysis and the impact of each independent variable was reported on response surfaces.

Experimental

Materials

Sodium hypophosphite (SHP), sodium hydroxide, BTCA, isopropanol, zinc acetate, lithium hydroxide, and sodium carbonate were supplied by Merck Chemical Co., Germany. Non-ionic detergent (Rucogen DEN) composed of fatty alcohol ethoxylated was purchased from Rudolf Chemie Co., (Tehran, Iran). The 100 % raw wool fabric with twill structure, 374 g/m², yarn count of 20/2 Nm, and wrap/weft density of 18/16 yarn/cm was purchased from Iran Merinous Co (Iran).

Instrument

The contents of finishing baths were prepared using an ultrasonic bath (200 V, 50 W, 40 kHz). The observations of scanning electron microscopic (SEM) on treated fabrics were performed using an EM-3200 electron microscope (KYKY, China). The transmission and absorbance spectra were recorded at UV region (200–400 nm) using UV/VIS spectrophotometer (CARRY 500 scan, Varian, Australia). Thermal oven was used to dry and cure the samples. The stained and treated samples were exposed to UV-A (320–400 nm) irradiation of an HPA 400S lamp (400 W, Philips, Belgium). The CIE color coordinates of samples were measured using reflectance spectrophotometer (color-guide sphere, D/8° spin, Germany).

Method

The wool fabric samples were prepared in 12 × 6 cm² swatches and scoured with 1.5 % non-ionic detergent at 40 °C for 50 min at liquor to goods ratio of 30:1. The preparation process of employed ZnO-np has been described by researchers (Farouk et al. 2009). A two-neck round bottom distillation flask was used to suspend 2.8 g (zinc acetate 2H₂O) in 100 mL isopropanol by reflux heating for 3 h. 0.75 g lithium hydroxide was dissolved in 100 mL isopropanol at room temperature by magnetic stirring. The zinc acetate suspension was cooled to 0 °C before the lithium hydroxide solution was added drop wise under vigorous stirring. The mixture was treated in an ultrasonic bath (200 V, 50 W, 40 kHz) at room temperature for about 2 h (Abd El-Hady et al. 2013).

The different aqueous solutions of BTCA bio-cross-linker with different concentrations of BTCA (5.00–10.00 % w/v) and SHP (3.00–6.00 % w/v) were prepared based on weight of bath: O.W.B (Table 1) using required distilled water. The scoured natural wool fabrics were impregnated in freshly prepared aqueous solutions at 55 °C for 50 min. The BTCA cross-linked fabrics were

dried at 80 °C for 6 min and then cured at 140 °C for 4 min. Treated fabrics were rinsed with hot water and cold water and finally dried at room temperature. The suspended solutions of ZnO-np were firstly prepared by suspension of different concentration of ZnO-np prepared previously in isopropanol (0.1–1.50 % w/v based on O.W.B) and sonicated for 20 min (Table 1). The BTCA bio-cross-linked wool fabrics were impregnated in suspended solutions of ZnO-np at 55 °C for 20 min. The treated samples were then dried at 75 °C for 8 min and cured at 115 °C for 6 min. The cured fabrics were ultrasonically washed at 55 °C for 15 min in a solution of 1.0 g/L Na₂CO₃ and 1.0 g/L non-ionic detergent (Rucogen DEN) based on O.W.B in order to remove ZnO-np having no bonding reaction with wool fabrics and then dried at room temperature.

The self-cleaning technology of synthetic and food color stains was conducted through discoloration analysis of color stains after exposing to UV-A radiation for 25 min. The treated natural wool samples were placed on flat surface and then one drop of coffee, black mulberry, Direct Blue 71, and Disperse Red 1 (1 %) was dripped vertically on the surface using burette (50 mL), form 1 cm above the wool fabric. The color stain on the wool surfaces was created with approximate diameter of 1.50 cm. The color stained wools were then dried at room temperature. Virtually, the amounts of ΔE^* for the blank and treated different wool samples were measured. Total color difference (ΔE^*) as color reduction is determined by Eq. 1 on the basis of measured CIE color coordinates:

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

where ΔL^* is the color lightness difference; Δa^* is red/green difference; and Δb^* is yellow/blue difference. Hence, the ΔE_T^* of stained samples were measured before and after exposing to UV-A (400 W). The degree of self-cleaning technology of different samples is compared by Eq. 2.

$$(\Delta E_T^*) = (\Delta E_2^*) - (\Delta E_1^*) \quad (2)$$

A drop of water from specific distance was placed on the surface of fabrics in order to evaluate the hydrophilic features of treated samples, and then spreading time of water drops was recorded by a stopwatch. This experiment was evaluated based on British standard 4554:1970 test method. The burning method was utilized to determine the actual ZnO-np loading on weight of fabric (O.W.F.). Weight-treated samples according to ASTM 5630, D 2584 were placed in a porcelain crucible and kept in an oven with a range of room temperature to 600 °C for 180 min. The calculations were conducted in such a manner that the remainder weight was subtracted from the remainder

Table 1 Central composite design for water absorption time and color reduction (ΔE^*) of the control and treated wools stained with of Direct Blue 71 and Disperse Red 1 as synthetic stains and coffee and black mulberry as food stains

Run	Factor			Responses				Time of water absorption (s)
	ZnO-np (%)	BTCA (%)	SHP (%)	ΔE^* (coffee)	ΔE^* (black mulberry)	ΔE^* (Direct Blue 71)	ΔE^* (Disperse Red 1)	
Control	0.00	0.00	0.00	4.28	4.12	4.59	4.37	2750.1
1	1.50	10.00	6.00	13.96	12.99	16.15	15.93	135.4
2	0.10	5.00	3.00	1.89	3.92	4.11	5.21	152.6
3	1.50	5.00	3.00	2.94	4.77	6.03	7.14	84.6
4	0.45	8.75	5.25	9.63	10.96	14.76	12.36	172.6
5	1.50	7.50	4.50	7.16	15.43	14.92	15.11	111.7
6	1.15	8.75	5.25	11.47	13.66	16.18	13.61	158.3
7	0.80	7.50	4.50	8.86	16.08	16.82	17.28	85.3
8	0.80	10.00	6.00	14.85	13.98	16.76	17.98	113.1
9	0.10	10.00	6.00	11.86	5.92	13.06	11.28	218.7
10	0.10	5.00	3.00	1.88	3.89	4.16	5.23	151.5
11	0.80	6.25	3.75	6.11	15.93	11.13	14.35	67.5
12	1.50	5.00	3.00	2.91	4.73	6.06	7.17	85.8
13	0.10	7.50	4.50	3.28	7.78	11.26	9.38	180.3
14	0.10	5.00	3.00	1.83	3.86	4.14	5.19	153.4
15	1.50	10.00	6.00	13.92	12.96	16.11	15.95	134.3
16	0.10	10.00	6.00	11.83	5.94	13.09	11.31	220.5
17	0.80	5.00	3.00	3.84	6.96	7.26	8.27	58.2

weight of the blank sample, and then the percentage of ZnO-np loading on wool based on O.W.F was obtained. Washing durability of treated samples was conducted according to AATCC test method 61(2A)-2003. In this approach, each cycle of washing process is equivalent to five home laundries in ambient conditions at 38 ± 3 °C.

Design of experimental (DOE)

The CCD was used for experimental plan with three variables. These variables included the amounts of SHP catalyst, BTCA bio-cross-linker, and ZnO-np co-catalyst concentrations. The ranges of these variables are: SHP (3.00–6.00 % w/v), BTCA (5.00–10.00 % w/v), and ZnO-np (0.10–1.50 % w/v) using trial version of Design Expert 8.0.1.0 software from Stat-Ease, Inc. (USA). The details of the design of natural wool samples with BTCA bio-cross-linker and SHP catalyst in the presence of ZnO-np are presented in Table 1 (Run 1–17). Also the influence of the variables on the results Y_1 (ΔE^*) and Y_2 (time of water absorption) was adjusted using the following third-order polynomial function:

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

In this equation, b_0 is an independent term according to the mean value of the experimental plan, b_i is regression

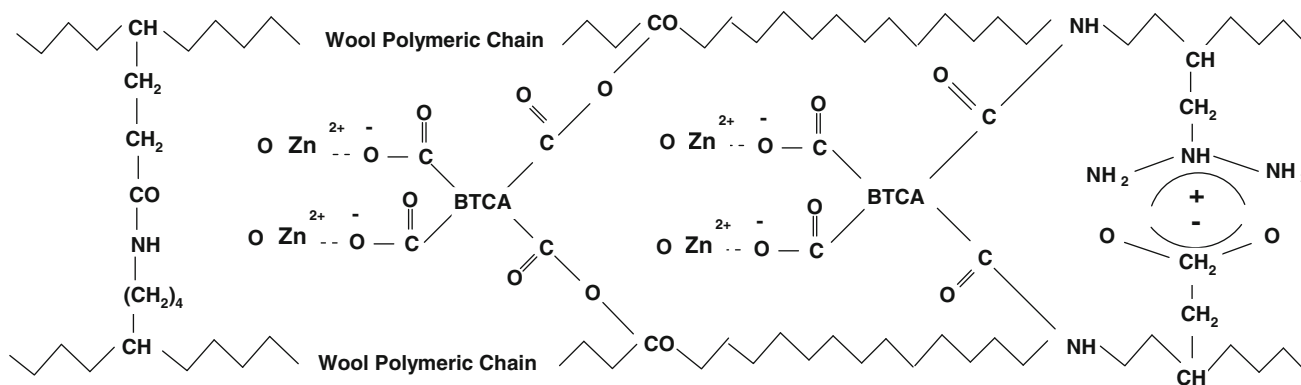
coefficients that explain the influence of the variables in their linear form, b_{ij} is regression coefficients of the interaction terms between variables, and c_i is the coefficients of quadratic form of variables.

Results and discussion

Hydrophilicity features

The results indicate that the water drop absorption time for the ZnO-np/BTCA wool samples decreased significantly compared with control sample (Table 1). Some researches which have been mostly evaluated in papers published relating to wool and its surface modification has been summarized in Table 2.

In this study, the hydrophilicity of natural wool samples increased through ZnO-np and BTCA bio-friendly treatment. It can also be obviously seen in Table 1 that by increasing the amount of ZnO-np up to 0.80 %, the amounts of water absorption time decreased (as Run: 8 and 9 or 2 and 17), while with constant concentration of ZnO-np and gradual increase of BTCA in impregnated bath, the amounts of water absorption time increase (as Run: 7, 8, 11, 17). In this research, the ZnO-np were bonded to wool through free carboxylates anions of BTCA bio-cross-linker. ZnO-np have high affinity towards hydroxyl and



Scheme 1 Suggested mechanism of electrostatic linkages between ZnO-np with BTCA and ester linkages between BTCA with wool

Table 2 The various theories related to wool main components and its surface modifications

Author	Year	Related papers
Kantouch et al.	1978	Shrink-resist treatment with potassium permanganate
Brown et al.	1951	Chemical modification with formaldehyde solutions
Hsieh et al.	2004	Antimicrobial and physical properties with citric acid and chitosan
Bahi et al.	2004	Surface characterization of chemically modified wool
Demir et al.	2008	Synergetic effects of alternative methods in wool finishing
Montazer and Pakdel	2011	Self-cleaning and color reduction by TiO ₂ -np
Montazer et al.	2012	Superior self-cleaning features using TiO ₂ /Ag nanocomposite
Nazari	2014	Proteases pretreatment to enhance antimicrobial and UV protection using TiO ₂ -np

carboxyl groups of carboxylic acids. The pH of impregnated bath was around 4.5 which led to positive charges of ZnO-np; subsequently their tendency towards carboxyl groups of BTCA with negative charge increased. This caused a higher absorption of ZnO-np on the wool surface as illustrated in Scheme 1 (Nazari 2014). Although the mechanism of the suggested Scheme 1 has not been investigated experimentally, but other similar mechanisms (Behzadnia et al. 2014) may also be presented in the literature (Yuranova et al. 2007).

Similarly, the surface hydroxyl molecules density had an excellent effect on improving the hydrophilicity producing more hydrogen bonds with molecules of waters (Euvananont et al. 2008). Therefore, it is reported that the contact angles can be decreased through light irradiation and water can be absorbed faster on the surface of wool fabric (Montazer et al. 2011).

Self-cleaning technologies

The influence of BTCA bio-cross-linker for stabilizing ZnO-np on the surfaces of wool fabric on color reductions (ΔE_T^*) of the treated wool samples under UV-A (400 W) irradiation is summarized in Table 1. Figure 1 demonstrated that degradation activity was more in ZnO/BTCA treated

samples than in control ones. In samples treated with moderated concentrations of ZnO, the color stains seemed lighter after 25 min of UV-A irradiation (Run: 2, 3, 5, 6) and were almost completely removed (Run: 8) because the amount of ZnO-np on the surface of treated sample is enough, whereas in control samples, the color stains were clearly observed on the fabric surface. This result showed that ZnO-np can degrade synthetic and food color stains on wool fabrics. Conversely this feature was not significant in control wools.

Therefore, the low reduction of natural and synthetic color stains under UV-A irradiation appeared for control ones (Table 1). Similar behavior was obtained for variation of color differences (ΔE_T^*) for each of natural and synthetic color stains based on different concentrations of ZnO-np and BTCA bio-cross-linker. ΔE_T^* values of finished fabrics gradually increased with the increase of ZnO-np at constant BTCA as it could be presented for set of each following Runs (Run: 2, 3, 10, 12, 14, 17, Run: 5, 7, 13, Run: 4, 6, and Run: 1, 8, 9, 15,16). This could be due to the presence of more ZnO-np on the natural wool samples that absorb UV irradiations more effectively. In other words, ZnO-np are capable of efficiently absorbing UV wavelengths and also more production of active radicals ($\cdot\text{OH}$) and consequently effective degrading the color stains produced by

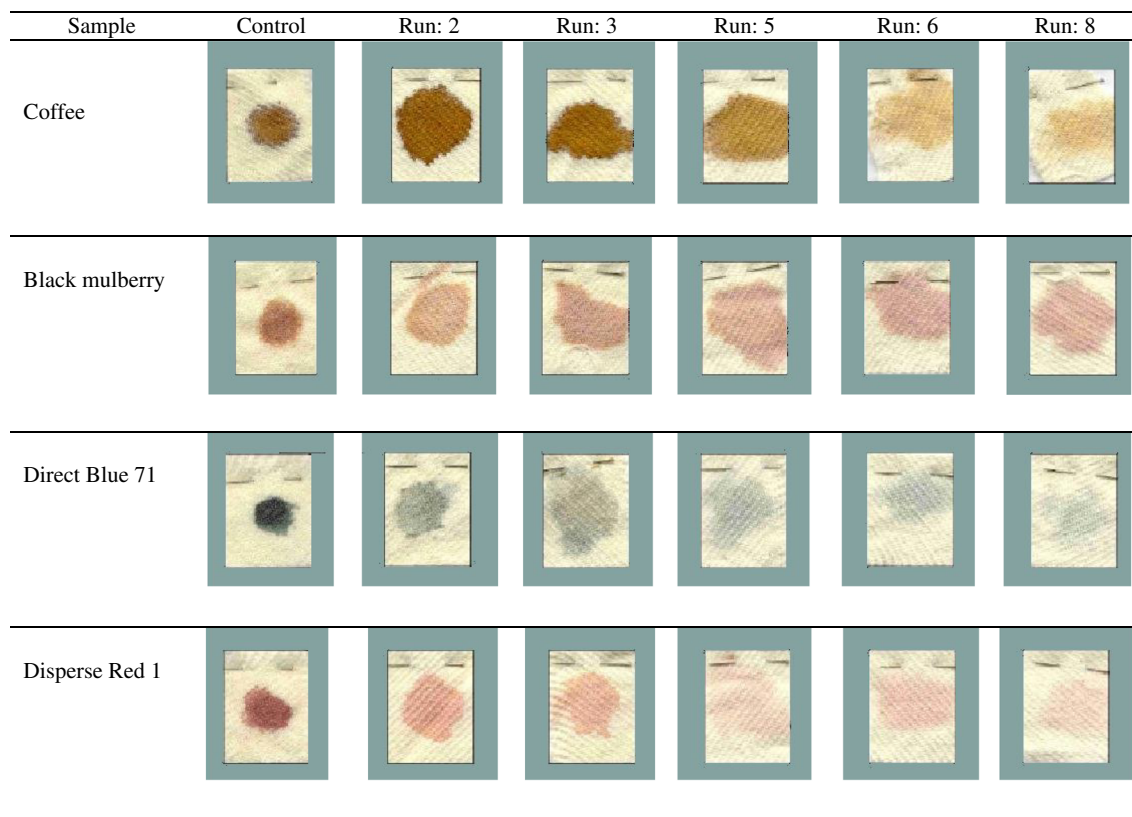
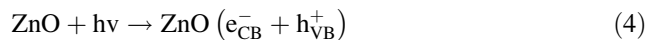


Fig. 1 Discoloring of treated wool samples (control, Run: 2, Run: 3, Run: 5, Run: 6, and Run: 8) stained by coffee, black mulberry, Direct Blue 71, and Disperse Red 1. (Color figure online)

Disperse Red 1, Direct Blue 71, black mulberry, and coffee. This may be attributed to the suitable energy produced by UV irradiations for transforming the electrons on ZnO-np surfaces from valence band to the conduction band. The famous reactions for the production of electrons and holes created on the ZnO-np as a result of UV irradiation and consequently the oxidation and reduction reactions for color photo-degradation and also self-cleaning technology mechanism were illustrated by researchers (Kandula and Jeevanandam 2014).

The color reduction activity of ZnO-np on wool fiber was attributed to the dispersed ZnO-np which were satisfactorily stabilized on the fiber surface. Conduction-band electrons and valence-band holes would be generated on its surface during photo-catalysis when ZnO-np was illuminated by UV irradiations with energy greater than its band gap energy Eq. (4). Holes could then react with water molecules adhering to the surface of the photo-catalyst to form highly reactive hydroxyl radicals ($\cdot\text{OH}$) Eq. (5). Here Oxygen acted as an electron acceptor by forming a superoxide radical anion ($\cdot\text{O}_2^-$) on the catalyst surface Eq. (6). The super-oxide radical anions may act as oxidizing agents or as an additional source of hydroxyl radicals via the subsequent formation of hydrogen peroxide. The powerful

oxidants associated with hydroxyl radicals were able to oxidize color materials Eq. (7).



The performance of ZnO-np slightly decreased at 1.50 % ZnO-np. This could be due to the satiating of functional groups existed in the BTCA bio-cross-linker, the agglomeration of ZnO-np on the surface of wool fabric or in the finishing bath and consequently decreased the efficiency of ZnO-np photo-degradation. Therefore, using experimental design to find out the effects of each variable and their interactions and also obtaining the optimum color reduction conditions on ZnO-np/BTCA bio-cross-linked wool fabrics is very beneficial.

In addition, Table 1 represented the increase of color reduction values at constant ZnO-np and more BTCA bio-cross-linker as it could be seen for set of each following Runs (Run: 1, 3, 5, 12, 15, Run: 2, 9, 10, 13, 14, 16, and Run: 7, 8, 11, 17). The BTCA bio-cross-linking led to the

higher adsorption and stabilization of ZnO-np and lower release of ZnO-np from the cross-linked wool surface of fabric. This possibly increased the degradation activity of ZnO/BTCA cross-linked wool fabrics for discoloring of food and synthetic color stains. Therefore, the formation of anionic multifunctional structure resulted from the function of BTCA bio-cross-linker acted as a stabilizing agent of ZnO-np on the surface of natural wool fabric. Interestingly, the performance of ZnO-np in the degradation of coffee color stains was slightly decreased at concentrations greater than 7.50 % BTCA as the decrease of ΔE_T^* values was observed. Protein fibers capable of changing light to self-cleaning technology for degrading its color stains, dirt, and harmful microorganisms in a process of photo-catalytic purification are very interesting materials for various applications (Tung and Daoud 2009). So BTCA bio-cross-linker not only restricted the self-cleaning technology but also had a noticeable influence on the degradation of natural and synthetic color stains. Consequently BTCA-based zero formaldehyde cross-linkers accompanying with ZnO-np had a complementary effect on the treated wool fabrics that exhibited a considerable increase in the durable self-cleaning technologies. The self-cleaning technology developed in this research, eliminated the necessity of frequent washing of wool fabric in order to remove synthetic and natural color pollutants. In a way that frequent washing along with increasing temperature had detrimental effect on the strength and appearance of woolen textiles; also it is assumed as high cost and time-consuming process. Consequently, the obtained durable self-cleaning technology had accessibility for industrial applications, while eliminating the utilization of formaldehyde cross-linkers and providing antishrinkage and self-cleaning suitable technologies for woolen fabric. However, economical processes relating to this research require more examining and optimizing based on the economic cost and benefit accordance with industrial scales.

Statistical analysis

RSM is a powerful statistical technique for testing multiple variables (Box et al. 1978) because of fewer required experimental trials compared to the “one-factor-at-a-time” method (Montgomery 2004). This research was conducted based on CCD and RSM. Seventeen experimental CCD designed runs were conducted according to Table 1. In this model, the impacts of independent variables including ZnO-np, SHP, and BTCA concentration on response surfaces were assessed. It explained water drop absorption time and color differences (ΔE_T^*) of ZnO-np/BTCA cross-linked wool samples stained with Direct Blue 71 and Disperse Red 1 as color synthetic stains and coffee and black mulberry as food color stains under the ultraviolet irradiation. Several statistical models were obtained based on results of relations

between surface responses and independent factors whose related responses were functions of its independent variables.

Statistical models related to water drop absorption time and color reductions (ΔE_T^*) of stained wool fabrics with Direct Blue 71, Disperse Red 1, coffee, and black mulberry are presented in Eqs. (8–12):

$$\begin{aligned}
 \text{Absorption time}_{(s)} = & +2223.83 - 354.26 \\
 & \times [\text{ZnO-np}] - 901.22 \times [\text{BTCA}] \\
 & + 6.81 \times [\text{ZnO-np} \times \text{BTCA}] + 306.72 \\
 & \times [\text{ZnO-np}^2] + 126.79 \times [\text{BTCA}^2] + 2.39 \\
 & \times [\text{ZnO-np}^2 \times \text{BTCA}] - 0.87 \times [\text{ZnO-np} \times \text{BTCA}^2] \\
 & - 89.73 \times [\text{ZnO-np}^3] - 5.64 \times [\text{BTCA}^3]
 \end{aligned} \tag{8}$$

$$\begin{aligned}
 \text{Color reduction}_{(\text{Direct Blue 71})} = & -41.87 + 2.06 \\
 & \times [\text{ZnO-np}] + 14.68 \times [\text{BTCA}] + 2.29 \\
 & \times [\text{ZnO-np} \times \text{BTCA}] - 7.56 \times [\text{ZnO-np}^2] \\
 & - 1.34 \times [\text{BTCA}^2] - 0.06 \times [\text{ZnO-np}^2 \times \text{BTCA}] - 0.13 \\
 & \times [\text{ZnO-np} \times \text{BTCA}^2] + 1.58 \times [\text{ZnO-np}^3] \\
 & + 0.04 \times [\text{BTCA}^3]
 \end{aligned} \tag{9}$$

$$\begin{aligned}
 \text{Color reduction}_{(\text{Disperse Red 1})} = & -197.25 - 6.78 \\
 & \times [\text{ZnO-np}] + 84.72 \times [\text{BTCA}] + 6.17 \\
 & \times [\text{ZnO-np} \times \text{BTCA}] - 14.48 \times [\text{ZnO-np}^2] \\
 & - 11.40 \times [\text{BTCA}^2] - 1.00 \times [\text{ZnO-np}^2 \times \text{BTCA}] \\
 & - 0.27 \times [\text{ZnO-np} \times \text{BTCA}^2] + 6.41 \times [\text{ZnO-np}^3] \\
 & + 0.50 \times [\text{BTCA}^3]
 \end{aligned} \tag{10}$$

$$\begin{aligned}
 \text{Color reduction}_{(\text{black mulberry})} = & -212.10 - 13.37 \\
 & \times [\text{ZnO-np}] + 89.51 \times [\text{BTCA}] + 8.46 \\
 & \times [\text{ZnO-np} \times \text{BTCA}] - 15.70 \times [\text{ZnO-np}^2] \\
 & - 11.86 \times [\text{BTCA}^2] - 0.76 \times [\text{ZnO-np}^2 \times \text{BTCA}] \\
 & - 0.42 \times [\text{ZnO-np} \times \text{BTCA}^2] + 5.59 \times [\text{ZnO-np}^3] \\
 & + 0.50 \times [\text{BTCA}^3]
 \end{aligned} \tag{11}$$

$$\begin{aligned}
 \text{Color reduction}_{(\text{coffee})} = & +4.89 - 8.48 \\
 & \times [\text{ZnO-np}] - 0.57 \times [\text{BTCA}] + 4.47 \\
 & \times [\text{ZnO-np} \times \text{BTCA}] - 2.70 \times [\text{ZnO-np}^2] \\
 & - 0.19 \times [\text{BTCA}^2] - 0.21 \times [\text{ZnO-np}^2 \times \text{BTCA}] \\
 & - 0.26 \times [\text{ZnO-np} \times \text{BTCA}^2] - 0.22 \times [\text{ZnO-np}^3] \\
 & + 0.03 \times [\text{BTCA}^3]
 \end{aligned} \tag{12}$$

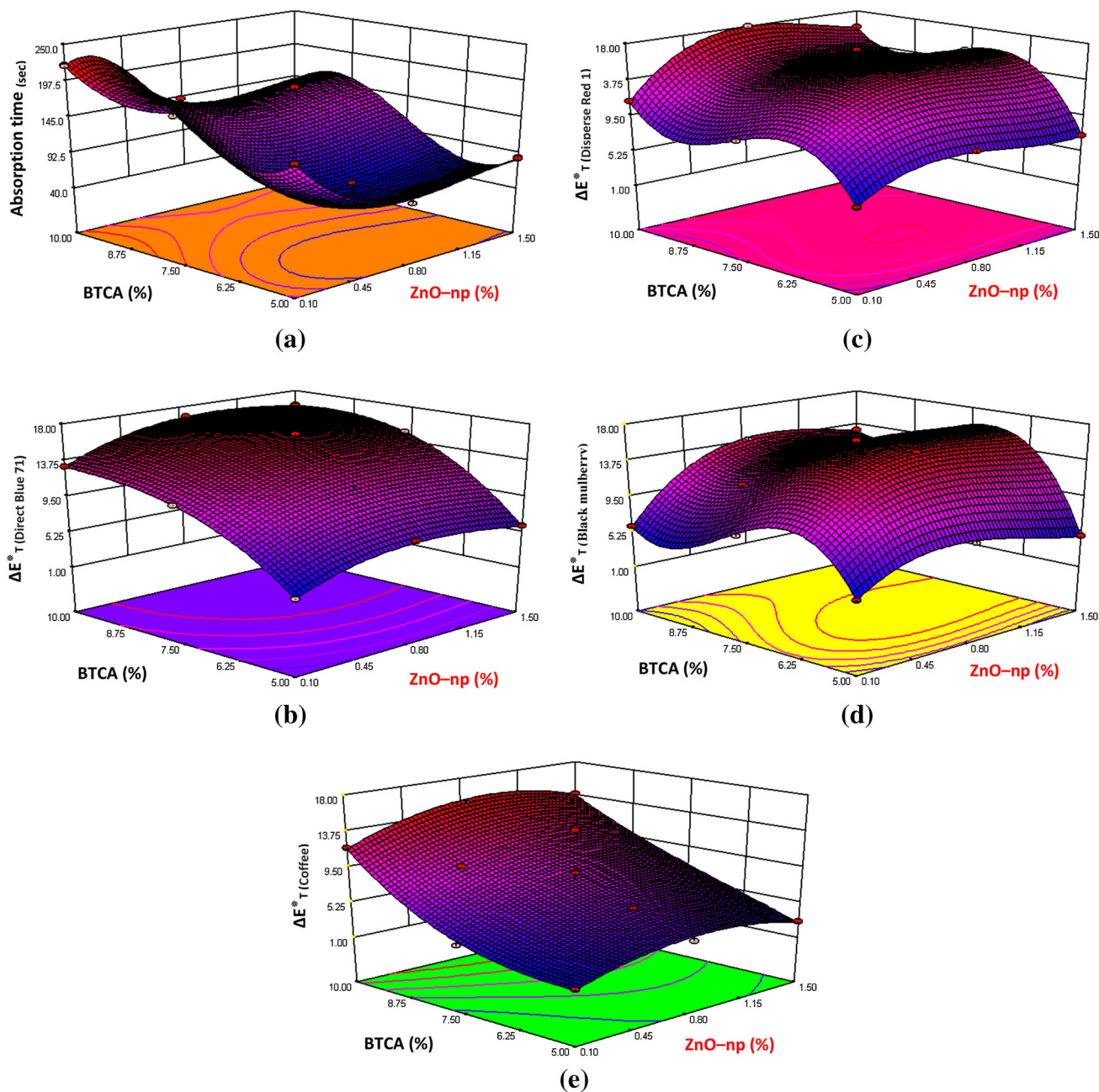


Fig. 2 Response surfaces for the absorption time (s) and the color differences (ΔE^*) of stained wool samples: (a) absorption time (s), (b) Direct Blue 71, (c) Disperse Red 1, (d) black mulberry, and (e) coffee as a function of BTCA and ZnO-np concentration. (Color figure online)

Response surfaces were drawn via achieved statistical models (Eqs. 8–12) and the relation between independent variables and accordingly drop absorption time and color reductions (ΔE_T^*) of synthetic and food color stains were found. Therefore, the response surfaces of drop absorption time and ΔE_T^* of stained wool fabrics with Direct Blue 71, Disperse Red 1, coffee, and black mulberry are suggested in Fig. 2a–e. It is recognized that BTCA bio-cross-linker plays a greater role in increasing of color reductions (ΔE_T^*) in comparison with ZnO-np.

Figure 2a–e represented the response surfaces of model for (a) absorption time and color reductions (ΔE^*) of stained wool samples with (b) Direct Blue 71, (c) Disperse Red 1, (d) black mulberry, and (e) coffee. The optimum condition of hydrophilicity and self-cleaning each of synthetic and food color stains was evaluated by Design of Expert software and are shown in Table 3. Thus, a significant lightening of color was observed in optimized samples after 25 min of UV-A irradiation (Fig. 3). In a way that obtained results from the performance of ZnO-np at

optimized condition for color reduction and self-cleaning is nearly equal with using TiO₂-np (Montazer and Pakdel 2011) and lower than results obtained from TiO₂/Ag nanocomposite (Montazer et al. 2012) accompany with poly carboxylic cross-linking agent on wool fabrics.

ANOVA was used to analyze the data and obtain the interaction between process of independent variables and responses. The results were then evaluated by ANOVA to assess the “goodness of fit” (Tables 4, 5, 6, 7, 8).

The lack of fit described the variation of data around the fitted model (Sugashini and Meera Sheriffa Begum 2013). If the model did not fit the data well, this would not be significant (Vedaraman et al. 2013). It was observed that designed model for water absorption time of treated wool samples was statistically significant at *F* value of 36.63 and values of prob > *F* (<0.0001) (Table 4). Therefore, it was

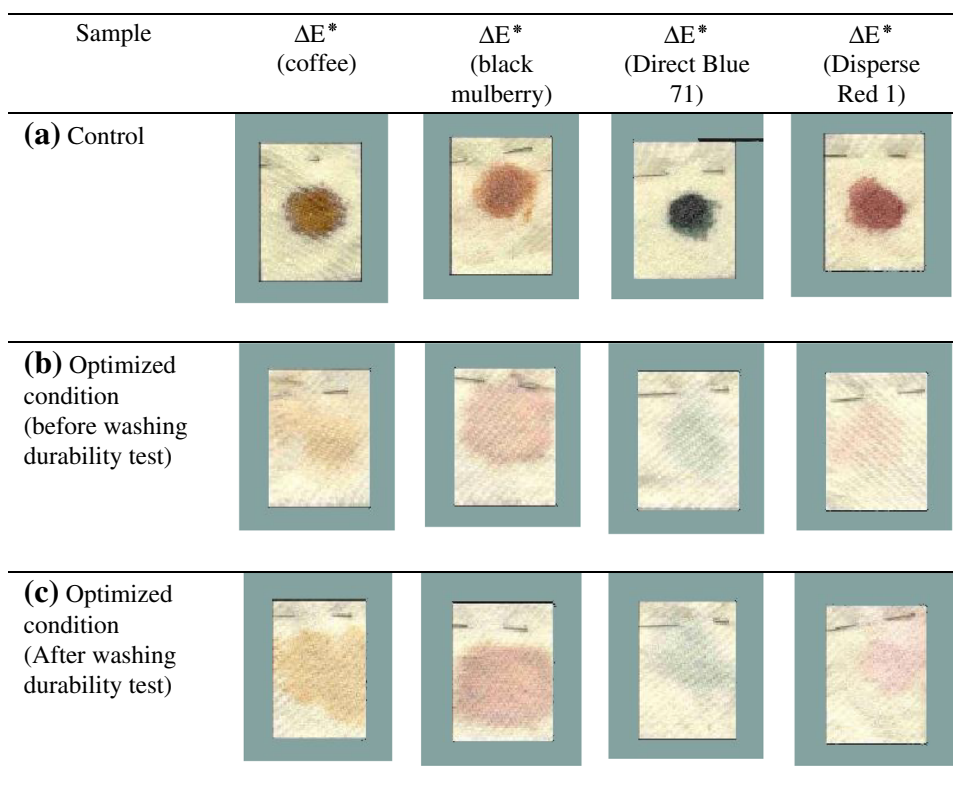
concluded that designed models for self-cleaning technology of stained wool with Direct Blue 71 and Disperse Red 1 were statistically significant at *F* value of 67.45 and 51.05 and values of prob > *F* (<0.0001), respectively (Tables 5, 6). Also it was observed that chosen models of stained wool samples for self-cleaning technology with black mulberry and coffee were significant at *F* value of 600.09 and 153.53 and values of prob > *F* (<0.0001), respectively (Tables 7, 8).

The fit of the model could be evaluated through R-squared coefficients. The results of Table 4 indicated that the only 2.08 % of total variables for water absorption time model of treated wool samples could not be explained by this model (Navid et al. 2014). Also the results of Tables 5 and 6 indicated that the only 1.14 and 1.50 % of total variables for self-cleaning technology models of Direct Blue 71 and Disperse Red 1 stained wool samples, respectively, could not be explained by these models (Navid et al. 2014). Therefore, R-squared of self-cleaning technology models of black mulberry and coffee stained wool samples could not explain 0.13 and 0.50 % of total variables, respectively (Tables 7, 8). A lower value of coefficient of variation (CV %) showed that conducted experiments were precise and reliable especially for the self-cleaning technology model of black mulberry stained samples (CV = 2.74 %) which indicated a good precision and reliability of experiments (Rashid et al. 2013).

Table 3 The optimum condition of ZnO-np/BTCA treatment on wool hydrophilicity and self-cleaning properties

Optimized property	ZnO-np (%)	BTCA (%)	Desirability
Absorption time (s) = 51.7	0.62	5.63	1.000
ΔE^* (Direct Blue 71) = 16.91	0.99	9.56	1.000
ΔE^* (Disperse Red 1) = 17.99	0.81	10.00	1.000
ΔE^* (Black mulberry) = 16.20	1.08	6.50	1.000
ΔE^* (Coffee) = 15.37	0.80	10.00	1.000

Fig. 3 Images of discoloration of the coffee, black mulberry, Direct Blue 71, and Disperse Red 1 stains on different wool samples (a control, optimized condition, b before, and c after washing durability test). (Color figure online)



Durability of washing

The washing durability of ZnO-np/BTCA wool fabrics treated after washing test was measured. The color reduction (ΔE_T^*) results are summarized in Table 9 and color variations are presented in Fig. 3.

The self-cleaning technology obtained in the optimized conditions exhibits a higher washing durability. It is because of sufficient existence of BTCA bio-cross-linker on fabric surface which was capable of stabilizing ZnO-np on the bio-cross-linked wool samples and consequently caused the increase of their durability against wash cycles. There existed an ionic interaction between groups of carboxylate anionic related to BTCA poly carboxylic acid and ZnO-np cation. Similar kind of interaction has been

previously reported in the presence of TiO₂-np photo-catalyst and poly carboxylic acid (Yuranova et al. 2007). It turned out that partial discoloration of CI Basic Blue 9 as a stain on the cross-linked cationized and conventional cotton with BTCA bio-cross-linker under UV and daylight irradiation presented a long-term stable performance for TiO₂-np (Nazari et al. 2011). The BTCA was bio-cross-linker that had the ability to improve the absorption of more ZnO-np on the natural wool surface since they contained four functional groups. The mechanism of electrostatic linkages between ZnO-np with BTCA and ester linkages between BTCA with wool was suggested in Scheme 1. Therefore, the reason of the small decrease in self-cleaning technology efficiency after washing durability test could be attributed to the removal of the few ZnO-np

Table 4 ANOVA results for response surface cubic model of water absorption time (s) of treated wool samples

Source	Sum of squares	Df	Mean square	F value	p value Prob > F
Model	37354.14	9	4150.46	36.63	<0.0001 significant
A [ZnO-np]	3.42	1	3.42	0.030	0.8670
B [BTCA]	5276.51	1	5276.51	46.56	0.0002
AB	158.55	1	158.55	1.40	0.2755
A ²	8253.56	1	8253.56	72.83	<0.0001
B ²	57.76	1	57.76	0.51	0.4984
A ² B	14.02	1	14.02	0.12	0.7354
AB ²	23.67	1	23.67	0.21	0.6615
A ³	229.72	1	229.72	2.03	0.1975
B ³	2492.46	1	2492.46	21.99	0.0022
Residual	793.25	7	113.32		
Lack of fit	788.48	2	394.24	413.68	<0.0001 significant
Pure error	4.77	5	0.95		
Cor Total	38147.38	16			

R-squared: 0.9792, adjusted R-squared: 0.9525, CV %: 7.92

Table 5 ANOVA results for response surface cubic model of color differences (ΔE^*) of stained wool samples with Direct Blue 71

Source	Sum of squares	Df	Mean square	F value	p value Prob > F
Model	383.24	9	42.58	67.45	<0.0001 significant
A [ZnO-np]	0.46	1	0.46	0.73	0.4226
B [BTCA]	7.02	1	7.02	11.13	0.0125
AB	0.73	1	0.73	1.15	0.3190
A ²	12.47	1	12.47	19.76	0.0030
B ²	28.13	1	28.13	44.57	0.0003
A ² B	0.010	1	0.010	0.016	0.9023
AB ²	0.57	1	0.57	0.90	0.3744
A ³	0.071	1	0.071	0.11	0.7468
B ³	0.13	1	0.13	0.21	0.6624
Residual	4.42	7	0.63		
Lack of fit	4.42	2	2.21	3721.29	<0.0001 significant
Pure error	2.967E-003	5	5.933E-004		
Cor total	387.66	16			

R-squared: 0.9886, adjusted R-squared: 0.9739, CV %: 7.03

Table 6 ANOVA results for response surface cubic model of color differences (ΔE^*) of stained wool samples with Disperse Red 1

Source	Sum of squares	Df	Mean square	F value	p value Prob > F
Model	307.51	9	34.17	51.05	<0.0001 significant
A [ZnO-np]	0.12	1	0.12	0.18	0.6815
B [BTCA]	3.34	1	3.34	4.98	0.0608
AB	4.01	1	4.01	6.00	0.0442
A ²	29.92	1	29.92	44.71	0.0003
B ²	15.87	1	15.87	23.72	0.0018
A ² B	2.44	1	2.44	3.64	0.0979
AB ²	2.42	1	2.42	3.62	0.0987
A ³	1.17	1	1.17	1.75	0.2273
B ³	19.54	1	19.54	29.19	0.0010
Residual	4.68	7	0.67		
Lack of fit	4.68	2	2.34	6161.92	<0.0001 significant
Pure error	1.900E-003	5	3.800E-004		
Cor total	312.19	16			

R-squared: 0.9850, adjusted R-squared: 0.9657, CV %: 7.22

Table 7 ANOVA results for response surface cubic model of color differences (ΔE^*) of stained wool samples with black mulberry

Source	Sum of squares	Df	Mean square	F value	p value Prob > F
Model	357.27	9	39.70	600.09	<0.0001 significant
A [ZnO-np]	1.01	1	1.01	15.20	0.0059
B [BTCA]	7.84	1	7.84	118.49	<0.0001
AB	21.02	1	21.02	317.79	<0.0001
A ²	44.42	1	44.42	671.53	<0.0001
B ²	65.88	1	65.88	995.88	<0.0001
A ² B	1.43	1	1.43	21.60	0.0023
AB ²	5.59	1	5.59	84.57	<0.0001
A ³	0.89	1	0.89	13.46	0.0080
B ³	20.11	1	20.11	303.99	<0.0001
Residual	0.46	7	0.066		
Lack of fit	0.46	2	0.23	353.70	<0.0001 significant
Pure error	3.250E-003	5	6.500E-004		
Cor total	357.73	16			

R-squared: 0.9987, adjusted R-squared: 0.9970, CV %: 2.74

available on the cross-linked wool surface as a result of evaluating washing durability. Therefore, the ZnO-np/BTCA cross-linked wool contained the great durability property including ideal self-cleaning technology in the optimized conditions. Also the percentage of actual content of ZnO-np (based on O.W.F) loaded on wool samples was measured using burning test and the results are presented in Table 10. It is clear that actual percentage of created weight increase for treated wool sample is 2.13 % at optimized condition (before washing durability test) but after the washing durability test, insignificant decrease is observed in actual content percentage of ZnO-np (2.08 %). In a way that main part of ZnO-np at optimized condition

preserved themselves on treated wool sample with strong connection. This consideration confirms that using BTCA with statistical optimized concentration is capable of absorption and stabilization increase of ZnO-np on wool surfaces. Consequently it was observed that BTCA bio-cross-linker could perform as ZnO-np stabilizer and preserved more ZnO-np on the surface of the cross-linked wool fabrics.

SEM images

Figure 4a–d demonstrated the SEM images of (a) control wool, (b) sample Run: 2, treated at optimized condition

Table 8 ANOVA results for response surface cubic model of color differences (ΔE^*) of stained wool samples with coffee

Source	Sum of squares	Df	Mean square	F value	p value Prob > F
Model	354.31	9	40.59	153.53	<0.0001 significant
A [ZnO-np]	1.12	1	1.12	4.24	0.0786
B [BTCA]	10.12	1	10.12	38.28	0.0005
AB	0.63	1	0.63	2.40	0.1652
A ²	15.79	1	15.79	59.72	0.0001
B ²	8.41	1	8.41	31.82	0.0008
A ² B	0.11	1	0.11	0.40	0.5465
AB ²	2.20	1	2.20	8.31	0.0235
A ³	1.339E-003	1	1.339E-003	5.064E-003	0.9453
B ³	0.074	1	0.074	0.28	0.6126
Residual	1.85	7	0.26		
Lack of fit	1.85	2	0.92	1225.79	<0.0001 significant
Pure error	3.767E-003	5	7.533E-004		
Cor total	367.16	16			

R-squared: 0.9950, adjusted
R-squared: 0.9885, CV %: 6.82

Table 9 Durability evaluation of wool fabrics treated in control and optimized condition (before and after washing test)

Different condition	ZnO-np (%)	BTCA (%)	SHP (%)	ΔE^* (coffee)	ΔE^* (black mulberry)	ΔE^* (Direct Blue 71)	ΔE^* (Disperse Red 1)
a: Control	0.00	0.00	0.00	4.28	4.12	4.59	4.37
b: Optimized condition (before durability test)	0.89	10.00	6.00	15.47	14.39	16.80	17.94
c: Optimized condition (after durability test)	0.89	10.00	6.00	14.39	13.26	15.53	16.81

Table 10 Actual content of Zn-np in wool fabrics treated at optimized condition (before and after washing test)

Optimized condition	ZnO-np (%) (O.W.B)	ZnO-np (%) (O.W.F)
Before washing durability test	0.89	2.13
After washing durability test	0.89	2.08

(c) before, and (d) after wash durability test. SEM analysis of control and treated samples (Fig. 4a–d) confirmed that the surfaces of treated samples were covered by ZnO-np. Because of small dimension properties, high surface activity, and large specific surface area ZnO-np had a tendency to be agglomerated easily (Zhang and Yang 2009). Bigger particles could be easily removed from the fabric surface, while the smaller particles could penetrate into the fabric matrix and adhered stronger to the fabric surface. These images showed the more ZnO-np loading on the treated sample at optimized condition (Fig. 4c) than the other samples. Therefore, the small decrease of ZnO-np presence was observed on the surface of sample Fig. 4 d than the sample Fig. 4c. This could be due to the removal

of some ZnO-np from the wool surface after the process of wash durability evaluation. BTCA bio-cross-linker significantly maintained the majority of ZnO-np on the cross-linked wool surfaces even after completing the evaluation of washing durability test and this showed achieving of durable self-cleaning technology and hydrophilicity wool fabrics. Also SEM image of sample (Run: 1) with the highest amount of ZnO-np (1.50 %) shows the agglomeration of ZnO-np on the wool fabric which leads to the reduction of their efficiency (Fig. 4e). However, BTCA-based zero formaldehyde cross-linkers not only cross-linked between protein chains of wool structure as a poly carboxylic, but also caused the stabilization of ZnO-np on the surface of natural wool fabric.

UV transmission and absorbance spectra

The UV transmission, absorbance spectra of control, treated wool with 0.10 % ZnO-np, 5.00 % BTCA, and 3.00 % SHP (Run: 2), and 0.89 % ZnO-np, 10.00 % BTCA, and 6.00 % SHP (optimized condition) in the UV region (200–400 nm) are presented in the Figs. 5, and 6, respectively. The wool samples treated with BTCA and ZnO-np

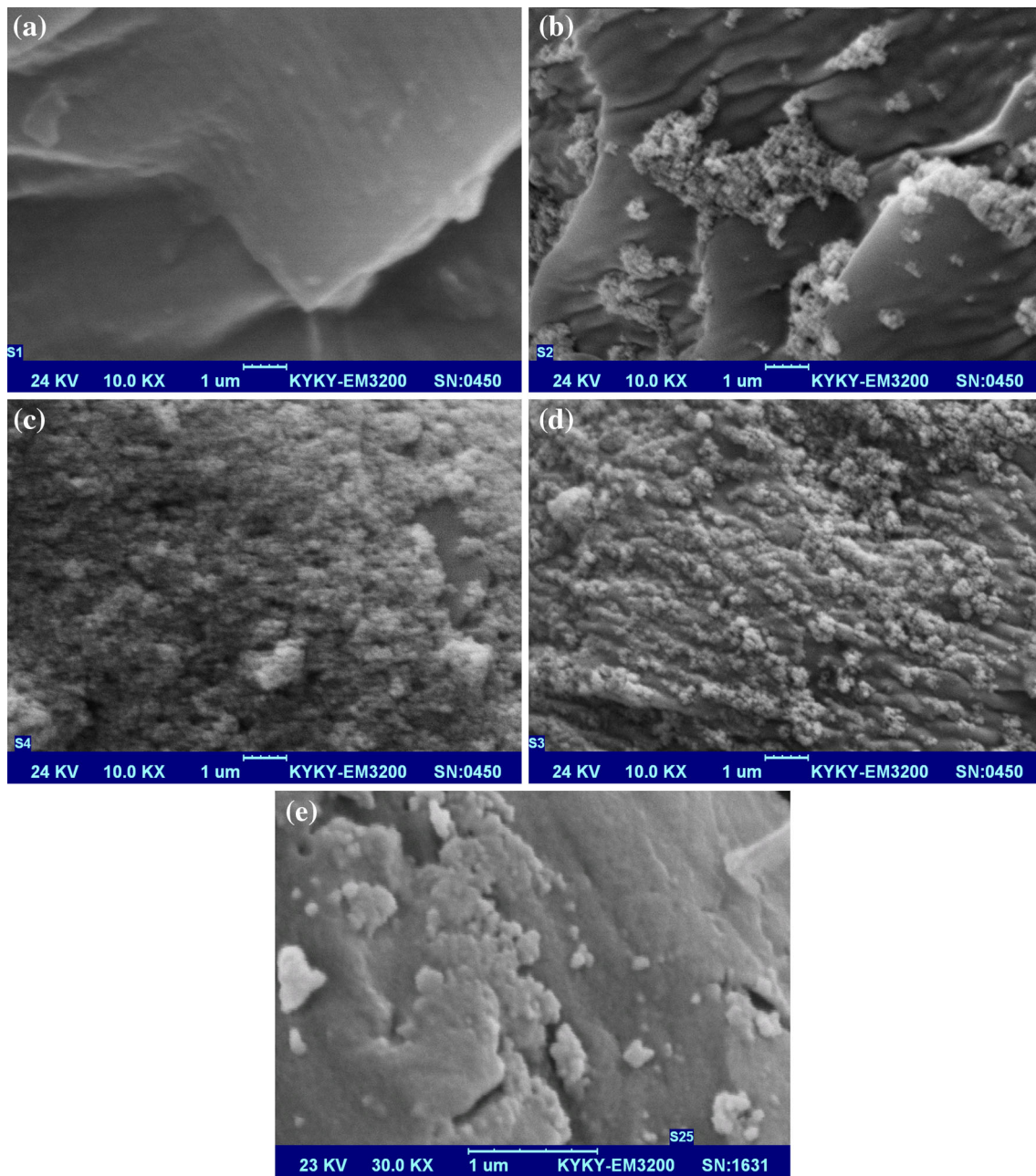


Fig. 4 SEM images of different wool samples **a** control, **b** Run: 2 (0.10 % ZnO-np, 5.00 % BTCA, and 3.00 % SHP), optimized condition (0.89 % ZnO-np, 10.00 % BTCA, and 6.00 % SHP)

c before, **d** after washing durability test (10,000 \times), and **e** Run: 1 (1.50 % ZnO-np, 10.00 % BTCA, and 6.00 % SHP) (30,000 \times)

had low UV transmission especially in UVB region (290–315 nm) and UVA region (315–400 nm) due to the UV absorption of ZnO-np. The lowest transmission was related to the treated wool at the optimized condition. Therefore, the absorbance extents of the treated wool samples (Figs. 5b and 5c) were more than control sample (Fig. 5a). This image clearly demonstrated that the most

absorption through ZnO-np/BTCA-treated wools occurred in the UV regions (200–400 nm). Therefore, ZnO-np absorbed the light with the wavelengths lower than 400 nm and the obtained treated wool sample indicated UV absorption property. ZnO-np acted primarily as a UV absorber resulting in a slower UV transmission rate, and the results are consistent with previous findings.

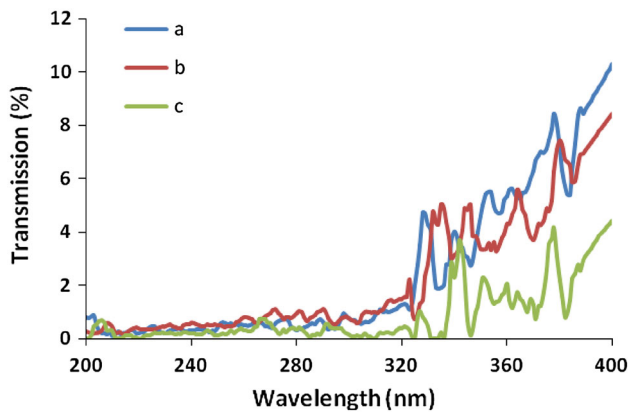


Fig. 5 UV transmission spectra of wool sample treated with ZnO-np and BTCA (*a*) control, (*b*) Run: 2 (0.10 % ZnO-np, 5.00 % BTCA, and 3.00 % SHP), and (*c*) optimized condition (0.89 % ZnO-np, 10.00 % BTCA, and 6.00 % SHP)

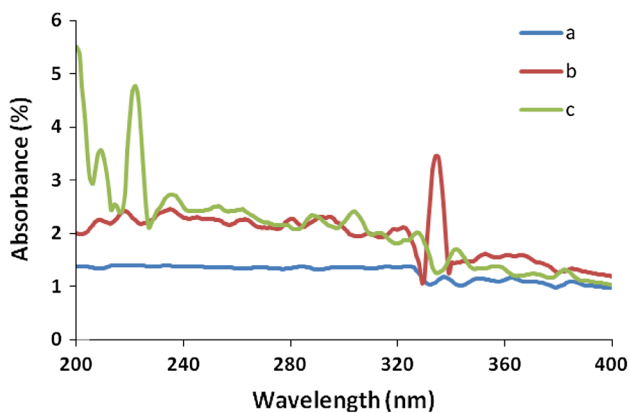


Fig. 6 UV absorbance spectra of wool sample treated with ZnO-np and BTCA (*a*) control, (*b*) Run: 2 (0.10 % ZnO-np, 5.00 % BTCA, and 3.00 % SHP), and (*c*) optimized condition (0.89 % ZnO-np, 10.00 % BTCA, and 6.00 % SHP)

Conclusion

This research intended to modify the bio-degradable wool surface to enhance ZnO-np adsorption and stabilize them on the fabric surface using BTCA as an eco-friendly cross-linker to produce a fabric with enhanced self-cleaning technology and hydrophilicity property. The increase in the bond ability of ZnO-np on the wool surface was investigated by surface modification induced by introducing extra hydroxyl and carboxyl groups using BTCA bio-cross-linker and SHP as a catalyst. According to the statistical analysis, the bio-cross-linked fabrics with BTCA and ZnO-np easily enable degradation of the synthetic and food color stains, while the treated wools became more hydrophilic. It can be concluded that at a given concentration of ZnO-np, BTCA bio-cross-linker, and catalyst, the color reduction

(ΔE^*) values of stained wool samples with the Direct Blue 71 and Disperse Red 1 are higher than those of coffee, black mulberry. Consequently BTCA bio-cross-linker with ZnO-np had a complementary effect on treated wool samples which demonstrated a noticeable increase in the durable self-cleaning technology and hydrophilicity property. It is also completely formaldehyde free, easily available, and soluble.

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