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Cationization of Cotton Fiber by Chitosan and Its Dyeing with Reactive Dye without Salt

M.A. Rahman Bhuiyan[1,*], Abu Shaid[1], M. A. Khan[2]

[1]Department of Textile Engineering, Dhaka University of Engineering & Technology, DUET, Gazipur-1700, Bangladesh
[2]Institute of Radiation and Polymer Technology, Bangladesh Atomic Energy Commission, P.O. 3787, Dhaka-1000, Bangladesh
*Corresponding Author: arahman@duet.ac.bd

Abstract Conventional dyeing process of cotton fabric with reactive dyes requires the use of large amount of electrolyte as exhausting agent. Thus the discharged wastewater from dye house creates unavoidable environmental threats due to very high salt concentration. This paper presents the possibility of salt free dyeing of cotton fabric with reactive dye by treating the fabric with chitosan. Exhaustion of dye by the fabrics was increased by treating them with chitosan prior to dyeing. It has been noticed that absorption of dye has significantly increased with the increment of chitosan concentration. The K/S value, i.e. dye absorption of chitosan treated fabrics was found as 1.6, 1.7, 2.2 and 2.9 respectively for 1%, 2%, 3% and 4% chitosan concentration whereas the K/S value of untreated fabric was 1.9. Fastness of the dyed samples had also been investigated through color fastness to washing, perspiration and rubbing. No fastness deterioration had been experienced for the dyed fabric treated with chitosan. However in case of chitosan treatment at high concentration, the wet rubbing fastness was found slightly inferior to untreated dyed samples which can be explained as the consequence of higher depth of shade due to high absorption of dyestuff by the fabric.

Keywords Chitosan, Cotton, Reactive Dye, Dye Absorption

1. Introduction

Cotton is a natural cellulosic fiber. The polymer chain of cotton consists of several hundreds to more than thousand β (1 - 4) D-glucose units [1] linked to each other. It builds up negative charges on its surface when immersed in water, resulting an inverse effect on exhaustion of anionic dyes such as reactive dye. Reactive dye is the worldwide acceptable dye for the coloration of cotton goods due to their ease of applicability, cost, brilliancy of color and high wet fastness properties [2]. High wash fastness property of reactive dye with cellulose is due to the formation of covalent bond with fiber polymer [3]. The reactive system of this dye enables it to react with the hydroxyl groups in cellulose by nucleophilic addition or substitution reaction.

As the reactive dyes are anionic and cotton fibers gain anionic surface charge in water, the charge repulsion adversely affects the dye bath exhaustion. Large quantities of electrolyte (30-100 g/l) [4] are added to overcome this problem. These electrolytes are neither exhausted nor destroyed and hence remain in the discharged dye liquor which leads to enormous environmental problems [5].

Many researchers in different countries worked to minimize [6] or eliminate [7-10] the use of electrolyte concentration in reactive dye liquor. The introduction of cationic sites within the cellulose is the most expected technique [11] to increase the dye adsorption. Cationic sites can be introduced either by aminization or cationization [12]. Treatment of cotton with chitosan is an aminization technique to introduce cationic site within the fiber polymer structure.

Chitosan [β-(1-4)-2-amio-2-deoxy-D-glucopyranose] is a nontoxic and biodegradable [13] biopolymer, abundantly found in nature; specially in the exoskeletons of crustaceans [14,15], arthropods and mollusks [16,17] as well as the cell walls of certain fungi [14, 17-20] in the form of chitin. Chitin is deacetylated in alkaline medium to obtain chitosan. Chitosan can be applied on cotton fiber in various methods [2]. Cotton fibers form cross linking with chitosan [21] resulting positive dyesites on the fiber surface. As a result anionic dyes such as direct, acid and reactive dyes can easily be adsorbed by electrostatic attraction due to the created cationic nature [11] of the fiber surface.

From the above discussion it can be concluded that the application of chitosan on cotton fiber contributes to the possibility of reactive dyeing without electrolyte with desired level of exhaustion. In addition the introduction of more hydroxyl groups in cellulose due to the cross linking of chitosan with fiber polymer can enhance the exhaustion of dye by fiber. The current paper investigated the dyeability and color performance of chitosan treated cotton fabric treated with chitosan dyed without salt and compared the results with the fabric dyed with salt.

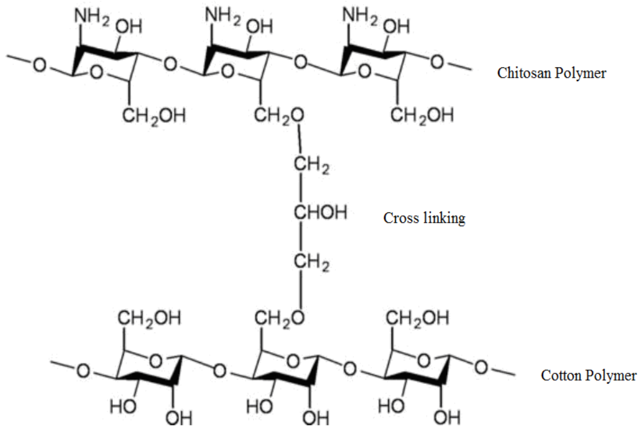

Figure 1. Cross-linking of chitosan with cotton fiber polymer

2. Experimental

2.1. Materials

Scoured, bleached (105^{0}C, 30 min) and enzyme (50^{0}C, 20 min) treated 100% single jersey cotton knit fabric (120 GSM) was used in all the experiments. Chitosan chips (color off white, deacetylation >70%) were collected from the laboratory of Institute of Radiation and Polymer Technology (IRPT), Bangladesh Atomic Energy Commission, Dhaka, Bangladesh. The dyeing of fabric was performed by using commercial reactive dye (Novacron Red FN2BL) form Swiss Colours Ltd., Bangladesh. Auxiliary chemicals like Detergent (Imeron PCLF) and Leveling agent (Drimagen E3R) were collected from Clariant, Bangladesh and used as received. Acetic acid (CH_3COOH), Glauber salt ($Na_2SO_4.10H_20$) and Soda ash (Na_2CO_3) was collected from Merck, India and all were of analytical grades.

2.2. Equipment

The treatment of fabric with chitosan and dyeing was carried out in Sandolab Infrared Lab dyeing machine (Copower Technology Ltd., Taiwan). The color depth of dyed goods was analyzed by spectrophotometer (Data Color 650, USA). Color fastness to wash, rubbing and perspiration was measured by wash fastness tester (Gyrowash, model: 415/8) perspiration fastness tester (Perspirometer, model: HX-30) and rubbing fastness tester (Crock meter, model: 670) from James H Heal & Co, UK.

2.3. Method

2.3.1. Sample Preparation

Fabric samples arranged for dyeing without salt were treated with chitosan solution prior to dyeing. Chitosan solution was prepared by dissolving the chips in distilled water in the presence of 2% acetic acid. Then the fabric was treated in solution for 60 minutes at 60^{0}C temperature, squeezed to remove excess solution and dyed with reactive dye.

2.3.2. Recipe for Dyeing

Cotton fabrics were dyed with the reactive dye at 1% (on the weight of fabric) shade without salt (in case of chitosan treated fabric) and with salt (for untreated fabric). Four different percentages of chitosan (1%, 2%, 3% and 4%) were used to treat the fabrics. General recipes are given in the table 1&2.

2.3.3. Dyeing Curve

5.0 g (± 5%) fabric samples were dyed with salt and without salt in exhaust dyeing method. The dyeing temperature was maintained at 60^{0}C. All the dyeing parameters were remaining constant for both treated and untreated fabrics.

Table 1. Recipe for 1.0% (owf) shade with salt

Ingredients	Dyes (%)	Salt g/l	Soda ash g/l	Wetting agent g/l	Leveling agent g/l	*M:L
Amount	1.0	20	8.0	1.0	1.0	1:10

Table 2. Recipe for 1.0% (owf) shade without salt

Ingredients	Sample-1	Sample-2	Sample-3	Sample-4
Chitosan (%)	1	2	3	4
Dyes (%)	1.0	1.0	1.0	1.0
Soda ash (g/l)	8.0	8.0	8.0	8.0
Wetting agent(g/l)	1.0	1.0	1.0	1.0
Leveling agent (g/l)	1.0	1.0	1.0	1.0
*M:L	1:10	1:10	1:10	1:10

*Material Liquor ratio

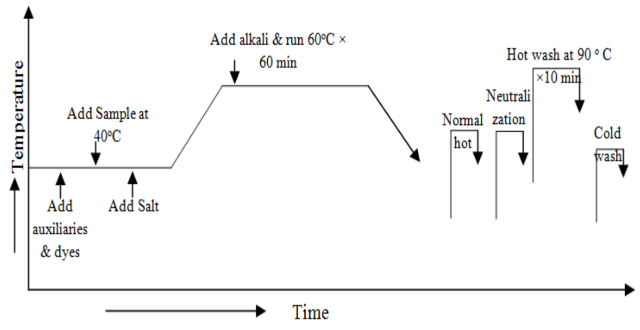

Figure 2. Conventional dyeing sequence of cotton fabric with reactive dye

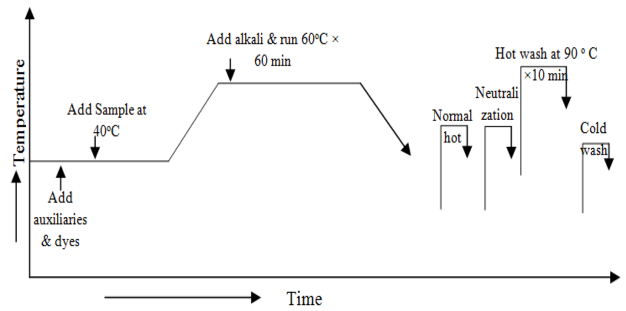

Figure 3. Dyeing sequence of chitosan treated cotton fabric with reactive dye

2.3.4. Dyeing Performance Test

The performance of dyed fabric i.e. depth of color was analyzed by spectrophotometer. The color depth of the dyed fabrics was analyzed by measuring the K/S values of samples. Color measuring instrument (spectrophotometer) determines the K/S value of a given fabric through Kubelka-Munk equation as follows [22].

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

Where R = reflectance percentage, K = absorption co-efficient and S = scattering co-efficient of dyes. This value represents the attenuation ratio of light due to absorption and scattering is found based on reflectance. Colorfastness to washing, rubbing and perspiration was measured according to ISO 105 C03, ISO 105 X 12: 1993 and ISO 105 E04 respectively [23].

3. Results and Discussions

3.1. Color Depth Analysis

The depth of color of dyed fabric was analyzed by K/S value. This value numerically represents the nature of the coloring material layer and an easy way to determine a color as a concentration. The color concentration decreases as the value for reflectance increases, and vice versa. The depth of shade i.e. K/S value found for all the dyed fabric samples are shown in the figure 4.

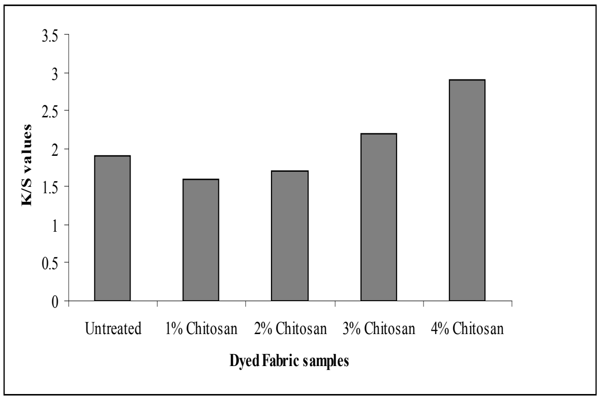

Figure 4. Dye absorption of treated and untreated fabric samples

The above figure shows that the dye absorption, i.e the K/S value increases with the increasing of chitosan concentration in the fiber. The increased K/S value in the chitosan treated fabric indicates the presence of higher amount of the dye absorbed in the chitosan treated fabric. Though the fabric with lower chitosan concentration may not absorb dyes as much as in case of the fabric dyed with salt, still when the chitosan concentration in fabric is increased, the same depth of shade was experience. Moreover increased chitosan concentration provided higher depth of shade. The enhancement of dye absorption occurred due to the formation of additional hydroxyl groups.

3.2. Comparison of Color Fastness

Three types of color fastnesses such as color fastness to rubbing, washing and perspiration of the dyed fabrics were measured. Color fastness to washing and perspiration were assessed in respect of color change and staining on multifiber fabric (acetate, cotton, nylon, polyester, acrylic, wool). Rubbing fastness was evaluated in dry and wet condition. Fastness ratings of different types of dyed samples are presented in the Table -3 & 4.

The tables show that the fastness ratings of chitosan treated and untreated fabrics are almost similar both in case of color fastness to washing and perspiration (color change and staining). However, in case of rubbing fastness, the wet rubbing of chitosan treated fabrics have shown lower rating than untreated fabric, especially for higher chitosan concentration. The chitosan present in the fabric enhances the dyesite causing deeper shade. Hence, as a general consequence of achieving deeper shade, the chitosan treated fabric samples have shown slightly lower fastness rating in comparison to lighter untreated fabric.

Table 3. Color fastness to rubbing and washing (color change and color staining)

Fabric sample	Rubbing fastness		Washing fastness Color staining						
	Dry	Wet	Color change	Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Dyed with salt	5	4	4/5	5	4/5	5	5	4/5	4/5
Dyed with Chitosan 1%	4/5	3	4/5	4/5	4/5	5	5	4/5	4/5
Dyed with Chitosan 2%	4/5	3	4/5	5	4/5	5	5	4/5	4/5
Dyed with Chitosan 3%	4/5	2/3	4/5	4/5	4	5	5	4/5	4/5
Dyed with Chitosan 4%	4	2/3	4/5	4	4	5	5	4/5	4/5

Table 4. Color fastness to perspiration (color change and color staining)

Fabric sample	Color change	Color staining					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Dyed with salt	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Dyed with Chitosan 1%	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Dyed with Chitosan 2%	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Dyed with Chitosan 3%	4/5	4/5	4/5	4/5	4/5	4/5	4/5
Dyed with Chitosan 4%	4/5	4/5	4/5	4/5	4/5	4/5	4/5

4. Conclusion

Treatment of cotton with chitosan increased the cationic sites in the fiber polymer that results higher absorption of reactive dye. The concentration of chitosan in fabric played a noticeable effect on dyeability. In this study, the increment of chitosan concentration gives the similar or more dye absorption i.e. higher K/S value of fabric compared to the fabric dyed with salt. The fastness properties of the chitosan treated fabrics also show almost similar ratings of the untreated fabric. Hence the treatment of cotton with chitosan for improved reactive dyeability provides a significant scope for further investigation to suit today's need of eco friendly dyeing.

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