IMPROVED NATURAL DYEING OF COTTON BY PLASMA TREATMENT AND CHITOSAN COATING. OPTIMIZATION BY RESPONSE SURFACE METHODOLOGY

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In this study, cotton fibers were dyed with pomegranate rinds as a natural dye. To improve the dyeability of cotton fibers, chitosan was applied on the surface of the fibers. To enhance the application and adhesion of chitosan, oxygen plasma pretreatment was utilized. The procedure was optimized by response surface methodology and the most effective conditions for chitosan coating of cotton fibers, with the objective of obtaining the highest color strength, were found. The sample prepared under the optimal conditions was studied by scanning electron microscopy (SEM). The SEM images confirmed the existence of chitosan on the surface of the fibers. The chitosan-coated and naturally dyed samples demonstrated high antibacterial activity toward both gram-negative and gram-positive bacteria.

Keywords: cotton, pomegranate rinds, chitosan, plasma, natural dye, optimization

INTRODUCTION

Researchers in the field of textile dyeing and finishing have been recently showing increasing interest in using natural dyes. Synthetic dyes are usually harmful to the environment and human body, while natural dyes are mostly considered non-toxic.[1] Achieving special aesthetic qualities of naturally dyed textiles, in combination with their higher acceptability regarding environmental friendliness, grants them added value as craftwork or industrial products.[2] However, natural dyeing of textile fibers, especially in the case of cotton, faces several difficulties. Two of the key problems are low absorption and limited fastness properties. These are usually overcome by the use of mordants in the dyeing procedure.[3]

Cotton is the most widely used natural fiber in the textile industry on a global level, as it is inexpensive, absorbent, breathable and soft. Despite the high affinity of synthetic dyes for cotton, this fiber has poor dyeability with natural dyes. Several approaches have been reported to solve this problem.[4] Enzymatic pretreatment,[5-6] mordanting using metallic salts,[7-8] pretreatment with natural or synthetic tannin,[5,9] plasma treatment,[10] gamma radiation,[11-15] cationization,[9,16-18] dyeing in the presence of ultrasonic energy,[1,19] combination of ozone and ultrasonic treatment,[20] chitosan treatment[21] and acrylic acid grafting[4] are methods that have been employed for boosting the dyeability of cotton with different natural dyes.

Plasma technology as an environmentally friendly surface treatment process can enhance the adhesion, wettability, dyeability and reactivity of cotton fibers.[22] It can be used for the enhancement of chitosan adsorption onto cotton fabric.[23-26] It can produce the functional sites needed for the attachment of chitosan to the surface of the fibers. Chitosan biopolymer can bring in cationic moieties to cotton fibers and enhance their affinity for anionic dye molecules.[24] Furthermore, chitosan-coated cotton has been reported to exhibit high antibacterial activity.[23,26-27] Natural fibers, such as cotton, provide suitable conditions for bacterial growth, therefore antimicrobial finishing of textiles has become important. Lots of plants customarily used for dyeing have medicinal properties and some of them have shown considerable antimicrobial activity when employed for coloration of textile fibers.[28]

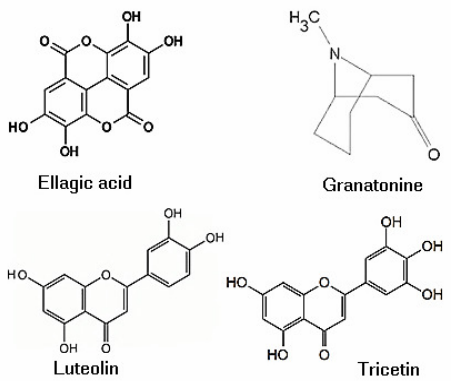

Figure 1: Chemical structures of coloring matters present in pomegranate rinds

Pomegranate (*Punica granatum*) belongs to the family Punicacea. It is native of Persia and grows in a number of countries of the world. Pomegranate rinds contain a high concentration of tannins, such as ellagic acid, besides granatonine, luteolin, and tricetin as coloring agents (Fig. 1).[3,28-29] Earlier studies indicated that pomegranate dyed textiles exhibit antibacterial activity.[30-31]

In this study, oxygen plasma was utilized for improving chitosan attachment to cotton fibers. The aim of the study was to prepare a cotton fabric that would be amenable to coloration with the selected natural dye with the highest K/S, in addition to achieving satisfactory antibacterial activity. The chitosan-coated samples were dyed with an extract of pomegranate rinds and the effects of the coating process parameters, including plasma treatment time, chitosan concentration and impregnation time, on the color strength of the dyed samples were investigated and optimized using response surface methodology.

The traditional method of optimization, which is based on varying each factor separately, while keeping the others constant, is energy and time consuming, and mostly insufficient for disclosing the optimal conditions of the process. Response surface methodology (RSM) encompasses the simultaneous experimental design, process analysis, optimization and statistical modelling of processes including more than one variable. RSM is a lessarduous way for evaluation of the effect of operation parameters, and the interactions among individual factors. Box-Behnken design (BBD) is the most frequently utilized design, compared to other RSM designs, with advantages such as higher efficiency and fewer experimental runs.[32]

Scanning electron microscopy (SEM) was employed to investigate the alterations of the surface morphological properties of cotton samples after plasma treatment and chitosan coating. The antibacterial activity and the color fastness of dyed samples to washing and light exposure were also evaluated.

EXPERIMENTAL

Materials

Pure cotton fabric with plain weave (100 g/m², yarn count Nm = 40) was obtained from Mazandaran Textile Co., Iran. Medium molecular weight chitosan (75-85% deacetylated) and Triton X-100 (nonionic surfactant) were purchased from Sigma Aldrich (USA).

Extraction of natural dye

Pomegranate rinds were first washed with distilled water, air dried and then powdered using a laboratory grinding mill (mesh No. 60). To prepare the original solution of the dye, each 100 g of powder was put into 1 liter of distilled water and boiled for 2 h and then filtered. Because of evaporation, the volume of the solution was reduced, so, distilled water was added to the filtrate to attain the initial volume and obtain a stock solution with a concentration of 10% w/v.

Design of experiments

In this study, experimental design software was used for the design of test runs and statistical evaluation of responses (Design Expert V7.0, Stat-Ease Inc., USA). Box-Behnken design was employed in order to evaluate the impact of three important

variables of the surface modification process on the color strength of cotton samples dyed with the aqueous extract of pomegranate rinds. Preliminary studies were done for determining the practically feasible range for the process variables. The required information about the coded process variable factors is shown in Table 1.

Plasma treatment

Low-pressure plasma equipment working in the radiofrequency (13.56 MHz), model Junior advanced, made by Europlasma, Belgium, was used. Oxygen plasma was utilized for the surface functionalization of cotton fibers. For this purpose, the air inside the plasma treatment chamber was pumped out to reach the pressure of 100 mTor. Oxygen was introduced into the chamber with a constant flow rate of 100 sccm (standard cubic centimeters per minute) during the plasma treatment. Plasma was generated at 150 W for different durations according to the experimental design. Finally, atmospheric air was released into the chamber to reach atmospheric pressure and the plasma treated sample was removed.

Chitosan treatment

Plasma treated samples were immediately impregnated in a solution of chitosan (concentration adjusted according to the experimental design) containing 1% v/v acetic acid for a predefined time. Then, the samples were padded with 100% wet pick-up and dried at 80 °C for 30 min. The dried samples were thoroughly washed with a solution containing 1% w/v Triton X-100 at 50 °C for 15 min to remove non-reacted chitosan from the surface of the fabric samples.

Dyeing

Dyeing of the raw and chitosan treated samples was performed using 10% owf of the natural dye (L:G = 40:1) at the natural pH of the solution (around 6). The starting temperature of the dyeing was 40 °C and the dye bath temperature was raised to boil in 30 minutes. The dyeing was continued at boil for 1 hour. Rinsing with tap water and air drying were the last steps of the dyeing procedure.

Color strength measurements

The reflectance data of colored specimens were collected using a Color-eye 7000A spectrophotometer (X-rite, USA), utilizing a D65 illuminant and a 10° standard observer. The following equation was used to calculate the color strength (K/S) of each colored test sample:

$$K/S = (1-R)^2/2R \quad (1)$$

where R is the observed reflectance at the wavelength of maximum absorbance, K is the absorption coefficient and S is the light scattering coefficient.

Scanning electron microscopy (SEM)

Scanning electron micrographs were taken utilizing an AIS2100 scanning electron microscope (Seron Technology, South Korea) to consider the effect of plasma and chitosan treatments on the surface morphology of cotton fibers.

Color fastness tests

ISO 105-C01: 1989(E) and ISO 105-B02: 1994(E) standard tests were employed to evaluate the color fastness of dyed samples to washing and light, respectively.

Antibacterial activity test

The antibacterial effectiveness of the samples was determined according to AATCC test method 100-2004. In this test, *Staphylococcus aureus* ATCC 6538 was selected as Gram-positive and *Escherichia coli* ATCC 8739 as Gram-negative bacteria. In this test, a circular swatch was inoculated with 1 ml of inoculums and incubated at 37 °C for 24 h. Before and after incubation on the agar plate, the colonies of both bacteria were counted with a microscope. The percent reduction in the number of bacteria after 24 hours of contact with the dyed samples was calculated and showed the efficacy of the antibacterial treatment.

Table 1
Experimental ranges of factors

Factor	Name	Unit	Low level	High level
A	Plasma treatment time	min	0	5
B	Impregnation time	min	10	60
C	Chitosan concentration	% w/v	0.2	1

RESULTS AND DISCUSSION

Model fitting and statistical analysis

Test samples were prepared as indicated by the experimental design. All prepared samples were dyed using the same recipe. The experimental conditions and color strengths (K/S) of the dyed specimens are shown in Table 2. The color strength data obtained from the spectrophotometer and calculated using equation 1 were fitted to different models, and their consequent ANOVA results are presented in Table 3. The quadratic

function was the most appropriate model for describing the process.

Table 4 demonstrates the analysis of variance (ANOVA) results of the organized model for responses. The high model F-value (88.13) indicates the significance of the established model. For each model term, a P-value less than 0.05 implies that the relevant factor is significant at the 95% confidence level, whereas the factors having P-values greater than 0.1 are usually considered as insignificant. In the present case, A, C, AC, A^2 and B^2 are significant model terms. When many insignificant model terms are found, model reduction can improve the model. In this study, some insignificant interactions of the variables were eliminated using the model reduction function of Design Expert software. A high R^2 coefficient (0.99) confirmed the acceptable conformity of the proposed model to the trial data.

The values of "Predicted R-Squared" and "Adjusted R-Squared" are 0.9380 and 0. 9788, respectively, which implies a logical agreement between them and the R-Squared. "Adeq Precision" is a kind of signal-to-noise ratio. A high value (usually greater than 4) indicates that a suitable model has been selected.[33] In this study, the ratio of 35.909 can be considered as an adequate signal, which confirms that the selected model can successfully navigate the design space.

Equation 2 shows the established model in terms of coded factors after the elimination of insignificant interactions:

$$K/S = 2.68 + 0.24A + 0.051B + 0.79C - 0.11AC + 0.29A^2 - 0.15B^2 \quad (2)$$

Table 2
Experimental design of plasma treatment procedures and responses

	Factor 1	Factor 2	Factor 3	Response
Run	A: Plasma treatment time (min)	B: Impregnation time (min)	C: Chitosan concentration (% w/v)	K/S
1	2.50	35.00	0.60	2.60
2	5.00	10.00	0.60	2.92
3	2.50	35.00	0.60	2.71
4	2.50	35.00	0.60	2.62
5	0.00	35.00	1.00	3.55
6	2.50	60.00	0.20	1.71
7	2.50	35.00	0.60	2.86
8	5.00	35.00	1.00	3.85
9	2.50	60.00	1.00	3.48
10	5.00	60.00	0.60	3.17
11	2.50	10.00	1.00	3.24
12	2.50	35.00	0.60	2.62
13	0.00	10.00	0.60	2.68
14	5.00	35.00	0.20	2.58
15	2.50	10.00	0.20	1.67
16	0.00	35.00	0.20	1.86
17	0.00	60.00	0.60	2.53
18	0.00	0.00	0.00	0.99

Table 3
ANOVA results of fitting the experimental data to various models

Source model	Std. dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	Note
Linear	0.21	0.9285	0.9132	0.8693	
2FI	0.22	0.9400	0.9073	0.7802	
Quadratic	0.11	0.9900	0.9788	0.9380	Suggested
Cubic	0.11	0.9947	0.9774		Aliased

Table 4
ANOVA results of the established model for responses

Factor	F-Value	P-Value
Model	88.13	<0.0001
A	43.60	0.0002
B	2.47	0.1548
C	482.73	<0.0001
AB	2.56	0.1480
AC	6.24	0.0371
BC	0.25	0.6333
A^2	30.94	0.0005
B^2	11.17	0.0102
C^2	0.51	0.4958
Lack of fit	0.88	0.5495

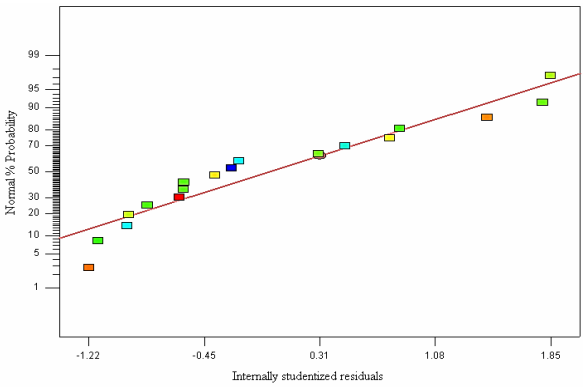

Figure 2: Studentized residuals *vs*. normal percentage probability plot for responses

Effect of process parameters on color strength

An important prerequisite for the validity of statistical analysis is that the data come from a normal distribution. The best ways to check the data for normality is constructing a normal probability plot of the residuals (the difference in the value obtained from the experiment and the predicted value or fitted value). In this plot, the residuals are considered as normally distributed if they fall approximately along a straight line.[34] As can be seen in Figure 2, all the residuals were linear, forming an approximately straight line and there is not any apparent problem with normality of the data.

Figure 3 shows the effects of the process factors on the color strength of dyed samples. It can be seen that increasing the plasma treatment time up to 2.5 min had no significant effect on color strength, but further increase resulted in increasing the K/S, due to enhancing the surface etching of fibers and to the introduction of more active chemical groups on the surface, leading to better penetration and adhesion of chitosan, which is responsible for increasing dye sorption (Fig. 3a). Increasing the impregnation time up to 35 min led to a small increase in K/S, and further increase caused the color strength to decrease. It seems that 35 min impregnation time is enough for sufficient adhesion of chitosan on the surface of cotton fibers (Fig. 3b). Increasing chitosan concentration led to increased K/S, which is due to the introduction of more amine groups as active sites for sorption of dye molecules (Fig. 3c). Figure 3d and e show the 3D surface plots, indicating the simultaneous effects of factors A-C and A-B on color strength, respectively.

Optimization of the process

The optimal conditions for obtaining the maximum K/S (according to the objective) were predicted using the optimization function of Design Expert software. The levels of all factors were selected to be "in the range". The optimized conditions are shown in Table 5. The values of the predicted and experimental K/S were very close, which means that the empirical model derived from RSM can be used to satisfactorily delineate the relationship between the process variables and the response (color strength of the dyed sample) in this study.

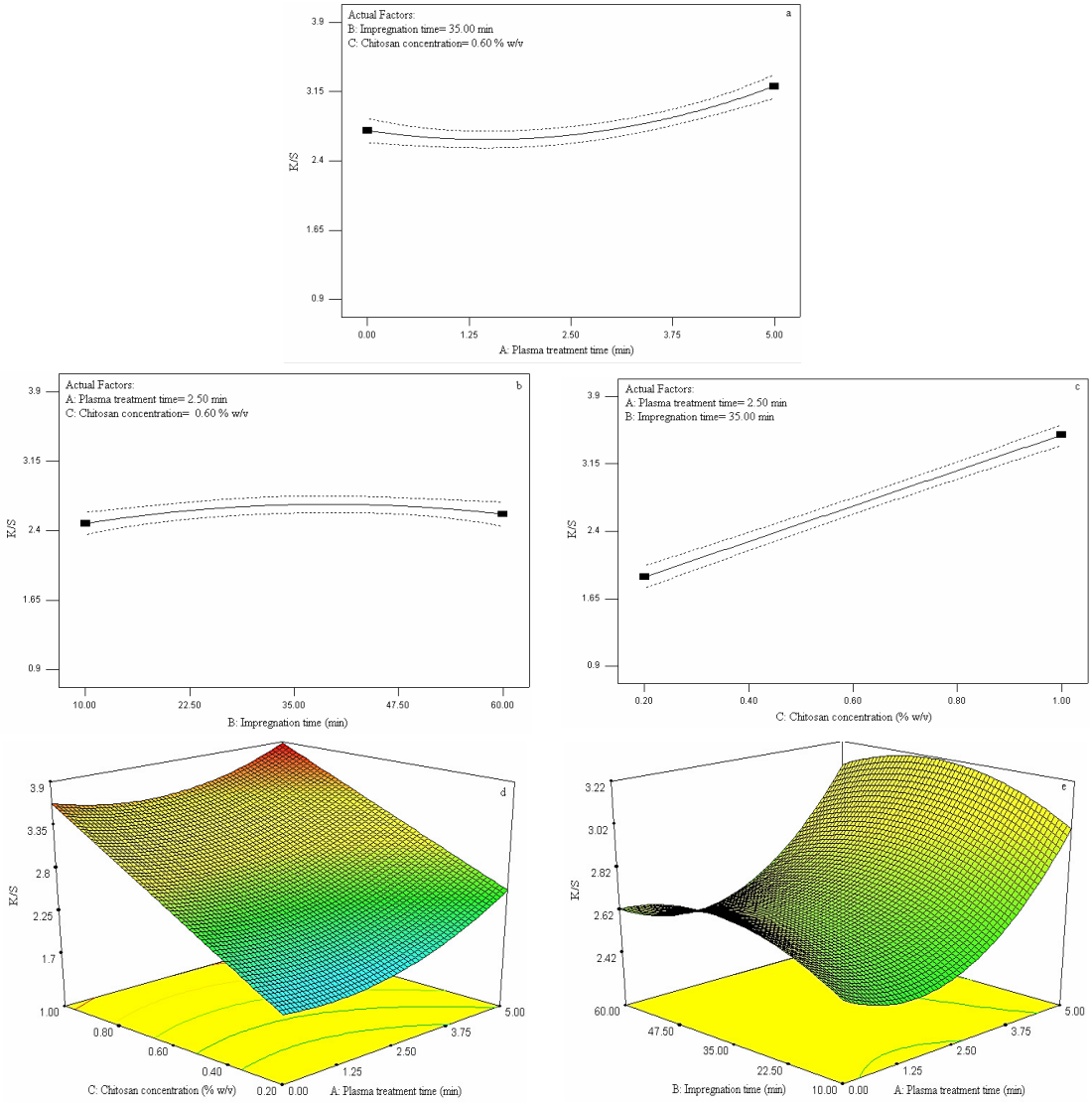

Figure 3: Individual and simultaneous effects of each factor on color strength of dyed samples

Table 5
Optimal conditions to obtain maximum color strength

A: Plasma treatment time (min)	B: Impregnation time (min)	C: Chitosan concentration (%w/v)	Predicted K/S	Experimental K/S	Desirability
5.00	35.00	1.00	3.88	3.85	1.00

SEM investigations

Figure 4 shows the surface morphology of raw, plasma treated and chitosan coated cotton fibers (according to the optimal conditions). The raw cotton fibers showed a smooth and even surface. The SEM image of raw cotton is typical of mature cotton fibres, with visible fibril outlines and collapsed inward. Compared to Figure 4a, the etching of the surface layer of cotton fibers caused by oxygen plasma treatment is evident in Figure 4b. Comparing these two samples with chitosan treated fibers, it can be seen that a thin layer of chitosan has been deposited on the surface of cotton fibers in Figure 4c.

Color fastness

Table 6 shows the color fastness properties of raw, plasma treated and chitosan coated cotton fibers (according to the optimal conditions). Although the fastness properties of raw cotton sample were acceptable for a typical natural dye on cotton, it can be seen that plasma and chitosan treatments have improved both the washing and light fastness of the dyed samples. The highest washing fastness was obtained when the cotton fabric was treated with oxygen plasma and coated with chitosan. It can be due to the ionic interaction between the amine groups of chitosan and hydroxyl groups of the dye molecules.

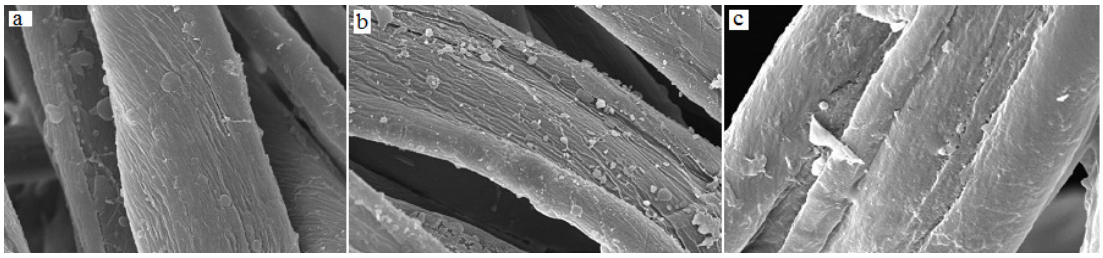

Figure 4: Surface morphology of raw (a), plasma treated (5 min, b) and chitosan coated (1% w/v, c) cotton fibers

Table 6
Fastness properties of dyed samples

Sample	Washing fastness	Rubbing fastness
Raw cotton, dyed	4	5-6
Plasma treated cotton (5 min), dyed	4-5	6
Chitosan coated cotton (1% w/v), dyed	6	7

Table 7
Percent reduction in the number of two bacteria on the surface of different samples

Bacteria	Raw cotton	Plasma treated cotton (5 min)	Chitosan coated (1% w/v) cotton, non-dyed	Chitosan coated (1% w/v) cotton, dyed
S. aureus	0	0	99.90	99.99
E. coli	0	0	99.91	99.99

Antibacterial activity

The plasma treated and chitosan coated samples (under optimal conditions) were tested as to antibacterial activity and compared with the untreated sample. Both dyed and non-dyed chitosan coated samples showed high antibacterial activity against both Gram-negative and Gram-positive bacteria. Table 7 shows the results of the antibacterial tests, confirming the high antibacterial activity of the finished samples. It is known that both chitosan and the polyphenols of pomegranate rinds possess antibacterial activity.[27,35] This functionality was imparted to the finished and naturally dyed samples as well.

CONCLUSION

In this study, cotton fibers were functionalized using chitosan biopolymer. Plasma treatment was used to improve the adhesion of chitosan onto cotton fibers. The finished samples were dyed with pomegranate rinds as a source of natural dye. The process of plasma treatment and chitosan coating was optimized using response surface methodology with a view to obtaining the highest color strength after natural dyeing. The results showed that plasma treatment can enhance the color strength of the dyed sample. The sample prepared under the optimal conditions was tested for antibacterial activity and showed great functionality against Gram-negative and Gram-positive bacteria.

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REFERENCES

[1] M. B. Ticha, W. Haddar, N. Meksi, A. Guesmi and M. F. Mhenni, *Carbohyd. Polym*., **154**, 287 (2016).

[2] P. S. Vankar, "Handbook on Natural Dyes for Industrial Applications", National Institute of Industrial Research, New Delhi, India, 2007, pp. 3-26.
[3] S. S. Kulkarni, A. V. Gokhale, U. M. Bodake and G. R. Pathade, *Univers. J. Environ. Res. Technol.*, **1**, 135 (2011).
[4] A. Haji, *Cellulose Chem. Technol.*, **47**, 303 (2013).
[5] P. S. Vankar, R. Shanker and A. Verma, *J. Cleaner Prod.*, **15**, 1441 (2007).
[6] E. Tsatsaroni and M. Liakopoulou-Kyriakides, *Dyes Pigm.*, **29**, 203 (1995).
[7] P. S. Vankar, R. Shanker and J. Srivastava, *Dyes Pigm.*, **72**, 33 (2007).
[8] H. T. Deo and B. K. Desai, *Color. Technol.*, **115**, 224 (1999).
[9] K. Hong, J. Bae, S. Jin and J. Yang, *Cellulose*, **19**, 507 (2012).
[10] M. Gorjanc, A. Savić, L. Topalić-Trivunović, M. Mozetič, R. Zaplotnik *et al.*, *Cellulose*, **23**, 2221 (2016).
[11] F. Batool, S. Adeel, M. Azeem, A. Ahmad Khan, I. Ahmad Bhatti *et al.*, *Radiat. Phys. Chem.*, **89**, 33 (2013).
[12] I. A. Bhatti, S. Adeel, M. A. Jamal, M. Safdar and M. Abbas, *Radiat. Phys. Chem.*, **79**, 622 (2010).
[13] A. A. Khan, N. Iqbal, S. Adeel, M. Azeem, F. Batool *et al.*, *Dyes Pigm.*, **103**, 50 (2014).
[14] S. Naz, I. A. Bhatti and S. Adeel, *Indian J. Fibre Text. Res.*, **36**, 132 (2011).
[15] F.-U. Rehman, S. Adeel, S. Qaiser, I. Ahmad Bhatti, M. Shahid *et al.*, *Radiat. Phys. Chem.*, **81**, 1752 (2012).
[16] W. Haddar, I. Elksibi, N. Meksi and M. F. Mhenni, *Ind. Crop. Prod.*, **52**, 588 (2014).
[17] W. Haddar, M. Ben Ticha, A. Guesmi, F. Khoffi and B. Durand, *J. Cleaner Prod.*, **68**, 114 (2014).
[18] S. Fu, D. Hinks, P. Hauser and M. Ankeny, *Cellulose*, **20**, 3101 (2013).
[19] H. Benli and M. İ. Bahtiyari, *Cellulose*, **22**, 867 (2015).
[20] H. Benli and M. İ. Bahtiyari, *J. Cleaner Prod.*, **89**, 116 (2015).
[21] P. Morakotjinda and W. Nitayaphat, *Appl. Mech. Mater.*, **749**, 89 (2015).
[22] A. Patiño, C. Canal, C. Rodríguez, G. Caballero, A. Navarro *et al.*, *Cellulose*, **18**, 1073 (2011).
[23] M. Naebe, Q. Li, A. Onur and R. Denning, *Cellulose*, **23**, 2129 (2016).
[24] A. Haji, S. S. Qavamnia and F. K. Bizhaem, *Ind. Text.*, **67**, 109 (2016).
[25] M. Naebe, A. Onur and X. Wang, in *Procs. The 13th Asian Textile Conference*, Geelong, November 3-6, 2015, pp. 595-598.
[26] C.-E. Zhou and C.-W. Kan, *Cellulose*, **21**, 2951 (2014).
[27] F. Ferrero, M. Periolatto and S. Ferrario, *J. Cleaner Prod.*, **96**, 244 (2015).
[28] A. Davulcu, H. Benli, Y. Şen and M. İ. Bahtiyari, *Cellulose*, **21**, 4671 (2014).
[29] C. Lal, M. C. Sharma, D. B. Shakyawar, A. S. M. Raja, K. K. Sharma *et al.*, *Arch. Appl. Sci. Res.*, **3**, 350 (2011).
[30] Y.-H. Lee, E.-K. Hwang and H.-D. Kim, *Materials*, **2**, 10 (2009).
[31] F. S. Ghaheh, A. S. Nateri, S. M. Mortazavi, D. Abedi and J. Mokhtari, *Color. Technol.*, **128**, 473 (2012).
[32] A. A. Oladipo, M. Gazi and E. Yilmaz, *Chem. Eng. Res. Des.*, **104**, 264 (2015).
[33] R. S. Rahbar and A. Haji, *J. Appl. Polym. Sci.*, **130**, 1337 (2013).
[34] J. Antony, "Design of Experiments for Engineers and Scientists", Butterworth-Heinemann, Burlington, 2003, pp. 37-38.
[35] N. S. Al-Zoreky, *Int. J. Food Microbiol.*, **134**, 244 (2009).