1026-1265/2002

Treatment of Cotton with Chitosan and Its Effect on Dyeability with Reactive Dyes

Shadi Houshyar[1] and S. Hossein Amirshahi[2*]
Department of Textile Engineering, Isfahan University of Technology, Isfahan 84154, I.R.Iran

Received 07 February 2001; accepted 02 December 2001

ABSTRACT

Dyeing behaviour of chitosan pretreated cotton fabric with reactive dyes is the subject of this study. Cotton fabric is treated with chitosan using five different techniques, consisting of exhaustion, pad-dry, pad-batch, pad-steam and pad-dry-steam methods. To find the influence of concentration of chitosan on the dyeability behaviour, different amounts of chitosan were used and the suitable concentration was determined. It is observed that chitosan pretreatment increases the exhaustion of reactive dyes and the highest dye up-take is achieved for pad-dry method. The effect of the period of storage of chitosan treated sample before dyeing process on dyeability of fabrics is examined by comparison of samples which was dyed immediately after treatment with the one which was kept for 48 h after treatment. The results show that dyeing immediately after treatment leads to higher dyeability and the effect of treatment decreases for the samples which were pkept for 48 h before dyeing process. The light and wash fastnesses of treated samples are measured and some reduction in light and wash fastnesses were observed.

Iranian Polymer Journal, 11 (5), 2002, 295-301

Key Words:
chitosan,
cotton,
pretreatment,
dyeability,
reactive dyes.

(*)To whom correspondence should be addressed.
E-mail: hamirsha@aut.ac.ir
Present address:
(1) Department of Applied Chemistry, RMIT University, Melbourne, Victoria, 3001 Australia.
(2) Department of Textile Engineering, Amir Kabir University of Technology, Tehran, P.O.Box: 15875-4413, I.R. Iran.

INTRODUCTION

Usually, the main use of reactive dyes is in the dyeing of cellulosic fibres. They have been considered to be of potential interest for dyeing cellulosic fibres due to their brilliancy and high wet fastness properties. However, dyers who are working with this group of dyes, have been faced with some serious problems which can be categorized as follows:

-Incomplete absorption of dyes during the exhaustion which originates from the lack of sufficient affinity between the dye and fibre.

-Incomplete reaction between fibres and dye.

-Destruction of band between fibre and dyes during the fixation.

- Hydrolyses of dyes during dyeing process.

The above problems become very important in heavy deep dyeing of cotton with reactive dyes. The low affinity between dyes and fibres which leads to weak or medium exhaustion, and the existence of some limitation in complete fixation of dyes specially in deep dyed samples such as dark shades, make this type of dyeing very expensive.

However, the application of chitosan as an auxiliary step in dyeing or printing of textile materials and leathers has been reported [1]. The chemical characterization and behaviour of chitin and chitosan were published in literature [2-3]. Davidson and Due [4] reported a better dyeability for treated wool by chitosan and Burkinshaw and Jarvis [5] found that the pretreatment of leather with chitosan increases the shrinkage temperature. Rippon [6] investigated that the pretreatment of cotton with chitosan eliminates the difference in colour between the dyed immature and mature cotton fibre in the dyeing process with direct dyes. Later, Metha and Combs [7] confirmed the Rippon results by additional works.

In order to improve the dyeability of cotton fibres with reactive dyes, we have pretreated the fibres with chitosan by various application methods. The results of this type of pretreatment on dyeability as well as its effects on light and wash fastnesses of treated and dyed samples are studied in this paper.

EXPERIMENTAL

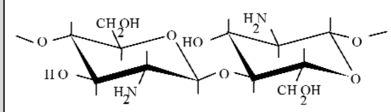
Materials

Scoured and bleached plain weave cotton fabric was used in all experiments. The weight of specimens in all the tests was 5 g.

A commercial grade, Kytex-L, of chitosan from Hercules, was used. Table 1 shows the properties of the used chitosan as well as its chemical structure. Chitosan solution was prepared by dissolution of 3 g of the chitosan in 1 L of aqueous acetic acid solution at room temperature by slow and continuous stirring (1rpm) for 5 min. Then, the solution was filtered to remove any insoluble materials.

Four commercial reactive dyes were used: namely Remazol Blue R Special (C.I Reactive Blue 19), Sumifix Supra Navy Blue 2GF, Kayacion Blue P-GR

Table 1. Specification of applied chitosan.

Chemical structure	
Physical form	Powder
Colour	Off white
Odor	Nil
Ash content	2% max
Deacetylation	> 85%
pH	6.5
Protein content	1% max

(C.I Reactive Blue 5) and Procion Blue MXR (C.I Reactive Blue 4). The reactive groups of the applied dyes were, respectively, vinylsulphone, bifunctional type, monochlorotriazine and dichlorotriazine and were supplied by Hoechst, Sumitomo Chemical, Nippon Kayako Chemical and ICI, respectively. All other chemicals were laboratory grades.

Methods

Samples were washed by a solution of 2 g/L of nonionic detergent called "Tinoventin JU 400% (Ciba)" at 60°C for 30 min before undergoing any treatment. In order to determine the suitable method for chitosan application to cotton, five different methods were applied for treatment of cotton with chitosan:

1- Pad (110% pick-up), batched for 30 min and finally rinse in distilled water.

2- Pad (110% pick-up), dried in laboratory stente for 3 min at 150°C and finally rinsed in distilled water.

3- Pad (110% pick-up), was steamed in laboratory steamer for 30 min at 100°C and finally rinsed in distilled water.

4- Pad (110% pick up), dried in a laboratory beaker for 3 min at 150°C, steamed in laboratory steamer for 30 min at 100°C and finally it was rinsed in distilled water, and

5- Exhaustion was carried out in fully computerized laboratory dyeing machine at L:R 28:1 at 60°C for 45 min.

Different amounts of chitosan were applied. Table 2 shows the amount of applied chitosan in different techniques.

Dyeing was done at liquor to good ratio of 28:1 in an Ahiba Turbomat laboratory-dyeing machine. The pretreated fabrics with chitosan were wetted and then

Table 2. The concentration of chitosan for different application methods.

Method(s)	Amount of applied chitosan									
Exhaustion (%OWF*)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Pad (g/L)	1	2	3	4	5	6	7	8	9	10

(*) OWF: On weight of fabric

dyed with 1% (on weight of fabric) of each dyestuff following the procedures recommended by dyes manufacturers for dyeing by exhaustion dyeing method (Figures 1-4).

Due to different characteristics of selected dyes, the amount of common salt and alkali were adjusted to suppliers' recommendation.

In order to evaluate the dye uptake of treated samples, two different methods were applied. Firstly, the visible spectra of dye bath at the end of dyeing was measured for bathes containing reference and treated samples by a Cary 3 UV-visible spectrophoto-meter. Then, the effect of treatment was evaluated by calculation of percentage dye increment, ID, by using eqn (1).

Where, C_R and C_T represent the amount of dyes at

$$I.D = \frac{C_R - C_T}{C_R} \times 100 \quad (1)$$

the end of dyeing procedure for reference and treated samples, respectively.

Secondly, the reflection values of the samples were measured by a reflectance spectrophotometer named Texflash from Datacolor. In order to determine the dye absorption, the K_λ/S_λ values of the dyed samples were measured at the wavelength of minimum reflection by using eqn (2).

$$\frac{K_\lambda}{S_\lambda} = \frac{(1-R_\lambda)^2}{2R_\lambda} \quad (2)$$

Where, R_λ refers to the reflection value of the sample.

In order to study the effect of storage duration of treated samples on the dyeing behaviour, two series of treated cotton fabrics were prepared and dyed, one series immediately after treatment and the other series 48 h later. The differences were evaluated by the calculation of K_λ/S values of the dyed samples.

The light and the wash fastnesses of samples were tested by ISO 105-B: 1989(E) and ISO 105-CO5: 1989(E), respectively [8].

RESULTS AND DISCUSSION

In order to determine the effect of treatment types and the effect of the application methods on the reactive dye uptake, the samples were individually dyed with 1% Remazol Brilliant Blue R Special by recommended exhaustion dyeing method. The K_λ/S_λ values of samples after classical fixation and washing procedures were calculated by using eqn (1). Table 3 shows the effect of chitosan concentration on the dyeability of cotton fabrics. The maximum K_λ/S_λ values were obtained by using 8 g/L of chitosan in pad methods and 0.6% on weight of fabric in exhaustion method. It is extremely difficult to evaluate the treatment [1].

However, in this research, in order to evaluate the effect of the applying technique, samples which were treated by equal amounts of chitosan by different methods, were dyed by Remazol Brilliant Blue R Special. Figure 5 shows the results for untreated and different treated samples. The K_λ/S_λ values for treated fabrics were significantly higher than untreated one and the differences between various application methods were not too significant. However, the highest value was achieved by pad-dry technique and the exhaustion method led to minimum K/S value in the five different applying methods. Obviously, the lack of suitable affinity between cotton and chitosan is demonstrated by poor absorption of solute which led to minimum changes to cotton dyeability.

The dye binding properties of chitosan has been studied and it is reported that chitosan has an extremely high affinity for many classes of dyes including reactive dyes. Since the best results were obtained with pad-dry method, so, in order to study the effect of reactive group of dyestuff on the colour yield of treated materials, the pretreated samples were dyed by mentioned

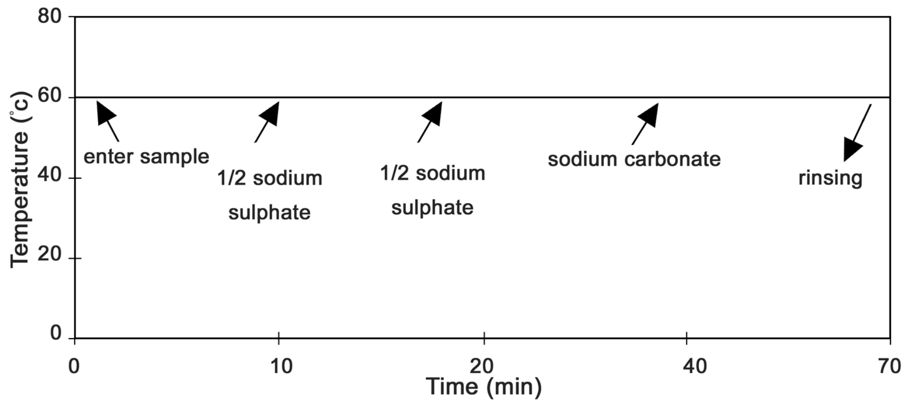


Figure 1. Dyeing method for treated samples by vinylsulphone reactive dye.

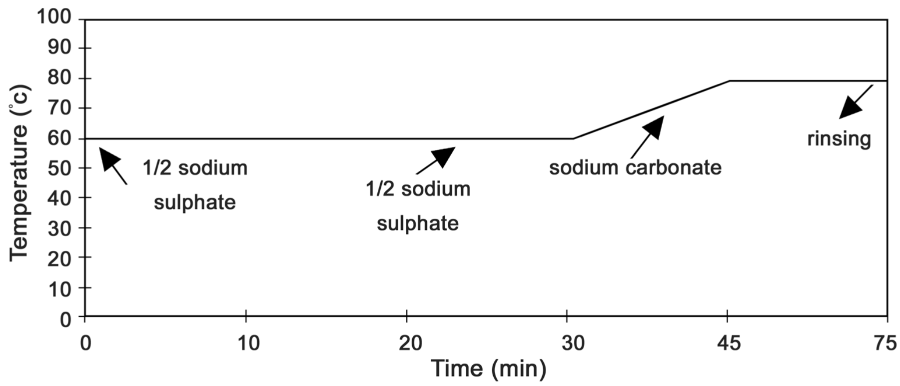


Figure 2. Dyeing method for treated samples with monochlorotriazin reactive dye.

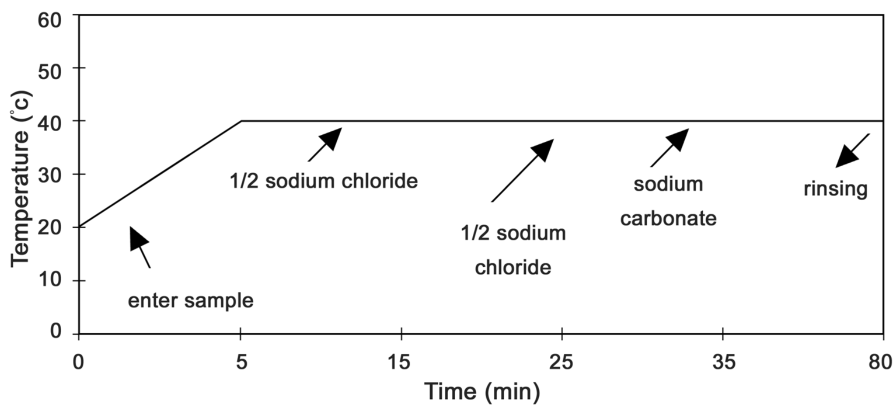


Figure 3. Dyeing method for treated samples with dichlorotriazin reactive dye.

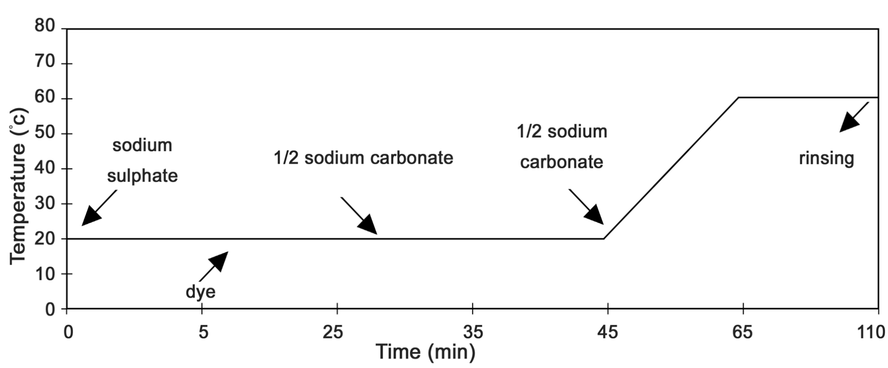


Figure 4. Dyeing method for treated samples with bifunctional reactive dye.

Table 3. Effect of chitosan concentration in three different methods of application on dye uptake of treated samples.

Method of application of samples with chitosan					
Exhaustion		Pad-batch		Pad-dry	
Concentration (%)	K/S	Concentration (g/L)	K/S	Concentration (g/L)	K/S
0.1	1.98	1	1.99	1	2.02
0.2	2.02	2	2.03	2	2.03
0.3	2.14	3	2.06	3	2.14
0.4	2.16	4	2.15	4	2.23
0.5	2.14	5	2.23	5	2.26
0.6	2.37	6	2.38	6	2.47
0.7	2.43	7	2.47	7	2.64
0.8	2.42	8	2.54	8	2.76
0.9	2.43	9	2.46	9	2.69
1.0	2.42	10	2.47	10	2.53

reactive dyes. Again, eqn (1) was used to evaluate the effect of the types of four different reactive groups on the treated fabric. Table 4 shows that the maximum changes were achieved for Sumifix Supra Navy Blue 2 GF which is a bifunctional reactive dye, while the Kayacion Blue PGR which contains a monochlorotriazine reactive group showed the minimum change. According to Table 4, the effect of treatment was more significant for high reactive dyes and it decreased for low reactive dyes such as Kayacion Blue PGR.

Figure 6 shows the K_λ/S_λ values of samples, which were dyed immediately, and 48 h after treatment. As this figure shows, the K_λ/S_λ values decreased by keeping them after treatment. It means that maximum dye uptake can be achieved by continuous treatment dyeing process.

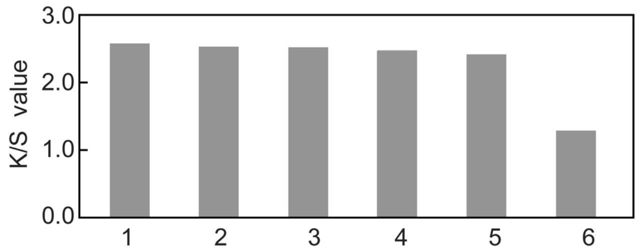
The light and wash fastnesses of treated-dyed samples were measured and compared with untreated fabrics as references. Tables 5 and 6 show the results, respectively. The light fastnesses of treated samples were slightly decreased for treated samples while; we expected higher light fastness for them due to their deeper depths. The moisture absorption of chitosan treated cotton fabrics were studied on wool and cotton and it is claimed that the wettability of the substrate was slightly enhanced [1,9]. According to literature [10], the light fastness of textile materials was affected by the effective moisture, significantly. So, any depletion

Table 4. The percentage of improvement in dyeability of treated samples for four different reactive dyes.

Reactive dye→	Remazol	Sumifix	Kayacion	Procion
Concentration of remaining dye in dye-bath for reference sample (mg/L).	0.0073	0.0026	0.0051	0.0035
Concentration of remaining dye in dye-bath for reference sample (mg/L).	0.0035	0.0002	0.0044	0.0025
Increasing of dyeability, I.D. (%).	52	91	13	22

Table 5. The light fastness of four applied reactive dyes on reference and treated samples.

Reactive dye	Type of treatment	Light fastness
Procion blue MXR	Exhaustion	5
	Pad-batch	4-5
	Pad-dry	4-5
	Non (reference)	5
Kayacion blue PGR	Exhaustion	5
	Pad-batch	5
	Pad-dry	4-5
	Non (reference)	5
Remazol brilliant blue R	Exhaustion	4-5
	Pad-batch	4
	Pad-dry	4
	Non (reference)	5
Sumifix supra navy blue 2GF	Exhaustion	2-3
	Pad-batch	2-3
	Pad-dry	2
	Non (reference)	3



(1) Pad-dry; (2) Pad-dry-steam; (3) Pad-batch; (4) Pad-steam; (5) Exhaustion; (6) Reference.

Figure 5. The values of K/S for dyed samples which were treated with different methods.

of light fastness of treated samples can originate from this type of changing.

The wash fastnesses of treated samples were also decreased in comparison with reference fabrics. The maximum decrease belonged to the pad-dry applying method, which led to maximum colour yield. It can be assumed that chitosan sorption on cotton is due to ionic interaction between the negative charges of hydroxyl groups in the cellulose chains and the protonated amino groups of chitosan and to the hydrogen bonding between hydroxyl groups of fibres and similar groups in chitosan as well as van der Waals' forces [1,3].

Table 6. The wash fastness of four applied reactive dyes on reference and treated samples.

Reactive dye	Type of treatment	Colour changes	Staining cotton	Viscose
Procion blue MXR	Exhaustion	2-3	4-5	
	Pad-batch	2-3	4-5	5
	Pad-dry	2-3	4-5	5
	Non (reference)	4	5	5
Kayacion blue PGR	Exhaustion	4-5	4-5	5
	Pad-batch	4-5	4-5	5
	Pad-dry	4-5	4-5	5
	Non (reference)	5	5	5
Remazol brilliant blue R	Exhaustion	2	4	4-5
	Pad-batch	1-2	4	4
	Pad-dry	1-2	3	3-4
	Non (reference)	5	4-5	5
Sumifix supra navy blue 2GF	Exhaustion	4	3-4	5
	Pad-batch	3	3	4
	Pad-dry	2-3	3	3-4
	Non (reference)	5	4-5	5

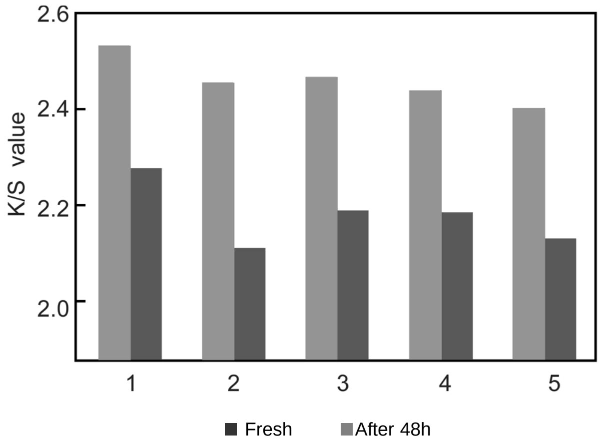


Figure 6. The K/S values for treated samples which were dyed immediately or kept for 48 h after treatment process.

Therefore, a part of reactive dyes which is absorbed by chitosan, could be removed from treated cotton during the washing process and led to significant decrease in washing fastness.

CONCLUSION

Treatment of cotton with chitosan increased the dye absorption of reactive dyestuff. The concentration of chitosan played a noticeable effect on cotton dyeability as well as the applying technique. Five exhaustion, pad-batch, pad-steam, pad-dry and pad-dry-steam methods were applied for treatment of cotton fabrics with chitosan. The highest dye uptake was achieved by pad-dry method while the exhaustion showed the minimum effect.

In order to determine the effect of applied dyes to the treated fabrics, four different types of reactive dyes consisting of vinylsulphone, mono- and di-chlorotriazine and bifunctional reactive groups were used. The maximum dyeing yield was achieved by the bifunctional dyestuff while the monochlorotriazine showed the minimum changes.

The light fastnesses of treated and dyed samples were slightly decreased while the wash fastnesses of treated fabrics were decreased more significantly which would be a point for future investigation to optimize the procedure. The degree of decreasing for light and wash fastnesses depended on the types of application methods.

REFERENCES

1. Jocic D., Julia M.R., and Erra P., “Application of a chitosan/nonionic surfactant mixture to wool assessed by dyeing with reactive dye”, *J. Soc. Dyers Colour,* **113,** 25-31 (1997).
2. Muzzarelli A.A., *Chitin,* Pergamon, Oxford (1977).
3. Muzzarelli A.A., *Natural Chelating Polymers,* Pergamon, Oxford (1973).
4. Davidson S. and Xue Y., “Improving the dyeability of wool by treatment with chitosan”, *J. Soc. Dyers Colour.,* **110,** 24-29 (1994).
5. Burkinshaw M. and Jarvis A.N., “The use of chitosan in the dyeing of full chrome leather with reactive dyes”, *Dyes and Pigments,* **31,** 35-52 (1996).
6. Rippon J.A., “Improving the dye coverage of immature cotton fibres by treatment with chitosan”, *J. Soc. Dyers Colour.,* **100,** 298-303 (1984).
7. Mehta R.D., and Combs R., “Coverage of immature cotton neps in dyed fabrics using chitosan after-treatment”, *Am. Dyest. Rep.,* **110,** 43-45 (1997).
8. *Standard Methods for the Determination of Colour Fastness of Textile*, Society of Dyers and Colourists, Bradford, UK (1966).
9. Houshyar S., “Improvement of reactive dyeability of cotton by chitosan pretreatment”, Master Thesis, Isfahan University of Technology, Iran (1999).
10. Nunn D.M., *The Dyeing of Synthetic Polymer and Acetate Fibres*, Society of Dyers and Colourists, Bradford, UK (1979).