

# Leaching and Fastness Behavior of Cotton Fabrics Dyed with Different Type of Dyes Using Sol-Gel Process

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**ABSTRACT:** Cotton fabrics were dyed with reactive, direct, and basic dyes by sol-gel process and exhausting process. As to this aim, the solutions of reactive, direct, and basic dyes were prepared by sol-gel process and then cotton fabrics were treated at 80°C for 10 min with these solutions and dried at 120°C for 20 min. Dyeing solutions contained tetraethyl orthosilicate and 3-glycidoxypropyl-trimethoxysilane as precursor, ethanol and water as solvent for sol-gel process. The wash fastness, light fastness, rubbing fastness and the degree of leaching, the light fading value, and dyeing yield of dyeings were evaluated. Moreover, the effect on dyeing yield, fastnesses, leaching, and fading properties of adding of sodium acetate trihydrate in dyeing solutions for sol-gel process was firstly studied. It was found that the dyeing yield of dyed cotton fabrics with the direct dyes significantly improved with using sol-gel process with adding

sodium acetate trihydrate in comparison with exhausting process. The color fastness values to washing and to light of the basic dyeing increased with using sol-gel process without adding sodium acetate trihydrate in comparison with exhausting process. The degree of leaching of dyed fabrics with the basic and reactive dyes decreased with using sol-gel process with adding sodium acetate trihydrate in comparison with exhausting process. The light fading value of dyed cotton fabrics with the basic and direct dyes after 120 h irradiation decreased with using sol-gel process with adding sodium acetate trihydrate in comparison with exhausting process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 97–105, 2008

**Key words:** coatings; thin films; solution properties; gels; dyes/pigments

## INTRODUCTION

Direct dyes are water-soluble, contain anionic substituents, have good substantivity to cellulose (especially cotton), and sorption characteristics with usually governed by accessibility of the fibers and/or Langmuir-type isotherms. Most direct dyes have azo structure, particularly in the disazo and trisazo chemical classes. Addition of salts or electrolytes, such as sodium sulfate or sodium chloride, promotes exhaustion of these dyes on cotton. There is still some dispute whether or not the sorption isotherm of these dyes is due to hydrogen bonding or is due to van der Waals' forces. Added electrolytes neutralize the negative charge of the cellulosic fiber that would repel a direct dye anion, and thus promote exhaustion, binding of the dye onto the fiber surface and facilitate diffusion of it into the fiber pores.<sup>1</sup> Direct dyes are one of the most popular dye classes used on cotton and its blends. They offer such advantages as wide color ranges, excellent dye penetration, low cost, short dyeing time, and dyeing stability at boiling temperature, etc. Direct dyes have the advantage that they can be directly applied to

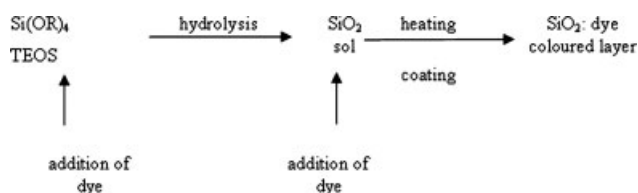
cotton fabrics by simple means, however, their fastness to wet processing, particularly wash fastness, is poor. This may be due to their strong hydrophilicity and penetration of dyes inside the fiber as there is no chemical bond formation between the dyes and cotton.<sup>2</sup>

Reactive dyes also contain anionic substituents with sulfonic acid groups to increase their solubility in water, chromophoric groups or systems, and a linking group to an electrophilic structure that contains a good leaving group (halogen, sulfate, or methanesulfonate). They become substantive to fiber by covalent bond formation. Reactive dyes have high color fastness values to particularly wash fastness because of covalent bonding with dyes and cotton.

Basic dyes are water-soluble and contain cationic groups. The positive charge on the dyes may be localized on a quaternary ammonium group or delocalized over the entire aromatic structure (such as in triarylmethanes, methines, xanthenes, and other heterocyclic systems). These dyes are applied primarily to acrylics and occasionally to polyester and polyamide fibers. Although basic dyes gave brilliant colors on wool, silk, and cellulosic fibers, they had poor fastness properties on these types of fibers.<sup>1</sup>

Dyes bond to textile materials with Van-der Waals forces, ionic, covalent bonding, and apolar interactions etc. depending on the types of dyes and sub-

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**Figure 1** Schematic drawing of sol-gel layer formation.<sup>9</sup>

strates for dyeings with exhausting processes. In the case of sol-gel processing, dyes can be embedded into sol-gel coatings and deposited on textile materials. Sol-gel technique allows different dyes to be embedded in modified silica matrices.<sup>3–6</sup>

Sol-gel process generally involves the use of metal alkoxides which undergo hydrolysis and polymerization reactions to give gels. The rates of the various reactions and the properties of the final material depend on, among others, the precursor used, pH of the precursor solution, the water concentration, and temperature.<sup>7</sup>

To produce silica coatings by a sol-gel process, hydrolysis of an alkoxysilane precursor tetraethyl orthosilicate (TEOS) is firstly performed. The products of hydrolysis are silica particles of low to medium crosslinking in solution, which can form silica layers during a coating and annealing process.<sup>8</sup> For embedding dyes in such silica coatings, the dye can be dissolved in the solution before hydrolysis or in the already prepared silica sol (Fig. 1). In principle, the dye molecules are immobilized during the coating procedure, so there should be no difference if the dye is dissolved before or after hydrolysis. Depending on the dye and the composition of the matrix, the dye can be fully immobilized into the silica network to yield high wash fastness.<sup>5,6,9–11</sup>

Moreover, wash fastness is a particular requirement for textiles. Light fastness and leaching stability of dyed coatings are essential for long-term and outdoor applications.<sup>2,6,12,13</sup> Modifying dye solutions with crosslinkable silane compounds further improves the leaching (and also the photobleaching) fastness of those dyes.<sup>14</sup> Increased light fastness was reported after incorporation into a silica matrix.<sup>9,15–17</sup> Up to now, only few articles have reported on textile dyeing using of the sol-gel technique.<sup>6,9,14</sup>

Mahlting et al. coated polyester, polyamide, and cotton fabric by acidic sol-gel process with using cationic dye Malachite Green (MG) and anionic dye Guinea Green (GG). They found that the use of silica matrices for coloration led to improved washing fastness on the three types of textiles (polyester, polyamide, cotton) as compared with the samples dyed without any silica sol for all dyes investigated. They reported that the dyes were probably more immobilized within silica network than within the fiber, so the wash fastness is improved. The reduction of

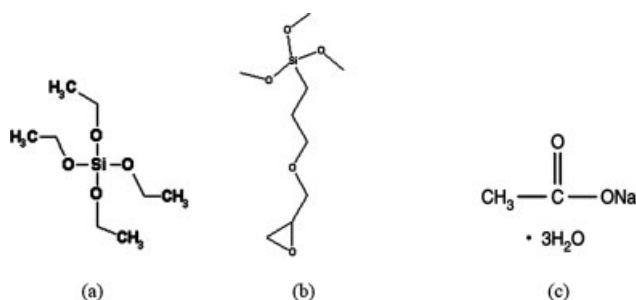
leaching was especially significant with the positively charged dye. In contrast to the positively charged triarylmethane dyes, the negatively charged dye molecules reveal a lower affinity to silica and together with the high solubility of this dye in aqueous solutions a higher degree of leaching as compared with results for anionic dye. In the case of coloration of cotton material, dye bleaching (degree of fading) with silica coating is reduced for cationic dye and anionic dye for 120 h bleaching compared without silica coating, if the dye is embedded into the silica coating compared with the colored textile without silica.<sup>13</sup>

Mahlting and Textor demonstrated that the application together with the silica sol or the aftertreatment of dyed textile with silica sol lead to significant improvement of leaching fastness. Also, the low bleaching fastness (degree of fading) of the triphenylmethane dyes (Malachite Green and Guinea Green) can be enhanced significantly. It made no significant difference for leaching fastness whether the dye is embedded into the silica coating (method D) or the once dyed fabric is coated by silica (method C) but in case of method C the color degree is higher. In case of the separately application of firstly sol and secondly dye (method B), they proposed that the dye molecules should be placed on the surface of the silica coating and are not embedded, so the decrease in leaching was only small.<sup>18</sup>

In this study, the embedding of three dyes with different class (Sirius Red F3B as direct dye, Maxilon Yellow GL 200% as basic dye, and Cibacron Red FN-R as reactive dye) into silica coatings deposited on the cotton fabric was investigated. The silica coatings were prepared using a sol-gel processes started from the precursors TEOS and 3-glycidoxypropyl-trimethoxysilane (GPTS). The dyeing yield, wash fastness, light fastness, rubbing fastness and the degree of leaching, and the light fading value of dyeings were evaluated. Moreover, the effect on dyeing yield, fastnesses, leaching, and fading properties of adding sodium acetate trihydrate in dyeing solutions for sol-gel process was firstly studied.

## METHODS

Scoured and bleached 100% plain-weave cotton fabrics (weight 126 g/m<sup>2</sup>, 17 picks/cm, 21 ends/cm) with dimensions of 10 × 10 cm<sup>2</sup> were used in this research. All chemicals used were reagent grade. The solutions were firstly prepared by mixing TEOS, C<sub>8</sub>H<sub>20</sub>O<sub>4</sub>Si (Fluka, 98%) with water and ethanol (C<sub>2</sub>H<sub>5</sub>OH) (96%, Iron Chemistry, Turkey). The pH value of the solution was measured at pH 6.52. The pH of solutions was measured using pH Meter (WTW Inolab, Germany). Secondly, sodium acetate



**Figure 2** Chemical formula of (a) TEOS, (b) GPTS, and (c) sodium acetate trihydrate.

trihydrate ( $\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ ) (powder, Horasan Chemistry, Turkey) was added if required and then GPTS ( $\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$ , 98%, Aldrich) and dyes were added (Fig. 2). Dyes were added in the solution before hydrolysis. In principle, the dye molecules are immobilized during coating process, so there should be no difference if the dye is dissolved before or after hydrolysis.<sup>12</sup> The molar ratio of TEOS: Ethanol :  $\text{H}_2\text{O}$  : GPTS : Na-acetate trihydrate was 0.49 : 8.6 : 17.8 : 0.18 : 0.018. This modified silica sol was prepared as described in literature.<sup>12</sup> These solutions were vigorously stirred for 10 min at magnetic mixer at room temperature in air. Transparent solutions were obtained. The used recipe to prepare the sols was given in Table I. After the adding of GPTS, the pH of solution did not change. After the adding of sodium acetate trihydrate, the pH of solution was measured at 7.81. GPTS is a crosslinking compound that is able to perform different kinds of reactions during sol-gel process.<sup>12</sup> Bath ratio of solutions was prepared as 1 : 50 (fabric : solution). Sirius Red F3B (C.I. Direct Red 80) as direct dye, Maxilon Yellow GL 200% (C.I. Basic Yellow 45) as basic dye, and Cibacron Red FN-R (C.I. Reactive Red 238) as reactive dye were used in this study. The chemical composition of dyes displayed in Figure 3. The dyes were exhausted by the fabrics at 80°C for 10 min using WB 14 Model-Memmert water bath and then the fabrics were squeezed using a Rapid Fulard (Model P-A1, Labortex, Taiwan) with pick up of about 87% at a nip pressure of 2 kg/cm<sup>2</sup>. The fabrics were dried at 120°C for 20 min using Nuve KD400 Oven (Turkey). Mahltig et al studied annealing conditions for 1 h at 120°C.<sup>12,13,18</sup> However, we studied for only 20 min at 120°C after exhausting for 10 min at 80°C. Figure 4(a) showed the flow chart of dyeing with sol-gel process. Dyeing with exhausting process was defined as E symbol, while dyeing using of TEOS and GPTS with sodium acetate trihydrate by sol-gel process was defined as TN symbol and dyeing using of TEOS and GPTS without sodium acetate trihydrate by sol-gel process was defined as T symbol.

After dyeing with sol-gel processes and exhausting process, the fabrics were treated as washing off

procedure, which was recommended by CIBA Specialty Chemicals. The procedure was 10 min rinsing at 50°C, 10 min neutralizing at 50°C with acetic acid, 15 min soaping at 90°C with using of 2 mL/L Arpol IV (nonionic surfactant, Argon Chemistry, Turkey), 10 min rinsing at 50°C (for dyeing with only reactive dye) and 10 min cold rinsing. Later the washed fabrics were dried at room temperature.

Dyeing with exhausting process was achieved as the recipes on Table II and the dyeing graph in Figure 4(b). All experiments of dyeing were carried out twice.

### Analysis methods

Color fastness to washing was determined according to BS EN ISO C06 at 40°C. The dyeing yields of the fabrics were determined with  $K/S$  values at wavelength obtained maximum absorption.  $K$  is the absorption of light and  $S$  is the scattering of light. The  $K/S$  values of dyed fabrics were measured by a Minolta (3200D) spectrophotometer in D65 (daylight source) and at 10° measurement angle.  $K/S$  values were calculated with following eq. (1) (Kubelka-Munk).

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

where  $R$  is the percent of remission value,  $K$  is the absorption of light, and  $S$  is the scattering of light.  $K/S$  values measured at the maximum absorption wavelength of 540, 550, and 430 nm for direct dye, reactive dye, and basic dye, respectively.

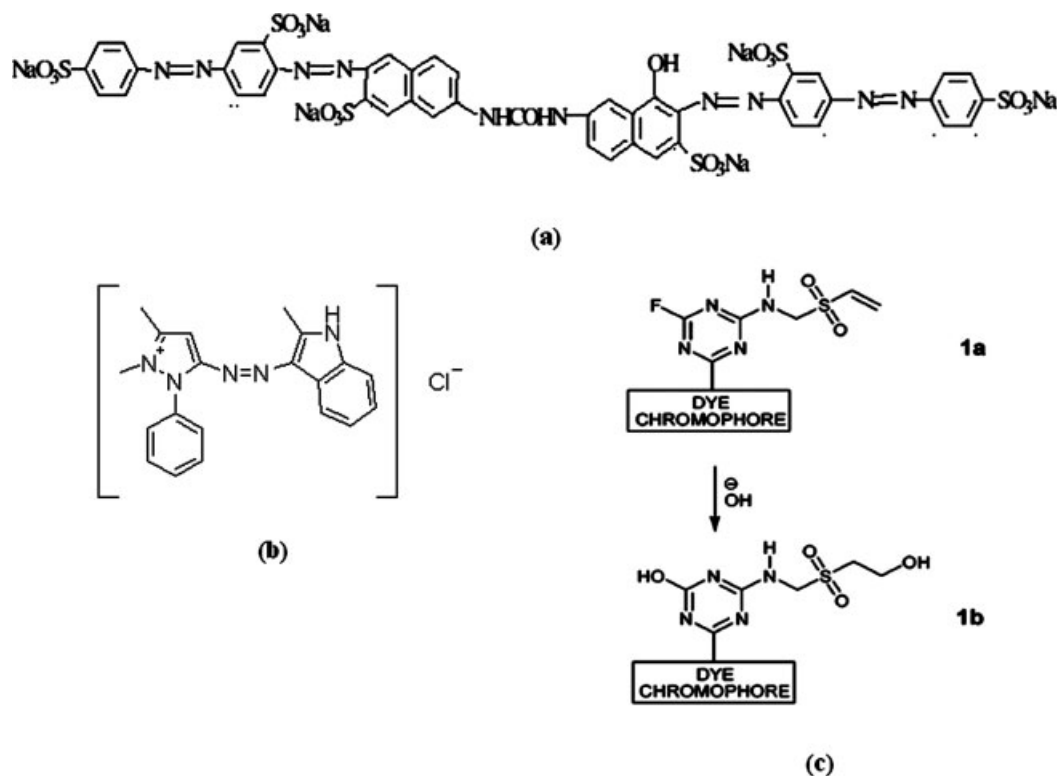
Moreover total color difference ( $\Delta E$ ) values between dyed fabrics by exhausting process and by sol-gel process were calculated from values of  $L^*$ ,  $a^*$ , and  $b^*$  of CIELAB system as eq. (2).

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

where  $\Delta E$  is the total color difference between reference and sample,  $\Delta L^*$  is the difference of lightness coordinates between reference and sample,  $\Delta a^*$  is the difference of redness–greenness coordinates between reference and sample, and  $\Delta b^*$  is the difference of yellowness–blueness coordinates between reference and sample.

**TABLE I**  
The Recipe Used in the Sols Preparation

Chemical agents	Recipe
TEOS	11 cm <sup>3</sup>
Ethanol	50 cm <sup>3</sup>
H <sub>2</sub> O (distillated)	32 cm <sup>3</sup>
GPTS	4 cm <sup>3</sup>
Sodium acetate trihydrate (if required)	0.2457 g
Dye (on weight of fabric, o.w.f.)	4%



**Figure 3** The chemical composition of dyes: (a) C.I. Direct Red 80,<sup>19</sup> (b) C.I. Basic Yellow 45,<sup>20</sup> (c) C.I. Reactive Red 238.<sup>21</sup>

Leaching stability of dyeing was evaluated with reflection curve of dyed fabrics before and after washing according to washing conditions on BS EN

ISO C06 standard with 150 mL of 5 g/L European Color Fastness Establishment (ECE) phosphate reference detergent (B) (without optical brightening



**Figure 4** Flow charts of dyeing with (a) sol-gel process, (b) exhausting process.

agent) at 45 rpm, 60°C for 3 h using Linitest Plus (Atlas Material Solutions, Germany). In this study, we used especially strong washing condition to get a better view of improvements in wash fastness with the sol-gel processing. The reflection values of the fabrics were also measured by a Minolta (3200D) spectrophotometer. The degree of leaching  $L$  (in %) was calculated analogous to Ref. 6 from the most significant minimum of the reflectance spectrum using the eq. (3).

$$L = \frac{100(r_A - r_B)}{(100 - r_B)} \quad (3)$$

where  $r_B$  represents the reflectance before and  $r_A$  the reflectance after the leaching tests (a value of  $L = 100\%$  corresponds to a completely decolorized fabric, whereas  $L = 0$  means the originally dyed material). The physical meaning of this leaching determination is illustrated by Figure 5.

The light fading (LF) tests were performed with a Xenotest Alpha HE (EtkiSti, Istanbul, Turkey). All textiles were exposed for 20 and 120 h in the Xenotest, and the percentage of faded dye LF was determined by means of a Minolta (3200D) spectrophotometer analogously to the leaching test [Eq. (3)]. A value of 100% for the light fading means that fabric was completely decolorized when measured at the absorption maximum of the dyeing.<sup>3</sup> The test method is closer to the photochemical behavior of the dyestuff than the use of a gray or blue scale. A light fading value of 5% (after 20 h irradiation) or 12% (after 120 h irradiation) measured by reflectance on the fabric corresponds to a light fastness scale classification of 4–5 compared with the DIN blue scale standard.<sup>12</sup>

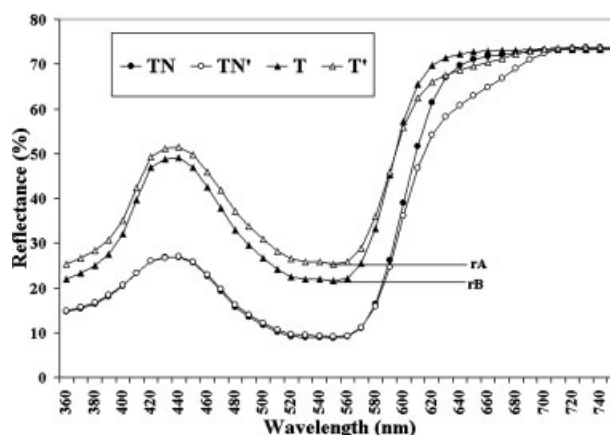
A statistical analysis of the  $K/S$  values was evaluated with the SPSS statistic program (Chicago, IL) with a 95% confidence interval. Analysis of variance according to Duncan's test with One-Way ANOVA at the comparison of obtained  $K/S$  values of the dyed cotton fabrics with different dyeing processes was achieved ( $\alpha = 0.05$ ).

**TABLE II**  
The Recipes of Dyeing with Exhausting Process

Dye type	Recipe 1	Recipe 2	Recipe 3
	Reactive dye	Direct dye	Basic dye <sup>a</sup>
Sodium hydroxide (36 °Be)	2% (v/v)	–	–
Sodium sulphate	6% (w/v)	10% owf	5% owf
Sodium carbonate	0.5% (w/v)	2% owf	–
Dye	4% owf	4% owf	4% owf
Bath ratio	1 : 50	1 : 50	1 : 50

<sup>a</sup> pH was adjusted to 3.5 with acetic acid for dyeing solution.

o.w.f.: of weight of fabric.



**Figure 5** Method for determining leaching ( $\sim$  wash fastness) as illustrated by reflectance measurements on dyeing with C.I. Reactive Red 28 (at 550 nm): reflectance curves before and after washing. TN and T are respectively, sol-gel process with or without using sodium acetate before washing, TN' and T' are respectively, sol-gel process with or without using sodium acetate after washing.

## RESULTS AND DISCUSSION

### The effect on dyeing yield ( $K/S$ values) of dyeing by sol-gel process

The obtained average  $K/S$  values and  $\Delta E$  values of dyed fabrics with different dye types and different dyeing processes were shown on Table III. Analysis of variance according to Duncan's test with One-Way ANOVA at the comparison of obtained  $K/S$  values of dyed fabrics with different dye types and different dyeing processes was achieved ( $\alpha = 0.05$ ).

There were statistically significant differences between  $K/S$  values of dyed fabrics by different processes with direct dye according to one-way analysis of variance (Sig. 0.011) (Table IV). The obtained  $K/S$  values of dyed fabrics with direct dye with regard to dyeing process increased by following as  $TN \geq T > E$ . Average  $K/S$  value of dyed fabrics with direct dye by using sol-gel process with adding sodium acetate trihydrate was 5.93, while average  $K/S$  value of dyed fabrics with direct dye by using exhausting process was 0.95. The  $K/S$  values of samples dyed by using E method with direct dye were very low because the dyeings carried out in 1 : 50 of bath ratio at 80°C for 30 min to use the same conditions with respect to temperature and bath ratio at all dyeings which contain dyeings by using sol-gel process and exhausting process. Thus dyes were removed during washing procedure. Moreover, our other aims are to shorten the time of dyeing which is 1 or 1.5 h for conventional dyeing and is to provide dyeing at low temperature while dyeing with direct dye is carrying out at 100°C for conventional dyeing. The  $K/S$  values of samples dyed by using TN method at 80°C with concentration of direct dye

**TABLE III**  
**The Color Fastness to Washing and to Rubbing, Dyeing Yield (*K/S* values) and  $\Delta E$  Values of Dyed Fabrics with Different Type of Dyes and Different Dyeing Process**

Dye Type		Color change rating	Color staining rating	Rubbing fastness		Average <i>K/S</i> value ( $\Delta E$ value)
				Wet	Dry	
Direct dye (540 nm)	E <sup>a</sup>	4	4/5	4/5	5	0.95 (36.99)
	TN <sup>b</sup>	3/4	4/5	4	4/5	5.93 (61.43)
	T <sup>c</sup>	3/4	4/5	4	4/5	4.44 (58.29)
Reactive dye (550 nm)	E	3/4	5	5	5	3.87 (61.49)
	TN	3/4	5	4/5	5	4.28 (62.84)
	T	3/4	5	4/5	5	1.77 (46.71)
Basic Dye (430 nm)	E	1/2	3/4	4	4/5	4.46 (62.91)
	TN	3/4	4/5	4/5	5	2.23 (54.47)
	T	3/4	4/5	4/5	5	3.03 (57.49)

<sup>a</sup> E is dyeing with exhausting process.

<sup>b</sup> TN is dyeing with sol-gel process using of TEOS and GPTS with sodium acetate trihydrate.

<sup>c</sup> T is the dyeing with sol-gel process using of TEOS and GPTS without sodium acetate trihydrate.

of 4% owf were very high in comparison with that of E method. Thus we provided dyeing with high *K/S* values at short time and low temperature by sol-gel process.

There were statistically significant differences between *K/S* values of dyed fabrics by different processes with reactive dye according to one-way analysis of variance (Sig. 0.031) (Table V). The obtained *K/S* values of dyed fabrics with reactive dye with regard to dyeing process increased by following as  $TN \geq E > T$ . It was found that the difference of average *K/S* values of dyed fabrics with direct dye by using exhausting process (3.87) and sol-gel process with adding sodium acetate trihydrate (4.28) was not significant. There was significant difference between average *K/S* values of dyed fabrics with reactive dye by using sol-gel process with (4.28) and without (1.77) adding sodium acetate trihydrate.

Takahashi et al. reported that the higher the pH in aging are the larger the volume and size of mesopores become.<sup>22</sup> Moreover, Panitz and Geiger found that the dye retaining capacity of the xerogel increases with increasing pore size.<sup>10</sup> Thus to study at basic pH such as 7.81 may be caused the larger pore size and so higher dye retaining in silica xerogel in comparison with acidic hydrolysis condition in T method and earlier studies. Besides the pH

value of the sol without adding sodium acetate was 6.52. Thus higher *K/S* values of samples were obtained at the higher pH values with adding sodium acetate.

Moreover, we provided higher dye yield with partially immobilizing into silica oxide of dyes, namely with physical embedding of dye and partially with the attraction and substantivity of dyes to fibers with especially available sodium acetate as electrolyte which provide neutralization of the negative charge of the cellulosic fiber that would repel a direct or reactive dye anion, and thus promote exhaustion, binding of the dye onto the fiber surface and facilitate diffusion of it into the fiber pores.

Moreover, during exhausting at 80°C for dyeing at T and TN method, the promoting of exhaustion, binding of the dye onto the fiber surface and facilitating diffusion of it into the fiber pores could be expected for anionic dyes such as reactive and direct dyes. Thus in our study, dyes on fiber surface can be partially encapsulated in silica matrix during heat treatment at 120°C after partially binding and attraction of the dye onto the fiber surface the fiber during exhausting process at 80°C to further improve the leaching fastness properties of dyeings.

It was determined that there were not statistically significant differences between *K/S* values of dyed fabrics by different processes with basic dye accord-

**TABLE IV**  
**The Table of Analysis of Variance with One-Way ANOVA to the Obtained *K/S* Values of Dyed Fabrics with Direct Dye by Different Dyeing Processes**

	Sum of squares	df	Mean square	F	Sig.
Between groups	26.088	2	13.044	28.439	0.011
Within groups	1376	3	0.459		
Total	27.464	5			

**TABLE V**  
**The Table of Analysis of Variance with One-Way ANOVA to the Obtained *K/S* Values of Dyed Fabrics with Reactive Dye by Different Dyeing Processes**

	Sum of squares	df	Mean square	F	Sig.
Between groups	7.282	2	3.641	13.656	0.031
Within groups	0.800	3	0.267		
Total	8.082	5			

**TABLE VI**  
**The Table of Analysis of Variance with One-Way ANOVA to the Obtained *K/S* Values of Dyed Fabrics with Basic Dye by Different Dyeing Processes**

	Sum of squares	<i>df</i>	Mean square	<i>F</i>	Sig.
Between groups	5.113	2	2.556	4.523	0.124
Within groups	1.695	3	0.565		
Total	6.808	5			

ing to one-way analysis of variance (Sig. 0.124) (Table VI).

Silica coatings contain an isoelectric point between  $pH_{IEP}$  1.5 and 4.5<sup>8</sup> and carry, therefore, a negative charge, if the washing procedure is performed at pH 7. Basic dye contains a positive net charge and could interact electrostatically the silica matrix containing a negative charge.<sup>10</sup> Because of low wash fastness on other textile materials, basic dyes are commonly only used for the dyeing of polyacryl fabrics. In this case, also the interaction between cationic dyes and negative sites in acrylic textile substrates are discussed in literature.<sup>23</sup> By improvement of the washing fastness, the sol-gel technique may enable also the use of such dyes on other textile materials. In dyeing with exhausting process, some temporary modification of the affinity is obtained by acidifying the dyebath to suppress the ionization of the acidic groups in the fibers.<sup>24</sup> The *K/S* values of dyed samples with basic dye without adding sodium acetate at pH 6.52 and that of dyed samples with exhausting process at pH 3.5 were higher than that of dyed samples with adding sodium acetate at pH 7.81. Thus we can suggest that the T method based on acidic sol-gel process was more proper for dyeing with basic dye in comparison with TN method at higher pH values with respect to dye yield results.

#### The effect on wash fastness of dyeing by sol-gel process

The investigated direct, reactive, and basic dyes contain different fastness properties due to their different electrical net charge. The wash fastness results for color change and color staining obtained by sol-gel process and exhausting process were shown in Table III. It is clear that the color fastness values to washing for color change and color staining of dyed fabrics with the direct and reactive dyes obtained using sol-gel process and exhausting process did not change with related to dyeing processes. The results were in concordance with Ref. 2. However, the color fastness values of dyed fabrics with the basic dye obtained using sol-gel process with adding sodium acetate trihydrate (TN) in comparison with exhausting process (C) increased from 1/2 to 3/4 for color change and from 3/4 to 4/5 for color staining in

concordance with Ref. 13 (see Table III). Silica is known to exhibit a negative electrical net charge at pH 7.<sup>12</sup> It can be supposed that the washing fastness improved results either by the physical embedding of the dye by the silica coating<sup>25,26</sup> and also by attractive electrostatic interactions between the positively charged dye molecules to the negatively charged silica.<sup>12,13</sup> Despite obtained the lower *K/S* values by using T and TN method, it can be observed stronger effect of physical embedding for that of TN and T method than electrostatic interaction between cationic dye molecules and negative charge of cellulosic fiber for that of E method with respect to washing fastness. In contrast to this, direct dye and reactive dye contains a negative charge, so no direct electrostatic attraction to the silica matrix can be expected.<sup>12</sup>

When the cotton fabric was treated with this sol, the wash fastness results obtained were of an acceptable level for commercially reject/accept limit (Table III). It is presumed that the colloidal particles formed a network on the cotton fiber and the dye molecules were fixed into this network. The results indicate that GPTS gels fix onto the surface of the sample firmly, which may prove indirectly chemical reactions between the gel and the fiber do exist.<sup>2</sup>

#### The leaching stability of dyeing

The leaching stability of dyeing was determined after washing during 3 h in ECE washing test at 60°C. The degree of leaching *L* (in %) was calculated from the most significant minimum of the reflectance spectrum using the Eq. (3). The higher degree of leaching of dyed fabrics with the basic dye using exhausting process (48.53%) was exhibited in comparison with the values obtained using sol-gel process with (9.69%) and without (6.09%) adding of sodium acetate trihydrate (Table VII). The leaching stability of dyed fabrics with the basic dye was significantly improved with using sol-gel process with and without adding sodium acetate trihydrate in comparison with exhausting process consistent with Ref. 20. It can be supposed that the improved leaching fastness results either by the physical embedding of the dye by the silica coating<sup>25,26</sup> and also by attractive electrostatic interactions between the positively charged dye molecules to the negatively charged silica.<sup>12,13</sup>

For reactive dye, the leaching after 3 h washing reached to values of 4.82% in the case of the using sol-gel process without adding sodium acetate trihydrate, 0.91% in the case of the using exhausting process, 0.45% in the case of the using sol-gel process with adding sodium acetate trihydrate. Namely, the leaching stability of reactive dyeing by using sodium acetate for sol-gel process was improved in comparison with that of sol-gel process without sodium ace-

**TABLE VII**  
**The Degrees of Leaching and Light Fading for 20 and 120 h of Dyed Fabrics with Different Type of Dyes and Different Dyeing Process**

Degree of leaching (%)						
Dye type/Process	E		T		TN	
Reactive dye	0.909		4.82		0.446	
Direct dye	1.08		1.37		1.12	
Basic dye	48.53		6.098		9.69	
Degree of light fading (%)						
Process	E		T		TN	
	20 h	120 h	20 h	120 h	20 h	120 h
Reactive dye	2.54	9.77	7.81	25.54	3.16	14.2
Direct dye	5.83	25.16	2.14	9.85	1.57	6.14
Basic dye	1.33	10.28	3.45	7.44	1.84	7.9

tate. In Figure 5, the reflectance curves of dyed fabrics with T and TN process before and after washing confirmed these results. The reflectance value at 550 nm before washing of dyed fabrics with reactive dye by T method was lower than that of after washing, while the reflectance values at 550 nm before and after washing of dyed fabrics with TN method did not change. As mentioned, to study at basic pH such as 7.81 may be caused the larger pore size and so higher dye retaining and decreasing of the amount of leachable dye in silica xerogel in comparison with acidic hydrolysis condition in T method.<sup>10</sup>

The degree of leaching of dyed fabrics with the direct dye slightly changed with using sol-gel process (1.12%) with adding sodium acetate trihydrate in comparison with exhausting process (1.08%) (Table VII). However the leaching value was sufficiently low.

#### The light fading and light fastness of fabrics

The light fading (LF) value of dyed fabrics with the basic dye decreased from 10.28 to 7.9% with using sol-gel process with adding sodium acetate trihydrate in comparison with exhausting process after only 120 h irradiation. Mahltig et al. mentioned that the improvement of light fastness of sol-gel embedded dyes could result from different reasons.<sup>13</sup> First, the dye molecules trapped inside the silica matrix could be more protected from other photodecomposition products, so further reactions with this type of products are not favored.<sup>15</sup> Secondly, the enhanced light fastness can be explained by interactions with the host matrix, analogously to the interaction of cationic dye with a negatively charged silica matrix.<sup>23</sup> Because of the partially ionic bonding of the positively charged dye to the negatively charged silica matrix the energy of the photoexcited dye can be dissipated by transfer to the surrounding silica matrix. They suggested that this second mechanism should be especially valid for the positively charged dye.

Moreover the light of fading values of anionic dyes with adding sodium acetate at higher pH value decreased as without adding sodium acetate whereas the values of cationic dyes with adding sodium acetate were increasing slightly (but acceptable) analogously for leaching values. Thus we can suggest the T method based on mild acidic sol-gel process for dyeing with basic dye while not suggest TN method.

The LF value of dyed fabrics with the direct dye decreased in either 20 (from 5.83 to 1.57%) or 120 h irradiation (from 25.16 to 6.14%) with using sol-gel process with adding sodium acetate trihydrate in comparison with exhausting process. However, the light fading value of dyed fabrics with the reactive dye increased with using sol-gel process with adding sodium acetate trihydrate in comparison with exhausting process after either 20 (from 2.54 to 3.16%) or 120 h irradiation (from 9.77 to 14.2%) (Table VII). The increasing can result from very reactive molecular structure of the reactive dye molecule.

The LF values of all of dyes after 120 h irradiation such as 14.2% for reactive dye, 6.14 for direct dye, and 7.9 for basic dye by using TN method were sufficiently low.

A LF value of 5% (after 20 h irradiation) or 12% (after 120 h irradiation) measured by reflectance on the fabric corresponds to a light fastness scale classification of 4–5 compared with the DIN blue scale standard.<sup>12</sup> Thus, we can suggest 4–5 values of light fastness of dyeing with direct dye and basic dye and 4 values of light fastness of dyeing with reactive dye by using TN method.

#### The effect on rubbing fastness of dyeing by sol-gel process

The wet and dry rubbing fastness results of dyed fabrics by sol-gel process were shown in Table III. It



is clear that wet and dry rubbing fastness values of dyed fabrics with the direct dye, reactive dye, and basic dye by using sol-gel process did not significantly change with comparison on the values of the samples by using exhausting process. When the cotton fabric was treated with this sol, the rubbing fastness results obtained were of an acceptable level. It confirms that the dye molecules should be embedded in silica matrix on the cotton fabric, but the dye molecules should not be placed on the surface of the silica coating.

### CONCLUSIONS

This study concerns basic research and the aim was to present in which way a modified silica sol could be applied to gain optimal dye stability on textiles. The results presented could help in future to develop optimized coloration procedures on textiles using the sol-gel technology.

It was concluded that the TN method based on basic sol-gel process can be suggested for dyeing with reactive and direct dye with increased dye yield (from 0.95 to 5.93 for direct dye and from 3.87 to 4.28 for reactive dye) and acceptable color fastness, low leaching values and low fading degrees in comparison with that of dyeing with exhausting process. On the other hand, T method based on acidic sol-gel process for dyeing with basic dye provided the improved color fastness (from 3/4 to 4/5 to washing for color staining), leaching values (from 48.53 to 6.098%), and degree of fading (from 10.28 to 7.44%) while decreasing dye yield in comparison with that of dyeing with exhausting process. Moreover, we deduced that the sol-gel procedure provided possibility dyeing at lower temperature and shorter time with direct dye while compared with conventional dyeing. In conclusion, sol-gel process could also provide that one could dye cotton fabric with basic dyes as dyeability of same dye on different textiles.

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