Salt-free Reactive Dyeing on Surface modified Cotton Fabric

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Abstract : ***In the recent scenario, the textile industry is well known as most polluted industry due to vast use of dyes and dyeing chemicals; mainly salt and alkali. Reactive dye is major category of dye for dyeing of cellulosic also uses high concentration of electrolytes in the process. The amount of unused electrolyte causes pollution in the environment. By many literatures it is observed that reduction of electrolyte in the reactive dyeing process is possible either modifying the dye or modifying the cotton surface. In the recent research work, approach is to reduce or eliminate addition of electrolyte in the dyeing treatment on modified cotton fabric by treating it with synthesized dyeing auxiliary. Acceptable results are observed in case of dyed cotton fabric. The physical properties of dyed cotton fabric were studied with fabric strength and scanning electron microscope (SEM); which showed excellent results. The chemical properties of dyed fabric were analyzed for colour strength and fastness property. The good fastness properties of modified dyed cotton fabrics are achieved in comparison to control fabric.***

Keywords : Surface Modification, Cyanuric Chloride, Cotton, Reactive Dye, Electrolyte.

INTRODUCTION

Cotton being the whole and soul of the textile industry; everything is dependent on cotton fibres here. Almost 40% of world fibre market is relied upon cotton production and processing [1]. There are various methods and treatments for cotton wet processing that includes dyeing and finishing. As we all know cotton garments offer breathability, moisture absorption ability and comfort due to presence of hydroxyl groups in its structure which plays major role in higher water uptake of the fibre [2]. Cotton offers strong affinity towards various dyes such as, direct dye, reactive dye and vat dye. Among all such dyes, reactive dye on cotton offers strong bond formation and gives excellent washing, rubbing and light fastness properties. There are various types of reactive dyes divided on the basis of structure and reactive groups attached. Reactive dye ranges offer wide, almost complete choice of colour shades. In textile industry, reactive dye on cotton is very demanding due to their useful chemical properties. Cotton in presence of water produces negative charge due to ionization of hydroxyl groups present. So, large amount of electrolyte is used to reduce repulsion between anionic dye and negatively charged cotton in presence of water [3]. The presence of high salt concentration in reactive dyeing effluent is a major cause of concern to environment which disturbs the biochemistry of water organisms [4].

In the present research, an approach has been made to eliminate or reduce the amount of electrolyte such as Glauber's salt used in the dyeing process of reactive dyes. This can be done by introducing cationic agent into the process prior to dyeing. Chemical modification is the process which modifies the cotton structure to improve desired chemical properties of fibre adding cationic sites onto the surface of substrate [5]. In cotton fibre, the hydroxyl groups present are mainly reacted with the cationic agent [6]. Such treatments are used to improve functionality and also the dyeing ability of cellulosic fibers using cationic agents [7], [8]. The cationic agent used for this study is cyanuric chloride amine derivative (CYCA) which contains amine group bonded to triazine ring. Many studies showed that presence of such group offers improved dyeability with increased dye exhaustion and fixation degree [9].

The cotton is first modified with CYCA as a cationic agent which increases the dye reactivity and then dyed with reactive dye in alkaline condition where comparative study was done with and without salt addition. The colour strength (k/s) and fastness properties of dyed fabric were studied. Effluent study of dye solution was characterized by chemical oxygen demand (COD) and Biological Oxygen Demand (BOD). Also, the testing for modified cotton is done with the help of Scanning Electron Microscopy (SEM) and tensile strength.

II. EXPERIMENTAL

A. Materials:

i. Fabric-

The cotton used for recent research work was purchased from Piyush Syndicate Ltd. with 115 GSM which was soaped, washed, rinsed and dried before using for further treatment.

ii. Dyestuff and Chemicals

Reactive Dye – Procion Red HE7B was used for dyeing of untreated cotton and modified cotton, supplied from Colourtex Industries Pvt. Ltd., Mumbai. All the chemicals used for synthesis and dyeing were of Laboratory grade procured from S D Fine Limited, Mumbai.

B. Methods

i. Synthesis of CYCA with N,N-Dimethylethylene diamine

Cyanuric Chloride was dissolved in ethanol and sodium hydrogen carbonate was added in the mixture with continuous stirring at 10ºC for 5 hours. After this process N, N-dimethyl ethylene diamine was added drop wise into above solution at room temperature and further stirred for 30 mins. The prepared white solution was poured into ice water and then precipitated product i.e. cyanuric chloride amine derivative (CYCA) was filtered and dried [10].

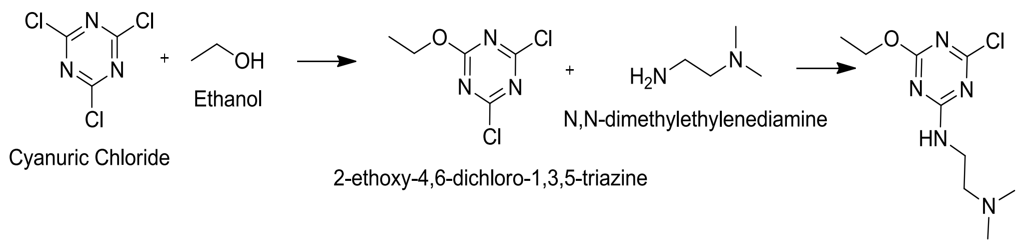

Fig. 1 Synthesis of CYCA

ii. Chemical Modification of Cotton Fabric by CYCA-

The purpose of the chemical modification is to increase the reactive sites on the cotton surface. This improves the dyeability of cotton fabric with increasing dyeing affinity to reactive dyes [11].

a. Application of CYCA on Cotton

The solution of CYCA at different concentrations was applied on cotton fabric with two methods namely; exhaust application (0.5% to 2%) and padding application (0.5gpl to 2gpl). The formulation was optimized with respect to four parameters i.e. concentration, temperature, pH and time.

Exhaust application: The cotton fabric was treated with 1.5% solution of CYCA at 80□C for 60mins and then washed with water, rinsed and dried.

Padding application: The cotton fabric was dipped in 1.5gpl solution of CYCA at room temperature for 5mins and then padded through padding mangles with 2dip-2nip. Treated cotton fabric was then dried at 80ºC for 1min and cured at 120ºC for 5 mins.

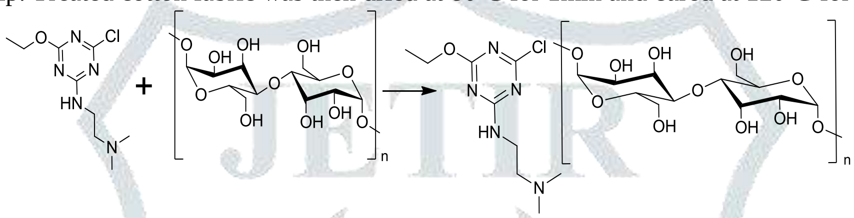

Fig. 2 Application of CYCA on Cotton Fabric

iii. Reactive Dyeing

Modified cotton and control cotton fabric was dyed with Reactive dye i.e. Procion Red HE7B, in comparison with and without addition of electrolyte in the dyeing process. The fabric was dyed with 4% shade with 1:30 Material to Liquor Ratio (MLR). The dyeing was started at room temperature (RT) and dyed for 10 mins, and the temperature was raised to 85□ C.

Dyeing Profile;

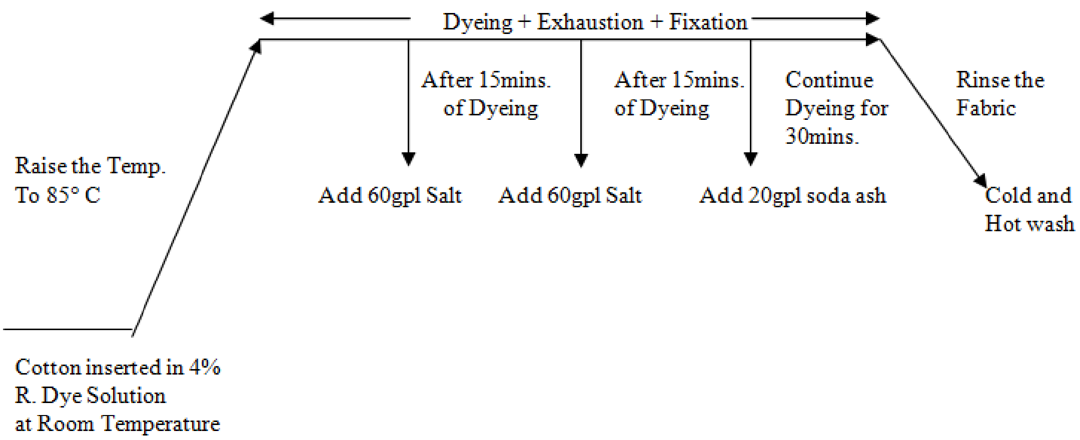

Fig. 3 Reactive Dyeing with Electrolyte

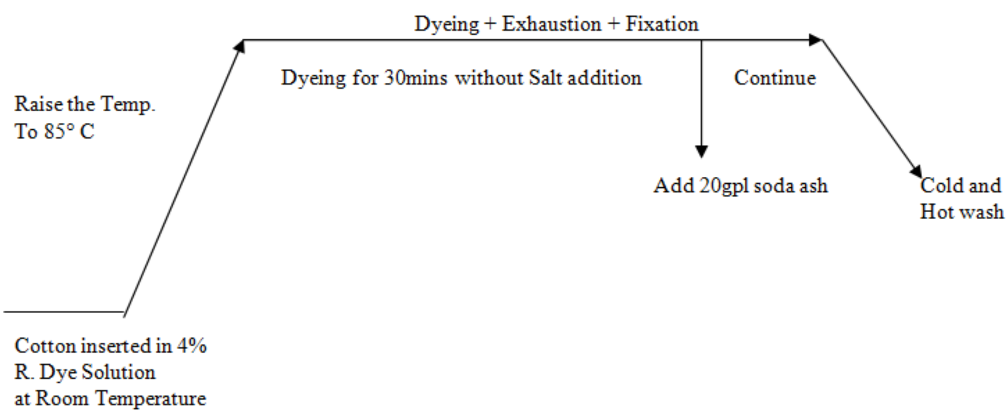

Fig. 4 Reactive Dyeing without Electrolyte

iv. Analysis

Analysis of chemical and surface modified cotton was characterized by FTIR and scanning electron microscopy (SEM) and the evaluation of modified reactive dyed cotton was done by fabric strength, colour strength (k/s) and fastness study which was further compared with that of control reactive dyed cotton fabric.

a. Fourier Transform Infrared Spectroscopy (FTIR)

The unknown functional groups are identified by absorption of infra-red at maximum wavelength (□max) in Fourier Transform-Infrared Spectroscopy (FTIR). The instrument used for FTIR analysis is SHIMADZU FTIR-8400S.

b. Scanning Electron Microscopy (SEM)

Changes in surface morphology of the fabrics are studied through a focused beam electron by producing an image in scanning electron microscopy. The preparation of samples for SEM was done with standard procedure with metal vapor coating on the surface of the sample to make it conductive for further testing [12]. The instrument used for Field Gun Emission-Scanning Electron Microscope (FEG-SEM) is JEOL JSM-7600F FEG-SEM.

c. Measurement of Colour strength

Light reflectance of unknown compound is measured to analyze the colour strength (k/s) of dyed fabric. The instrument used is Computer Colour Matching (CCM) Premier Colourscan Spectra scan 5100+ spectrophotometer. When dyed fabric is subjected to CIE LAB instrument it measures the colour depth in terms of L*, a*, b*, C*, H*.[13]- [15]

This colour strength is measured by “KUBELKA-MUNK” equation which is as follows;

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

Where,

K = Absorption co-efficient

R = Reflectance of dyed samples

S = Scattering co-efficient at λ_{max}

d. Tensile properties (Tensile, Elongation)

The physical property of the fabric is tested by its strength. The load is applied on the sample in fibre axis. ASTM 5303 standard is used with 3.0 cm x 15.0 cm sample specification. The instrument used for the fabric testing is H5KS Single Column Universal Tester (Tinius Olsen).

e. Fastness to Washing

The wash fastness of dyed control cotton and modified cotton was performed using Launder-o-meter. The standards used for wash fastness was ISO 105 C03. The light fastness of the dyed cotton was evaluated by AATCC-16E method. The rubbing fastness of dyed fabric was tested in Crock-o-meter using ISO 105 X12 testing method. The gray scale was used for assessment of colour fastness in terms of change in colour and staining [16].

f. Dye Exhaustion

The evaluation of dye exhaustion i.e. the dye uptake capacity of cotton fabric was done by UV-Visible spectrum where the maximum wavelength (λ_{max}) of dye absorption was measured [17]. The instrument used is UV-1800 spectrophotometer from Shimadzu, Japan. To calculate dye exhaustion percentage (E%) following equation is used;

$$E\% = \left(1X\frac{A}{A0}\right) X\,100 \qquad (2)$$

Where;

A = Absorbance of the dye after dyeing

A0 = Absorbance of the dye before dyeing

g. Effluent Study

Effluent is the wastewater which is generated in the process plant containing water, chemicals, dyes etc. and discarded upon completion of process. This causes water pollution [18]. The Physicochemical analysis of dye solution with and without addition of electrolyte was performed by Chemical Oxygen demand (COD) and Biological Oxygen Demand. The COD was measured in Reactor and photometer-HACH DR 900-DRB 200 and the BOD was tested in BOD Track-B050C003849.

Table I Water Quality standards for textile industry effluent by CPCB, India

Sr. No.	Effluent Quality Standards for Textile Mills	
	Parameters	**Maximum Limits**
1.	pH	6.5-8.5
2.	COD (mg/L)	250
3.	BOD (mg/L)	100

III. RESULTS AND DISCUSSIONS

A. FTIR Analysis

CYCA is formed when cyanuric chloride reacts with amine derivative. The functional groups produced in the process are located in Fig. 5. The sharp peak of 800.40 cm^{-1} indicates the presence of halogen groups i.e. chlorides (-Cl) attached to triazine ring present. The presence of aromatic C=C is detected by the sharp peak at 1568.02 cm^{-1} and C=O stretching is observed at 1568 cm^{-1}. Also, there is sharp peak of 2° amines at 2989.46 cm^{-1} which proves the presence of amines. These amines are mainly responsible for cationization of cotton.

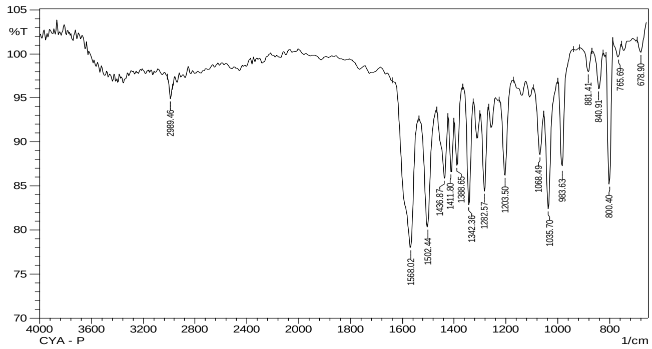

Fig. 5 FTIR of CYCA

B. Chemical Modification

For salt-free reactive dyeing of cotton, CYCA was applied on cotton fabric through padding application. In current study, the CYCA product is used as chemical surface modifying agent in which cotton fabric gets more cationic sites for attachment with various functionalities. The large numbers of electrolytes are used for reactive dyeing to draw the anionic dye to the surface before getting diffused and fixed. The electrolytes play an important role in this first phase of dyeing i.e. adsorption, where they are needed to drive dye molecules from water to the surface of fibre [5]. After modification of cotton when dyed with reactive dye, the dye molecules are easily attracted to modified cotton without addition of electrolyte with strong ionic linkage. By comparing Figs. 6 & 7 it is observed that in Fig. 7 chlorides are seen at 810.05 cm-1, which are absent in Fig 6. In Fig. 7 the small peak of aromatic C=C and 2□ amines are indicated at 1569.95 cm-1 and 2927.74 cm-1 respectively.

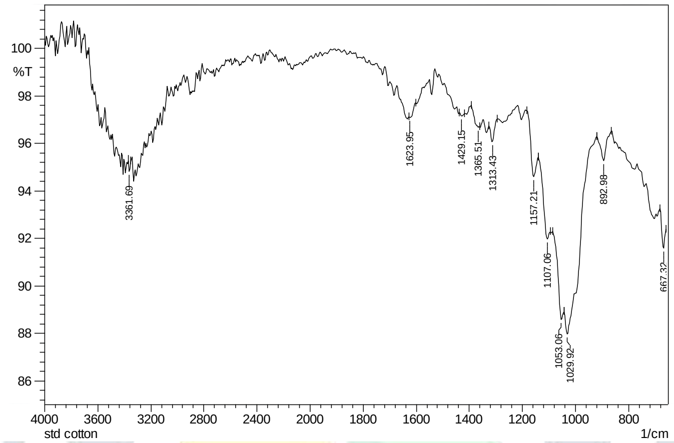

Fig. 6 FTIR of standard cotton

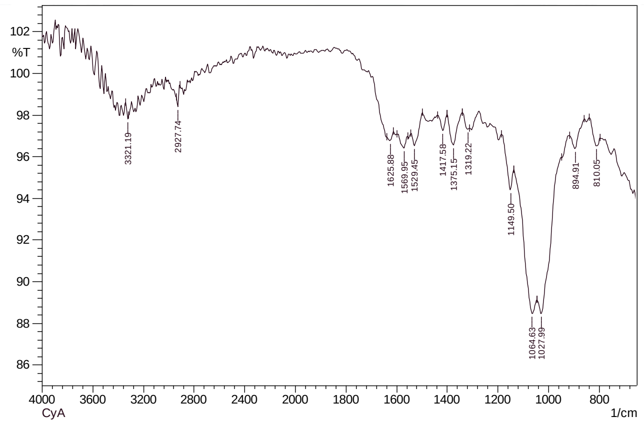

Fig. 7 FTIR of CYCA modified cotton

C. SEM Analysis-

Scanning electron micrographs with Energy Dispersive X-Ray spectroscopy (EDS) examines the surface morphology of the modified and control cotton fabric along with the detection of the elements present on the surface. According to the Fig. 8 (a) normal cylindrical smooth surface of cotton fibres can be seen while in case of Fig. 8 (b) micrograph, the rough surface of modified cotton is observed with deposition of CYCA product. In SEM-EDS of modified cotton as illustrated in Fig. 9 (b), there is presence of Chlorides, Nitrogen, Oxygen and Carbon elements on the surface of modified cotton however Chlorine and Nitrogen are absent in the Fig. 9 (a) of control cotton.

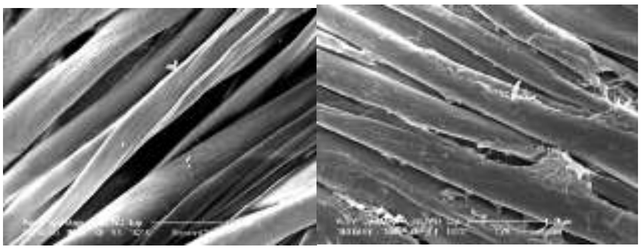

Fig. 8 SEM Analysis (a) Control Cotton (b) CYCA Modified Cotton

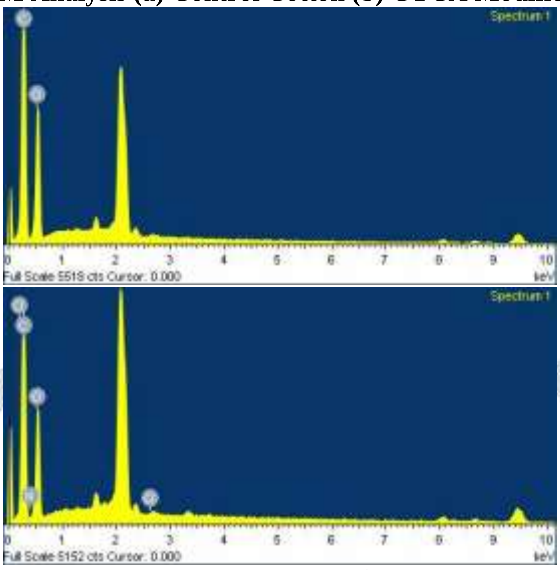

Fig. 8 SEM-EDS Analysis Control Cotton (b) CYCA Modified Cotton

D. Tensile Properties

The tensile strength is measured when maximum load is applied on it without any external force. From Table II it is observed that there is no drastic deterioration in the tensile strength of the CYCA modified cotton as compared to that of the standard cotton fabric. In the chemical modification treatment of cotton a strong bond is formed between cotton fibre and CYCA product and it results in the improvement in the strength of the fabric.

Table II Tensile properties

Sr. No.	Fabric	Breaking Strength (kgf)	Extension %
1.	Standard cotton	27.33	25.17
2.	Reactive dyed cotton	27.56	25.90
3.	CYCA modified cotton	28.63	23.04
4.	CYCA modified reactive dyed cotton	29.03	24.89

E. Dyeing:

From Table III and IV it is clear that the colour strength, dye exhaustion and dye fixation of the modified dyed cotton is the highest than those of control dyed cotton fabric. Cotton being an anionic in nature does not have cationic sites. CYCA agent being cationic nature on application on cotton fabric forms a strong covalent linkage with cationic sites. When such modified cotton is treated with reactive dye the exhaustion is found to be higher without addition of electrolytes because the anionic reactive dyes get attracted towards cationic sites of modified cotton.

i. Colour Strength-

From the Table III the % fixation of modified cotton dyed fabric shows higher values that that of the control dyed fabric.

Table III Colour Strength (K/S) and % Fixation after dyeing of cotton

Sr. No.	Fabric	Colour Strength (K/S)		% Fixation
		Before washing	Before washing	
1.	Reactive dyed cotton	29.6254	29.6254	75.80
2.	CYCA modified reactive dyed cotton with electrolyte	14.2882	14.2882	91.17
3.	CYCA modified reactive dyed	11.5985	11.5985	81.53

	cotton without electrolyte			

ii. Dye Exhaustion

The % Exhaustion of CYCA + Reactive dye solution without electrolyte is highest when compared to control dye solution. From Table IV it is proved that absence of electrolyte in reactive dyeing process gives good results.

Table IV % Dye Exhaustion of the Dye solutions

Sr. No.	Dyeing solution	Absorbance at λ_{max}		% Dye Exhaustion (%E)
		Before dyeing (A_0)	After dyeing (A)	
1.	Control Reactive Dye Solution	1.023	0.706	69.01
2.	CYCA + Reactive Dye Solution with Electrolyte	0.803	0.643	80.07
3.	CYCA + Reactive Dye Solution without Electrolyte	0.712	0.632	88.76

iii. Wash fastness Testing

As illustrated in Table V wash fastness of the modified dyed cotton shows good results due to the better fixation of the dye molecules into the fibre as compared to the control dyed cotton.

Table V Wash Fastness of Reactive Dyed Cotton

Sr. No.	Fabric	Wash Fastness	
		Change in colour	Staining
1.	Reactive dyed cotton	2-3	3
2.	CYCA modified reactive dyed cotton with salt	3	3-4
3.	CYCA modified reactive dyed cotton without salt	3-4	3

iv. Light Fastness

From the Table VI, it is observed that there is no significant change in the light fastness of the modified dyed cotton as compared to control dyed cotton fabric though cationisation is known to decrease the light fastness.

Table VI Light Fastness of Reactive Dyed Cotton

Sr. No.	Fabric	Light Fastness
1.	Reactive dyed cotton	2-3
2.	CYCA modified reactive dyed cotton with salt	3
3.	CYCA modified reactive dyed cotton without salt	3-4

v. Rubbing Fastness

The excellent rubbing fastness especially in wet condition is seen in case of modified dyed cotton when compared to control dyed cotton due to the increase in the fixation of dye molecules into cotton. This is a significant development.

Table VII Rubbing Fastness of Reactive Dyed Cotton

Sr. No.	Fabric	Rubbing Fastness	
		Dry	Wet
1.	Reactive dyed cotton	3	2
2.	CYCA modified reactive dyed cotton with salt	4	4
3.	CYCA modified reactive dyed cotton with salt	4	4

G. Effluent Analysis

Reactive dyeing is the most important dyeing process in textile industry. Electrolytes are vastly used for dyeing and unused electrolyte with dyes is a major cause of water pollution. So the attempt is made to eliminate the usage of electrolyte in this process. The dye solution which does not contain electrolytes shows near to lower values of COD, BOD that the standard dyes solution which is then compared to standards as per Table I.

Table VIII Effluent study of dye solutions

Sr. No.	Type of Effluent	Effluent Analysis			
		pH	Colour	COD (ppm)	BOD (ppm)
1.	CYCA Solution	6	Clear Solution	1649	250
2.	Control reactive Dye Solution	11	Red	3455	750
3.	Reactive dye solution of modified cotton with electrolyte	11	Red	1755	300
4.	Reactive dye solution of modified cotton without electrolyte	8	Red	760	150

IV. CONCLUSION

The cotton fabric when treated with Cyanuric Chloride Amine derivative introduces cationic sites onto it. Such modified cotton can be dyed with reactive dyes without addition of electrolytes into the dyeing process. The modified dyed cotton produces well to excellent wash, rubbing and light fastness properties with increased exhaustion and fixation onto its surface. The chemical treatment of the cotton does not affect the fabric strength, light fastness and also wet rubbing fastness is rather improved which makes this development a significant one.

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