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Salt Free Reactive Dyeing of Cotton Fabric by Cationization with Keratin Obtained from Sheep Wool

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Abstract

In this investigation an attempt was made to cationize cotton fabric by treatment with keratin hydrolysate extracted from sheep wool for salt free dyeing with reactive dye. In conventional method of dyeing of cotton with reactive dyes requires more electrolytes for exhaustion and alkali for fixation. Besides this there is also low dye exhaustion, due to similarity of negative charge of dye and cellulose fiber tends to repeal each other requiring high amounts of salt in the dyeing bath to overcome repulsive charge between cotton and reactive dyes. Therefore the discharged wastewater from dye house creates avoidable environmental threats and aquatic life problems due to very high dye concentration. To solve these problems, cationization of cotton fabric by treatment with keratin hydrolysate extracted from sheep wool for salt free dyeing with reactive dye was done. The extractions were tried at different combinations of NaOH, MLR, time and temperature and optimized based on the maximum absorption obtained at λ_{max} and maximum percentage yield. The extracted keratin was applied on cotton by pad-dry-cure techniques. Then dyed with reactive dye without salt and evaluated. The K/S value of cationed cotton was better than that of conventional which is 4.96 and 4.51 respectively. Dye exhaustion and fixation percentage obtained was 78.65% and 84.27% respectively for the cationed sample while 70.34% and 75.61% for the conventional sample. The colorfastness to washing, rubbing and light of the cationized cotton were found almost similar to that of the conventional dyeing. Tensile and tear strength of cationized and the conventional dyed cotton were found almost the same. A slight increase in flexural rigidity and crease recovery angle in the cationized cotton was observed. From this study it can be revealed that keratin hydrolysate was found to be effective for cationization in salt-free dyeing of cotton.

Keywords: Cotton; Keratin hydrolysate; Cationization; Salt free dyeing; Color strength; Fastness

Introduction

Cotton is the world's most widely used natural fiber for making various textile products. Cotton fibers stand out and are used widely because of their special qualities, which include softness, versatility, absorbency, hydrophilicity, comfort permeability, no static electricity, ease of dyeing, and biodegradability [1-3]. The main dyes for dying cotton fibers are reactive dyes, which have strong reactions with cotton fibers, bright colors, a wide color spectrum, versatile application methods, and excellent color fastness [4-8]. Reactive dyes are distinguished from other dyes by their capacity to form covalent bonds carbon atoms of dye reactive group and oxygen atoms of cotton hydroxyl groups under alkaline conditions [9].

Reactive dyes, the most regal dyes, continue to dominate the cotton dyeing industry today because of their numerous versatile qualities, including wide color gamuts, practical fastness features, and simplicity of use. Cotton develops a negative charge as a result of the hydroxyl groups in cellulose being ionized in the dyeing water. Despite the fact that the majority of dye classes that work for cotton are anionic in solution. An electrolyte like sodium chloride or sodium sulfate can be used to reduce the intense static repulsion that exists between the cotton fiber and the anionic reactive colors. The amount of salt used might range from 30g/l to 150g/l, depending on the color depth and dye composition [9-13].

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The depletion of the dye is accelerated by adding enough salt, which accelerates the transfer of dyes from the dyeing solution to the surface of the cotton fiber. Reactive cotton dye fixations work by creating a covalent link between the dye molecule and the hydroxyl of cotton fiber at a high pH (>10.5). Additionally, some dyestuff molecules may interact with OH- in the alkaline solution, resulting in low dye fixation [13,14]. The dyeing chemists have consequently shown a great deal of interest in processes that employ a lot of salt and fix reactive dyes slowly. Strongly colored effluents from the dyeing process that have complicated chemical compositions have significantly harmed the environment [13,15].

For the purpose of enhancing dye adsorption, a significant amount of inorganic salt, such as sodium sulphate, must be applied for reactive dyeing. It is important to note that 30-50% of the dye is still lost during conventional dyeing, even when salt is applied at a rate of 30-150 g/L [9,16]. Inorganic salts that are not biodegradable and are present in significant quantities in dyeing wastewater when it is discharged haphazardly can cause water pollution and salinization of the soil [17]. Therefore, to achieve the environmental friendliness and effective exploitation of resources in deep color dyeing procedures, avoiding the employment of salt and improving dye fixation are vital [6-9,18].

It is crucial to find an alternate strategy to minimize environmental issues, remove or reduce salt consumption, and improve color usage.

Chemically altering cotton fiber to impart cationic charges has received a lot of attention recently as a key to achieving the desired dyeing performance with current dyes. The affinity of anionic dyes for cotton was greatly increased by adding cationic groups to cotton fibers, enabling the dyeing of cotton garments without salt and increasing the efficiency of reactive dyes. The dyeing of cationized cotton is a potentially environmentally friendly technique because it uses less chemical, water, and energy [19-21].

One of the most widely studied methods for salt-free dyeing is chemical modification of cellulosic fibers using cationic reagent for cationization. In this study keratin hydrolysate extract was used as cationic reagent for cationization of cotton for salt-free dyeing. Cationic functional groups were introduced on the surface of the cotton fibers to improve dye exhaustion. These cationic groups have an overall positive charge, which causes the cotton fiber to acquire a positive charge in water. Since reactive dyes have an overall negative charge, an attraction between the two occurs, improving exhaustion and enabling salt-free, high fixation dyeing.

The best approach to overcoming cotton's lack of affinity for reactive dyes is therefore to change the cotton fiber to promote dye-fibre interaction, which has led to salt-free or low-salt reactive dyeing being a significant subject of study in recent years [6-10].

With this background knowledge, the current study was designed with the objective of modifying the cotton fiber's surface by cationizing an extract of sheep wool's keratin hydrolysate for a salt-free dying method using reactive dyes.

Keratin can be extracted from animal hard tissues including wool, feathers, hooves, and horns especially for use in the cosmetic industry. Keratin comes in two forms, powder & liquid form. Keratin is completely insoluble in cold or hot water. Due to its inherent biocompatibility and biodegradability behaviors, keratin is found to be very useful for a wide range of applications.

Sheep wool unsuitable for processing in the textile industry belongs to most important keratin wastes. The most typical indicator of proteins of keratin group is high content of amino acids cystine, cysteine and methionine [22].

Due to its non-reactive character and strong resilience, keratin can be processed only with great difficulty; for this reason it has to be partly hydrolysed. Many different procedures and methods can be applied to obtain keratin hydrolysates. Breakdown of keratins by means of hydroxides has been known quite long; alkalis applied most are NaOH, KOH and $Ca(OH)_2$ [23,24]. Gousterova et al decomposed wool in a solution of KOH and NaOH and heated the obtained mixture by microwave technique [25]. Abouheif et al broke down wool and feathers by employing a 3 % solution of boiling NaOH [26].

Many researchers carried out cationization of cotton fiber by using synthetic chemicals of ammonium salts but these chemicals cause irritation to skin and other health problems. Also cationization of cotton fiber by using chitosan, amino acid extract, etc but their extraction processes are long and costly due to using of large amount chemicals. Beside this extraction of keratin hydrolysate had been done by some scholars however, the methods of extraction, extraction conditions optimized and the class of reactive dye used is different. As well dyeability properties and effect of cationization on cotton has been studied well in this study. In this investigation an attempt has been made to cationization of cotton fiber by treatment with keratin hydrolysate extracted from sheep wool for salt-free dyeing of cotton with reactive dyes.

Materials and Methods

Materials

For this study sheep wool waste were collected from kombolcha (Amar tannery seller), half bleached 100% cotton fabric with count 21 Ne warp and weft count with 24 ends per inch and 18 picks per inch was obtained from Kombolcha Institute of Technology (KIOT) laboratory.

Chemicals and Reagents

Sodium hydroxide was used for extraction of keratin hydrolysate. Reactive blue H5R (C.I. Reactive Blue 13), Sodium hydroxide, Sodium carbonate, Sodium chloride, acetic acid, wetting agents and sequestering agents were used throughout this research work to carry out dyeing of cotton fabric. All the chemicals and reagents used in this study was laboratory grade.

Equipment's and Apparatus

All the dyeing accessories were also used in this study. Lab-scale IR Dyeing machine, Padding Mangle, Mini-dryer, PerkinElmer FT-IR Spectrometer, Data color 850 spectrophotometer, PerkinElmer UV/VIS Spectrometer Lambda 25, Crock-Meter, Auto-Wash, Fadometer with xenon arc lamp, Elmendorf tear strength tester, Universal tensile strength tester, Shirley crease recovery tester were used in this study.

Collection and Preparation of Sheep Wool Waste

In this study the sheep wool wastes were collected from kombolcha local tannery sell and leather tannery industries. The wool waste was washed with tap water and standard detergent in order to remove external impurities. Then the washed

sample materials were dried in sunlight and size reductions of the sheep wool were carried out for better extraction efficiency of keratin.

Extraction of Keratin

Keratin was extracted from wool by immersing in caustic soda. Wool keratin was extracted by hydrolysis with caustic soda at different combinations of temperature, time, concentration of NaOH and MLR. The optimum extraction parameters were determined after measurement of its absorption using UV-Vis spectroscopy and percentage yield. Then after the extracted solutions was filtered with filter paper and stored in container until further use.

Extraction Conditions Optimization

In order to determine the maximum yield percentage of keratin hydrolysate from sheep wool waste extraction were tried at different extraction conditions like extraction temperature, extraction time, material to liquor ratio and concentration of caustic soda.

Extraction of the keratin hydrolysate was tried at extraction temperature of 40, 60, 80 and 100 $^{\circ}C$; at different extraction time of 60, 80, 100 and 120 min; at caustic soda concentration of 10, 20, 30 and 40g/l. A four factor four level Taguchi design of expert were used for optimization of this extraction parameters and a total of sixteen experiments were carried out as per the design experiment software.

Then after the optimum extraction conditions were identified by determining the percentage yield of keratin. Percentage yield of extract were determined using equation (1):

$$\text{Yield } (\%) = \frac{[W1 - W2]}{W1} * 100 \qquad (1)$$

Where W1 is original weight of sheep wool, and W2 is residual weight of sheep wool after treatment.

Cationization of Cotton

The extracted keratin hydrolysate solutions were applied on cotton fabric by pad-dry-cure techniques.

Cationization of cotton was done by application of the extracted keratin hydrolysate solutions on cotton fabric by padding technique in a laboratory two bowl padding mangle (two dips and two nips) at 100% wet pickup. The cotton fabric was immersed in 40g/l of keratin haydrolysate solutions and squeezed at 3 bar pressure of the squeezing rollers. The padded and squeezed cotton fabrics were dried at a temperature of 90°C for 5 minutes and subsequently cured at 130°C for 2 minutes.

Confirmation of Cationization

Cationization of the cotton fibers were confirmed by measuring the presence of new functional groups in the cotton fiber, measuring dye absorption and K/S value of the dyed samples.

Dyeing Parameters Optimization

The cationed cotton fabric was dyed with Reactive blue H5R dye without utilization of salt. Optimization of dyeing parameters such as dyeing temperature, dyeing time, MLR were carried out. Dyeing was carried out at 70 $^{\circ}C$, 80 $^{\circ}C$, 90 $^{\circ}C$ dyeing temperature; for 60, 90 and 120 min dyeing time; at 1:10, 1:20 and 1:30 material to liquor ratio. During dyeing of the cationed cotton fabric electrolytes/salt was not added in the dye-bath. For optimization of dyeing conditions of cationed cotton a three factor three level Taguchi design of expert were used and a total of nine experiments were carried out as per the design expert software. The optimum dyeing conditions was determined by measuring the color strength (K/S) value of the dyed fabric samples and fastness properties.

Dyeing of the Cotton fabric with Conventional Methods

The half bleached cotton fabric was dyed with R-blue H5R (C.I. Reactive Blue 13) for 3% shade. Lab-scale IR dyeing machine with a material-to-liquor ratio of 1:30 was used throughout the study. Start dyeing with the bath containing dye solution and fabric sample at 50 ^{0}C. After 20 minutes half of the pre-dissolved 30g/l glauber salt was added. The dyeing was continued while raising the temperature to 85˚C in 25 minutes and the remaining 30g/l pre-dissolved glauber's salt was added in the intermediate. The dyeing was continued at 85˚C for 15 minutes and 20g/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 5g/l 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 the Cationed Cotton Fabric

Keratin cationized cotton fabric was dyed with R-blue H5R (C.I. Reactive Blue 13) in a Lab-scale IR dyeing machine with a material-to-liquor ratio of 1:30 and for 3% shade. The fabric was entered at 50˚C to the dyebath solution and the temperature was raised to 80˚C in 30 minutes at the rate of 1˚C per minutes. Dyeing was continued for 20 min at 80˚C and then 20g/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 5g/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 then allowed to dry in drying chamber. During dyeing of the cationized cotton with reactive dye, electrolytes/salt has not been added in the dye-bath in this dyeing method.

Color Strength Measurement

The reflectance values at all wave length was measured by using Data color 850 spectrophotometer, The reflectance (R) value of dyed cloth at the maximum wave length of absorbency (λmax) is found and the K/S is calculated using the built –in software of the computer color matching system. Kubelka-munk equation (2) given as-

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

Where, K/S and R stands to color strength and reflectance at maximum wave length (λmax) respectively.

Determination of Exhaustion percentages

The optical density of the dye before and after dyeing was measured using UV/VIS Spectrometer at the maximum absorption of the sample. The dye bath exhaustion percentage (%E) was calculated using Equation (3).

$$\%\ E = \frac{[A0 - A1]}{[A0]} * 100 \qquad (3)$$

where A0 and A1 are the absorbencies at maximum wave length of dye originally in the dye bath and residual dye after dyeing, respectively.

Determination of Fixation percentages

The reflectance (R) values at all wavelengths were measured. The maximum K/S value of dyed fabric at the certain wavelength was measured using Color Eye 3100 before and after soaping. The percentage of dye fixation (% F) was calculated using equation (4):

$$\%\ F = \frac{\left(\frac{K}{S}\right)_b}{\left(\frac{K}{S}\right)_a} * 100 \qquad (4)$$

Where K/S is the color yield with the values before soaping (b) and after soaping (a)

Determination of Total Dye Utilization

The total dye utilization percentage (%T) was calculated using equation (5).

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

Testing of Fastness Properties

Color fastness properties such as washing, rubbing and light fastness of the dyed samples were evaluated according to ISO 105-C06: 2010 [27], ISO 105-F09: 2009 [2,7] and ISO 105-B02: 2013 [2,7] standard methods respectively.

Testing of Physical Properties

Physical properties such as tensile strength, tear strength, stiffness and crease recovery angle of the dyed samples were tested according to ASTM D 5035-95 [6], ASTM D1424-09 [6], AATCC Test 66-2003 [28] and ASTM D1388-2007 [28] standard methods respectively.

Result and Discussions

Optimization of keratin extraction Parameters

In each trial experiment 20gm of chopped wool was used for extraction of keratin in different combinations of the extraction parameters as given in Table 1.

The extraction was carried out in a closed IR dyeing apparatus with a mechanism for computer-assisted parameter control. The optimum extraction parameters were determined by evaluating the absorption of the extracted keratin under UV-Visible spectroscopy and percentage yield for each trial experiments. Table 1 shows that the optimum values of extraction were 35 g/l NaOH, 1:20 MLR, 85 $^{\circ}C$ and 60 min with an efficiency of 96.64%.

In Table 1 it was observed that maximum absorption of keratin hydrolysate extract and higher percentage yield was obtained in experiment number 14. In trial experiment 14, a percentage yield of 96.64% and UV absorption of 5.6 keratin extract from sheep wool waste were obtained. As a result, it was concluded that the optimum extraction conditions of keratin are at 35g/l NaOH, MLR of 1:20, extraction temperature of 85 $^{\circ}C$ and extraction time of 60 minutes. This extraction parameter has given the maximum absorption of keratin hydrolysate extract solution and the maximum percentage yield of keratin.

Figure 1 shows the UV absorption of keratin hydrolysate extract solution value with their respect number of trial experiment. It was observed that higher absorption value was obtained at experiment number 14. Figure 2 shows higher percentage yield of keratin extract was obtained in experiment number 14. Figure 1 indicates that maximum absorption and Figure 2 indicates that higher percentage yield (dissolution) were obtained when wool fiber waste was treated with 35g/l caustic soda at 85 $^{\circ}C$ for 1 hours and at 1:20 material to liquor ratio. This treatment was performed at 12 pH level.

This means that the treatment of the wool fiber waste with caustic soda at this optimized extraction conditions gives maximum efficiency of extraction of keratin solution and maximum absorption of keratin solution.

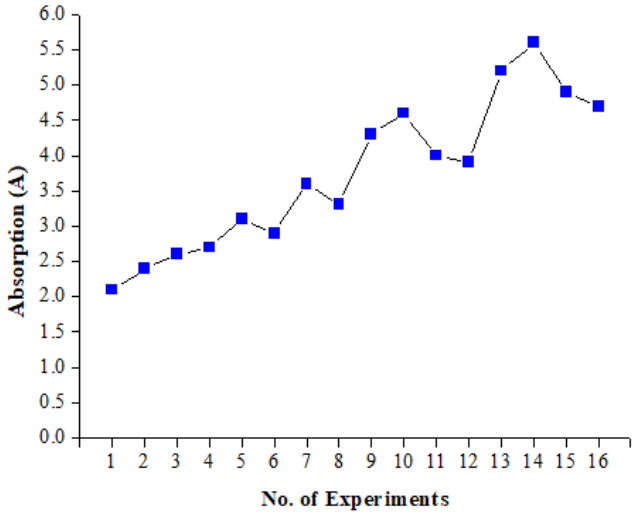

Figure 1: UV Absorption of the extracted keratin.

Table 1: Absorption and Percentage Yield of keratin.

No. of Experiments	Conc. of NaOH (g/l)	Liquor to material (ml/g)	Extraction Temperature ($^{\circ}C$)	Extraction Time (Min)	Yield (%)	UV Absorption (A) at λmax 270 nm
1	5	10	55	60	59.75	2.1
2	5	20	70	80	61.6	2.4
3	5	30	85	100	64.22	2.6
4	5	40	100	120	67.86	2.7
5	15	10	70	100	74.45	3.1
6	15	20	55	120	71.21	2.9
7	15	30	100	60	78.26	3.6
8	15	40	85	80	76.33	3.3
9	25	10	85	120	86.25	4.3
10	25	20	100	100	88.58	4.6
11	25	30	55	80	84.4	4.0
12	25	40	70	60	83.52	3.9
13	35	10	100	80	94.32	5.2
14	35	20	85	60	96.64	5.6
15	35	30	70	120	92.13	4.9
16	35	40	55	100	89.92	4.7

Table 2: K/S Value of cationized cotton.

No. of Experiments	Dyeing Temperature (°C)	Dyeing Time (min)	MLR	K/S Value
1	65	60	1:10	3.21
2	65	90	1:20	3.47
3	65	120	1:30	3.73
4	80	60	1:20	4.24
5	80	90	1:30	4.96
6	80	120	1:10	4.48
7	95	60	1:30	4.53
8	95	90	1:10	4.65
9	95	120	1:20	4.71

Table 3: K/S value of various samples at 460 nm wavelength.

Samples	Reflectance (%)	K/S value
Cationized	8.45	4.96
Conventional	9.15	4.51
Control	15.67	2.27

Table 4: CIE L * a ×*b values at D65 and 10° observer.

Samples	Color Parameters							
	L*	a*	b*	X	Y	Z	Yellowness	Whiteness
Control	91.64	2.31	-7.12	68.52	72.48	68.96	9.63	59.81
Conventional	61.88	-5.94	-21.37	33.24	23.63	27.62	45.02	56.11
Cationized	60.35	-4.67	-26.77	31.85	22.44	27.98	39.70	54.84

Table 5: Dye exhaustion percentage of different samples.

Fabric Samples	Maximum Absorbance before dyeing (Ao)	Maximum Absorbance after dyeing (A1)	Percentage Exhaustion (% E)
Control	5.2687	3.2287	38.72
Conventional	2.6682	0.7914	70.34
Cationized	2.1583	0.4608	78.65

Table 6: Dye Fixation percentage of different samples.

Fabric Samples	Maximum K/S before Soaping at 460 nm	Maximum K/S after Soaping at 460 nm	Fixation Percentage (F %)
Control	1.28	2.27	56.38
Conventional	3.41	4.51	75.61
Cationized	4.18	4.96	84.27

Cationization of Cotton fabric

The cotton fabric was immersed in 40 g/l of keratin hydrolysate extract and then subjected to squeezing to facilitate the penetration of keratin solution into the fiber and also to remove excess solutions. Then the padded fabric was dried and cured subsequently at 90°C and 130°C for 5 and 2 minutes respectively.

Confirmation of Cationization

FTIR spectrum of both the treated and untreated cotton fabric was illustrated in Figure 3. The presence of amino acid in the cationized cotton fabric was confirmed with the use of FTIR technique. The result of the above Figure 3 showed that there was a change in chemical composition after cationizing by pad-dry-cure method; the amino acid was fixed to the fabric.

As compared with the untreated cotton, two new absorption bands were observed in the treated cotton at 1653 cm-1 and 2348 cm-1. The first absorption bands was observed at peak 1653 cm-1 and clearly indicate the presence of vibrations bending N-H primary amines and found strong to medium intensities. The other new absorption band was observed at peak 2348 cm-1 which is the characteristics of –CH2- stretching. Such absorption bands, however, are practically non-existent in the spectrum of untreated cotton. This observation adequately revealed that the amino group was chemically absorbed on the treated cotton fibers by pointing to the presence of primary amines. It demonstrated that cationic keratin polymer and cotton textiles reacted.

Cationized Cotton Dyeing Parameters Optimization

In this study in order to investigate the dyeing conditions of the cationized cotton fabrics the dyeing conditions were optimized by carrying out the dyeing at different combinations of dyeing conditions. In Table 2 the different combinations of dyeing conditions with their respective K/S value was shown.

Table 2 and Figure 4 indicate that higher color strength value was obtained when the cationized cotton fabric was dyed at 80 °C for 90 minutes and at 1:30 material to liquor. K/S value of 4.96 was obtained at trial experiment number 5. The optimum dyeing of keratin hydrolysate cationized cotton fabric which has given higher color intensities at 460 nm wavelength was at 80 °C dyeing temperature, 90 min dyeing time and 1:30 MLR. The higher the color intensity 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.

Table 3 and Figure 5 indicate that a higher K/S values was obtained in the cationized cotton fabric at 460 nm wavelength. This shows that more dye molecules was exhausted by the cationized cotton than the untreated. The reason behind achievement of higher color strength in the cationized cotton sample was due to the higher dyeability properties of amine groups of the cationized cotton than hydroxyl groups of the untreated cotton.

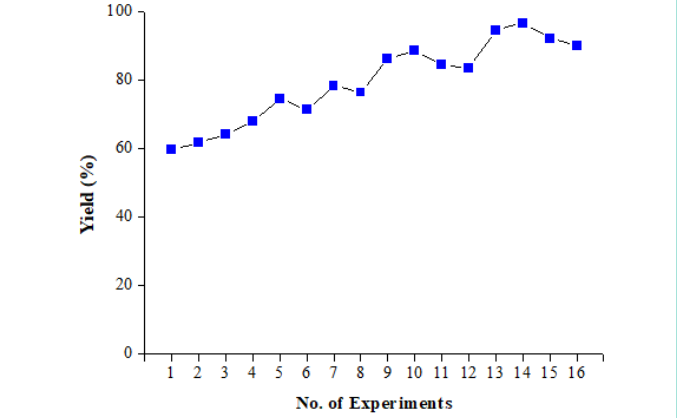

Figure 2: Percentage yield of keratin.

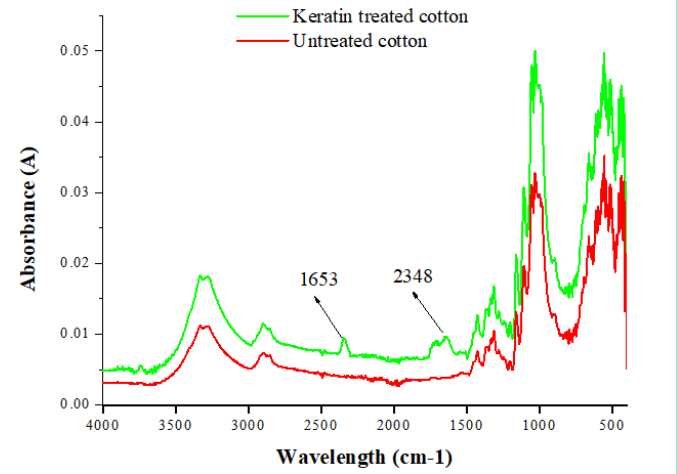

Figure 3: FTIR curve of treated and untreated cotton fabric.

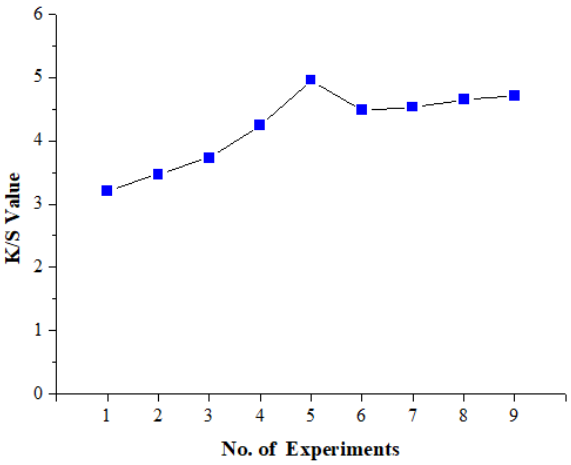

Figure 4: K/S value of cationized cotton at different combinations of dyeing parameters.

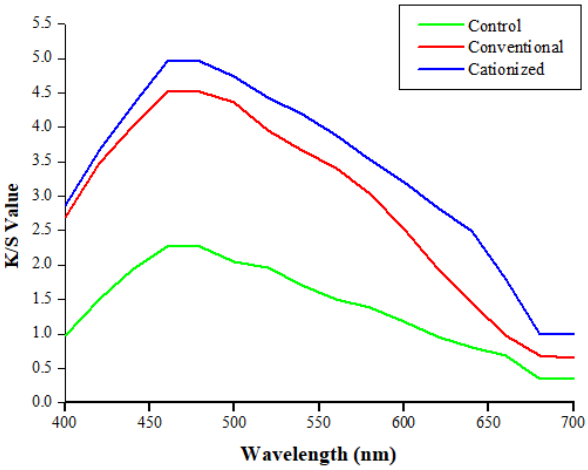

Figure 5: K/S values of cationized and untreated cotton after dyeing.

The greater K/S value in the cotton treated with keratin hydrolysate extract indicates that more dye was absorbed into the treated fabric. The K/S values of the cationized cotton fabric that was coloured with reactive dye using a salt-free dyeing procedure were greater than those of the fabric that was traditionally dyed with salt. The creation of positive charge may be the cause of the increased dye uptake of treated cotton fabric.

In the non-conventional reactive dyeing process, there is strong attraction between the cationic dye sites on the modified cotton and the anionic dyes existed which led to obtain a very high exhaustion rates without addition of electrolytes to the dye-bath.

Moreover, the development of additional amine groups, which increases dye attachment sites, was the cause of the improved dye uptake in the cationized cotton. This demonstrates the effectiveness of the keratin solution treatment in permitting the salt-free dyeing of cotton fabric.

Color coordinate values of the cationized, untreated and control cotton sample were also studied and presented in Table 4.

According to Table 4, there was no discernible change between the treated and untreated fabrics' "L*" values (lightness). The trichromacity coordinates showed no discernible difference between the cationized and uncationized fabric. Uncationized cotton displayed greater "a*" values, which are greener, while cationized cotton displayed more "b*" values, which are bluer. The yellowness index of the cationized fabric was lower than that of the conventional fabric. The whiteness index was likewise lower, demonstrating the deeper hue of the cationized cotton. This demonstrates that the cationized fabric absorbs a significant amount of dye.

UV-Visible Dye Absorption

The residual dye baths after dyeing of the untreated and treated samples were subjected to UV/VIS Spectroscopy measurement and the result was presented in Figure 6.

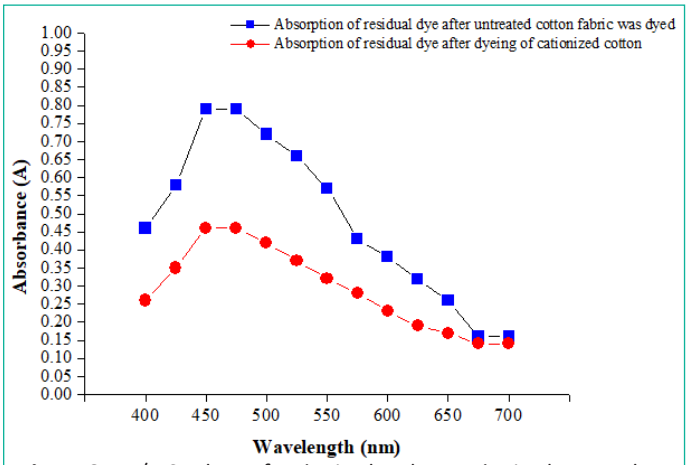

Figure 6: UV/VIS values of cationized and un-cationized cotton dyeing residuals.

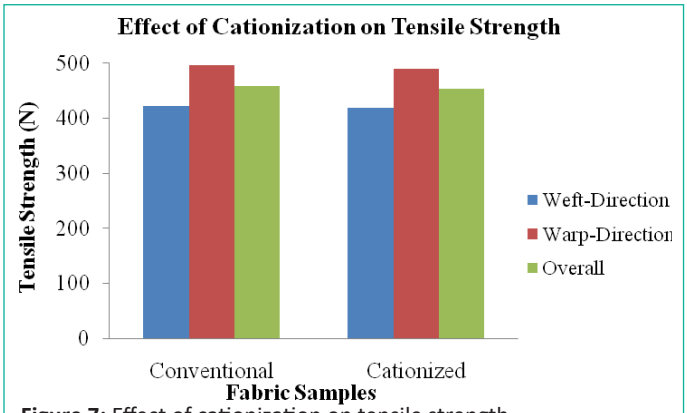

Figure 7: Effect of cationization on tensile strength.

A higher absorption peak indicates that there is more dye still in the dye bath. It is evident that more dye was absorbed in the cationized sample when comparing the maximum absorption peak intensity to the conventional sample. Equation (3) was used to calculate the dye bath exhaustion percentage, which was 70.34% for the conventional sample and 78.65% for the cationized sample. This demonstrates once more how successful the fabric's cationization by sheep wool extract was.

Effect on Dye Exhaustion

The optical density of dye solution before and after the dyeing was measured using UV/VIS spectrophotometer at the maximum wavelength of absorbance (λmax). The maximum absorbance at 460 nm wavelength was taken to determine the dye exhaustion percentage.

The exhaustion of Reactive blue H5R dye on cationized fabric was calculated measuring absorbance before and after dyeing using equation [3]. The results obtained were presented in Table 5 below.

From Table 5 it was observed that the cationized fabric had high dye exhaustion percentage indicating that there was better utilization of dyes. This also shows that the effluent that leaves the dye bath was less colored. The improvement of the dye exhaustion was by 39.93% from the untreated and salt free dyed sample and by 8.31% from the conventional one. The improved

dye uptake of the modified materials may be attributed to the generation of positive charge. It was found that cationization caused remarkable improvements in dye uptake of cotton.

Effect on Dye Fixation

The percentage fixation was calculated measuring the K/S value before and after soaping using Equation (4), and the results were summarized in Table 6.

Table 6 demonstrates that the fixation percentage of the cationized cotton was higher than that of the uncationized cotton colored with salt. The percentage of fixation increased by approximately 27.89% compared to the untreated, salt-free cotton dyed fabric and by approximately 8.66% compared to the uncationized cotton fabric dyed with salt. The decrease in the likelihood of dye hydrolysis was the source of the improvement in dye fixing. The evaluations for washing fastness in Table 8 also showed an improvement in fixation. Adding alkali during fixation promotes the dye's reactivity with the fiber or with the water already in the system. The reactivity of the dye affects how quickly the reaction proceeds. Because the dyes that the fiber uses up preferentially react with the fiber, higher dye exhaustion also leads to higher levels of fixation. On the cationized cotton, it was also discovered that the fixing of dyes had significantly enhanced. The negative surface charge of the fiber might be effectively screened by such treatment, allowing reactive dye to be exhausted and fixed even in the absence of salt.

Effect on Total Dye Utilization

The percentage dye utilization of the cationized and conventional method dyed sample was calculated and the results were summarized in Table 7.

Table 7 demonstrates that the cationized cotton offered a better percentage of color utilization than the traditional sample fabric dyed with salt. By cationizing cotton using keratin hydrolysate obtained from discarded sheep wool, the dye utilization increased from 53.18% to 66.27%. The amount of dye consumption improvement was approximately 44.44% from the untreated and salt-free dyed fabric and approximately 13.09% from the traditional procedure. This means that dyeing cationized cotton can result in a savings of about 13.09% dye.

Fastness Properties

Color fastness to washing, rubbing and light of the cationized fabric was compared with conventionally dyed cotton fabric. Washing fastness was evaluated in terms of color change and staining while rubbing fastness was assessed in terms of dry and wet conditions.

Table 8 shows that the washing fastness of the cationized cotton obtained was very good however one grade down in color change assessment as compared to the conventional. This may be due to hydrolyzed dyes able to form ionic bond with sheep wool keratin hydrolysate on cotton surface, and ionic bonds are weaker than covalent bonds. The result shows that the dry rubbing fastness of all samples was giving not any change and all samples scored very good grade. This may be because of the formation of strong ionic bond between the anionic dye molecule and the cationic cotton surface. The cationized sample also scored good grade in the wet rubbing fastness but one step down than that of the conventional dyed sample. This may be due to the tendency of the hydrolysed dyes being able to form hydrogen bond with amine groups of keratin on cotton surface.

Table 7: Total dye utilization percentage of different samples.

Fabric Samples	Percentage total dye utilization (% T)
Control	21.83
Conventional	53.18
Cationized	66.27

Table 8: Fastness properties of cationized cotton.

Samples	Washing fastness		Rubbing fastness		Light fastness
	Staining	Color change	Dry	Wet	
Control	4/5	4/5	4/5	4	6
Conventional	5	5	4/5	4/5	6
Cationized	5	4/5	4/5	4	5

Cationized cotton dyed sample resulted one step downed light fastness compared to other samples. The reason for one step reduction in the light fastness of cationized cotton was most likely due to the fact that the dye penetrability was good in the cationized fibers with the intended dye fixation method, which assisted in obtaining high light fastness.

Effect of Cationization on Cotton Tensile and Tear Strength

The effect of cationization on tensile and tear strength of cotton fabric were evaluated and compared with conventional procedure dyed samples as shown in Figure 7 and Figure 8.

Tensile and tear strength of cotton fabric dyed with the conventional dyeing method and cationized cotton fabrics were found to be almost the same. Figure 7 and Figure 8 shows that there is a small loss 1.31% and 0.41% in tensile and tear strength respectively. This indicates that cationization of cotton have not affected the strength of the fabric.

Effect of Cationization on Stiffness

The effect of cationization on stiffness of cotton fabric was evaluated and compared with conventional procedure dyed samples as shown in Figure 9.

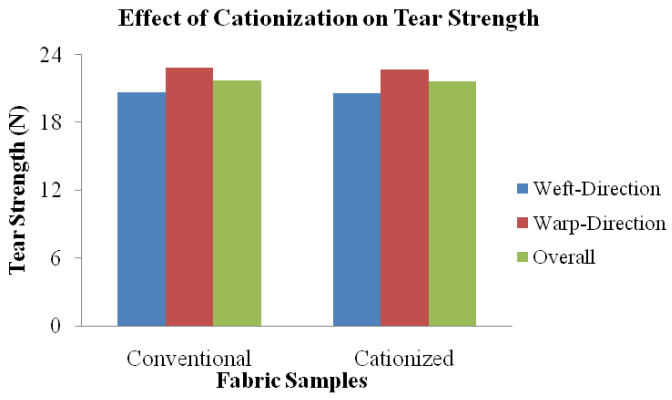

Figure 8: Effect of cationization on tear strength.

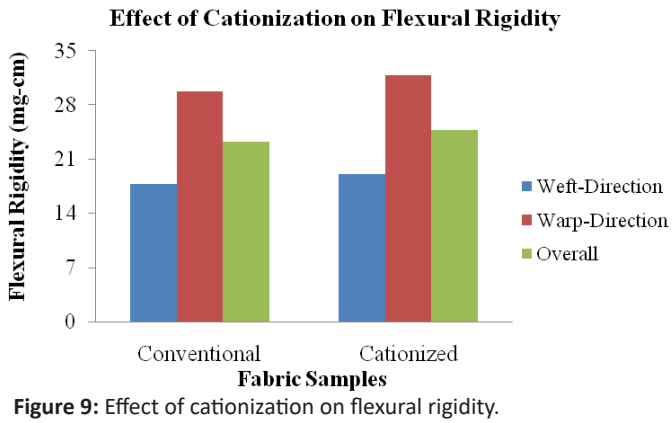

Figure 9: Effect of cationization on flexural rigidity.

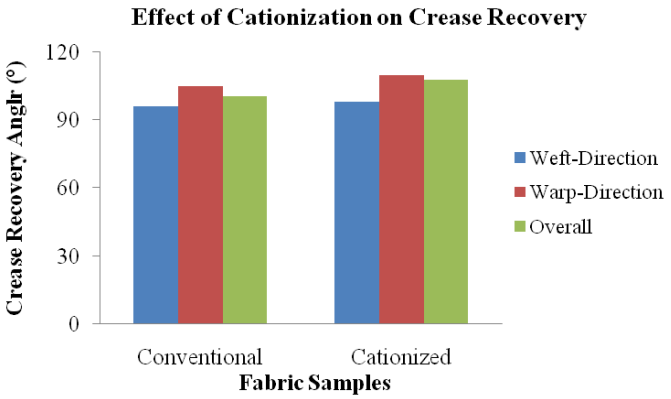

Figure 10: Effect of cationization on crease recovery.

From Figure 9 it is evident that the flexural rigidity of conventional dyed and cationized cotton does not reflect any major variation. The cationization of cotton with keratin slightly increased the flexural rigidity of cotton as a result of pretreatment. The increase in flexural rigidity shows that fabric became slightly stiffer as a result of cationization of cotton with keratin extract of sheep wool. In addition, the stiffness of a fabric in bending is very dependent on its thickness, the thicker the fabric, the stiffer it is if all other factors remain the same.

Effect of Cationization on Crease Recovery

The effect of cationization on crease recovery angle of cotton fabric was evaluated and compared with conventional procedure dyed samples as shown in Figure 10.

From Figure 10 it was observed that there is an increase in crease recovery angle of the cotton fabric in both weft and warp directions when treated with keratin hydrolysate. Cationization increased the crease recovery angle of the cotton fabrics.

Conclusions

From this investigation it was observed that salt free reactive dyeing of cotton with reactive dye by cationization with keratin provided excellent results. The keratin was extracted from sheep wool waste by exhaust technique and applied on bleached cotton fabric by pad-dry-cure techniques. The cationized cotton provided cationic dye sites and thus has been dyed with Reactive blue H5R (C.I. Reactive Blue 13) without salt and the result had been compared with the conventional dyed sample with salt. The dyed fabric was tested for its color strength and CIE L*a*b*, FTIR spectrum, dye exhaustion, dye fixation, color fastness and physical properties. Dyeing of cationized cotton gave better color strength compared to conventional method. Dye exhaustion, dye fixation and color fastness of the dyed samples was improved after the cationization. Keratin cationized cotton showed 8.31 % improvement in dye exhaustion, 8.66 % in dye fixation and 13.09 % in the total dye utilization as compared to the conventional sample. The dye hydrolysis is reduced in the keratin modified cotton dyeing as the dye exhaustion percentage of cationized dyeing is higher. Colorfastness to washing, light, dry rubbing and wet rubbing of the keratin cationized dyed cotton fabric showed adequate and quite comparable result with conventional method dyed cotton. Cationization of cotton has not affected the tensile and tears strength of the fabric. However, the flexural rigidity and crease recovery angle of cotton was slightly increased by cationization. Therefore, from dyeing, economic and environmental point of view, it is possible to propose that extracted keratin from sheep wool waste can be used as bio-degradable eco-friendly cationic agent applied on cotton fabric for salt free reactive dyeing.

Author Statements

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Conflicting of Interests

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Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

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