

## Effect of TiO<sub>2</sub> nanoparticle on light fastness and degradation of dyed fabric with direct dye

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The photocatalytic degradation of various dye solutions has been studied using nanoTiO<sub>2</sub> (NTO) as a catalyst. The effect of NTO on the light fastness of dyed cotton fabric has been studied using two different dyes, namely Direct Blue 71 and Direct Red 31 with high and low light fastness respectively. After dyeing, the fabric is coated with NTO using a dip-pad-dry-cure process. The coated fabrics are then exposed to UV light for different periods of time. The results indicate that the coated cotton fabrics show a significant photo-oxidative activity under UV light. The color change of cotton fabric dyed with Direct Blue 71 with high light fastness is found less than that of the sample dyed with Direct red 31 with low light fastness.

**Keywords:** Cotton fabric, Direct dye, Light fastness, Nano TiO<sub>2</sub> Photo-oxidation activity

### 1 Introduction

Rapid development in the nanofabrication techniques has increased the production of different advanced nano-sized semiconductors. Photocatalysis has attracted great attention as a cleanup technology, since it is an economic and convenient method for the complete decomposition of organic species into H<sub>2</sub>O and CO<sub>2</sub>. Nano TiO<sub>2</sub> (NTO) was found to be the best-known photocatalyst widely used in textile industry. The use of NTO also affects the color of textiles. Dyeing is one of the most important processes in textile industries and hence the study of the elements influencing color of textile has become an important subject<sup>1</sup>.

In recent years, the textile industry has increasingly focused its interest on nanotechnologies<sup>2</sup>. Titanium dioxide (TiO<sub>2</sub>) has been used as the photocatalyst agent. It has different useful applications to produce high quality samples<sup>3</sup>. It is observed that NTO has good photo catalytic activity. This activity leads to self-cleaning effect on cotton fabric<sup>4,7</sup>. NTO was also used to produce smart fabrics with antibacterial, stain resistant, and UV protection properties<sup>8</sup>. Numerous studies on the application of NTO for photocatalytic oxidation (PCO) or the removal of azo dyes and other organic pollutants in aqueous wastewater solutions have been reported<sup>9-16</sup>.

The oxidation process commonly involves irradiation by UV ( $\lambda < 400$  nm) when a semiconductor catalyst like TiO<sub>2</sub> is present. By the absorption of light energy equal

to or larger than the band gap energy, a valence band electron of the semiconductor is excited to the conduction band ( $e^-_{CB}$ ), leaving a positive hole in the valence band ( $h^+_{VB}$ ). The positive hole is a strong oxidant, which can directly oxidize a compound, or react with electron donors such as water or hydroxide ions to form hydroxyl radical ( $\cdot OH$ ). On the other hand, one effective electron acceptor is molecular oxygen (O<sub>2</sub>), which forms a superoxide anion radical (O<sub>2</sub><sup>-</sup>) after receiving the electron<sup>11</sup>. This hydroxyl radical and superoxide anion radical can degrade organic compounds. Thus these radicals can affect the dyed fabric and cause color change, also with the change in reflectance. The reflection properties of surfaces can be explained by the reflectance spectra, which have been measured at regular intervals in the visible spectrum. The reflectance spectra can be used to measure the color strength<sup>17</sup>. The purpose of this study was to investigate the influence of NTO photocatalyst on light fastness of cotton fabric dyed with direct dyes that eventually leads to color difference.

### 2 Materials and Methods

#### 2.1 Materials

Cotton fabric (bleached and mercerized) was purchased from Iran Poplin Corporation. The direct dyes used for dyeing cotton fabric, namely C.I. Direct Blue 71 and C.I. Direct Red 31 (Table 1) were obtained from K. K. J. Co., The titanium dioxide nanoparticles (21 nm diameter and BET area  $50 \pm 15$  m<sup>2</sup>/g) were obtained from Degussa (P25, Evonik).

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## 2.2 Instruments

Six dispersion solutions were prepared in distilled water by a Sonoplus DW 3200 sonicator. The reflectance spectra and color parameter of the samples were measured by XRite Color Eye 7000Å spectrophotometer. The reflectance spectra were measured at 31 wavelengths at 10 nm intervals from 400 nm to 700 nm. The color parameter was measured under 10 degrees standard observer and D65 standard illuminant. Relative color strengths ( $K/S$  values) were specified using the Kubelka-Munk equation. The color difference of the samples was measured using CIELab color difference equations as shown below<sup>17</sup>:

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

where  $\Delta E$  is the color difference between the sample and the standard;  $L^*$ , the white-black axis,  $a^*$ , the red-green axis; and  $b^*$ , the yellow-blue axis. A comparison was made between color coordinates of each dyed fabric and coated dyed fabric before and after the irradiation. The color difference of the samples was calculated using Eq. (1) in CIELAB color space. For pad-dry-cure process, a SDL pad thermosol was used.

The effect of  $\text{TiO}_2$  nanoparticles on the color of the fabric was analyzed using SEM and XRD results.

## 2.3 Dyeing of Cotton Fabrics

The cotton fabric was dyed with direct dyes (Fig. 1). Direct Blue 71 with high light fastness and Direct Red 31 with low light fastness were used. Dyeing liquor ratio was 40:1 and the amount of conman salt was 10 g/L.

## 2.4 Coating of NTO on Dyed Cotton Fabrics

$\text{TiO}_2$  nanoparticles were dispersed in water at 0.5, 1.0 and 2.0 wt/wt% concentration. These dispersions were

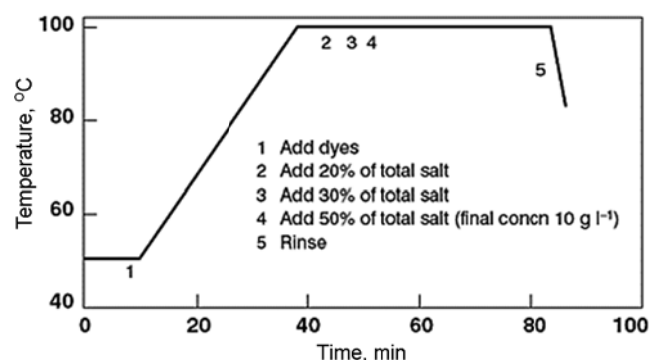
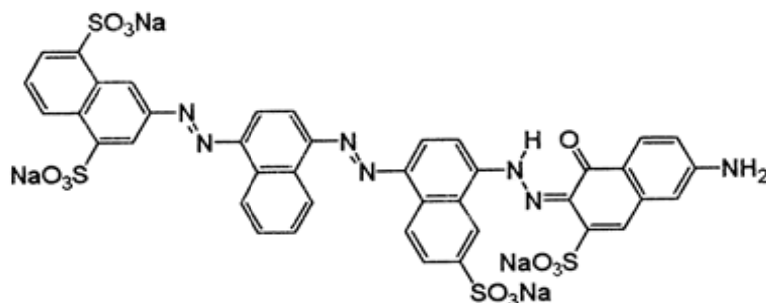


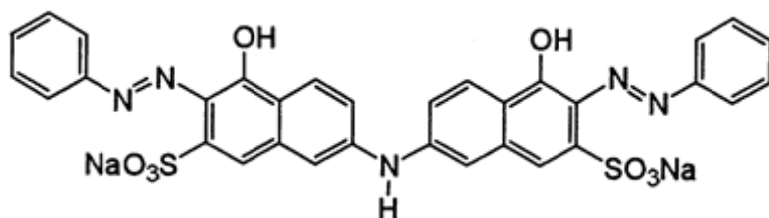
Fig. 1 — Dyeing cotton fabrics with direct dye<sup>18</sup>

Table 1 — Information of dyes

Parameter	Direct Blue 71	Direct Red 31
Chemical class	Trisazo	Disazo
C. I. Number	34140	29100
S. D. C. classification	B	A
Light fastness	4-5	1
	5	2



Direct Blue 71



Direct Red 31

sonicated for 20 min to prepare uniform dispersion. To transfer TiO<sub>2</sub> nano particles on the fabric surface evenly, each dyed sample was immersed in the prepared dispersion for 5 min. Then, the samples were passed through a padding mangle to eliminate surplus solution. All the samples were padded with 80% pick-up. After padding, the samples were taken out, dried for 5 min at 80 °C and then cured for 3 min at 130 °C. Relative color strengths and the color differences of the coated samples were measured before and after photo-oxidation process and exposure to light process<sup>19</sup>.

### 2.5 Construction of Photoreactor

All photocatalytic experiments were carried out in a reactor as shown in Fig. 2. Container dimensions were 100cm × 60cm × 100cm. The top of the container shield was open to the atmosphere and a fan was fitted at the bottom to circulate fresh air into the photoreactor. On

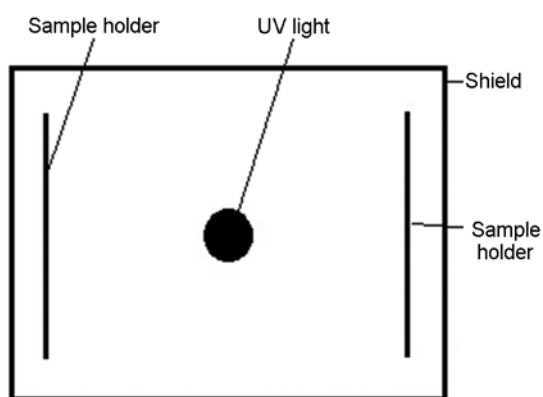


Fig. 2 — Top view of photoreactor

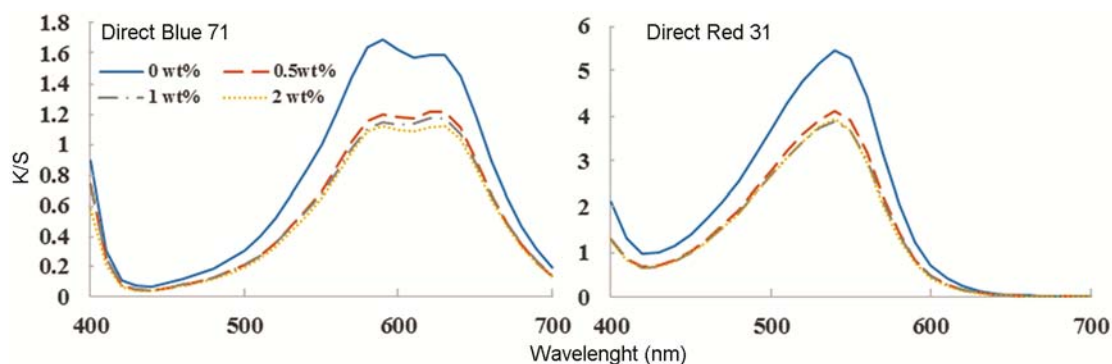


Fig. 3 — *K/S* spectra of modified fabrics with different concentrations of NTO

both sides of the shield there were sample holders. The UV lamp (HPMV 400W) was placed in the center of the shield. Four samples were tested in the reactor; using two dyed fabrics without NTO (blue and red), and six dyed fabrics, blue and red, each with 0.5, 1.0 and 2.0 wt/wt% of NTO concentration. The surface of the samples was dampened after every 15 min with a sprinkler. The dampened samples with NTO were exposed to photo-oxidation by UV. The sample were measured by RSD at the intervals of 2, 6, 8 and 16 h.

### 3 Results and Discussion

To impart photooxidation properties of TiO<sub>2</sub> coated fabric under UV irradiation, cotton fabrics were dyed with two classes of direct dyes with azoic structures (one with strong light fastness and the other with weak light fastness), and then coated with NTO at different concentrations.

The effect of TiO<sub>2</sub> coating on color of dyed fabrics was evaluated by measuring their reflectance spectra and colorimetric parameters, and the results are summarized in Table 2. The obtained results show that the nano-sized TiO<sub>2</sub> coating can change the color of dyed fabrics. According to Table 2, the color change ( $\Delta E_{ab}^*$ ) for both blue and red fabrics increases with increasing the concentration of NTO. On the other hand, the effect of NTO on color of the fabric with blue shade is more than that of the fabric with red shade.

Figure 3 shows *K/S* spectra of pristine and TiO<sub>2</sub> treated samples. It is observed that an increase in TiO<sub>2</sub> concentration will result in the increase in the reflectance

Table 2 — Colorimetric parameters and color difference of dyed fabrics before and after coating with NTO

NTO wt/wt%	Direct Blue 71				Direct Red 31			
	L*	C*	h	$\Delta E$	L*	C*	h	$\Delta E$
0	62.27	35.94	267.50	0	49.20	47.31	352.53	0
0.5	66.65	33.40	264.42	5.39	53.44	47.25	351.75	4.29
1	66.95	32.81	264.46	5.92	53.74	46.19	351.58	4.74
2	67.57	32.75	263.76	6.58	54.25	47.11	352.15	5.06

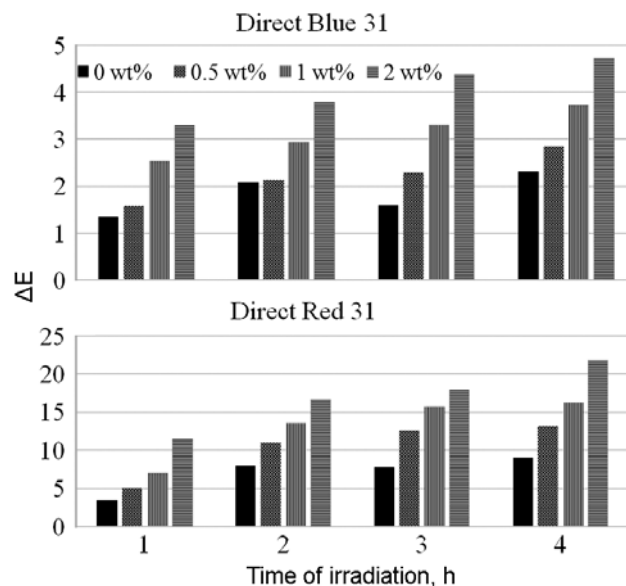


Fig. 4 — Color change of coated samples (blue and red) with specific concentrations of NTO in different time periods of irradiation NTO in different time periods of irradiation

spectra of coated samples and decreases the  $K/S$  values. Therefore, it can be inferred that the increase in NTO decreases the relative color strength of dyed fabrics.

To evaluate the extent of photodegradation of pristine and coated fabrics, samples are exposed to UV irradiation for different periods of time. The color change of samples are shown in Fig. 4, as color difference between reference and radiated samples. Also, the reflectance and  $K/S$  values of reference and radiated samples are depicted in Fig. 5. The changes in each coated sample with a specific concentration of NTO are examined at different time periods. In addition to the color difference caused by NTO, irradiation also photodegradizes the dyed fabric; and this irradiation causes changes in color, reflectance factor and reflectance function ( $K/S$ ). The photodegradation and reflection increase with increasing the time of irradiation, while relative color strength decreases with increasing the time of

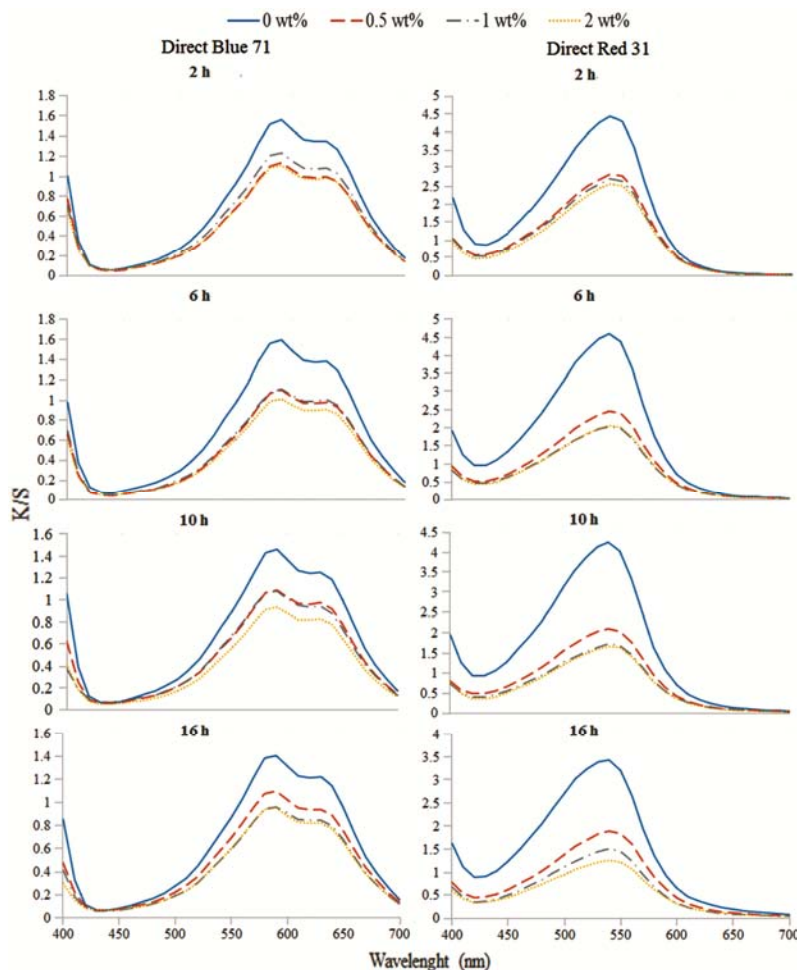


Fig. 5— $K/S$  spectra of dyed modified fabrics (blue and red) with different concentrations of NTO

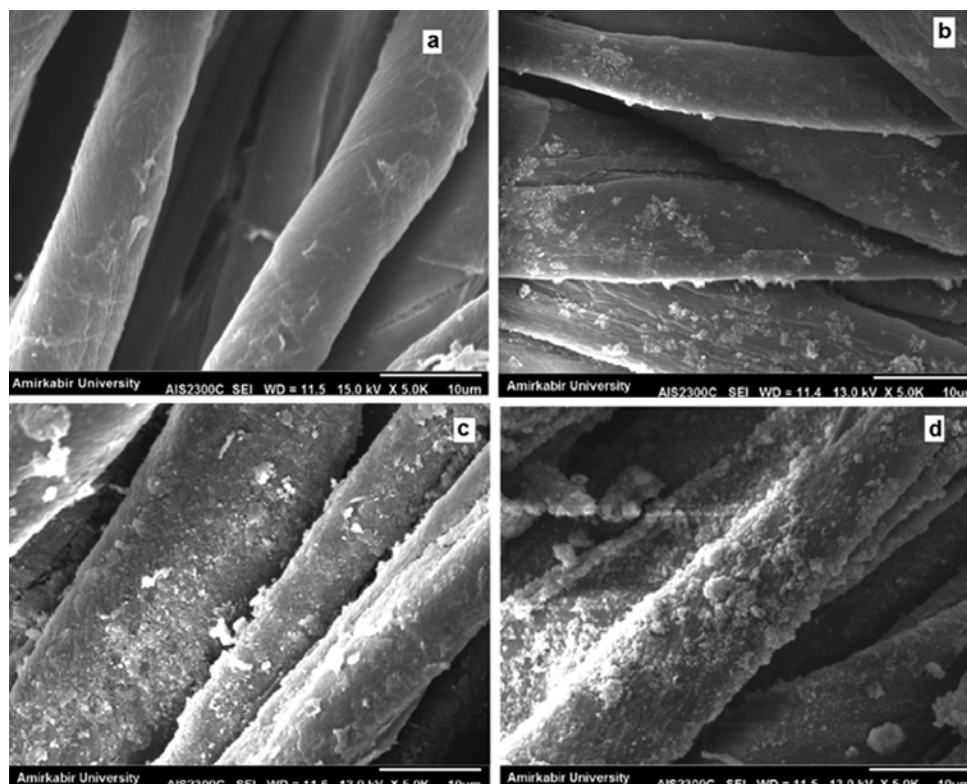


Fig. 6–SEM images of coated samples for (a) dyed fabric without NTO, (b) Dyed fabric with 0.5 wt/wt% NTO, (c) dyed fabric with 1 wt/wt% NTO, and (d) dyed fabric with 2 wt/wt% NTO

irradiation. The results obtained indicate that the color change in red samples is considerably higher than in blue samples. In this experiment, the dyed sample without NTO (introduced as 0 wt/wt%), like the coated sample, has been exposed to UV light and photodegraded to some extent. Also, the color change of the red sample with 0wt/wt% concentration after 2 h of irradiation is found similar to that of the blue sample with 2wt/wt% concentration after 16 h of irradiation. On the other hand, after irradiation at 16 h, the color change of the red sample with 0wt/wt% concentration is found more than in blue sample with 2 wt/wt% concentration. The obtained results indicate that the light fastness of the dye is an important and effective factor in the color change of the samples under irradiation. Consequently, the coating of dyed fabric with NTO for the purpose is possible by selecting the appropriate dye with higher fastness.

To study the surface morphology of the cotton fabric samples, the images of the dyed fabric and NTO treated dyed fabric samples are analyzed using scanning electron microscope. Figure 6(a) shows the surface of cotton dyed fabric sample without NTO. Figures 6(b), (c) and (d) show cotton surface treated with three concentrations of NTO (0.5, 1 and 2 wt/wt%

respectively). However, these images confirm the coating of NTO particles on cotton fabric by the padding process, but their distribution on the fibre surface is not quite uniform, probably because of the aggregation of some NTO particles on the cotton surfaces.

To reassure the presence of NTO on the surface of the samples, XRD is also obtained. The XRD patterns are obtained on a Philips PW1840 X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a scan rate of  $0.05^\circ (2\theta) \text{ s}^{-1}$ . The patterns are collected in the  $2\theta$  range =  $10^\circ$ – $70^\circ$  and in continuous scan mode. The accelerating voltage and the applied current are 40 kV and 30 mA respectively. Crystalline status of titanium particles over cotton fabric is obtained by XRD. The results confirm the presence principal diffraction peaks for the TiO<sub>2</sub> by comparing the XRD data with (JCPDF 01-84-1285). The intense peak at  $2\theta = 23.1^\circ$  is due to the cotton phase. The four broader peaks at  $2\theta = 25.3^\circ, 48^\circ, 55.1^\circ$  and  $62.7^\circ$  indicate the anatase phase of NTO.

#### 4 Conclusion

This work includes study on the photocatalytic activities of dyed cotton coated with NTO. The analysis of the data provides evidence that the

presence of NTO causes color change, increase in reflection and decrease in relative color strength. After treating the samples with NTO and irradiation of UV light, the resulting color change causes an increase in reflection and decrease in relative color strength. It is also observed that the light fastness of the selected dye can largely affect the extent of color change because of photodegradation, while the concentration of NTO and the time of irradiation can affect the color of the fabric.

### References

- 1 Kartini I, Ilmi I & Kunarti E S, *Indian Academy Sci*, 37(2014) 1419.
- 2 Ortelli S, Blosi M, Albonetti S, Vaccari A, Dondi M & Costa A L, *Photochem Photobiol A: Chem*, 276(2014) 58.
- 3 Mohamed R, McKinney D L & Sigmund W M, *Enhanced Materials Sci Eng: R: Reports*, 73(2012)1.
- 4 Pisitsak P, Samootsoot A & Chokpanich N, *KKU Res J*, 18(2013) 200.
- 5 Qi K Daoud W A, Xin J H, Mak C L, Tang W & Cheung W P, *Materials Chem*, 16(2006) 4567.
- 6 Wu D, Long M, Zhou J, Cai W, Zhu X, Chen C & Wu Y, *Surface Coatings Technol*, 203(2009) 3728.
- 7 Yuranova T, Laub D & Kiwi J, *Catalysis Today*, 122(2007) 109.
- 8 Dastjerdi R & Montazer M, *Colloids Surfaces B: Biointerfaces*, 79(2010) 5.
- 9 Abo-Farha S, *Am Sci*, 6(2010).
- 10 Daneshvar N, Salari D & Khataee A R, *Photochem Photobiol A: Chem*, 162(2004) 317.
- 11 So C, Cheng M Y, Yu J C & Wong P K, *Chemosphere*, 46(2002) 905.
- 12 Zhang D, *Russian Phys Chem A*, 87(2013) 129.
- 13 Zhang D, *High Energy Chem*, 46(2012) 206.
- 14 Atchudan R, Edison NJI, Perumal S, Karthikeyan D, Lee YR, *Photochem Photobiol A: Chem*, 333(2017) 92.
- 15 Rostami-Vartooni A, Nasrollahzadeh M, Salavati-Niasari M & Atarod M, *Alloys Compounds*, 689(2016) 15.
- 16 Zeinab M Abou-Gamra & Mohamed A Ahmed, *Adv Chem Eng Sci*, 5(2015) 373.
- 17 Westland S & Ripamonti C, *Computational Colour Science using MATLAB* (John Wiley & Sons, UK), 2004.
- 18 Broadbent A D, *Basic Principles of Textile Coloration* (Society of Dyers and Colourists Bradford), 2001.
- 19 Goudarzi U, Mokhtari J & Nouri M, *Fibers Polym*, 15(2014) 241.