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Dyeing and diffusion properties of modified novel cellulose with triazine derivatives containing cationic and anionic groups

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Abstract

Cellulose is chemically modified with the compounds containing cationic and anionic groups. Dyeing and diffusion properties of modified cellulose are discussed. The exhaustion and fixation of reactive dyes on modified cellulose are higher than those on unmodified cellulose. Compared with unmodified cellulose, the dyed modified cellulose also gets good washing fastness. The diffusion coefficients of dyes at different temperature are calculated. Compared with unmodified cellulose, the diffusion of dyes in the modified cellulose shows significant change.

Keywords: Modification; Dyeing properties; Diffusion coefficients; Cellulose

1. Introduction

It is well-known that cotton cellulose is highly appreciated for its outstanding characteristics such as comfortable hand, excellent softness for garment industry. Besides the traditional use as textile materials, cotton cellulose has been explored as a substrate for composite materials because of the presence of several functional groups that may be employed in various activation processes (Jiang, Meng, & Qing, 2006; Kulpinski, 2005; Xie, Hou, & Zhang, 2006; Fu, Hsiao, Pagola, Stephens, et al., 2001). However, it also suffers from some inferior properties such as low wet resiliency, low exhaustion of reactive dyes. It is one of important methods to modify cellulose with chemical method in order to improve some properties of cotton cellulose and change its surface chemical structure. A number of attempts have been made to modify cotton fiber using the compounds containing the cationic groups (Lee & Kim, 2001; Wang & Lewis, 2002; Xie, Hou, & Sun, 2006). Not surprisingly, the physical and mechanical properties of modified cellulose are quite different from those of conventional cotton fabric. The modified cellulose can be dyed without the salt in the dyehouse (Ma, Zhang, Tang, & Yang, 2005; Sang & Hudson, 2004; Xie, Sun, & Hou, 2006). However, molecular chains of modified cellulose with cationic compounds only have cationic groups. Its application and production in the composite material fields can be limited. When cellulose is chemically modified with the compounds containing cationic and anionic groups, the molecular chains of the modified cellulose have both cationic and anionic groups (shown in Scheme 1).

They change the surface chemical structure and property of cellulose fiber. The reports of modified cellulose with the compounds containing multi cationic and anionic groups are scarce. In our recent works, modified cellulose with cationic and anionic groups was investigated (Xie, Hou, & Sun, 2007). Modified cellulose showed a significant change of the chemical structure and physical morphology. The crystallinity and P.O of modified cellulose slightly decreased. The thermal stability of the modified cellulose slightly improved. In this paper, the dyeing and diffusion properties of the modified cellulose with the compounds containing cationic and anionic groups are further dis-

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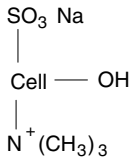


Scheme 1.

cussed. The composition are consisted of a 1,3,5-triazine derivative containing reactive groups, 2,4,6-tri-[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) and 2,4,-bichloro-[(6-sulfanilic acid anhydrous)-1,3,5-triazine (Bi-CSA).

2. Experimental

2.1. Materials

Desized, scoured and bleached cellulose were obtained from Beijing Textile Company. The 1,3,5-triazine derivative containing the reactive groups, 2,4,6-tri-[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) and 2,4,-bichloro [(6-sulfanilic acid anhydrous)-1,3,5-triazine (Bi-CSAT) were obtained from National Engineering Research Center for Dyeing and Finishing of Textiles (Shanghai). The reactive dyes were obtained from Shanghai Kehua Chemical Company.

2.2. Modification to cellulose with compounds

The 1,3,5-triazine derivative containing reactive groups, 2,4,6-tri-[(2-hydroxy-3-trimethyl-ammonium)propyl]-1,3,5-triazine chloride (Tri-HTAC) was dissolved in distilled water to give the certain concentration solution. 2,4,-bichloro[(6-sulfanilic acid anhydrous)-1,3,5-triazine (Bi-CSAT) was added in the Tri-HTAC solution to give the certain quantity solution (Tri-HTAC:Bi-CSAT = 5:1 w/w).

Tri-HTAC–Bi-CSAT solution was diluted in distilled water to give 8% solution by weight. To the solution was added 1.5% sodium hydroxide as catalyst. Samples of cellulose were treated with the Tri-HTAC–Bi-CSAT solution in the dyeing machine (PYROTEC-2000) at the liquor ratio being 1:10. The samples were kept at room temperature for 4 h. The treated fabrics were then washed with tap water until neutral and again washed in warm water using a domestic washing machine to remove unfixed compounds. The fabrics were dried at ambient conditions (the reaction shown in Scheme 2).

2.3. Dyeing of the modified and unmodified cotton fabric

The unmodified cotton was dyed in an IR dyeing machine (PYROTEC-2000), the liquor ratio being 1:15, sodium sulfate (60 g/l) and sodium carbonate (10 g/l). Fabrics were immersed in the dyebath at room temperature and the temperature was raised to 65 °C at the rate of 1 °C/min and continued at this temperature for 60 min. All the dyed samples were rinsed in hot water and soaped in the solution containing a nonionic surfactant (OP-10, 1 g/l) at 90 °C for 20 min at liquor ratio 1:15. The samples were removed, rinsed thoroughly in hot tap water until the rinsing water was clear and air-dried. For modified cellulose, the addition of electrolyte was omitted.

The exhaustion and fixation of dyes on cellulose was calculated by measuring the absorbance of the residual dyebath liquor. The percentages of dyebath exhaustion (E%) and fixation (F%) were calculated according to Eqs. (1) and (2), respectively.

$$\mathrm{E}\ (\%) = [1 - (A_1/A_0] * 100 \quad (1)$$

$$\mathrm{F}\ (\%) = [(A_0 - A_1 - A_2)/A_0] * 100, \quad (2)$$

where A_0 and A_1 are the absorbance of the dye solution at λ_{max} before and after dyeing, respectively, A_2 is the absorbance of the soaped dye solution.

2.4. Diffusion properties of the reactive dyes

The unmodified and modified cellulose fabrics were dyed in an IR dyeing machine (PYROTEC-2000), dye concentration 2 g/l, the liquor ratio being 1:500, pH 7. After dyeing, the samples were removed, rinsed thoroughly in hot tap water until the rinsing water was clear and air-dried. The dye absorption at each time was determined using a Shanghai 723 spectrophotometer. The K/S of dyed samples was determined using Datacolor Spectraflash SF600 Computer Color-Matching System. The standard curve of K/S value versus the dye up-takes was plotted. The dye up-takes on dyed samples were obtained through the standard curve of K/S value.

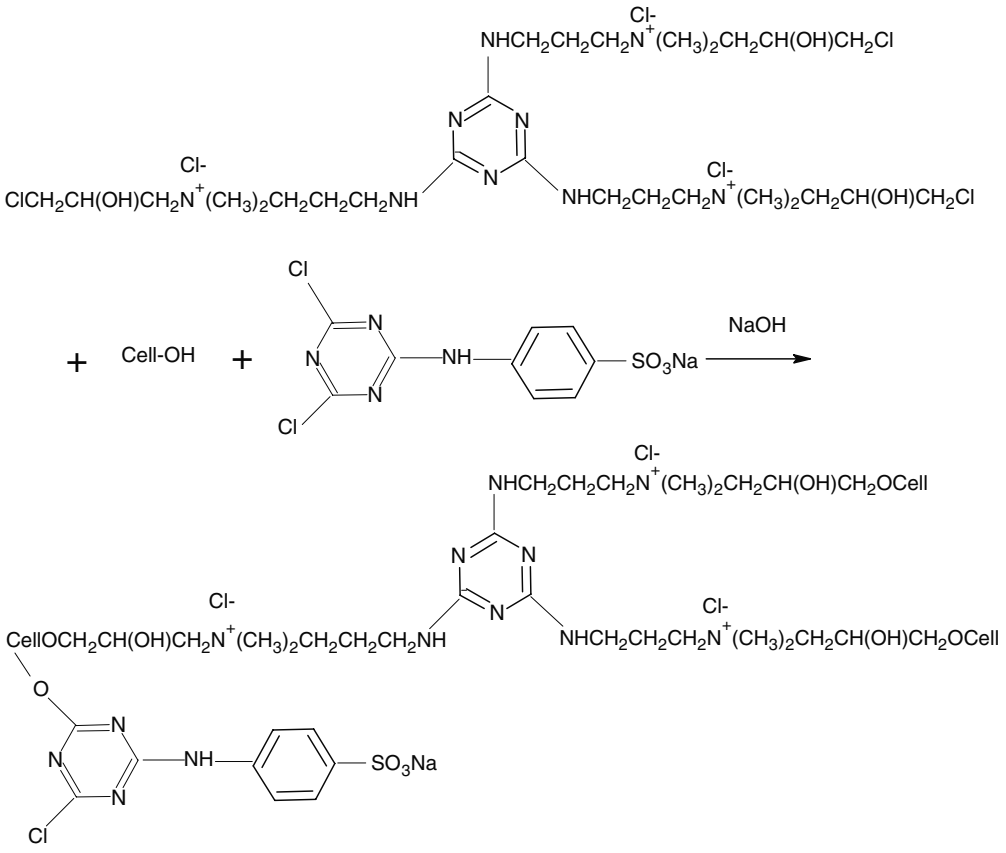
2.5. Fastness testing

Color fastness was evaluated according to the respective international standards: fastness to washing, ISO 105-C03:1989; fastness to rubbing, ISO 105-X12:1993.

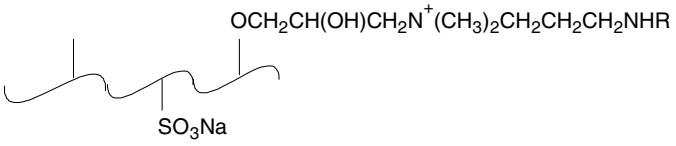
3. Results and discussion

3.1. Dyeing properties for the modified cellulose

After modified with Tri-HTAC–Bi-CSAT compounds, the chemical structure and surface properties of cellulose are changed. The modified cellulose fibers form new molecular structures containing not only cationic but also anionic groups (Scheme 3). Dyeing properties of the modified cellulose with reactive dyes were investigated. The exhaustion and fixation of reactive dyes on cellulose fiber are summarized in Table 1. It indicates that the exhaustions of reactive dyes on the modified cellulose were significantly higher than those of them on the unmodified cellulose. The fixations of reactive dyes on the modified cellulose were 13–24% higher than those of them on the unmodified



Scheme 2.



Scheme 3.

Table 1
Dyeing properties for the modified cotton cellulose with reactive dyes

Dyes samples	Unmodified cotton		Modified cotton	
	E (%)	F (%)	E (%)	F (%)
Reactive Red BF-3B	85.40	79.00	95.35	92.60
Reactive Yellow BF-3R	88.68	78.70	97.24	94.55
Reactive Black B	78.22	73.87	97.34	96.45
Reactive Blue BF-RN	82.32	76.32	96.73	95.62
Reactive Black BF	89.77	80.10	98.62	96.41
Reactive Red 3BSN	83.28	73.13	98.20	96.71
Reactive Yellow ED	90.50	75.00	97.89	95.16

cellulose. This will be of great benefit, as it can reduce dyes effluent discharge and salt in dyehouse effluent. The modified cellulose exhibited different behavior towards dyeing.

The fastness properties of dyed cellulose are shown in Table 2. It can be seen that wet rubbing fastness and washing fastness of dyed modified samples were similar with those of unmodified cellulose. The modified cellulose dyed with reactive dyes also got good fastness properties. This reconfirms that the modified cellulose using Tri-HTAC–Bi-CSAT compounds improved dyeing properties.

3.2. Diffusion of the reactive dyes into the modified cotton cellulose

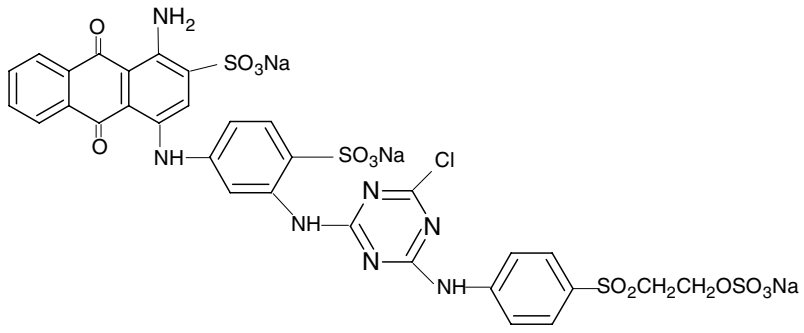
The modified cellulose exhibited different behavior towards dye exhaustion and diffusion due to the presence of a lot of cationic and anionic groups on the modified cellulose. In order to investigate the diffusion processing of the reactive dyes into the modified cellulose, Reactive Blue BF-RN was used to dye (the structure of Reactive Blue BF-RN shown in Scheme 4). Figs. 1 and 2 show the diffusion and exhaustion of the dye at different dyeing time on the unmodified cellulose and the modified cellulose at 25, 35, 45, 65 °C, respectively.

By comparing Figs. 1 and 2, it is clear that the dye uptakes were higher on the modified cellulose than those on the unmodified cellulose at any dyeing time. They demonstrate that diffusion rate of the reactive dyes into modified cellulose was faster than those of them into the unmodified cellulose. This conclusion was valid for each temperature and could be explained by more quaternary ammonium groups on modified cellulose exposed to the dye molecules than those on unmodified cellulose. The dyeing temperature had a significant influence on the dye uptake. The higher the temperature was, the more dye

Table 2
Fastness properties of dyes on cotton cellulose

	Dyes	Fastness to rubbing		Fastness to washing	
		Dry	Wet	SC	SW
Modified	Reactive Red BF-3B	4–5	4	4–5	4–5
	Reactive Yellow BF-3R	4–5	4	4–5	4–5
	Reactive Black B	4–5	3–4	4–5	4–5
	Reactive Blue BF-RN	4–5	4	4–5	4–5
	Reactive Black BF	4–5	3–4	4–5	4–5
	Reactive Red 3BSN	4–5	4	4–5	4–5
	Reactive Yellow ED	4–5	3–4	4–5	4–5
Unmodified	Reactive Red BF-3B	4–5	3–4	4–5	4–5
	Reactive Yellow BF-3R	4–5	4	4–5	4–5
	Reactive Black B	4–5	3–4	4–5	4–5
	Reactive Blue BF-RN	4–5	3–4	4–5	4–5
	Reactive Black BF	4–5	3–4	4–5	4–5
	Reactive Red 3BSN	4–5	4	4–5	4–5
	Reactive Yellow ED	4–5	3–4	4–5	4–5

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



Reactive Blue BF-RN

Scheme 4.

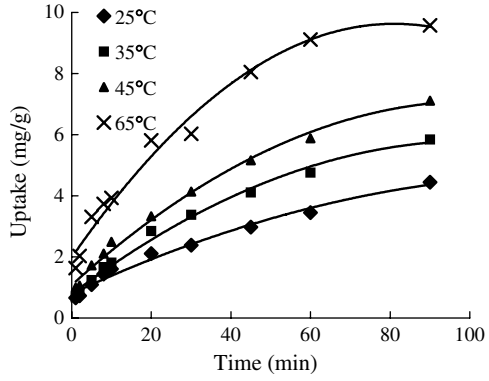


Fig. 1. Diffusion processing of Reactive Blue BF-RN into unmodified cotton cellulose at different dyeing time.

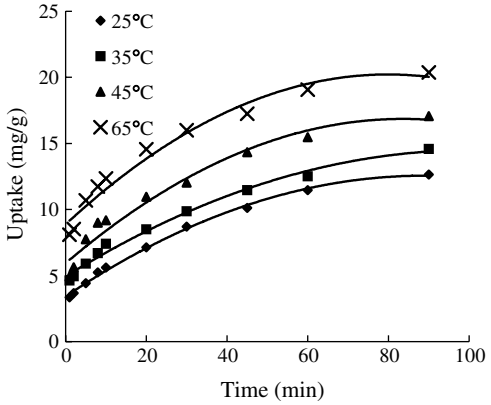


Fig. 2. Diffusion processing of Reactive Blue BF-RN into modified cotton cellulose at different dyeing time.

was sorbed by the fiber. The dye uptake increased initially with the dyeing time, and reached equilibrium after 60 min.

3.3. Diffusion rate constants

The transfer of a dye molecule from the dye solution into a fiber is usually considered to involve the initial mass transfer from the bulk solution to the fiber surface, adsorption of the dye on the surface, followed by diffusion of the dye into the fiber. The diffusion in a fabric is much more difficult than in solution because of dye-fiber interactions and mechanical obstruction by the fiber molecules in the pores. The diffusion of the dye within the fiber is rate controlling. Diffusion of

dyes into fibers during dyeing can take place under either finite or infinite dyebath conditions. In an infinite dyebath, the dye concentration does not change during the sorption process. In a finite dyebath, the dye concentration at the fiber surface continuously decreases during the sorption process. If the initial dye concentration is high, infinite dyebath conditions are maintained throughout the dyeing process. In the present paper, the diffusion coefficients are analyzed for infinite dyebath condition.

Fick's equations describe the diffusion of a dye within a fiber. One simplification is to assume that the external dyebath has a constant concentration. This gives what is known as steady-state diffusion. Another simplification is based on conditions at the beginning of the dyeing process. The amount of dyes in the fiber at any time is directly related to the square root of dyeing time t (Eqs. (3) and (4)) (Broadbent & Arthur, 2001).

$$\frac{\partial c}{\partial t} = D\left\{\frac{\partial^2 c}{\partial r^2} + \frac{z}{r}\left(\frac{\partial c}{\partial t}\right)\right\} \tag{3}$$

$$\frac{C_t}{C_\infty} = 2\sqrt{\frac{D_f t}{\pi}} \tag{4}$$

where C_t represents the dye concentration in the fiber at dyeing time t, C_∞ represents the dye concentration in the fiber at equilibrium. At a certain temperature, C_∞ is constant. If $D = 2C_\infty\sqrt{\frac{D_f}{\pi}}$

That gives Eq. (5).

$$C_t = Dt^{1/2}. \tag{5}$$

From the relation $C_t = Dt^{1/2}$, C_t being the dye concentration on the fiber at dyeing time t. D is diffusion coefficient.

Figs. 3 and 4 show the dye uptakes versus the square root of dyeing time t at 25, 35, 45, 65 °C, respectively. The diffusion coefficients D at different temperatures (shown in Table 3) were evaluated from the slopes of the corresponding linear plots. It could be seen that the values of diffusion coefficient were 2–3 times higher on the modified cellulose than those on the unmodified cellulose. There were more sites in the modified cellulose capable of attracting the dye molecular. The absorption rates of dyes on modified cellulose were significant improved. The diffusion coefficient increased as temperature rising.

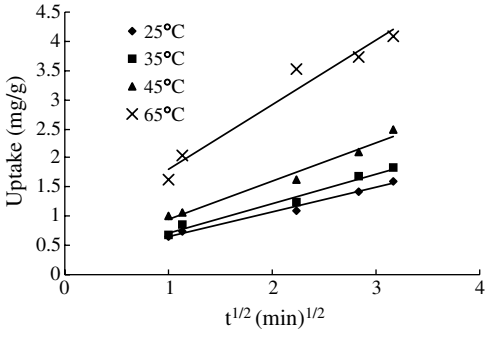


Fig. 3. Dye uptakes on unmodified cotton cellulose versus the square root of dyeing time.

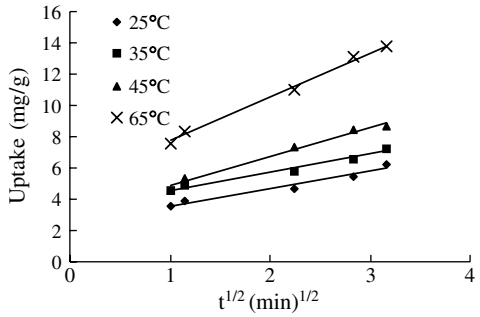


Fig. 4. Dye uptakes on modified cotton cellulose versus the square root of dyeing time.

Table 3
Diffusion coefficients D of Reactive Blue BF-RN

Temperature (°C)	D			
	Unmodified cotton		Modified cotton	
	BF-RN	R	BF-RN	R
25	0.4279	0.9814	1.1124	0.9968
35	0.5073	0.9885	1.1510	0.9923
45	0.6621	0.9924	1.8570	0.9889
65	1.1037	0.9935	2.8072	0.9831

4. Conclusions

Cellulose was chemically modified with Tri-HTAC–Bi-CSAT composition. The modified cellulose exhibited different behavior towards dyeing compared with the unmodified cellulose. The modified cellulose could be dyed with reactive dyes without the addition of salt and got better exhaustion, fixation and fastness properties. Compared with unmodified cellulose, the diffusion coefficients in the modified cellulose were higher.

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