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Functionalization of Cellulosic Fibers Using Chitosan: a Salt Free Dyeing Approach

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Abstract

This paper presents the possibility of salt free dyeing of cotton fabric with reactive dye by treating the cotton with chitosan from fish scale and used as a salt for dyeing of cotton with reactive dye. Cellulosic fiber acquires negative charge in aqueous medium and thus repels negatively charged dye anion during dyeing. Such repulsion between fibre and dye is offset by using large quantity of salt in dye bath, particularly for reactive dyes. A low dye bath exhaustion also leads to low dye fixation of reactive dyes on cotton. Therefore, the discharged wastewater from dye house creates avoidable environmental threats due to very high dye concentration. Hence, surface modification of cotton to increase dye-fibre interaction is thus the best route to overcome the lack of affinity of cotton to reactive dyes making salt-free reactive dyeing. In this investigation, an attempt was made to modify cotton with chitosan extracted from fish scales. The chitosan modified cotton was dyed with reactive dye and compared with the conventional dyed cotton. The color strength of the modified cotton fabric was better than that of conventional sample which is 18.88 and 18.02 respectively. Better fastness properties were experienced in treated cotton sample than the ordinary sample. The fastness properties obtained were better than the conventional sample. From this investigation it was revealed that surface modification of cotton by treatment with chitosan provided better dyeing properties and it can be the best possibility for salt free dyeing of cotton.

Keywords: Cotton; Chitosan; Modification; Salt free dyeing; Color strength; Fastness properties

Introduction

Cotton is a natural cellulosic fiber and the most popular among all the textile fibers. About 48% cotton fiber is consumed as clothing material all over apparel industry for a number of its unique characteristics such as softness, versatility, absorbance, hydrophilic in nature, comfort permeability, biodegradability, no static electricity, and breathability [1].

Dyeing of textile fibers comprehends utilization of various chemicals and auxiliaries for various purposes, such as exhaustion of the dyestuff from the dyeing liquor to the textile substrate, fixation of the dyestuff on the substrate, giving identical level dyeing results etc [2]. One of the most well-known classes of dyes for cotton dyeing is a class of reactive dyes. They are frequently considered as king of dyes for cotton owing to their simple application techniques. The dyeing of these fiber are generally done with reactive dyes due to its brilliancy, bright shade, variety hue, good color fastness properties, convenient usage, low energy consumption, high applicability, etc. 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 dye enables it to react with the hydroxyl group in cellulose by nucleophilic addition or substitution reaction [4].

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 quantity of electrolyte (30-100g/l) is added to overcome this problem [4]. Some problems such as low dye utilization, high degree of salt utilization and colored effluent due to unexhausted, unfixed, and hydrolyzed dyestuffs, and high volume of waste water discharged, always exist in the application of reactive dyes. The dyeing of 1kg of cotton with reactive dyes demands from 70-150liter water, 0.6-0.8kg NaCl and from 30-60g dye stuffs [3,4]. These electrolytes are neither exhausted nor destroyed and hence remain in the discharge dye liquor which leads to enormous environmental problem. Due to these problems this class of dyes is the most unfavorable one from the ecological point of view, these effluents produced gives high values of BOD/COD (Biological Oxygen Demand/Chemical Oxygen Demand) and increases salinity of the rivers affects the delicate biochemistry of aquatic life. More than 80,000 tons of reactive dyes are produced and consumed each year, making it possible to quantify the total amount of pollution caused by their use. To improve the dye substantivity of cotton in the absence of salt or low salt additions, one of the approaches is cationization of cotton. Majority of the chemicals used for introducing cationic sites in cotton are themselves not safe environmentally [1,5,6].

Chemical modification of cotton has been earlier studied by many researchers in different ways and means, which are widely available in the literature. Majority of the chemicals used for introducing cationic sites in cotton are themselves not safe environmentally. However, these problems can also be overcome by improving the dye substantivity of cotton in the absence of salt or with low salt additions [7]. One such approach is cationization of cotton which is critically explored in this investigation. Therefore, there is a need to explore the

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potentiality of the cationization route using eco-friendly chemicals. The use of natural amino groups, a polymer derived from chitosan derived from fish scales, is a step forward in this investigation.

As an important root to obtain the desired dyeing performance with existing dyes, chemical modification of cotton fiber to impart cationic charges have been widely researched in recent years. By introducing cationic groups into cotton fibers, the affinity of anionic dyes for cotton was significantly improved, which allows the dyeing of cotton fabrics without salt and to improve reactive dye utilization [8,9].

Cationization of cotton is one of the most widely researched modifications in recent years since both direct and reactive dyes carry anionic charges and they exhibit high affinity for positively charged cotton. Numerous chemicals and methods have been used to introduce cationic groups into cotton fiber [10-14]. By introduction of cationic groups into cotton fibers, the affinity of reactive dyes for cotton can be significantly improved. The ionic attractions between cationized cotton and reactive dyes can result in increased dye uptake, reduced or no electrolyte use, less dye washing off and less water and energy consumption. The environmental problems caused by dye and salt in effluent can be potentially mitigated by cationization pretreatment of cotton [13,14].

The development of chitosan is necessary to overcome those problems that are occurred while using salt; Due to its cationic in nature, nontoxicity biodegradability, antimicrobial activity, etc. Chitosan is composed two main functional groups, namely hydroxyl and amino groups as well as ether linkages. Chitosan and cellulose have analogous structure with the same β-glucoside linkages and the main discrepancy is the presence of primary amino groups at the greater part of the C-2 position in chitosan, in place of the hydroxyl groups in cellulose[15,16].

In this investigation an attempt was made to modify the surface of cotton with chitosan treated which is extracted from fish scales in order to dye cellulosic fibers with reactive dye without utilization of electrolytes in the dyeing process.

Materials and Methods

Fabrics and chemicals

In this investigation 100% half bleached plain weave cotton fabric having 24 ends per inch, 18 picks per inch and having an average areal density of 145 g/m^2 was used. Fish Scales and shells were taken from the local fish market for this study.

Chemicals used for extraction of chitosan, cationization of cotton and for dyeing of the cationized cotton was hydrochloric acid, methanol, acetic acid, acetone, sodium hydroxide, wetting agent, sequestering agent, sodium chloride, sodium carbonate and R-red H8B (C.I. Reactive red-31). All chemicals used were of laboratory grade.

Equipment/Apparatus and machinery

All dyeing accessories were used in this study such as weighing balance, lint test machine, pipet, beaker, stirrer, measuring cylinder, digital pH meter etc. The major equipment used in this study was Stove, Mini dryer, Color data 850 spectrophotometer, Perkin Elmer UV/VIS Spectrometer Lambda 25, Auto-Wash, Crock-Meter and light fastness tester.

Experimental procedures

Preparation of the fish scales: The collected fish scales were washed thoroughly with tap water to remove impurities and dirt on the surface, desiccated at room temperature and subjected to size reduction followed by drying at room temperature.

Extraction of chitin: In the extraction process of chitosan demineralization and deproteinization was done using hydrochloric acid solution (1.0M) and sodium hydroxide solution (1.0M) respectively. Demineralization of the fish skin and scale were carried out to obtain chitin by optimization of the extraction conditions. Demineralization was tried at 2%, 3%, 4% and 5% concentration of hydrochloric acid; at 1:10, 1:15, 1:20 and 1:25 material to liquor ratio; at 20, 24, 28 and 32 hours of treatment time and at room temperature. After that, the solution was filtered and the samples were washed with distilled water until neutral pH was achieved (pH 6.5-8.0). Then the samples were dried using the sun for 4 hours and then the drying process was continued using an oven at 70°C until constant weight were obtained.

In this demineralization process dilute hydrochloric acid was used to remove calcium carbonate and to prevent the hydrolysis of chitin.

The deproteinization were carried out by adding 2N sodium hydroxide in the ratio 1:10 (w/v) and then heated at 60°C by constantly stirring for 30 minutes. In this step sodium hydroxide is used to remove the protein. After that, the solution was filtered and the samples were washed with distilled water until neutral pH was achieved (pH 6.5-8.0). Chitin was obtained as intermediate product.

Extraction of chitosan: The isolated chitin was converted to chitosan by deacetylation process. The deacetylation process was conducted by soaking dried chitin prepared from deproteinization in a 50% NaOH at a temperature of 100 maintained for 6 hours.

Acetic acid solution (5%, w/v) was used to dissolve the achieved chitosan to the ratio of 1:10(w/v), solid to acidic solution. The solution was kept for 12 hours and centrifuged to get a clear chitosan solution. Sodium hydroxide solution (5%, w/v) was added in to the acidic chitosan solution until a precipitation of pure chitosan formed which was then washed until a neutral pH obtained and then dried [17,4].

Analysis of chitosan yield: The percentage dissolution (yield) was calculated using equation (i) by drying the residual after treatment.

$$\text{Chitosan extraction yield (\%)} = [W1\text{-}W2]/W1 \quad (1)$$

Where $W1$=original weight of fish scales, and $W2$= residual weight of fish scales after treatment

Cationization of cotton fabric

Cationization of the cotton fabric with the extracted chitosan was done by using exhaustion methods. Optimization of the cationization conditions of the cotton fabric was conducted. Cationization was tried using 5gpl of pure chitosan at 60, 70 and 80°C of cationization temperature; 15, 30 and 45 minutes of cationization time and 1:10, 1:15 and 1:20 material to liquor ratio.

The presence of chitosan in the cationized cotton was checked by measuring the dye uptake phenomenon using UV/VIS Spectrometer and by measuring the K/S value using color data 850. Cationization parameters for the exhaust method were optimized based on dyeing evenness, maximum K/S values and minimum scorching of fabric.

Conventional dyeing method

The half-bleached cotton fabric was dyed with R-red H8B (C.I. Reactive red-31) for 2% shade. The laboratory lint test dyeing machine with a material-to-liquor ratio of 1:20 was used throughout the study. The fabric was entered at 50oC to the dye bath with a dye and 1g/l levelling agent. After 20 minutes half of the pre dissolved 30g/l glaubular salt was added. The dyeing was continued while raising the temperature to 85°C in 25 minutes and the remaining 30 g/l predissolved glauber's salt was added in the intermediate. The dyeing was continued at 85°C for 10 minutes and 15 g/l soda ash was added to the solution and dyeing was continued for 35 minutes. After dyeing was completed soaping was carried out at boiling temperature for 20 minutes by using 2gpl standard soap. The dyed fabric was rinsed by carried out washing with warm water (60°C) for 5min and with cold water for 5 minutes.

Dyeing of cationized cotton

Chitosan cationized cotton fabric was dyed with R-red H8B (C.I. Reactive red-31) in a laboratory lint test dyeing machine with a material-to-liquor ratio of 1:10 and for 2% shade. The fabric was entered at 40°C to the dye bath solution and the temperature was raised to 75°C in 20 minutes at the rate of 1oC per minutes. Dyeing was continued for 10 min at 75°C and then 15 g/l sodium carbonate was added to the solution. After addition of sodium carbonate for the fixation of reactive dyes used in this study, the dyeing was continued for further 40 minutes. The fabric was then soaped with 2g/l standard soap at boiling temperature for 20 minutes. The dyed fabrics were then rinsed with warm water (60°C) for 5 min and with cold water for 5 min and finally dried in air.

The dye bath did not contain salt during the application of reactive dye unless otherwise specified.

Evaluation parameters

Determination of color strength (K/S): The color strength was measured using data color 850-spectrophotometer result in L x a x b, D-65 and 10° observer, the color intensities (K/S) of the cationized samples at different conditions was determined. The Reflectance (R) value of dyed fabric at the maximum wavelength of absorbency (λmax) was found and the K/S was calculated using the built-in software of the computer color matching system. Kubelka-Munk equation (2) given below has been used for K/S determination.

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

Where, K is the light absorption coefficient, S is the light scattering coefficient while R is the D65/10 light reflection. K/S values were calculated based on reflection values of untreated and treated cotton fabrics. This value symbolizes the reduction ratio of light owing to absorption and scattering achieved based on reflectance.

Determination of dye exhaustion (% E): The absorbance (optical density) of the dye solution was measured before and after the dyeing processes using a UV/VIS Spectrometer at the maximum wavelength of absorbance (λ max). The percentage of dye bath exhaustion (E) was calculated using equation (3):

$$\%E=\frac{(A_o-A_1)}{A_o}\times 100 \qquad (3)$$

Where A_o is the absorbance of dye solution before the commencement of dyeing and A_1 is the absorbance of dye solution after the dyeing process.

Determination of dye fixation (% F): The reflectance (R) values at all wavelengths were measured. The maximum *K/S* value of dyed fabric at the certain wavelength was measured by using data color 850 spectrophotometer before and after soaping. The percentage of dye fixation was calculated using equation (4).

$$\%F=\frac{(K/S)a}{(K/S)b}\times 100 \qquad (4)$$

Where *(K/S)b* and *(K/S)a* are the color strength before soaping and after soaping respectively.

Determination of total dye utilization (%T): The total dye utilization percentage (%*T*) was calculated by using equation (5).

$$\%T=\frac{E\times F}{100} \qquad (5)$$

Assessment of fastness properties: ISO 105 C06 2002 method on launder-O-meter was used to assess the wash fastness. The change in colour and degree of staining were evaluated using geometric grey scales. The light fastness was evaluated with light fastness tester (ISO 105 B02) and the rubbing fastness on crockmeter (ISO 105 F09 2009).

Result and Discussions

Color strength result

The color intensities (K/S) is used to express the reduction ratio of light owning to absorption and scattering achieved based on reflectance. The higher the color intensities is the more dye is fixed on the fabric and the low dye variation effect will have on the fabric because light is reflected more in a uniform surface. Using color eye 3100 reflectance spectrophotometer result in L x a x b, D-65 and 10° observer the color intensities (K/S) of cationized samples was

Figure 1: Preparations of the fish skin and scale.

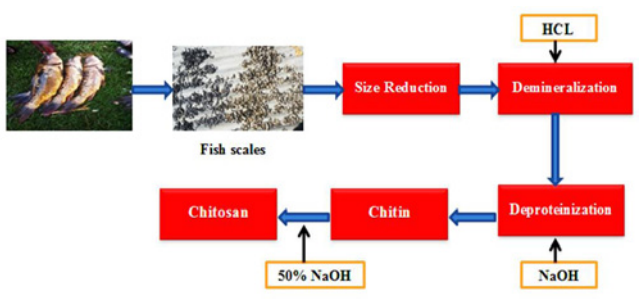

Figure 2: Overall process for extraction of chitosan from fish scales.

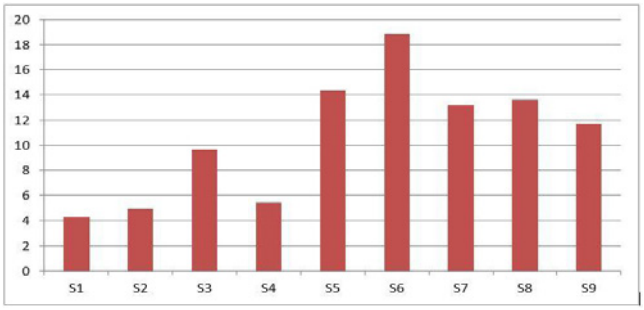

Figure 3: Optimization of the color strength value of cationized cotton.

Table 1: K/S value of chitosan modified cotton.

Samples	Reflectance (%)	K/S
Conventional	2.63	18.02
Cationized	2.65	18.88

Table 2: Percentage exhaustion of chitosan modified cotton.

Samples	Maximum Absorbance before dyeing (A_o)	Maximum Absorbance after dyeing (A_1)	Percentage Exhaustion (% E)
Conventional	4.93	1.3845	71.956
Cationized	4.69	0.807	82.793

Table 3: Percentage fixation of chitosan modified cotton.

Sample	Maximum K/S after washing	Maximum K/S before washing	Fixation (%)
Conventional	18.0228	21.981	81.992
Cationized	19.502	17.881	91.688

determined and it is as shown in Figure 3.

From the above Table 2 and Figure 3 it was showed that K/S value of sample at 530 nm wavelength was maximum (18.88). Hence, the optimized cationization conditions were 3% acetic acid, 60 min treatment time, 80°C temperature and 1:25 material to liquor ratio.

As shown in the above Table 1, the result shows that the color strength (K/S) values of the chitosan treated cotton fabric is almost similar to the unmodified cotton dyed with salt. There is no significant difference in color strength value between the modified and unmodified samples. This shows that surface modification of cotton using chitosan for salt free dyeing provides good dyeing properties.

Effect on percentage dye exhaustion (%E)

Uniform distribution of the dye in to the inter part of the fabric or transferring of the dye from dyeing bath to surface of the fabric. The optical density of dye solution before and after the dyeing was measured using UV/VIS spectrophotometer at the maximum wave length of absorbency (λ). The maximum absorbency at 530nm wave length was taken to determine the dye exhaustion percentage.

The result of the above Table 2 showed that the chitosan cationized fabric had high dye exhaustion percentage indicating that there was better utilization of dyes. This also shows that the effluent that leaves the dyebath was less colored. Because the pretreatment of cotton fabric with chitosan demonstrates the introduction of functional amino groups which increase the substantivity and also the reactivity of cotton. The cationic charged amino groups may

Table 4: Percentage dye utilization of chitosan modified cotton.

Sample	Percentage total dye utilization (% T)
Conventional	60
Cationized	76.4

Table 5: Washing fastness of chitosan modified cotton.

Sample	Color Change	Staining
Conventional	4/5	4/5
Cationized	5	4/5

be involved in the adsorption of anionic chromophores of reactive dyes. The improved dye ability is postulated due to the presence of amide groups (-CONH2) available from the chitosan which also tents to improve the reactivity of cellulosic substrate. Chitosan treated cotton which is dyed without utilization of electrolytes improved dye exhaustion by 13.1% from the unmodified cotton dyed with salt.

Effect on percentage dye fixation (%F)

The color strength of the dyed fabric sample before and after soaping was measured using data color 850 spectrophotometer. The percentage of dye fixation was calculated using the above equation (4).

As shown in the above Table 3 the cationized cotton provided higher fixation percentage than the uncationized cotton dyed with salt. The improvement of fixation percentage was around 10.6% from the uncationized cotton fabric dyed with salt. The reason behind the improvement in the dye fixation was because there is less chance for hydrolysis of dyes. The dye exhausted by the fiber preferentially react with the fiber, therefore higher exhaustion result in higher degree of fixation also. The fixation of the dye was also found to be improved greatly on the cationized cotton.

Effect on percentage total dye utilization (%T)

The total dye utilization percentage was calculated using the above equation (5).

The above Table 4 shows that the cationized cotton provided higher dye utilization percentage than the conventional sample fabric dyed with salt. The cationization of cotton with chitosan extracted from fish shell dye utilization was improved in 16.4% from conventional method. From this it can be concluded that, the dyeing of cationized cotton can save approximately 21.5% dye. Because of the cationized cotton have high exhaustion rate; in this case it will reduce the occurrence of hydrolysis of the dye.

Washing fastness

Color fastness to washing of the cationized fabric was compared with conventionally dyed cotton fabric. It was assessed in respect of color change and staining as shown in Table 5.

As shown in the above Table 5, the wash fastness of the cationized cotton fabric was almost similar to the conventional dyed cotton fabric. The color change grade of cationized cotton is higher than the conventional and there was no staining in all cases. Both dyeing methods scored very good grade by assessment with the standard grey scale reading. This may be due to the formation of strong bond between the fiber and the dye. In addition to this, the exhausted dye is fixed on the substrate.

Table 6: Rubbing fastness of chitosan modified cotton.

Samples	Staining	
	Dry	Wet
Conventional	4/5	4
Cationized	4/5	4

Table 7: Light fastness of chitosan modified cotton.

Sample	Color change
Conventional	7
Cationized	6

Rubbing fastness

Color fastness to rubbing of the cationized fabric was compared with conventionally dyed cotton fabrics. The staining of rubbing cloth was assessed with the grey scales for staining.

As shown in the above Table 6, color fastness to rubbing of cationized fabric was compared with conventionally dyed cotton fabric. The result shows that the dry and wet rubbing fastness of both samples was given not any change and both sample scored very good grade. This may be because of the formation of strong covalent bond between the anionic dye molecule and the cationic cotton surface. The cationized fabric had similar color change with conventional.

Light fastness

Light fastness measures the resistance to color change of dyed textile when exposed to day light. The light fastness of both untreated fabric dyed with salt and the cationized fabric dyed without salt was compared.

As it was observed from the above Table 7, the light fastness was assessed by comparing of the change in color of the specimen with that of the standard. The result showed that the light fastness of the untreated fabric was excellent. The light fastness of the fabric generally 4 is acceptable. From the above result, cationized cotton dyed sample resulted one step downed light fastness compared to the conventional.

Conclusion

From this investigation it was observed that salt free reactive dyeing of cotton with reactive dye by modification with chitosan provided excellent results. The chitosan was extracted from fish scales by exhaust technique and applied to cotton using pad-dry-cure techniques. The modified cotton provided cationic dye sites and thus has been dyed with reactive dye R8H (C.I. Reactive red-31) without salt and the result compared with the conventional dyed sample with salt. Chitosan modified cotton showed 13.1 % improvement in dye exhaustion, 10.6 % in dye fixation and 21.5% in the total dye utilization as compared to the conventional sample. The dye hydrolysis is reduced in the chitosan modified dyeing as the dye exhaustion percentage of cationized dyeing is higher than the conventional dyeing. In addition to this, both the dyeing time and temperature were reduced by 10°C and 20 minutes respectively in the cationized cotton dyeing technique. Compared with untreated cotton dyed with a conventional dyeing procedure, the chitosan modified cotton fabrics dyed without electrolytes have adequate and quite comparable colorfastness to washing, dry rubbing and wet rubbing fastness but slightly reduced light fastness. Besides, the chitosan modified dyeing process greatly reduced, the amount of water usage and time required to adequately rinse and remove hydrolyzed reactive dye. So, a significant savings in process costs was also achieved from the modified cotton dyeing method. Therefore, from dyeing, economic and environmental point of view, it was concluded that using this natural material for cationization is a good substitute for synthetic cationizing agents. This provides both a strategy for reducing risks and pollutant from salt and unutilized dye and also creates an opportunity for new markets and new businesses that could be implemented for selling of the waste product of fish.

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