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Chemical modification of cotton fabrics for improving utilization of reactive dyes

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ABSTRACT

The cotton fabric was chemically modified with the acrylamide through Michael addition reaction and Hoffman degradation reaction. And the optimum chemical modification conditions were determined. The molecular structure of the modified cotton fabric was identified by Fourier transform infrared spectroscopy (FTIR). The structures of both the raw and modified cotton fabrics were investigated by X-ray diffraction and scanning electronic microscopy. The raw and modified cotton fabrics were dyed using commercial reactive dyes with vinyl-sulfone groups. The results showed that the total dye utilization of modified cotton fabrics in the salt-free dyeing was higher than that of raw cotton fabrics in the conventional dyeing. And the color fastness properties and tear strength of modified fabrics were both satisfactory.

1. Introduction

The cotton fabric characteristically exhibits excellent physical and chemical properties in terms of water absorbency, dyeability and stability. Reactive dyes are often referred to as the king of dyes for cotton fabrics dyeing system. Their increased demand and popularity are for bright color, excellent color fastness, water-fast, simple application techniques and low energy consumption (Aksu & Tezer, 2000). However, it is necessary to use a large amount of salt (sodium chloride or sodium sulphate) to overcome the static repulsion between cotton fabrics and reactive dyes to promote dyeability in the traditional dyeing process. Even so, the reactive dyes are far from ideal because they are difficult to exhaust from the dyebath and the fixation reaction between dye and cotton fabrics is also inefficient. Depending on the different nature of the used dye and fabric, as much as 40–50% of the dye remained in the dyebath effluents (Aksu & DÖnmez, 2005; Jiang et al., 2011). Discharges of high electrolyte concentrations are undesirable since increased salinity of the rivers affects the delicate biochemistry of aquatic life. The residue of dyes and electrolytes has posed a significant environmental hazard.

Therefore, how to improve utilization of the reactive dyes and to reduce or eliminate the amount of electrolyte used in cotton dyeing has been an important problem concerned by many researchers. In the last recent years, there have been many efforts to improve the dyeability of cellulosic fabrics (Burkinshaw, Mignanelli, Froehling, & Bide, 2000; Cheng & Biswas, 2011; Corrales et al., 2007; Feng & Chen, 2008; Heinze & Liebert, 2001; Ibrahim, El-Zairy, El-Zairy, Eid, & Ghazal, 2011; Kitkulnumchai, Ajavakom, & Sukwattanasinitt, 2008; Lewis & Lei, 1991; Lewis & Mcllroy, 1997a; Lim & Hudson, 2004; Liu, Yang, Zhang, Liu, & Xiong, 2007; Shin & Yoo, 1998; Wang, Ma, Zhang, Teng, & Yang, 2009; Xie, Liu, & Wang, 2009; Zhang, Chen, Lin, Wang, & Zhao, 2008). Among those efforts, the surface modification of cellulosic fabrics has attracted much attention. The process is primarily to attach the cationic compounds on cotton fabrics by chemical binding or physical adsorption for enhancing the substantivity between anionic dye and cotton. Such treated cotton would be dyeable with reactive dyes under neutral or mildly acidic conditions in the absence of electrolyte in the dyebath (Wang & Lewis, 2002).

But the modification technology of cotton fabrics has some problems which restrained their application, for example, excessive cost, wearability of dyed fabrics (moisture, air permeability and tear strength) degeneration, health and safety of modification technology, complication of industry dyeing technology (Teng, Ma, & Zhang, 2010; Xu, Renfrew, & Phillips, 2005). Despite all of the above approaches, none has achieved commercial importance (Xu et al., 2005).

Introduction of amine groups into the cellulose structure produces a fiber that may be considered analogous to wool. Wool has a natural substantivity towards anionic dyes (Lewis & Mcllroy, 1997b) and the amino group can react more easily with reactive dyes than the hydroxyl group. A novel method to prepare aminoethyl cotton was proposed and investigated by treating cotton fabrics with ecologically sustainable and cheap acrylamide. This method could improve the substantivity of cotton for reactive dyes to achieve the goal of salt-free or low-salt dyeing.

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2. Experimental

2.1. Materials

The cotton fabric used in this work was desized, caustic-boiled, bleached, weighing approximately 100 g/m^2. The fabric was washed in the laboratory at 100 °C for 60 min using the distilled water. It was then dried at ambient conditions.

2.2. Chemicals

Sodium hydroxide, acrylamide, sodium nitrite, sodium carbonate, sodium chloride, sodium hypochlorite and other chemicals were of laboratory-grade chemicals from Sinopharm Chemical Regent Co., Ltd.

The commercial reactive dye, C.I. Reactive Black 5 and C.I. Reactive Blue 19 were supplied by Shanghai Dyestuff Co., Ltd., China, C.I. Reactive Yellow 176, C.I. Reactive Red 195, were supplied by Zhejiang Longsheng Group Co., Ltd., China. And their structures are given in Fig. A.1.

2.3. Chemical modification of cotton fabrics

The first step was Michael addition reaction. Acrylamide and sodium nitrite (2 g/L) were mixed in an aqueous solution. The pressure on the mangle was adjusted to give 100% wet pickup. Cotton fabrics were dipped and padded twice in the above solution. And then the above cotton fabrics were dipped and padded twice in the aqueous solutions of sodium hydroxide. The two-bath dipping and padding process kept at room temperature. The treated fabric was then subjected to heat treatment at a specific temperature for a certain length of time. After that, it was cooled to ambient temperature, then washed with distilled water, and finally dried in air.

The second step was Hoffman degradation reaction. The treated fabric was immersed in the beaker placed mixture solution of sodium hydroxide and sodium hypochlorite in the proper proportions. Then it was placed in the Thermostatic Water Bath for a specified period of time. After the reaction, the treated fabric was removed, washed with distilled water and dried. The final modified cotton fabric was thus prepared. Details of the conditions used are given in the text.

2.4. Kjeldahl nitrogen determination

The Kjeldahl method was used for analyzing the nitrogen contents of modified cotton fabrics using a Kjeltec 2300 Analyzer (Foss Tecator).

2.5. Characterization

Infrared spectroscopy (IR) experiments of the fabrics were performed using a Nicolet 460 FTIR under standard operating conditions.

The surface morphologies of the untreated and treated cotton fabrics were observed with LEO 1530 scanning electron microscope. All the samples were coated with gold before SEM testing.

The X-ray diffraction (XRD) patterns of the fabrics were measured stepwise in the 2θ between 5° and 60° by a X" Pert PRO diffractometer (PANalytical, Netherlands).

2.6. Dyeing procedures

2.6.1. Dyeing procedure for the modified cotton (aminoethyl cotton)

The dyeing was carried without the addition of salt. The modified cotton fabric was introduced in aqueous bath containing 4% dye (omf, weight percent of dye relative to fiber) at a liquor ratio of 1:30. The temperature was kept at 25 °C. After 30 min, the dyeing temperature was gradually increased to 60 °C in 20 min. Then 20 g/L sodium carbonate was added with stirring and the dyeing process was continued for 60 min. At the end of dyeing process, the dyed fabric was soaped in a solution of a nonionic surfactant (Triton X-100, 1 g/L) at 90 °C for 20 min at liquor ratio 1:30 and then thoroughly rinsed in tap water.

2.6.2. Dyeing procedure for the untreated cotton

The untreated cotton fabric was introduced in aqueous bath containing 4% dye (omf) at a liquor ratio of 1:30. In the dye bath, 25 g/L sodium chloride was added with stirring. The temperature was kept at 25 °C. After 30 min, another 25 g/L sodium chloride was added and the dyeing temperature was gradually increased to 60 °C in 20 min. Then 20 g/L sodium carbonate was added and the dyeing process was continued for 60 min. The dyed fabric was soaped in a solution of a nonionic surfactant (Triton X-100, 1 g/L) at 90 °C for 20 min at liquor ratio 1:30 and then thoroughly rinsed in tap water.

2.7. Determination of dye exhaustion and fixation

The absorbance of the dye solution was measured at λ_{max} before and after the dyeing processes using a Lambda 950 Spectrophotometer (PerkinElmer Co. Ltd.). The percentage of dyebath exhaustion (E) was calculated using Eq. (1), where A_0 and A_1 were the absorbance of the dye solution before and after the dyeing process, respectively. And the fixation of the adsorbed dye (F) was calculated using Eq. (2) and the total utilization of the original applied dye (T) was calculated using Eq. (3), where A_2 was the absorbance of the dyebath after soaping.

$$E = \frac{A_0 - A_1}{A_0} \times 100\% \quad (1)$$

$$F = \frac{A_0 - A_1 - A_2}{A_0 - A_1} \times 100\% \quad (2)$$

$$T = E \times F \quad (3)$$

2.8. Color yield analysis

The color yield or the color strength expressed as K/S value was calculated from the Kubelka–Munk equation as given below (Eq. (4)), where K is the absorbance coefficient, S is the scattering coefficient, and R is the reflectance ratio measured at the maximum absorbance of dye using a CM-2600d Spectrophotometer (Konica Minolta). After folding each fabric twice, measurements were taken at four different positions on the fabric surface and averaged.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (4)$$

2.9. Color fastness and tear strength testing

The washing properties were measured by SW-12 (Dongyuan testing Machinery) washing machine according to the standard, ISO 105-C06 (C2S). Meanwhile, the rubbing fastness properties were evaluated according to the standard, ISO 105-X12 on Y571B (Changzhou Textile Instrument Co., Ltd.) rubbing machine.

The tear strength of the modified and untreated cotton fabric was tested according to ASTM D 5734-1995 with YG (B) 033A tearing instrument (Wenzhou, China).

3. Results and discussion

3.1. FT-IR study of the modified cotton fabric

The treatment of the cotton fabric has been undertaken to bring a chemical modification according to the reaction in Fig. A.2. The FT-IR spectrum of untreated cotton, carbamoylethyl cotton and aminoethyl cotton was illustrated in Fig. 1. Compared with untreated cotton, the absorption peak at about 1671 cm^{-1}, which was assigned to the stretching vibration of the carbonyl (C=O) of the carbamoylethyl group, obviously appeared in the spectrum of carbamoylethyl cotton and disappeared again in the spectrum of the aminoethyl cotton. It indicated that acrylamide had reacted with cotton cellulose to form carbamoylethyl cotton through Michael addition reaction, and Hoffman degradation reaction occurred between carbamoylethyl cotton and sodium hypochlorite through decarbonylation. It was conformed that aminoethyl groups were attached to the cotton cellulose.

3.2. Surface morphology

Scanning electron microscopy (SEM) was used to investigate the change in the surface morphology of the treated cotton fabric, which could estimate the influence of modification process on the fabrics. Fig. 2(a) and (b) were SEM photos of the untreated fabric and the treated fabric. Although the surface of the untreated fabric was a little rougher compared with that of the treated one, no distinct change could be detected between them.

3.3. X-ray diffraction analysis (XRD)

The XRD patterns of the untreated and treated cotton are shown in Fig. 3. The results showed that the X-ray spectra of the cotton before and after modification were almost the same, a typical diffraction peak existed at $2\theta = 14.8^\circ$, 16.4°, 22.9°, and 33.8° in both Fig. 3(a) and (b) which are typical cellulose I crystalline form, in good agreement with previous report (Klemm, Heublein, Fink, & Bohn, 2005). It demonstrated that chemical modification does not change the main crystalline form of cotton fabrics.

3.4. The optimum conditions of Michael addition reaction

It was clear that the extent of the Michael addition reaction could be expressed as the nitrogen content (%N, wt) of carbamoylethyl cotton. The variables investigated by orthogonal test included baking temperature, baking time and the concentration of sodium hydroxide, as shown in Table 1. It could be observed that nitrogen content of carbamoylethyl cotton gradually increase with increasing sodium hydroxide concentration, baking temperature. In view of the acrylamide readily polymerized (Carpenter & Davis, 1957) and hydrolyzed with rising temperature and increasing sodium hydroxide concentration (Moens & Smets, 1957), the optimal technological parameters were as follows, the concentration of the sodium hydroxide was 24.6 g/L, baking temperature was 70 °C and baking time was 2 h.

In addition, in order to ensure that the amount of the aminoethyl group attached on the cotton fabric was sufficient to exhaust reactive dyes, the effect of acrylamide concentration was evaluated. The carbamoylethyl cotton prepared in different concentration of acrylamide was decarbonylated by Hoffman degradation reaction.

Table 1
Orthogonal test design and results of Michael addition reaction.

Experiment no.	Variables and their levels			Nitrogen content (%)
	Temperature (°C)	Time (min)	NaOH (g/L)	
1	50	60	8.2	0.63
2	50	120	16.4	1.08
3	50	180	24.6	1.15
4	60	60	16.4	0.94
5	60	120	24.6	1.17
6	60	180	8.2	0.95
7	70	60	24.6	1.25
8	70	120	8.2	0.98
9	70	180	16.4	1.14
I	2.86	2.82	2.56	
II	3.06	3.23	3.16	
III	3.37	3.24	3.57	
K_1	0.95	0.94	0.85	
K_2	1.02	1.08	1.05	
K3	1.12	1.08	1.19	
R	0.17	0.14	0.34	

The acrylamide concentration was 200 g/L in the padding solutions.

The obtained products were dyed with reactive dye (C.I. Reactive Black 5) and the results were shown in Fig. 4(a). The effect of acrylamide concentration was measured by the total dye utilization of the obtained product. It could be seen from Fig. 4(a) that the total dye utilization was enhanced greatly with the increase of acrylamide concentration from 50 g/L to 200 g/L. When acrylamide concentration was 200 g/L in the padding solutions, the nitrogen content of the carbamoylethyl cotton was 1.31%. But when it was above 200 g/L, a further increase in acrylamide concentration gave little further improvement in the total dye utilization. It meant that 200 g/L acrylamide aqueous solution could provide sufficient aminoethyl groups for dyeing.

3.5. The optimum conditions of Hoffman degradation reaction

During the progress of the Hofmann degradation, the isocyanato groups which are formed as transient intermediates reacted with water to yield the objective amino groups (Tanaka & Senju, 1976). The amount of aminoethyl group on the treated cotton fabric has an important effect on utilization of reactive dye. In order to obtain the best dyeability, the Hofmann degradation reaction conditions were optimized by orthogonal test based on the total utilization of reactive dye on aminoethyl cotton fabrics. The aminoethyl cotton fabrics prepared by Hofmann degradation reaction was dyed with reactive dye (C.I. Reactive Black 5) without the addition of salt. The factors investigated by orthogonal test included Hofmann reaction temperature, Hofmann reaction time and the active chlorine content, as shown in Table 2. In particular, the molar ratio of sodium hydroxide and the active chlorine was kept at 2:1 in every reaction solution system according to mechanism of Hofmann degradation reaction. The results indicated that the process conditions optimized were as follows, reaction temperature was 40 °C, reaction time was 60 min and the active chlorine content was 1.68 g/L. Furthermore, it could be seen from Table 2 that the reaction temperature are the most important determinant in the Hoffman degradation reaction. Therefore, single-factor experiments at different temperatures were carried out to examine the reaction efficiency, as Fig. 4(b) showed. The total dye utilization increased with increasing temperature from 0 °C to 40 °C. So combined with the result of Table 2, the optimum modification temperature was still chosen at 40 °C.

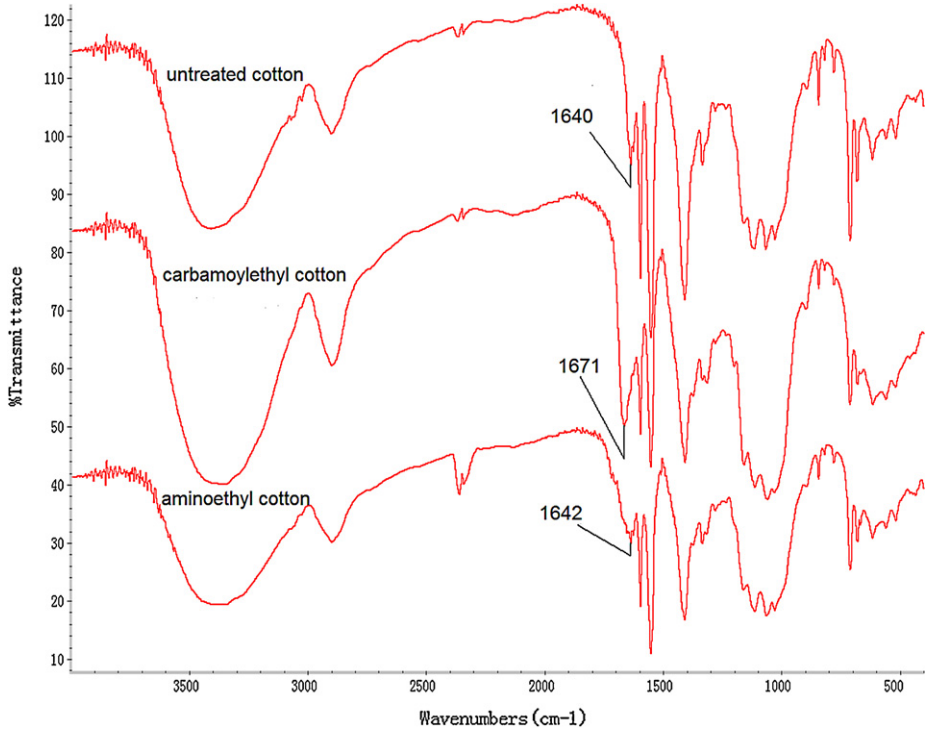


Fig. 1. FTIR spectrum of untreated cotton fabric and modified cotton fabric.

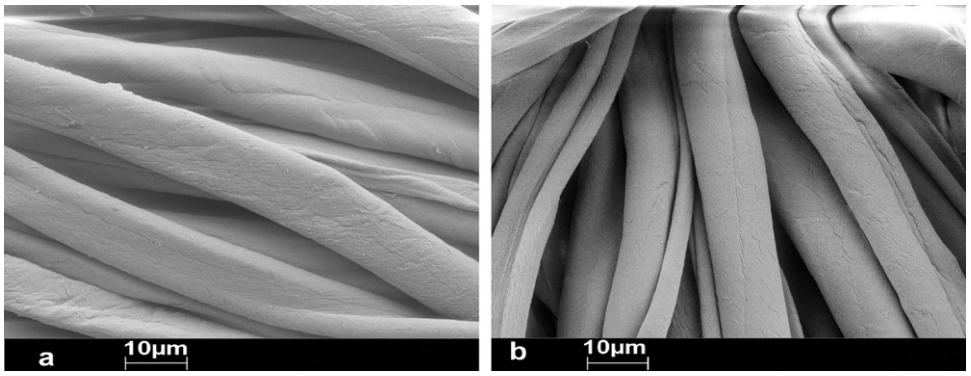


Fig. 2. SEM photos of untreated cotton fabric (a) and treated cotton fabric (b).

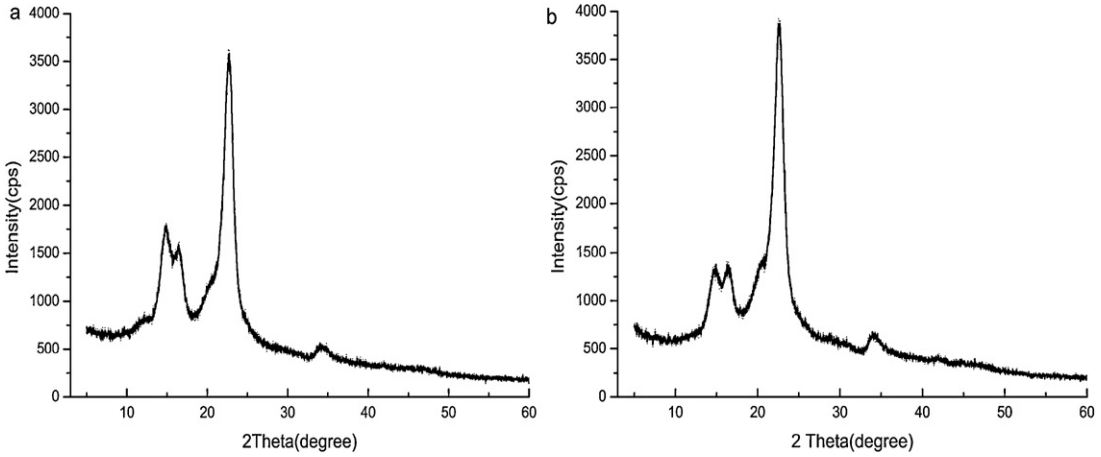


Fig. 3. X-ray diffraction patterns of untreated cotton fabric (a) and treated cotton fabric (b).

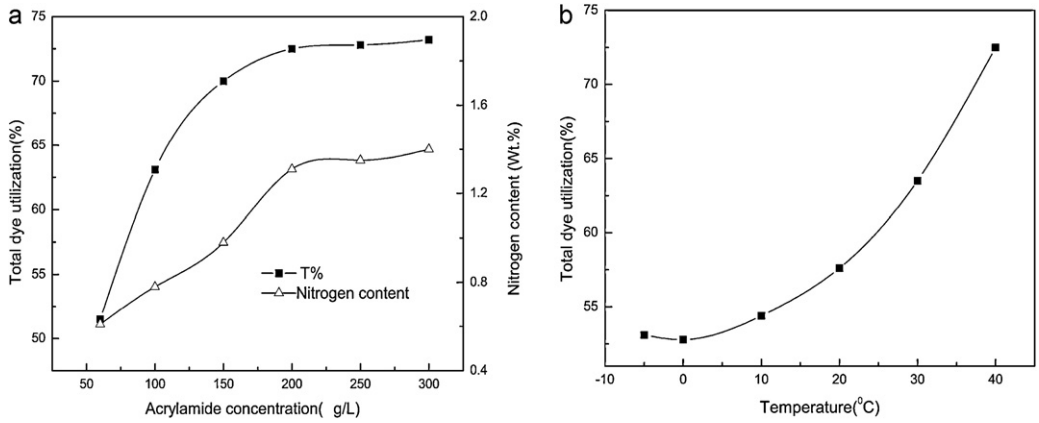


Fig. 4. The total dye utilization as a function of acrylamide concentration (a) and Hoffman degradation reaction temperature (b).

Table 2
Orthogonal test design and results of Hoffman degradation reaction.

Experiment no.	Variables and their levels			*T* (%)
	Reaction temperature (°C)	Reaction time (min)	Active chlorine content (g/L)	
1	40	30	1.68	68.6
2	40	60	2.10	71.4
3	40	90	2.52	63.6
4	50	30	2.10	65.9
5	50	60	2.52	61.2
6	50	90	1.68	54.5
7	60	30	2.52	36.2
8	60	60	1.68	50.3
9	60	90	2.10	31.9
	203.6	170.7	173.4	
II	181.6	182.9	169.2	
III	118.4	150.0	161.0	
K1	67.87	56.90	57.80	
K2	60.53	60.97	56.40	
K3	39.47	50.00	53.67	
R	28.40	10.97	4.13	

Nitrogen content of the treated fabric (carbamoylethyl cotton) is 1.31%. The liquor ratio of Hoffman reaction is 1:30.

3.6. Fastness properties and tear strength

The color fastness properties and tear strength of untreated and treated cotton fabric are summarized in Table 3. From Table 3, the color fastness properties of treated cotton fabric were the same good as those of the untreated cotton fabric. The tear strength of the dyed modified cotton was slightly lower than that obtained from the untreated one. It indicated that the chemical modification of cotton fabrics had no adverse effect on the fastness properties of the dyes and tear strength of cotton fabrics. It were still comparable to the results obtained from untreated cotton and could meet the application requirements for the dyed fabrics.

Table 3
Fastness properties of C.I. Reactive Black 5 and tear strength of the dyed cotton.

Fabric	Wash fastness			Rub fastness		Tear strength (N)	
	Shade change	Staining		Dry	Wet	Warp	Weft
		Cotton	Wool				
Untreated	4–5	4–5	4–5	4–5	3	22.9	17.4
Treated	4–5	4–5	4–5	4–5	3	22.1	16.8

Table 4
Dyeing effect of untreated and modified cotton using various reactive dyes with vinyl-sulfone groups.

Reactive dye name	Untreated cotton		Treated cotton	
	T (%)	*K*/*S*	*T* (%)	*K*/*S*
C.I. Reactive Black 5	52.9	21.68	72.5	24.78
C.I. Reactive Blue 19	56.8	16.08	75.5	21.73
C.I. Reactive Yellow 176	64.2	16.56	65.5	18.02
C.I. Reactive Red 195	67.4	19.33	69.5	19.93

3.7. Suitability of other reactive dyes with vinyl-sulfone groups

Besides C.I. Reactive Black 5, other reactive dyes with vinyl-sulfone groups were also examined to assess their suitability for dyeing the prepared aminoethyl cotton fabric. The treated cotton was dyed without salt and untreated cotton was dyed with 50 g/L sodium chloride. As shown in Table 4, the total dye utilization and color yield of the prepared aminoethyl cotton were higher than those of untreated cotton with various reactive dyes. Compared with the original cotton fabric, the prepared aminoethyl cotton displayed enhanced color strength using salt-free dyeing.

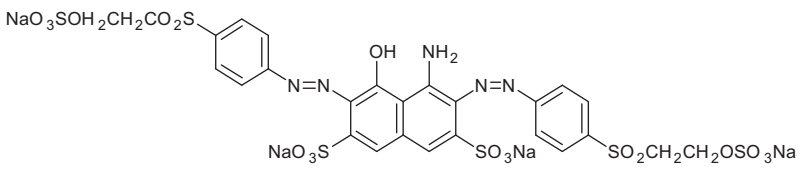
4. Conclusions

The aminoethyl cotton fabric was prepared and its structure was confirmed by FTIR spectroscopy. And the optimum chemical modification conditions were determined. The optimum conditions of the Michael addition reaction were as follows, the cotton fabrics was padded separately in 200 g/L acrylamide solution and 24.6 g/L sodium hydroxide solution in sequence, baking temperature was 70 °C and baking time was 2 h. The optimal process of the Hofmann degradation reaction was that the carbamoylethyl cotton was immersed in the aqueous solution containing sodium hypochlorite and sodium hydroxide at 40 °C for 60 min. In this solution active chlorine content was 1.68 g/L and sodium hydroxide concentration is 3.8 g/L.

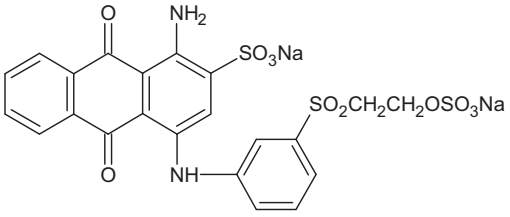
This study confirmed that the modified cotton could be dyed using reactive dyes with vinyl-sulfone groups in the absence of salt. Besides, color fastness properties and tear strength of the modified fabrics were both satisfactory. It provides a easy and feasible way to realize salt-free dyeing of reactive dyes.

Appendix A.

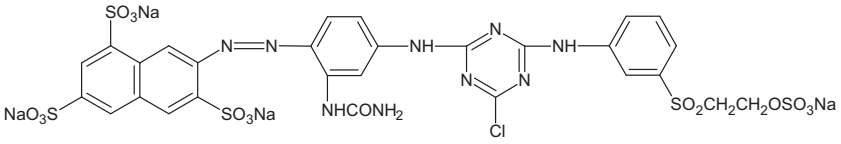
See Figs. A.1 and A.2.



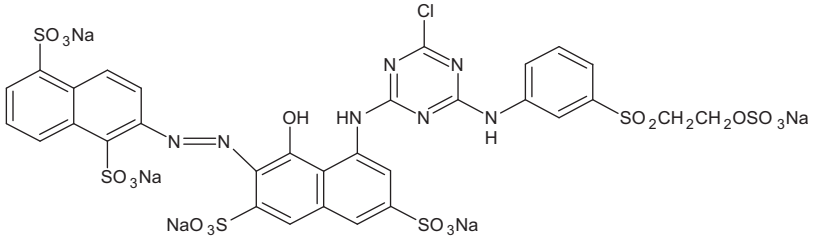
C.I. Reactive Black 5



C.I. Reactive Blue 19



C.I. Reactive Yellow 176



C.I. Reactive Red 195

Fig. A.1. Chemical structures of the reactive dye used in this study.

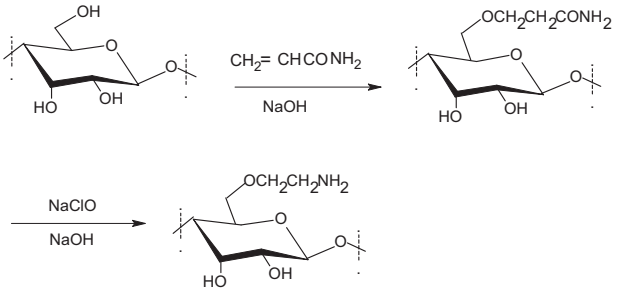


Fig. A.2. Scheme of the modification reaction.

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