

SUSTAINABLE DYEING OF MODIFIED COTTON FABRIC WITH REMAZOL DYES IN THE ABSENCE OF SALT AND ALKALI

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This research work investigates the chemical modification of cotton cellulose with a cationizing agent (CHPTAC, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride), which resulted in the enhanced dye uptake and increased color strength (*K/S*) on the dyed cotton fabric in the absence costly auxiliaries, such as sodium chloride and sodium hydroxide. The modified and unmodified cotton fabric samples were dyed using the exhaust dyeing method on a high-temperature dyeing machine with several reactive dyes of the Remazol class in different shade depths. The dyed samples were washed, dried and tested for *K/S* and colorfastness properties (washing, rubbing, and light), using standard test protocols. The results revealed that the color strength and the colorfastness properties of the modified dyed cotton fabric were significantly better than those of unmodified cotton. Thus, this study attempted a sustainable approach in cotton dyeing without using salt and alkali.

Keywords: cotton, cationization, Remazol dyes, color strength, colorfastness

INTRODUCTION

Sustainable approaches in the textile industry are highly appreciated by scientists to keep our planet Earth green for our future generations.¹ Cotton is abundantly used in the form of fiber, yarn, fabric, and garments due to its distinctive comfort and aesthetic properties.²⁻⁵ The dyeing of cotton fibers with reactive dyes requires a significant amount of electrolytes to have sufficient uptake. These salt additions are not consumed in the dyeing process and later after the coloration of the fabrics, these salts find their way into the effluents and disturb the balance of salts in the oceans and other water bodies.^{6,7} This could also threaten the whole aquatic life in the rivers and oceans. Reactive dyeing of cellulosic fibers also requires adding a significant amount of alkali to be fixed covalently with the cellulosic fibers. Both salt and alkali additions damage agricultural lands, as well as the whole environment.⁶⁻⁹

To overcome these issues of salt and alkali additions during the dyeing of cotton with reactive dyes, numerous works have been established. Cotton carries a negative dominant

charge in the aqueous medium, which results in repulsion between anionic dyes and cotton.^{10,11} The cationization of cotton generates positive dominant charges, which enables dyeing with reactive dyes absolutely without salt and alkali.¹²⁻¹⁵ The incorporation of positively charged sites (Fig. 1) facilitates the dye molecules to penetrate well into the cellulosic fiber and to be resistant during washing as a consequence of the attractive forces between anionic dyes and cationized cotton fabric.¹⁶⁻¹⁹

Lewis and other researchers have extensively studied the chemical modification of cotton with significantly enhanced dye uptake using anionic dyes. Modified cotton fabric can be successfully dyed with the covalent fixing dyes at neutral pH, which could promote a sustainable dyeing process, as compared to conventional dyeing, where high amounts of salt and alkali are added to fix the dyes covalently with the cellulose. In textile printing with reactive dyes, the modified cotton fabrics revealed enhanced properties of fixation and color strength.^{20,21}

Usually, all the reactive dyes need higher amounts of salt to achieve a reasonable penetration for the covalent fixation of dye molecules, but Remazol dyes need even more electrolyte addition than all other reactive dyes due to bearing strong negative charges onto the dye molecules.²² Our research group reported the coloration of modified cotton with sulphur black dyes using no salt and alkali.⁵ This particular

research work focuses on dyeing of cotton with Remazol dyes with absolutely no electrolyte or alkali addition during the dyeing of the cotton chemically modified with CHPTAC. The dyeing of modified cotton with Remazol dyes dramatically enhanced the dye uptake and yielded higher color strength (*K/S*) values, as well as other colorfastness properties.

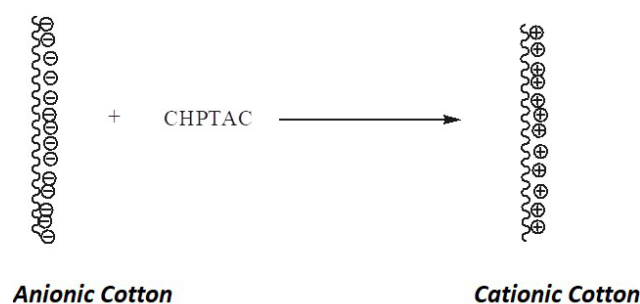


Figure 1: Conversion of anionic sites on cotton to cationic ones by treating with a cationizing agent

EXPERIMENTAL

Materials

Pretreated 100% cotton plain weave fabric having 120 GSM (80 EPI and 66 PPI) with 0.30 mm thickness was used during this project. The cotton fabric was provided by the Textile Processing Lab of National Textile University, Faisalabad. For the chemical modification of cotton, the cationizing agent 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC, 99%) was obtained from Sigma Aldrich (Faisalabad, Pakistan). Four commercially available Remazol dyes, namely, Remazol Black NN (99%), Remazol Yellow RGB (99%), Remazol Red RGB (99%), and Remazol Blue RGB (99%), were supplied by DyStar as laboratory research samples. Sodium chloride (99%), sodium carbonate (99%), sodium hydroxide (99%), and wetting agent (nonionic surfactants, such as alkylphenol ethoxylate) were laboratory-grade and used with purification. Distilled water was used throughout the research work.

Modification of cotton fabric

Preparation of pad solution: The cationizing agent CHPTAC (20 g) was mixed with distilled water (100 g) and sodium hydroxide (20 g) was added dropwise under continuous stirring for 20 min. Then, a wetting agent (2 g) was added to the above solution and stirred again for 5 min. Finally, distilled water was added to make the total pad solution of 200 g and stirred again for a short while before padding the fabric.

Padding cotton fabric: Pretreated cotton fabric was padded with the pad solution with a 100% pickup and subsequently batched for 18 hours by covering it with a polyethylene film to make it airtight. Then, the fabric

was properly washed several times with distilled water to make sure that there was hardly any hydrolyzed CHPTAC or any other chemical left inside the fabric. Finally, the fabric was dried and ready for dyeing. The potential reaction mechanism of CHPTAC and cellulose is given in Figure 2.

Hydrolysis of CHPTAC

Some of the cationizing agents might hydrolyze (Fig. 3), which needs to be washed out after batching the fabric overnight. Washing several times with distilled water removes the hydrolyzed cationizing agent from cotton.

Application of Remazol dyes

An HT dyeing machine was employed in the coloration of unmodified and modified cotton fabric samples using four reactive dyes, namely Remazol Yellow RGB, Remazol Red RGB, Remazol Black NN, and Blue RGB. In the case of unmodified cotton (Fig. 4), the dyeing solution was prepared by adding dye, water, salt, and a wetting agent; and the cotton fabric was added (liquor to goods ratio, 40:1). The temperature of the HT dyeing machine was adjusted to 60 °C. When the dyeing machine gained the required temperature of 60 °C, then sodium carbonate was added to the dyeing machine to achieve the required alkaline medium for the fixation of dye with the cotton. The dyeing machine was allowed to run for a further 45 min at 60 °C. After 45 min, the machine was switched off, the temperature was lowered and the dyed samples were washed off with the cold and hot water.

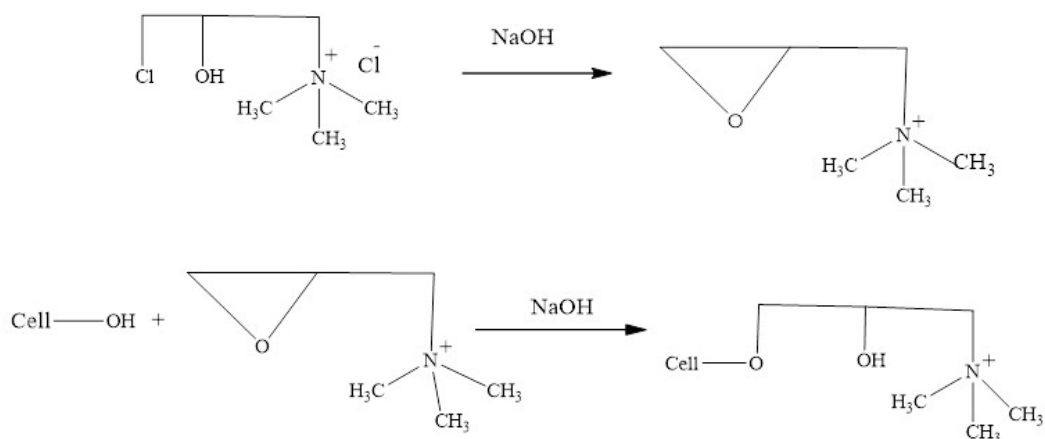


Figure 2: Proposed reaction mechanism of cellulose with the cationizing agent

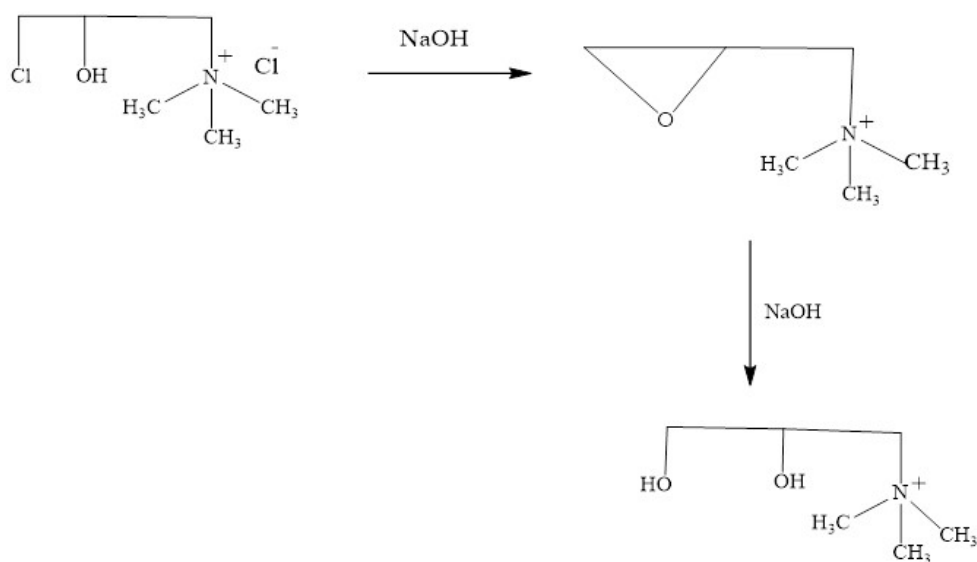


Figure 3: Hydrolysis of CHPTAC in the presence of concentrated NaOH

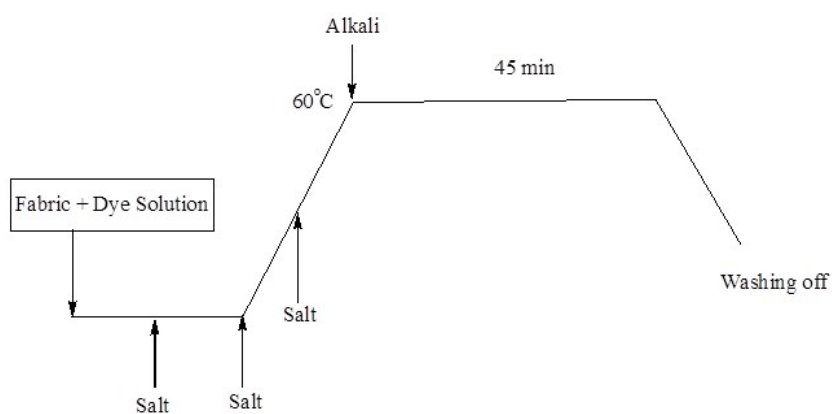


Figure 4: Dyeing profile for unmodified fabric with the given set of Remazol dyes

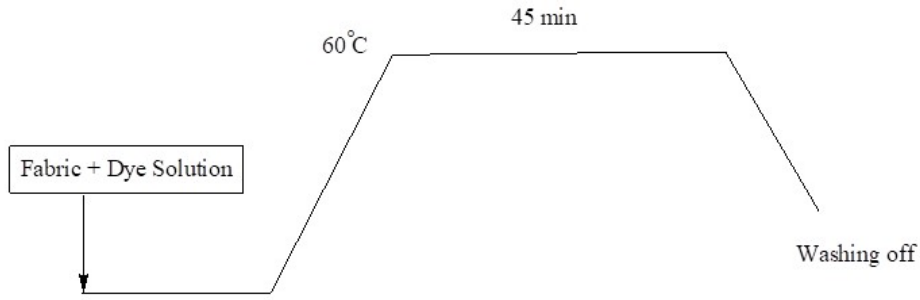


Figure 5: Dyeing profile for modified fabric with the given set of Remazol dyes

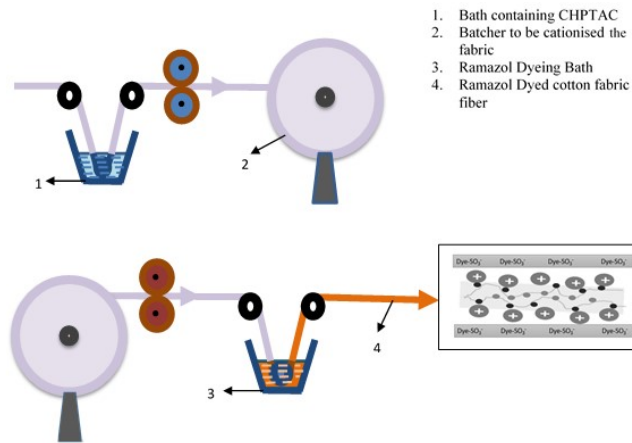


Figure 6: Process of cotton modification and dyeing

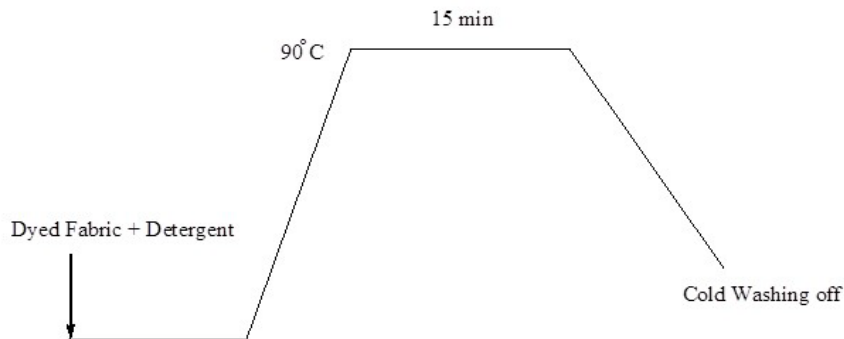


Figure 7: Schematic presentation of the soaping off process for dyed samples

However, the modified cotton fabric samples (Fig. 5) were dyed without adding any salt or alkali in the dye bath. The cationized cotton fabric samples and the dye solution with the shade depths of 0.5%, 1%, 2%, 4%, and 6% o.w.f. were only added in the dyeing tube without any other auxiliary. All these samples were run in the dyeing machine at 60 °C for 45 minutes. Later on, all the dyed samples were rinsed in cold and hot water simultaneously (Fig. 6).

Soaping off

The dyed cotton samples were soaped off (Fig. 7) by using non-ionic detergent (2 g/L) at 90 °C for 15 min with the liquor to goods ratio of 50:1.

Subsequently, the samples were cold washed with distilled water and dried.

Color strength measurements

A UV/Vis spectrophotometer (model: DATACOLOR 850) was employed in the measurements of color strength values of all dyed samples in different shades. The Kubelka–Munk equation was used to determine the color strength (*K/S*) values of unmodified and modified cotton dyed fabrics (Eq. (1)):

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

where R is the reflectance at the maximum wavelength (λ_{\max}) of absorbance and K/S is the ratio of absorption and scattering coefficients.

Colorfastness

The colorfastness to washing of the dyed samples was determined according to the ISO 105-C01 standard test protocol. The specimen was prepared according to the standard test method and stitched adjacent to the multifiber strip. Subsequently, the dyed samples were washed in the laundrometer at 60 °C for 30 min using sodium carbonate. Then, the specimen was rated for colorfastness to staining and shade change using the Grey scale (1-5). The AATCC test method 16-1993 was employed to determine the colorfastness of the dyed samples in a Xenon arc lamp chamber for 24 hours and the color fading of the dyed samples, as a consequence of exposure to light, was rated using the blue wool scale (1-8). The AATCC-8 standard test method was used to determine the colorfastness to rubbing (dry and wet) of the dyed samples using a Crock meter. The staining on the adjacent fabric was rated using the Grey scale (1-5).

RESULTS AND DISCUSSION

Color strength (K/S)

The K/S values obtained for the modified dyed cotton samples were higher than those for unmodified dyed samples (Fig. 8), which can be attributed to the fact that a greater number of anionic dye molecules are attached to the modified (cationic) dyed samples. The improved color strength shows that the dye molecules penetrated well inside the fiber and were fixed there due to the electrostatic forces found between the cationic cotton cellulose and the negatively charged dye molecules. The K/S values obtained for modified dyed samples were almost double

those for unmodified samples in red and yellow chromophores. However, in the case of Blue and Black Reactive dyes, the K/S values of modified cotton fabric samples were significantly higher than those of the unmodified counterparts. A very similar trend in K/S values was observed by Correia *et al.*²³ in the chemical modification of cotton fabric. They reported that cotton modification with CHPTAC did not cause any significant changes in surface morphologies, confirmed by their SEM investigations, which are in agreement with earlier published works.^{24,25}

Colorfastness assessment

The colorfastness to staining and the shade change results of unmodified and modified dyed cotton samples are given in Tables 1 and 2. The results for staining on multifiber strips obtained for the unmodified dyed samples and for the modified dyed samples with cationizing agent showed nearly similar ratings. However, the shade change results of modified samples were better than those of unmodified dyed samples. This phenomenon can be attributed to the stronger electrostatic forces between the dye and cationized fabric samples, which assist dye molecules in penetrating deeper into the fiber and strongly attaching to the available sites on cotton fabric. The slight increase in washing fastness of cationized dyed cotton samples is in considerable agreement with the literature.²⁶

The colorfastness to light results of the samples dyed with 2% shade depth are shown in Table 3. It was observed that the light fastness results for the unmodified and the modified dyed cotton fabrics were very similar.

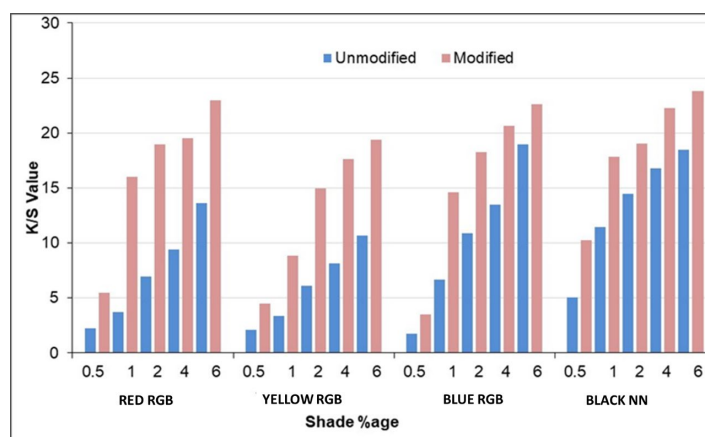


Figure 8: Color strength (K/S) values obtained for unmodified and modified cotton fabrics

Table 1
Colorfastness to washing (staining and shade change) of unmodified dyed cotton samples

Dyes	Shade, %	Staining						Shade change
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	
Remazol Red RGB	0.5	4	4	3-4	4	4	4	3-4
	1	4	3-4	4-5	4-5	4	4	4
	2	4	4	4	3-4	4	4	3-4
	4	4-5	3-4	4	4	4-5	4-5	4
	6	4-5	3-4	4	3-4	4	4-5	4
Remazol Yellow RGB	0.5	3-4	3	3-4	3-4	4	3-4	4
	1	4	4	4	3-4	4	4	3-4
	2	4-5	3-4	4	4	4-5	4-5	4
	4	4-5	4	4	4-5	4	4	3-4
	6	4	4	4-5	4	4	4	4
Remazol Blue RGB	0.5	0.5	3-4	3	3-4	3-4	4	3-4
	1	1	4	4	4	3-4	4	4
	2	2	4-5	3-4	4	4	4-5	4-5
	4	4	4-5	4	4	4-5	4	4
	6	6	4	4	4-5	4	4	4
Remazol Black NN	0.5	4-5	3-4	3-4	4-5	4	4	3-4
	1	4	3-4	4	4	4	4	3-4
	2	4	4	4	4-5	4	4	4
	4	4-5	3	4	4	4	4-5	4
	6	4	4	4-5	4	4-5	4	4

Table 2
Colorfastness to washing (staining and shade change) of modified dyed cotton samples

Dyes	Shade, %	Staining						Shade change
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	
Remazol Red RGB	0.5	4-5	4	4	4	4	4-5	4
	1	4	4	4-5	4-5	4-5	4	4-5
	2	4-5	4	4	4	4-5	4	4
	4	4-5	3-4	4	4-5	4	4-5	4-5
	6	4-5	3-4	4	4	4	4-5	4
Remazol Yellow RGB	0.5	4-5	4	4	4	4	4	4
	1	4-5	4	4	4	4-5	4	4
	2	4-5	3-4	4	4-5	4-5	4-5	4-5
	4	4-5	4	4	4-5	4	4	4
	6	4	4	4-5	4-5	4	4	4-5
Remazol Blue RGB	0.5	4-5	4	4	4	4	4	4-5
	1	4-5	4	4	4	4-5	4	4
	2	4-5	3-4	4	4-5	4-5	4-5	4
	4	4-5	4	4	4-5	4	4	4-5
	6	4	4	4-5	4-5	4	4	4-5
Remazol Black NN	0.5	4-5	4	4	4-5	4	4	4-5
	1	4	4	4	4	4-5	4	4
	2	4-5	4	4-5	4	4	4-5	4
	4	4-5	3-4	4-5	4-5	4-5	4-5	4-5
	6	4	4	4-5	4	4-5	4	4-5

Also, no influence of the cationizing agent in the case of the modified dyed cotton fabric, was noticed. The results are in agreement with earlier published results, which reported that light fastness mainly depends on the chromophore of the dyestuffs.²⁷

The dry rubbing fastness results of all the dyed samples, with different shades, gave relatively better results on the modified cotton fabric, as compared to the unmodified samples, as shown in Figure 9. However, the wet rubbing fastness results (Fig. 10) of the modified cotton fabric samples were better than those of the unmodified

fabric samples, even with the higher color strength values achieved due to cationization. The positively charged cotton fabric and negatively charged dye molecules have strong electrostatic attractive forces that enable the dye molecules to

resist from being rubbed off easily. The better rubbing fastness results are also supported by earlier published research focused on the cationization of cotton.²⁸

Table 3
Colorfastness to light results of unmodified and modified samples dyed with shade depth (2% o.w.f)

Dyes used	Unmodified cotton	Modified cotton
Remazol Red RGB	4-5	4-5
Remazol Yellow RGB	4-5	4-5
Remazol Blue RGB	4-5	4-5
Remazol Black NN	4-5	4-5

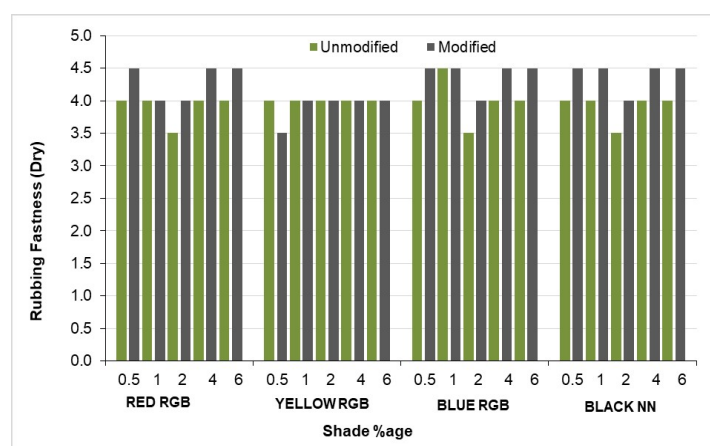


Figure 9: Dry rubbing fastness results of unmodified and modified cotton samples

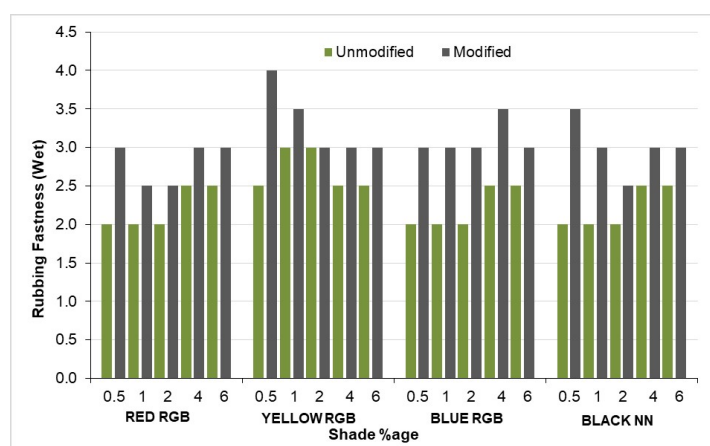


Figure 10: Wet rubbing fastness results of unmodified and modified cotton samples

CONCLUSION

This research work presented a successful sustainable approach to the reactive dyeing of cotton fabric using the exhaust method. Cotton fabric was modified with CHPTAC and dyed with four commercial reactive dyes in different shade depths (0.5%, 1%, 2%, 4% and 6% o.w.f.), without using any salt and alkali. Modified cotton samples revealed higher color strength K/S values

in all shade depths, as compared to unmodified counterparts. With pale shades on modified cotton fabrics, the color strength obtained is almost double than that of unmodified dyed samples. The modification with CHPTAC enhances the dye uptake and color strength of cotton due to the generation of positively charged sites. In addition, the modified dyed samples revealed better colorfastness to washing and rubbing results due

to the strong covalent bond formation. However, the lightfastness was not improved much, even in the case of modified cotton samples. Cationization was useful in enhancing the dyeability and colorfastness of reactive-dyed cotton samples.

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