Carbohydrate Polymers 101 (2014) 666–670

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Printing properties of the red reactive dyes with different number sulfonate groups on cotton fabric

Kongliang Xie*, Aiqin Gao, Min Li, Xiao Wang

College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China

ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form
24 September 2013
Accepted 29 September 2013
Available online 7 October 2013

Keywords:
Cotton
Print
Reactive dyes
Affinity
Color yield

ABSTRACT

Cellulose fabric is an important printing substrate. Four red azo reactive dyes based on 1-naphthol-8-amino-3,6-disulfonic acid for cotton fabric printing were designed. Their UV–Vis spectra and printing properties for cotton were investigated. The relationship between the chemical structures of the dyes and their printing properties on cotton fabric was discussed. The results show that the color yield (*K*/*S*) values of the printed fabrics decreased with the increase of sulfonate groups, but the fixation and penetration of the reactive dyes on cotton fabric increased. The reactive dyes with fewer number sulfonate groups were sensitive to alkaline and urea. Whereas, the reactive dyes with numerous sulfonate groups were not sensitive to urea and had good leveling properties, penetration uniformity, and good wet fastness for cotton fabric. Surface wettability of all cotton fabrics printed with four dyes was excellent. It is possible to print cotton fabric urea-free using the reactive dyes with numerous sulfonate groups.

1. Introduction

Cellulose fabric is one of the excellent natural materials and it is the most commonly printed substrate. Printed fabrics have wide applications in the different productions, such as garment, home textile, and composite materials (Hou & Sun, 2013; Jung, Wolters, & Berlin, 2007; Xie, Gao, & Zhang, 2013). Reactive dyes, mainly monochloro-triazine reactive dyes, is one kind of the most commonly used dyes for cellulose fabric printing because of its high wet fastness and brilliant color (Hebeish, Ragheb, Nassar, Allam, & Abd El Thalouth, 2006; Kanik & Hauser, 2003; Lewis, 2001). Reactive dyes for printing cotton must exhibit the properties, such as high solubility, low affinity, high diffusion and high printing paste stability. Red color for printing fabric is one of the most important color hues. Reactive Red K-2BP (C. I. Reactive Red 24) is an important commercial red reactive dye for cotton fabric printing in the dyestuff market.

Reactive Red K-2BP is derived from 1-naphthol-8-amino-3,6-disulfonic acid (H-acid) as the coupling component. The chemical structure has monochloro-triazine reactive group. The monochloro-triazine reactive group can react with cellulose fiber under the alkaline condition. It is widely used to print cellulose fabric and can be applied to match color as the red component in the reactive black dyes (El-Shishtawy, Nassar, & Ahmed, 2007; Nateri & Ekrami, 2010; Shams-Nateri, 2010). However, there are some problems in the practical application for cellulose fabric. Its solubility and diffusion in the printing paste is not satisfactory (Chen, 2006; Kantouch, Kantouch, & El-Sayed, 2006; Xie, Liu, & Wang, 2009). Deep red color in the high dye concentration for printing fabric may pose quality problem. Meantime, the fixation yield of Reactive Red K-2BP on cotton material is only about 70–80%. Furthermore, unfixed reactive dyes in wastewater may pose an environmental hazard (Hamaky, Tawfeek, Ibrahim, Maamoun, & Gaber, 2007; Kanik & Hauser, 2002; Wang & Wu, 2009).

In this paper, four red reactive dyes with different number sulfonate groups based on 1-naphthol-8-amino-3,6-disulfonic acid were synthesized. Their chemical structures and printing properties for cotton fabric were investigated and compared.

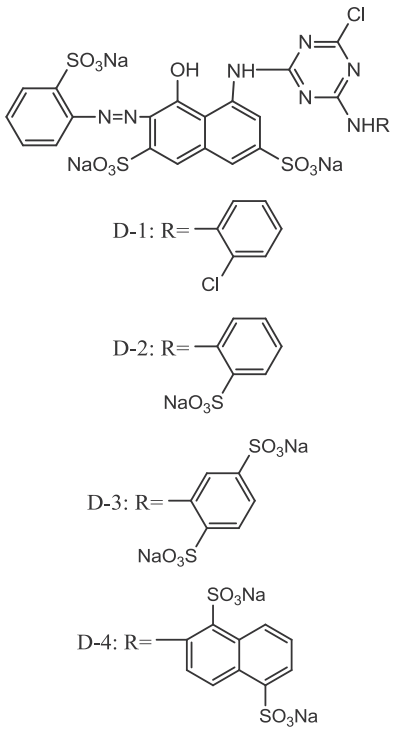
2. Experimental

2.1. Materials

1-Naphthol-8-amino-3,6-disulfonic acid (H-acid), 2-sulfonic acid aniline, and trichlorotriazine were obtained from Wujiang Taoyuan Chemical Company, Suzhou, China. Desized, scoured and bleached cotton fabric, weight 230 g/m^2, was obtained from Shaoxing Jinqiu Textile Company, Shaoxing, China. Other chemicals used were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

* Corresponding author. Tel.: +86 21 6779 2413; fax: +86 21 6237 8392.
E-mail address: klxie@dhu.edu.cn (K. Xie).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.09.107



Scheme 1. Chemical structures of the designed red reactive dyes.

2.2. Synthesis of the reactive dyes

Chemical structures of the designed red reactive dyes with different number sulfonate groups are shown in Scheme 1.

First, H-acid reacted with trichlorotriazine at 0–5 °C, pH 2–3. Then the substituted product containing dichlorotriazine group was used as coupling ingredient. The diazotization and coupling reaction were carried out in the similar way as described in the previous study (Wang & Wu, 2009; Xie, Liu, & Li, 2007a). The obtained azo dyes containing dichlorotriazine as the intermediate further reacted with aniline derivates (Xie et al., 2007a; Xie, Liu, & Li, 2007b). The synthesized red reactive dyes based on different substituted compounds, 2-choloro-aniline, 2-sulfonic acid aniline, 2,5-disulfonic acid aniline, or 1,5-disulfonic acid-2-amino-naphthalene, were named as D-1, D-2, D-3, D-4, respectively. The purification was achieved by recrystallization with alcohol, and then dried. FTIR spectrum of the dyes was measured by a OMNI 98 Sampler of the Nexus-670 FTIR-Raman Spectrometer (Nicolet Analytical Instruments, Madison, WI). ^{1}H NMR spectrum was recorded on a Bruker Avance 400 (Bruker Co., Faellanden, Switzerland).

D-1: The yield was 91% and λ_{max} being 534 nm. IR (KBr, cm^{-1}): 3377, 2148, 1572, 1645, 1598, 1558, 1491, 1432, 1390, 1324, 1139, 1046, 993, 791, 753; ^{1}H NMR (D_2O, δ_H, ppm): 8.96 (s, H, —OH), 8.58(s, H, —NH), 8.14(s, H, —NH), 8.06–8.16 (m, 3H, H of naphthalene), 6.97–7.29 (m, 7H, Ar–H), 7.50–7.79 (m, 2H, Ar–H).

D-2: The yield was 87% and λ_{max} being 533 nm. IR (KBr, cm^{-1}): 3342, 2341, 2100, 1786, 1648, 1566, 1485, 1437, 1354, 1327, 1214, 1090, 1049 994, 797; ^{1}H NMR (D_2O, δ_H, ppm): 9.37 (s, H, —OH), 8.78(m, 2H, —NH), 7.89–8.06 (m, 3H, H of naphthalene), 7.08–7.40 (m, 7H, Ar–H), 7.55–7.89 (m, 2H, Ar–H).

D-3: The yield was 89% and λ_{max} being 533 nm. IR (KBr, cm^{-1}): 3372, 2259, 2094, 1670, 1545, 1485, 1325, 1250, 1122, 1056, 978, 800, 624; ^{1}H NMR (D_2O, δ_H, ppm): 9.17 (s, H, —OH), 8.24–8.25(m, H, —NH), 8.01–8.07 (m, 3H, H of naphthalene), 7.28–7.57 (m, 7H, Ar–H), 7.58–7.97 (m, 2H, Ar–H).

D-4: The yield was 84% and λ_{max} being 532 nm. IR (KBr, cm^{-1}): 3303, 2263, 2097, 1794, 1647, 1555, 1485, 1383, 1324, 1246, 1046, 978, 800, 764; ^{1}H NMR (D_2O, δ_H, ppm): 9.07 (s, H, —OH), 8.77–8.98(m, H, —NH), 8.08–8.13 (m, 3H, H of naphthalene), 7.16–7.46 (m, 7H, Ar–H), 7.66–7.99 (m, 2H, Ar–H).

2.3. Preparation of the printing paste

The printing paste of the reactive dyes was prepared according to the following recipe: sodium alginate 60 g, reactive dye 80 g, resists salt (sodium 3-nitrobenzenesulfonate) 10 g, urea 50 g, a certain amount of sodium bicarbonate and water, for a total recipe of 1000 g.

2.4. Printing technique

A screen printing technique according to the previous described method was applied to cotton fabric (Xie et al., 2009). The fixation of the printed samples was carried out by steaming using an automatic thermostatic oven, Mathis CH-8156 (Wenner Mathis Co., Switzerland). Steaming was conducted at 102–105 °C for 12 min.

The printed fabrics were washed according to the following washing procedure: cold rinsing 5 min at 20 °C; warm washing 5 min at 40 °C; hot washing 10 min at 85 °C with the addition of nonionic surfactant OP-10, 1 g/l; warm washing 5 min and neutralizing at 40 °C with the addition of acetic acid, 0.5 g/l; and cold rinsing 5 min at 20 °C. The liquor ratio was 1:10 for the entire washing procedure. The washed samples were dried.

In order to determine the extent of dye fixation, the printed fabrics after washing were further extracted with aqueous solution of 50% DMF at 100 °C for 15 min and then rinsed with water and dried.

2.5. Color yield analysis

The color yield (K/S) of the printed fabric was determined by Datacolor SP600$^+$ spectrophotometer (Datacolor, Switzerland). The tristimulus values X, Y and Z of the samples were measured under illuminant D_{65} using the 10° standard observer in the spectrum visible region 360–700 nm. The color parameters L, a, b, were calculated. The reflectance at the wavelength of maximum absorption (λ_{max}) was used to calculate the color yield of the printed fabrics by the Kubelka-Munk Equation (Eq. (1)).

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where K is the absorption coefficient of the substrate, S is the scattering coefficient of the substrate and R is the reflectance of the printed fabric at λ_{max}.

2.6. Measurements of dye fixation and penetration

The extent of reactive dye fixation (F%) was determined and calculated using Eq. (2) (Ahmed, Youssef, El-Shishtawy, & Mousa, 2006). The method assumes that K/S value is proportional to the concentration of dye on fabric at the dye concentration employed.

$$F\% = \frac{(K/S)\ \text{after}_{DMF}}{(K/S)\ \text{after}_{soaping}} \times 100\% \quad (2)$$

where K/S after$_{soaping}$ and K/S after$_{DMF}$ are the K/S values of the printed fabrics before and after extracted with aqueous solution of 50% DMF, respectively.

Table 1
Printing properties of the reactive dyes on cotton fabric.

	λ_{max} (nm)	K/S	$\Delta K/S$	F (%)	P (%)	ΔE
D-1	534	27.87	0	93.20	4.51	0.26
D-2	533	27.47	−0.40	93.26	7.06	0.19
D-3	533	25.89	−1.98	95.16	8.85	0.21
D-4	532	26.13	−1.74	99.47	11.35	0.20

The penetration percent (P%) was calculated according to Eq. (3).

$$P\% = \frac{(K/S)_b}{(K/S)_f} \times 100\% \quad (3)$$

where $(K/S)_b$ and $(K/S)_f$ are the K/S values of non-printed back face and printed front face of fabric, respectively. The higher the percentage penetration is, the greater the extent of dye penetration is.

2.7. Wettability and fastness properties of the printed fabrics

Wettability of dyeing cotton was monitored. Three specimens in one group were tested. The length of specimen was 300 mm and the width was 50 mm. Three specimens in one group were hanged. The bottoms of samples were immersed in the distilled water at room temperature. After 30 min, the length of specimens with water was measured. The mean value of three specimens was calculated.

Color fastness was evaluated according to the respective international standards: fastness to washing, ISO 105-C03 (1989); fastness to perspiration, ISO 105-E04 (2009); fastness to rubbing, ISO 105-X12 (2003).

3. Results and discussion

3.1. Synthesis and printing properties of the red reactive dyes

In order to investigate the relationship between chemical structures and printing properties for cotton fabric, the reactive dyes with different number sulfonate groups were designed and synthesized. The synthesized red dyes, based on different substituted compounds, had different number sulfonate groups. D-1 had three sulfonate groups and D-2, D-3, D-4 had 4, 5, 5, sulfonate groups, respectively. UV–Vis spectra of the four reactive dyes were measured. It indicates that UV–Vis spectra of the four red reactive dyes were similar and the λ_{max} of them were 534 nm, 533 nm, 533 nm, 532 nm, respectively, H_2O as solvent.

A screen printing technique using the four red reactive dyes was applied to cotton fabric. According to the recipe of printing paste: sodium alginate 6%, reactive dye 8%, resist salt 1%, urea 5%, sodium bicarbonate 1.5%, steaming temperature was 102–105 °C and steaming time being 12 min. The color yield, fixation and penetration properties of the printed fabric were determined and listed in Table 1.

Table 1 demonstrates that K/S values decreased with the increase of sulfonate groups from D-1 to D-3. The number of sulfonate groups of D-4 was the same as that of D-3, just naphthalene instead of benzene ring. K/S value of D-4 was slightly higher than that of D-3. However, fixation (F%) of the four reactive dyes increased with the increase of sulfonate groups from D-1 to D-4. It can be seen that the reactive dye with numerous sulfonate groups had higher solubility in the paste, such as D-2, and D-3. Meantime, the penetrations (P%) of the reactive dyes on cotton fabric increased with the increase of sulfonate groups from D-1 to D-4. Comparison to printing properties of the reactive dyes, $\Delta K/S$ value of the printed cotton fabric with the dye having excellent solubility was lower, such as D-3. The results show that D-4 had higher color yield and good fixation and penetration. The mean color differences (ΔE) on five points could represent leveling properties and penetration uniformity of reactive dyes on cotton fabric. The color differences (ΔE) were calculated using the measured values of CIELAB (Eq. (4)).

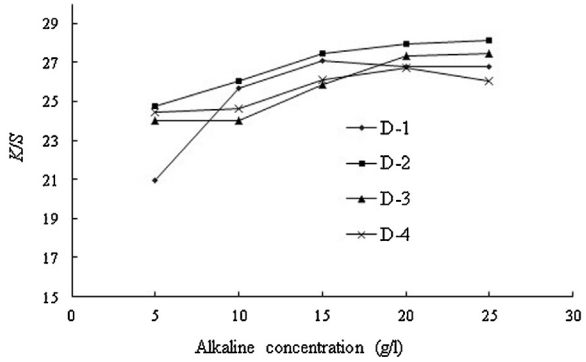


Fig. 1. Effect of alkaline on color yield of the reactive dyes on cotton fabric.

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (4)$$

ΔL, Δa and Δb are the difference in the color parameters of the printed fabrics. Mean values of color differences (ΔE) on five points were calculated.

The mean color differences (ΔE) of the four red reactive dyes indicate that D-2, D-3, D-4 had lower color differences than that of D-1. It also shows that the reactive dye with numerous sulfonate groups had good leveling properties and penetration uniformity.

3.2. Effect of alkaline on printing properties of cotton fabric

It is well known that the reaction and fixation between cellulose fiber and reactive dyes take place under the alkaline condition. Sodium bicarbonate is an important compound for printing fixation on cotton fabric.

The effect of sodium bicarbonate on the color yield (K/S) and fixation are shown in Figs. 1 and 2, respectively. It can be seen that K/S and fixation (F%) of the four reactive dyes increased with the increase of the concentration of sodium bicarbonate. The K/S and F% of D-1 on cotton fabric were lower than those of the other three reactive dyes at sodium bicarbonate 5 g/l. The reactive dye with fewer number sulfonate groups was sensitive to alkaline.

3.3. Effect of urea on printing properties

Urea is common compound in reactive dyes printing paste. Its main functions are an increase in the solubility of dye in the

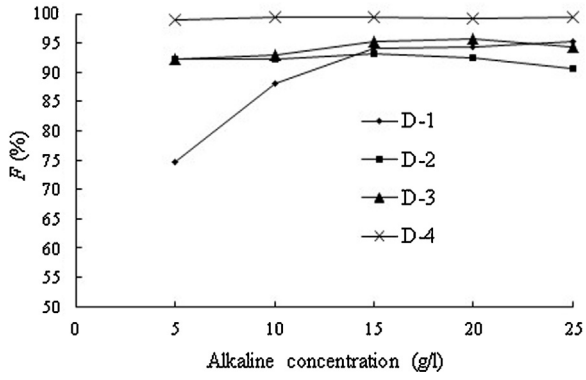


Fig. 2. Effect of alkaline on the fixation of the reactive dyes on cotton fabric.

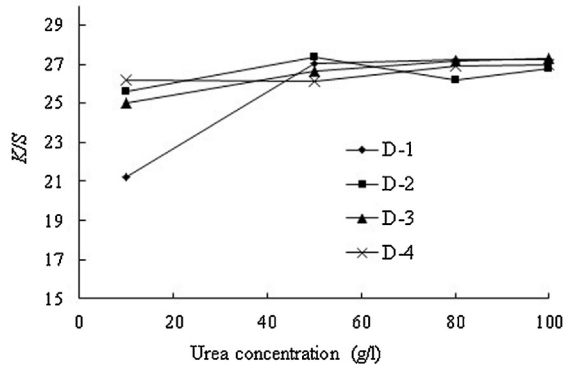


Fig. 3. Effect of urea on color yield of the reactive dyes on cotton fabric.

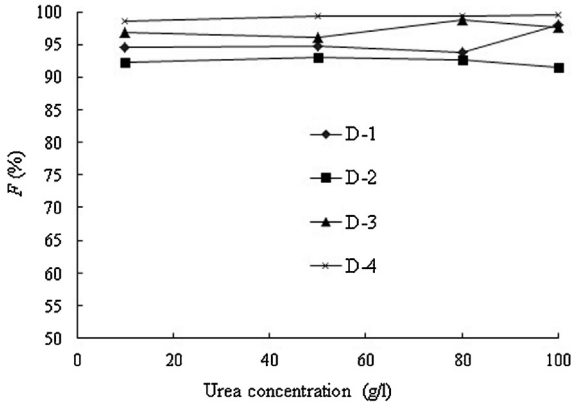


Fig. 4. Effect of urea on fixation of the reactive dyes on cotton fabric.

reaction medium, dye disaggregation, retardation of water evaporation during drying and swelling of cotton fiber in the printing process. The effect of urea concentration on the color yield (K/S) and fixation are shown in Figs. 3 and 4, respectively. Fig. 3 indicates that K/S of D-1 increased with the increase of urea concentration. Urea improved the solubility of D-1 in the reaction medium. The K/S values of D-2, D-3, D-4 had slight change with the urea concentration. Fig. 4 demonstrates that the fixations of the four reactive dyes were not obviously affected by the urea concentration. It is possible to print cotton fabric urea-free using the reactive dyes with numerous sulfonate groups. The use of urea could pose ecological and environmental problems associated with the high nitrogen content of the printing effluent (Ahmed et al., 2006; Kumbasar, 2007).

3.4. Color data of the printed fabrics

The colorimetric data of the printed fabrics with the four reactive dyes were measured and shown in Table 2. L^* is corresponding to the brightness, a^* to the red–green coordinate and b^* to the yellow–blue coordinate. As a whole, a combination of all these parameters enables one to understand the tonal variations. The L^* values of D-2, and D-3 were lower than that of D-1. L^* value of D-4 was similar to that of D-1. Color (C^*) of the four reactive dyes are similar to the situation of L^* values. It indicates that colors of D-2, and D-3 were slightly darker than that of D-1. Redness/greenness (a^*) values of D-2, and D-3 slightly decreased. Yellowness/blueness (b^*) values of D-2, D-3, D-4 were lower than that of D-1. In general, color shades of the four reactive dyes were similar both equipment and visual.

Table 2
Colorimetric data of the printed cotton fabrics.

Samples	L^*	a^*	b^*	ΔL	Δa	Δb	C^*
D-1	36.28	58.18	31.25	0	0	0	66.04
D-2	34.29	55.66	29.63	−1.99	−2.52	−1.62	63.06
D-3	34.96	56.98	30.19	−1.32	−1.2	−1.06	64.49
D-4	36.32	59.43	29.44	0.04	1.25	−1.81	66.32

Table 3
Wettability and fastness properties of the printed fabrics.

	Wettability (cm)	Fastness to rubbing		Fastness to washing		Fastness to perspiration	
		Dry	Wet	SC	SW	SC	SW
D-1	9.5	4–5	3–4	4	3–4	3–4	3–4
D-2	9.7	5	4	4	4	3–4	3–4
D-3	9.9	5	4	4	4	3–4	3–4
D-4	9.8	4–5	4	3–4	4	3–4	3–4

SC = staining on cotton; SW = staining on wool.

3.5. Wettability and fastness properties of the cotton fabrics printed

The wettability and fastness properties of the cotton fabric printed with the four reactive dyes are summarized in Table 3. Wettability properties of all cotton fabrics printed with four dyes were excellent. Wet rubbing and washing fastnesses of the printed samples with D-2, D-3, D-4 were slightly better than those of D-1. Perspiration fastness of D-2, D-3, D-4 was the same as D-1. This can be explained by the fact that the reactive dyes with numerous sulfonate groups have higher solubility and lower affinity for cotton fabrics. The unfixed reactive dyes and hydrolyzed dyes are easy to be washed away to improve wet fastness.

4. Conclusions

Four red reactive dyes based on 1-naphthol-8-amino-3,6-disulfonic acid had different number sulfonate groups. UV–Vis spectra and λ_{max} of the four reactive dyes were similar. Wettability of all cotton fabrics printed with four dyes was excellent. However, their printing properties were different. K/S values decreased with the increase of sulfonate groups from D-1 to D-3. The fixations and penetrations of the reactive dyes on cotton fabrics increased with the increase of sulfonate groups from D-1 to D-4. D-4, 1,5-disulfonic acid-2-amino-naphthalene instead of 2,5-disulfonic acid aniline, had higher color yield and good fixation and penetration. The reactive dye with fewer number sulfonate groups was sensitive to alkaline. The fixations of the four reactive dyes were not obviously affected by urea concentration. The reactive dye with numerous sulfonate groups had higher solubility in the paste and lower affinity for cotton fabrics. The reactive dye with numerous sulfonate groups have potential application in printing urea-free for cellulose fabric.

References

Ahmed, N. S. E., Youssef, Y. A., El-Shishtawy, R. M., & Mousa, A. A. (2006). Urea/alkali-free printing of cotton with reactive dyes. *Coloration Technology*, *122*, 324–328.
Chen, R. (2006). Review on printing dyes. *Textile Auxiliaries (Chinese)*, *23*, 1–11.
El-Shishtawy, R. M., Nassar, S. H., & Ahmed, S. E. N. (2007). Anionic colouration of acrylic fiber. Part 2: Printing with reactive, acid and direct dyes. *Dyes and Pigments*, *74*, 215–222.
Hamaky, Y. H. E., Tawfeek, S., Ibrahim, D. F., Maamoun, D., & Gaber, S. (2007). Printing cotton fabrics with reactive dyes of high reactivity from an acidic printing paste. *Coloration Technology*, *123*, 365–373.
Hebeish, A. A., Ragheb, A. A., Nassar, S. H., Allam, E. E., & Abd El Thalouth, J. I. (2006). Technological evaluation of reactive cyclodextrin in cotton printing with reactive and natural dyes. *Journal of Applied Polymer Science*, *102*, 338–347.
Hou, A., & Sun, G. (2013). Multifunctional finishing of cotton with 3,3′,4,4′-benzophenone tetracarboxylic dianhydride: Reaction mechanism. *Carbohydrate Polymers*, *95*, 768–772.

Jung, A., Wolters, B., & Berlin, P. (2007). (Bio)functional surface structural design of substrate materials based on self-assembled monolayers from aminocellulose derivatives and amino(organo)polysiloxanes. *Thin Solid Films*, *515*, 6867–6877.

Kanik, M., & Hauser, P. J. (2002). Printing of cationised cotton with reactive dyes. *Coloration Technology*, *118*, 300–306.

Kanik, M., & Hauser, P. J. (2003). Ink-jet printing of cationised cotton using reactive inks. *Coloration Technology*, *119*, 230–234.

Kantouch, A., Kantouch, F., & El-Sayed, H. (2006). Surface modification of wool fabric for printing with acid and reactive dyes. *Coloration Technology*, *122*, 213–216.

Kumbasar, E. P. A. (2007). Mixture printing pastes from high substituted guar gum and alginates on reactive printing of viscose. *Journal of Applied Polymer Science*, *103*, 745–751.

Lewis, D. M. (2001). Recent developments in reactive dyes: Chemistry and application processes. *Advances in Color Science and Technology*, *4*, 41–48.

Nateri, A. S., & Ekrami, E. (2010). Dye binary mixture formulation by means of derivative ratio spectra of the Kubelka–Munk function. *Color Research and Application*, *35*, 193–199.

Shams-Nateri, A. (2010). Prediction of dye concentrations in a three-component dye mixture solution by a PCA-derivative spectrophotometry technique. *Color Research and Application*, *35*, 29–33.

Wang, Z., & Wu, Z. (2009). A study of novel bisazo reactive red dyes with good wet fastness. *Coloration Technology*, *125*(4), 216–221.

Xie, K., Liu, Y., & Li, X. (2007a). Synthesis and properties of the novel surface-active dyes containing fluorocarbon groups: Part 1. Synthesis and dyeing properties of the novel surface-active dyes on silk fabric. *Materials Chemistry and Physics*, *105*, 199–203.

Xie, K., Liu, Y., & Li, X. (2007b). Synthesis and properties of the novel surface-active dyes containing fluorocarbon groups: Part 2. Dyeing diffusion kinetics of the novel surface-active dyes on silk fabric. *Materials Chemistry and Physics*, *105*, 204–207.

Xie, K., Liu, H., & Wang, X. (2009). Surface modification of cellulose with triazine derivative for improving printability with reactive dyes. *Carbohydrate Polymers*, *78*, 538–542.

Xie, K., Gao, A., & Zhang, Y. (2013). Flame retardant finishing of cotton fabric based on synergistic compounds containing boron and nitrogen. *Carbohydrate Polymers*, *98*, 706–710.