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Unconventional Dyeing of Cotton Fabric using Chitosan-Functionalized Reactive dye

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ABSTRACT

Reducing the use of exhausting agents conventional dyeing process of cotton fabric with reactive dyes is essential to diminishing the tremendous influence of dyes released in wastewater on the environment. However, it remains a significant challenge to achieve both excellent dyeing properties and a low risk of water pollution. In this study, to eliminate exhausting agents' usage in the reactive dyeing of cellulose fabrics, an attempt was made to functionalize reactive dyes with chitosan and subsequently dye cotton fabrics. As result, due to the physical interaction between chitosan and dye, the cotton fabric dyed with reactive dye-functionalized chitosan improved by 15% and 6.14 % in color strength compared with conventional dyeing and unconventional dyeing of cationization cotton fabrics, respectively. on other hand the cotton fabric dyed with reactive dye-functionalized chitosan also showed better fastness properties including washing, rubbing and lighting fastness. Considering the good dyeing properties of the reactive dye-functionalized chitosan, this promising technique may pave the way for the salt-free dyeing of cotton.. Also study the effect of Ammi visnaga oil on microorganisms.

KEYWORDS

Cotton Fabric, Reactive dye, Chitosan, Waste water

1 INTRODUCTION

Cotton fibers are extensively used in fabric production because of their exceptional characteristics of biodegradability; comfortability, air permeability, and no static electricity build-up [1]. Among water-soluble dyes, reactive dyes are highly desirable for practical applications for cotton fibers coloration because of their excellent properties such as high brilliance, diversly of hue, relatively low cost, consumes little energy, and excellent fastness [2].

Moreover, owing to the construction of a covalent bond between the dye molecules and the hydroxyl groups of the cellulose fibers, the reactive dyes have high wash fastness with cellulose fibers [3, 4 However, because reactive dyes possess a negatively charged ion and cellulose fibers develop a negative surface charge in an aqueous medium, dye bath exhaustion is hampered because of the aversion. [5, 6]. Thus, following the dye molecules' adsorption by the cellulose fiber, the hydroxyl groups of cellulose fibers cannot form covalent bonds because of unsatisfactorily nucleophilic.

To improve dye exhaustion, large amounts of salt (sodium sulfate and sodium chloride) are demanded to preserve the pH of the dye bath. In such conditions, covalent bonds between the reactive dyes and cellulosic fiber can be formed after the fixation [3]. However, hydrolyzed dyes are formed due to the contest of cellulose fiber and reactive dyes to react with alkali, which is required to increase the amounts of hydroxyl groups in cellulosic fibers [4]. After the dyeing process, hydrolyzed dyes should be removed from cellulose fiber using a large amount of water. Accordingly, the polluted water should be treated to protect the environment before discharge [5].

To solve the above-mentioned issue, many researchers have chemically modified cotton fabric to enhance the dyeability of the reactive dyes using various techniques, which are exceedingly known in previous studies [6-8]. Lewis and McIlroy have modified the surface of the cotton fabric with cationic groups [9]. Such methods frequently referred to as cationization, are performed by modifying cotton fabric with low molecular weight cationic agents or with cationic polymers. Moreover, in other studies researchers have dyed the modified cotton fabric with reactive dyes without using salt and alkali [10, 11]. Most of the modifications used for introducing cationic groups in cotton fabric is considered an additional process step and the treatment itself is not safe environmentally [12].

Cationization with natural cationizing polymers such as cationic starch [16, 17], chitosan [5, 18], and chitosan derivatives [19] have been investigated, which leads to making the cationization approach environmentally safer. The application of chitosan on cotton fabric dyeing donates to the potential of reactive dyeing without electrolytes with the desired level of exhaustion. Besides, chitosan increases hydroxyl groups in the cotton fabric due to the cross-linking of chitosan with fiber polymer, thus, the dye exhaustion improved [13].

This study investigates the dyeability of cotton fabric with cationization reactive dye without electrolyte, which introduced the positive charge after interaction with chitosan. Then the results obtained from this system were compared to the results from the dyeing systems of cationized cotton fabric with reactive dye after it has been treated with chitosan without salt and conventional dyeing.

2 Material and Methods

Material

In this exploration, 100% scoured bleached (90 ◦C, 45 min) treated plain woven cotton fabric with 60 ends per inch, 45 picks per inch, and an average areal density of 158 g/m2 was used. Sodium chloride, hydrochloric acid, sodium hydroxide, acetic acid, and hydrogen peroxide were provided by Misr chemical industries Egypt. Sodium carbonate, wetting agent, and BEZAKTIV RED dyes (C.I. Reactive red 1) were purchased from Ostim chemical company. All chemicals used were of laboratory grade without any further purification.

Cationization of Cotton

Cotton fabric samples were modified with chitosan for salt-free dyeing. Firstly, a homogeneous chitosan solution was prepared by dissolving the chitosan powder in distilled water in the existence of 2% acetic acid. Secondly, the fabric samples were soaked in chitosan solution for 60 minutes (min) at a temperature of 60º C. Later, the modified fabric samples were squeezed to remove the chitosan residue. Finally, the modified fabric samples were dried before use.

Chitosan-Functionalized Reactive dye

Firstly, 2.0 grams of the reactive dyes were dissolved in 200 mL of water, and 2.0 grams of chitosan were dissolved in 100 mL of water. Then both solutions were mixed and left for 24 hours at room temperature.

Conventional Dyeing Method

Conventional dyeing was carried out by dyeing full bleached cotton fabric with a 2% shade of C.I. Reactive red 1 with a liquor ratio of 1:50 in a laboratory automatic dyeing machine (model 4-12; Tokyo, Japan), which it's referred to as (S1). The dyeing process was started with a dye and 1g/L leveling agent at 60˚C then the cotton fabric was immersed for 10 min. The pre-dissolved 20 g/L Glauber salt was added to a due bath, three times every ten minutes 6g/L, 6g/L, and 7g/L respectively. The dyeing was continued while increasing the temperature to 80˚C, then 15 g/L of sodium carbonate was added to the solution. The dyeing was continued for 5 minutes to complete the dyeing. After that, the dyed fabric was washed with 2g/L standard soap at boiling temperature for 20 minutes. Finally, the dyed fabric was rinsed in warm water (60˚C) and cold water for 5 min for each. Then the dyed cotton fabric was dried.

Dyeing of Cationized Cotton

Chitosan-modified cotton fabric was colored with a 2% shade of C.I. Reactive red 1 with a liquor ratio of 1:50, referred to as (S2). The dyeing process was started at a temperature of 60˚C then the modified cotton fabric was immersed for 10 min. The dyeing was continued while increasing the temperature to 80˚C, then 15 g/L of sodium carbonate was added to the solution and continued for 5 minutes. After that, the dyed fabric was washed with 2g/L standard soap at boiling temperature for 20 minutes. Finally, the dyed fabric was rinsed in warm water (60˚C) and cold water for 5 min for each. Then the dyed cotton fabric was dried.

Dyeing cotton fabric with Chitosan - Functionalized Reactive dye

The full bleached cotton fabric, which it's referred as (S3), in a research facility build up a test coloring machine with a material-to-liquor ratio of 1:50 and for 2% shade. The fabric was dyed in the pre-mixed dye solution with chitosan solution. The fabric was entered at 60˚C for 10 min to the dye bath solution and the temperature was raised to 80 ˚C, then 15 g/l of sodium carbonate was added and the dyeing process continued for 5 minutes. The dyed fabric was rinsed by carried out washing with warm water (60˚C) for 5 min and with cold water for 5 minutes. The dyeing was continued while raising the temperature to 80˚C and 15 g/l soda ash was added to the solution and dyeing was continued for 5 minutes. After dyeing was completed, soaping was carried out at boiling temperature for 20 minutes by using 2g/l standard soap. The dyed fabric was rinsed by washing with warm water 60˚C for 5 min and with cold water for 5 minutes.

Characterization

FTIR

FT-IR was used to establish the nature of the interaction between reactive dye and chitosan before dyeing.

Color Strength

Color strength (K/S) was determined using data color 500 spectrophotometer results in L× a ×b, D-65, and 10˚ observers. The reflectance (R) value of dyed fabric at the maximum wavelength of absorbance (λ max) was found and the K/S was calculated using Kubelka-Munk equation

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

Where, *K* is the light absorption coefficient, *S* is the light scattering coefficient while *R* is the D 65/10 light reflection.

Dye bath exhaustion (% E)

The dye bath exhaustion (% E) was determined by measuring the dye solution absorbance before (0) and after (1) using a UV/VIS Spectrometer at the maximum absorbance wavelength (λ max). Then, the percentage of dye bath exhaustion (% E) was calculated using the following equation.

$$\%E = \frac{(A_0 - A_1)}{A_0} \times 100 \qquad (2)$$

Dye fixation (% F)

The dye fixation (% F) was determined from K/S value. The maximum K/S value of dyed fabric at a certain wavelength was measured by using a data color 500 spectrophotometer before (b) and after (a) soaping. The percentage of the dye fixation was calculated using the following equation:

$$\%F = \frac{(K/S)_a}{(K/S)_b} \times 100 \qquad (3)$$

Total dye utilization (% T)

The total dye utilization percentage (%T) was calculated by using equation (4).

$$\%T = \frac{E \times F}{100} \qquad (4)$$

Fastness properties

The wash fastness properties were assessed according to ISO 105 C06 2002 method on Launder-O-meter. The change in color and degree of staining was assessed using geometric grey scales. While the light fastness and rubbing fastness were evaluated with a light fastness tester (BSEN ISO 105 B04: 1994) and a crock meter (BSEN ISO 105 X12: 2001), respectively.

Result and Discussion

3.1 Mechanism of Dyeing Cotton Fabric using Chitosan-Functionalized Reactive Dye

The conventional dyeing process of cotton fabric with reactive dyes demands the use of a large amount of an exhausting agent (30-100 g/L). Consequently, the released wastewater from the dyeing factories makes inevitable environmental hazards because of extremely high salt concentrations. Accordingly, the challenge remains in reducing of use of the exhausting agent with excellent dyeing properties and low environmental pollution. Here the use of chitosan in the dyeing processes, whether in surface modification of cotton fabric or functionalization of reactive dye before dyeing can provide an excellent way to dye cotton fabrics with reactive dyeing without exhausting agents with perfect dyeing effects and less environmental pollution. As shown in figure 1, the bleached cotton material is immersed in the previously prepared chitosan functionalized reactive dye solution. In such conditions, the electrostatic interaction plays a foundation role, and here the interaction between the chitosan functionalized reactive dye and the cotton material is mainly through hydrogen bonding with the possibility of forming covalent bonds.

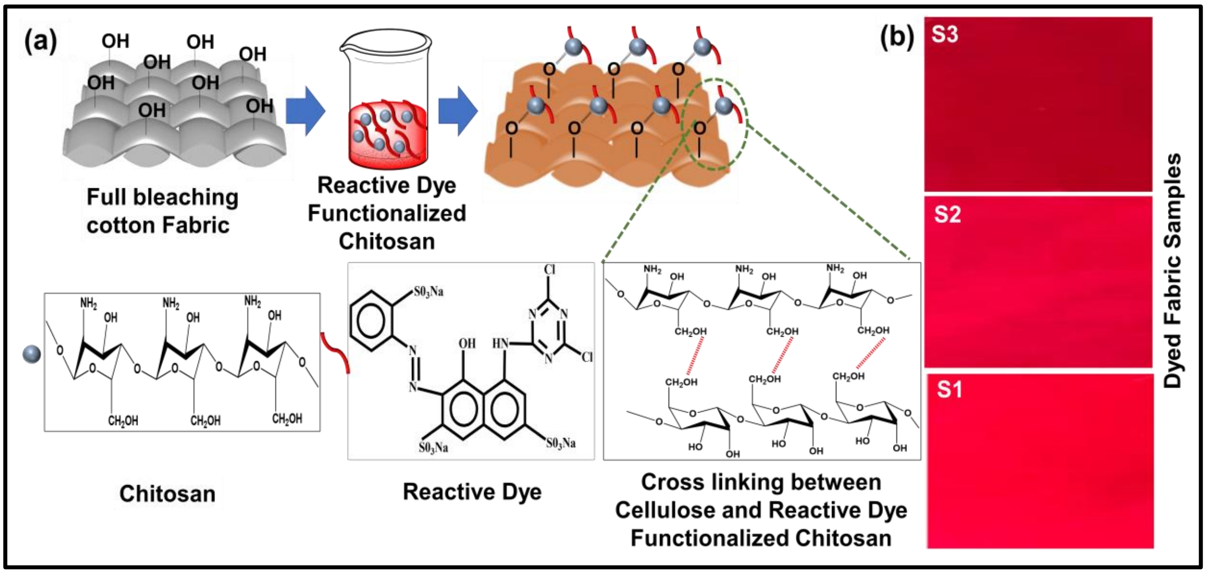

Figure 1 Scheme of Mechanism of Dyeing Cotton Fabric using Chitosan-Functionalized Reactive Dye.

3.2 Characterization the reaction between Chitosan and Reactive Dyeing

FTIR is used to establish the nature of the interaction between the reactive dye and chitosan. As shown in Figure.2, the essential characteristic peaks of the chitosan were shown at 3435 cm^{-1} (O–H stretch and N–H stretch, overlapped), 2871 cm^{-1} (C–H stretch), 1656 cm^{-1} (NH_2 deformation), 1603 cm^{-1} (N–H bend), and 1030 cm−1 (C–O stretch, hydroxyl group). For chitosan-red, the intensity of peaks was decreased and several shifts in the wave number. It was indicated that the interaction that occurs between chitosan and red dye was merely a physical interaction.

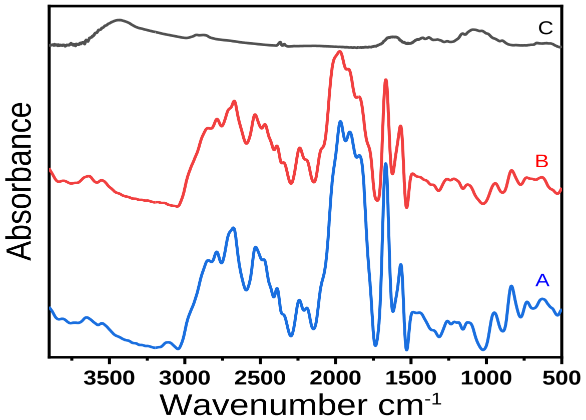

Figure.2 FT-IR Spectra of. (A) Reactive Dye, (B) Composition of Reactive Dye and Chitosan and (C Chitosan

3.3 Color strength result

The color strength of dyed fabrics was investigated by K/S value. Such value numerically illustrates the nature of the coloring fabric and is an easy method to define a color concentration. The color concentration drops as the reflectance increases. The color strength of shade namely the K/S value for all the dyed fabric samples was shown in Figure.2.

Figure 2 shows that the color concentration of cotton fabric dyed with chitosan functionalized reactive dye in the absence of the electrolyte is lower than cationized cotton fabric and fabric dyed in the existence of an electrolyte. The increased K/S value in the fabric dyed with cationized reactive dye designates a higher amount of the dye absorbed in the cotton fabric dyed with cationized reactive dye.

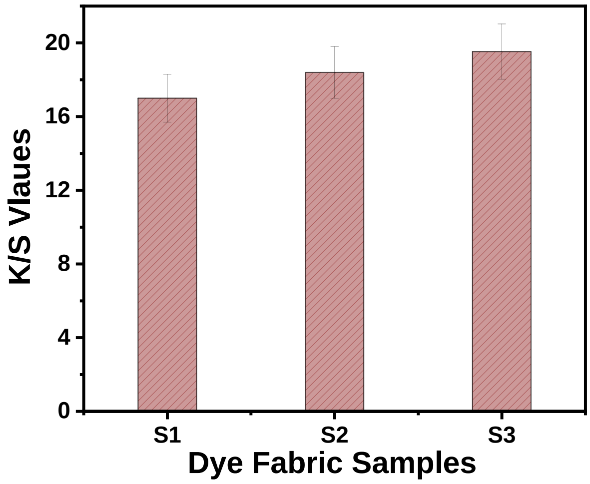

Figure 3. Dye Adsorption of Cotton Fabric dyed with different dye Systems (S1), (S2) and (S3)

The improvement of dye absorption happened due to the construction of further hydroxyl groups in the reactive dye, as shown in Figure 2. In addition, as shown in Figure 3, the depth of shade was found to be better when the cotton fabrics were dyed with the cationized reactive dye. We assume that the reason for this is since when dyeing with the chitosan functionalized reactive dye, all the amount of chitosan does not enter into the interaction with the active dye, but rather some of it has remained. The remained chitosan can interact with the cotton fabric, which directs to an enlargement in the fabric's absorption of the reactive dye. On the other hand, in the cationization of cotton fabric with chitosan before dyeing, all the added chitosan does not interact with the cotton fabric. In addition, we found that when washing and drying the cotton cloth after chitosan treatment, part of the polymer loses its bond with the fabric and is removed from the surface of the fabric.

3.4 Effect on percentage dye exhaustion (%E)

To get dispensing the dye into the inter part of the fabric, the dye concentration before and after the dyeing process was determined by UV/VIS. spectrophotometer at the maximum wavelength absorbance (λ). The maximum absorbance at 530 nm was carried out to calculate the dye exhaustion percentage.

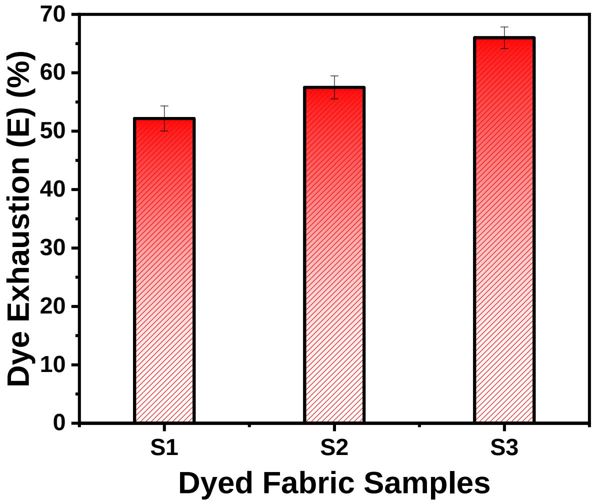

Figure 4. Percentage dye exhaustion (%E) of Cotton Fabric dyed with different dye Systems. (S1), (S2) and (S3)

The result in Figure 3 showed that the cotton fabric dyed with chitosan functionalized reactive dye has an elevated percentage of dye exhaustion, which indicates the better utilization of dyes. It is noteworthy that the effluent that leaves the dye bath was less colored. Because the functionalization of reactive dye with chitosan indicates the introduction of new functional amino groups which improves the substantivity and also the reactivity of cotton. The positive charge of the amino groups may be applied in the adsorption of the negative charge of chromophores of reactive dyes.

The enhanced dyeability is hypothesized due to the existence of amide groups of the chitosan which also can enhance the reactivity of reactive dye. The dye exhaustion of cotton fabric dyed with chitosan functionalized reactive dye improved by 14.8% and 26.5 compared with from the chitosan treated cotton, and unmodified cotton dyed with salt respectively.

3.5 Effect on percentage dye fixation (%F)

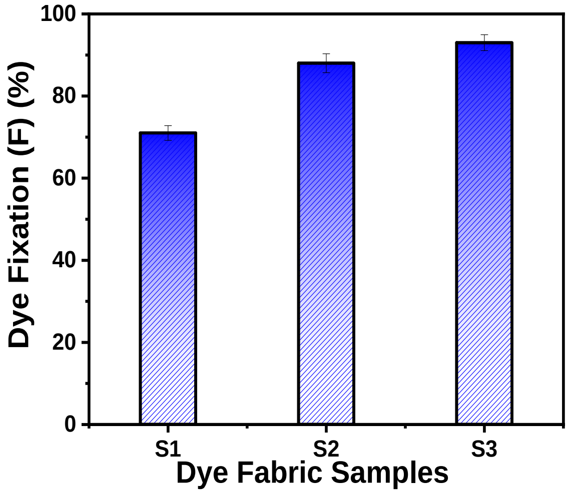

Figure.5 percentage dye fixation (%F) of Cotton Fabric dyed with different dye System. (S1), (S2) and (S3)

As shown in Figure 4, the cotton fabric dyed with chitosan-functionalized reactive dye provided a higher fixation percentage compared with the cationized and uncationized cotton. The enhancement of dye fixation was about 5.6% and 30% compared with the cationized cotton and uncationized cotton fabric, respectively. Such enhancement was due to minor accidental hydrolysis of dyes. The dye exhausted by the fabric probably reacts with the fabric, consequently higher dye exhaustion fulfills in a higher degree of fixation.

3.6 Effect on percentage total dye utilization (%T)

Figure 5 displays that the sample fabric dyed with chitosan functionalized reactive dye delivered a higher dye utilization percentage than the cationized and uncationized cotton fabric sample. The dye utilization was improved by 9.56% and 22.2% compared with cationized and uncationized methods, respectively

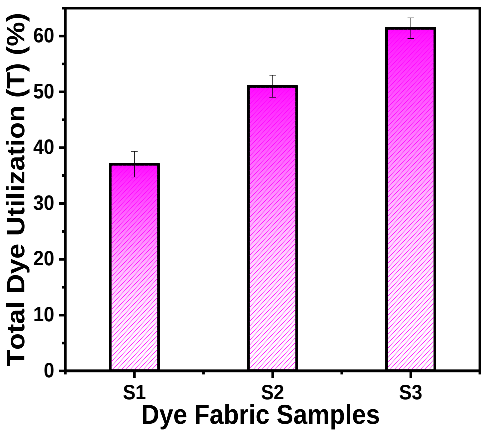

Figure.6 Total Dye Utilization (T) (%) of Cotton Fabric dyed with different dye Systems. (S1), (S2) and (S3)

3.7 Color fastness testing

Here, rubbing, washing, and light fastness were measured to assess the color fastness of the dyed cotton fabrics.

3.7.1 Washing fastness

The washing fastness of the cotton fabric dyed by chitosan functionalized reactive dye was compared with cationized and uncationized cotton fabrics. Here the color change and staining were considered of dyed cotton fabric. As shown in Table 1, the washing fastness of the cotton fabric dyed with chitosan functionalized reactive dye was slightly lower than the cationized and uncationized cotton fabric. All dyeing techniques achieved satisfactory grades by examination with the standard greyscale assignment. Here the results may be due to the construction of a robust bond between the fiber and the dye. In addition, the exhausted dye was fixed on the cotton fabric.

Table 1 Washing fastness of Cotton fabrics dyed with different systems

Sample	Color change	Staining
Conventional Dyeing	4	4
Cationized Cotton	4	4
Chitosan-Functionalized Reactive Dye	3/4	3/4

3.7.2 Rubbing fastness

The rubbing fastness of the chitosan functionalized reactive dye was compared with cationized and uncationized cotton fabric. The rubbing staining of dry and wet fabric was evaluated with the grey scales for staining. As shown in Table 2, the rubbing fastness of the chitosan functionalized reactive dye was compared with cationized and uncationized cotton fabrics. The result shows that the rubbing fastness of dry and wet fabrics was not given any change and all samples achieved satisfactory grades. The results may be because of the construction of the robust covalent bond between the chitosan functionalized reactive dye and cotton fabric.

Table 2 Rubbing fastness of Cotton fabrics dyed with different systems

Sample	Color change
Conventional Dyeing	4
Cationized Cotton	3/4
Chitosan-Functionalized Reactive Dye	3/4

3.7.3 Light fastness

The light-fastness estimates the resistance to the color change of dyed fabric when exhibited in daylight. The light fastness of all fabrics dyed with chitosan functionalized reactive dye, cationized and uncationized cotton fabric were compared. As can be seen from Table 3, the light-fastness was evaluated by comparing the change in color of the samples with the standard. The result showed that the light-fastness of the uncationized cotton fabric was excellent. From the below result, the cotton fabric dyed with chitosan functionalized reactive dye resulted in one step downed light fastness compared to the cationized cotton fabric.

Table **3 Light fastness of Cotton fabrics dyed with different systems**

. Sample	Staining	
	Dry	Wet
Conventional Dyeing	4	1/2
Cationized Cotton	4/5	2
Chitosan-Functionalized Reactive Dye	4/5	2

Conclusion

In summary, we established a new technique for salt-free dyeing of cotton with reactive dye based on chitosan functionalized reactive dye. Benefiting from the strong interaction between chitosan and reactive dye as well as cotton fabric, the cotton fabric dyed with chitosan functionalized reactive dye achieved high dye exhaustion, dye fixation, and total dye utilization. Furthermore, the cotton fabric dyed with chitosan functionalized reactive dye exhibited satisfactory color fastness including rubbing, washing, and light fastness. The successful dyeing of such chitosan functionalized reactive dye by using this easy technique may present a model for the design and development of the economic and environmental dyeing process.

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