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Cationic Modification of Grey Cotton Fabrics Using Chitosan

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ABSTRACT

The main problem in dyeing cotton fabrics with reactive dyes is the low affinity of the fabrics for the dyes due to the negative charge acquired by the fabrics in aqueous medium which led to repulsion between the anion of the dye and the negative charge of fabrics. To overcome such repulsion, large amount of electrolyte is required to improve the affinity of the fabrics for reactive dyes. This leads to the discharge of highly coloured effluent with high salt content, which causes unavoidable threat to the environment. These problems can be overcome by modifying the surface properties of the cotton fabrics to improve its substantivity so as to develop salt free reactive dyeing. In this study, environment friendly approach of cationization of cotton using chitosan was employed. Dyeing properties of cotton fabrics treated with chitosan was compared with that of the untreated fabrics using FTIR spectral analysis. Dye exhaustion and the fastness was investigated using UV-visible spectrophotometric analysis. The results have shown improvement in dye exhaustion for chitosan treated fabrics in reactive dyeing in the absence of salts. The colour fastness properties of the treated fabrics were also improved compared to the untreated fabrics.

KEYWORDS: *Cotton fabrics, Cationization, Chitosan, Dyeing and Reactive dyes.*

INTRODUCTION

Cotton is the most widely used fiber in Textile Industries, due to its excellent properties, such as, stability, comfort to wear, moisture absorption high dyeability and good wicking properties (Shahin, 2015). Dyeing of cotton fibers is generally done with Reactive dyes, due to its brilliancy, different hue, high wet fastness convenient usage and high applicability (Kunal *et al.*, 2012). However, with increasing popularity of reactive dyes in dyeing of cotton, environmental problems associated with their usage have received attention. Since cotton has low affinity for reactive dyes, large quantities of electrolytes like NaCl, Na_2SO_4 ranging from (40 – 100g/L) are usually used for better dye exhaustion (Aravin *et al.*, 2011). Despite the use of large quantity of salts, yet exhaustion and fixation of reactive dyes on cotton can still be as low as 50% for some dyes. Thus, waste water contains significant amount of dye and salt which can lead to discharge of serious environmental pollutants, (Chattopadhyay, 2001). It has been postulated that more than 80,000 tons of reactive dyes are produced and consumed every year, this is what necessitate the need of quantifying the total amount of pollution load caused by their usage. So, most researchers focused on introducing salt-free dyeing technology for reactive dyes (Kunal *et al*., 2012). Different approaches, have been introduced in order to control the above effluent problems, these include the modification of the dye structure to make it more substantive to cellulose.

Cationization of cellulose through chemical reactions with compound containing cationic groups or controlled dosing of dye and salt during the exhaustion process (Aravin *et al.*, 2011).

It has been found that pretreatment of cotton before dyeing can offer a simple and effective method of improving dye-fiber affinity, and avoiding the need of salt as an electrolyte in the dye bath (Nejbosa and Ivanka, 1998). In this study, chitosan was used for the modification of cotton fabrics and the fabrics dyed using conventional dyeing procedure without the use of salt.

Chitosan is a polysaccharide which shows unique chemical and biological properties, such as biodegradability, biocompatibility, nontoxicity and its solubility in acidic solutions makes it easily available for industrial purposes. The polysaccharide-base cationic biopolymer chitosan is a poly(1,4)-2-amino-2-deoxy- β-D-glucan usually obtained by deacetylation of insects and marine invertebrates (Crabs, and Shrimp) (Sheila *et al*., 2013).

Materials and Methods

Grey cotton fabrics obtained from Kurmi market Kano was used for the experiments. Pretreatment was done using chitosan cationic agent obtained by deacetylation of chitin obtained from the exoskeleton of shert-horned grasshopper.

Reagents used were; sodium hydroxide, sodium hypophosphite, sodium chloride, sodium trioxocarbonate, citric acid, acetic acid, hydrochloric acid and Remazol red B (C. I. Reactive red), which were analytical reagent grade.

Isolation of chitin and synthesis of chitosan. The polycationic biopolymer chitosan was extracted using the standard procedure shown in Figure 1.

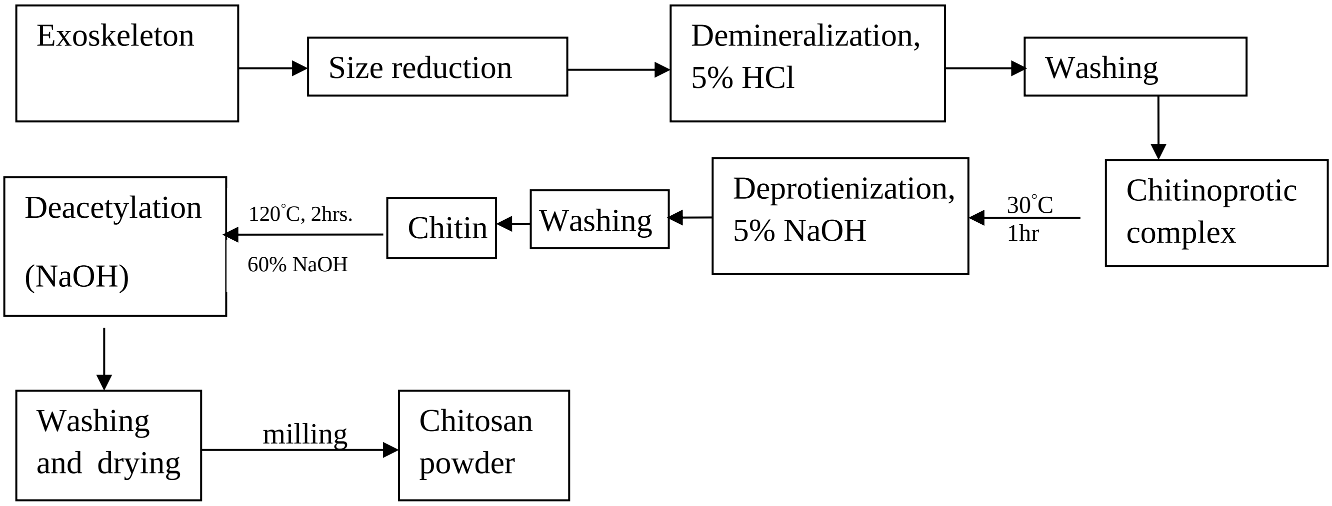

Fig. 1: Steps involved in the extraction of chitosan

Preparation of chitosan solution

Chitosan solutions were prepared at 0.5, 1.0, 1.5, 2.0, and 2.5% w/v. Each amount of chitosan was dissolved in 10% (v/v) acetic acid containing 6% citric acid and shake in an orbital shaker at 30˚C overnight. The solution was filtered to remove any insoluble materials.

Treatment of cotton fabrics with chitosan solution

1g each of grey cotton fabrics were soaked in chitosan solution for 1 hour at 60˚C with stirring. The fabrics were removed from solution squeezed to drain excess chitosan solution and then dried at 110˚C for 5 minutes in a hot air oven, and then dyed with C. I. reactive red 22 and C.I reactive Yellow 17, at (1%, 2, 4, 6 & 8% owf) without salt (Piyaporn *et al*., 2010).

Dyeing of chitosan modified cotton fabrics without salts

Cotton fabrics were dyed with Reactive Red 22 (Remazol red B.) at different shade (1,2,4, 8% o.w.f) without salts. Dyeing recipes are given in

Table 1. The fabrics were dyed using exhaust method. Dyeing was carried out at 60˚C for 60 min with stirring. After dyeing, the fabrics were washed to neutrality and air dried (Rahman *et al*.,2014).

Table 1: Recipe for cotton dyeing without salt and alkali

Conc. of Chitosan (%)	Concentration of Dyes (%) Remazol Red B. and Remazol Golden Yellow G				
0.5	1	2	4	6	8
1.0	1	2	4	6	8
1.5	1	2	4	6	8
2.0	1	2	4	6	8
2.5	1	2	4	6	8
M:L Ratio	1:20	1:20	1:20	1:20	1:20

Determination of dye exhaustion and fixation

The dye exhaustion (E) was determined using Equation (1). While dye fixation (F) was obtained according to equation (2) from the UV-Visible spectrophotometric results of the absorbance maximum of the dye liquor before and after dyeing as follows:

$$E = \frac{A_{\circ} - A_1}{A_{\circ}} \times 100\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

where:

$A_\circ$ and A_1 are the absorbance of the dye liquor before and after dyeing respectively, E is the Exhaustion.

$$F = \frac{A_\circ - A_1 - A_2}{A_\circ - A_1} \times 100\% \ldots\ldots\ldots\ldots\ldots\ldots (2),$$

where A_2 is the absorbance of the soap bath after soaping, while F is the dye fixation.

Measurement of Colour Fastness

The fastness properties of the dyed fabrics were tested, using (ISO 105, AO2 BS 1006 – AO2:1978) for colour change and (ISO 105, AO5, AO3 BS 1006-AO3:1978) for degree of staining:

While light fastness was assessed using AATCC test method 16-93 with micros Cal tester.

RESULTS AND DISCUSSION

Fourier transformed infrared spectroscopy (FTIR)

From Table 2, the IR spectral data a band at 3334, 3335, 3337, 3339cm^{-1} was observed for both chitosan and chitosan modified fabrics, which is due to OH stretching. Absorption peaks at 3285cm^{-1} was due to axial NH stretching in chitosan (Ibrahim and Reda, 2015). The peaks of 2902, 2818cm^{-1} for chitosan and the modified fabrics were due to CH_2 stretching vibration while absorption bands at 1687, 1657 and 1721 & 1709cm^{-1} were due to C = O stretching vibration. Absorption band at 1428, and 1530cm^{-1} were due to C – O stretching, CH_2, bending vibration and NH_2 stretching respectively. Absorption band at 1317, 1205, 1391, 1367 and 1371 cm^{-1} was due to C – H stretching in the pyranose ring and CH wagging (Feriel *et al.*, 2014).

This result is further confirmed by the FTIR spectrum in fig. 2(a-e).

OPTIMIZATION OF DYEING CONDITIONS

Effect of Modifying Agent on dye exhaustion

The relationship between the concentration of chitosan and the exhaustion of Remazol Red Band Remazol golden yellow G was studied by varying the concentration of chitosan (0.5, 1.0, 1.5, 2.0 & 2.5% as shown in Table 3 and Figure 3.

From Fig 3 It was observed that chitosan modified fabrics have shown high exhaustion values for both remazol gold yellow G and remazol red B of comparable strength. Exhaustion increasing gradually with increase in concentration of chitosan. From the results it was established that modification cotton fabrics using chitosan provides more cationic sites on the fabrics were anionic dyes can be fixed (Sheila *et al.*, 2013. This lead to high exhaustion of the dye bath leaving little or no coloured effluent. However, at higher concentration of chitosan above 2%, a decline in the dye exhaustion was observed. This might be due to the fact that increase in chitosan concentration beyond 2%, the fabrics becomes more covered by chitosan molecules, hence binding of the dye molecules with the functional groups of the fabrics decreases as reported by Abdur-Rehaman (2007).

Table 2: Spectral data for chitosan and chitosan modified fabrics.

Unmodified cotton fabrics	**Chitosan absorption bands cm^{-1}**	**Concentration of chitosan and their absorption bands cm^{-1}**					**Functional group**
	0	0.5	1.0	1.5	2.0	2.5	
3334	3334	3334	3334	3335	3337	3339	OH stretching
3285	3285	3285	-	-	-	-	N–H stretching
2902	2902	2902	2818	2818	2918	2902	CH_2 stretching
1687	1721	1721	1709	1721	1721	1657	C = O stretching vibration
1562	1428	1428	1428	1428	1428	1530	C – O, NH_2 stretching vibration
1317	1317	1317	1205	1391	1367	1371	CH stretching in the ring

Table 3: Dye exhaustion (%) on Chitosan Modified Cotton Fabrics

Exhaustion (%)	**Concentration of Chitosan %**					
	Unmodified	0.5	1.0	1.5	2.0	2.5
C.I Reactive yellow 17	48.63	56.96	63.24	68.36	72.65	56.23
C.I Reactive red 22	50.93	62.80	63.56	67.21	70.63	59.62

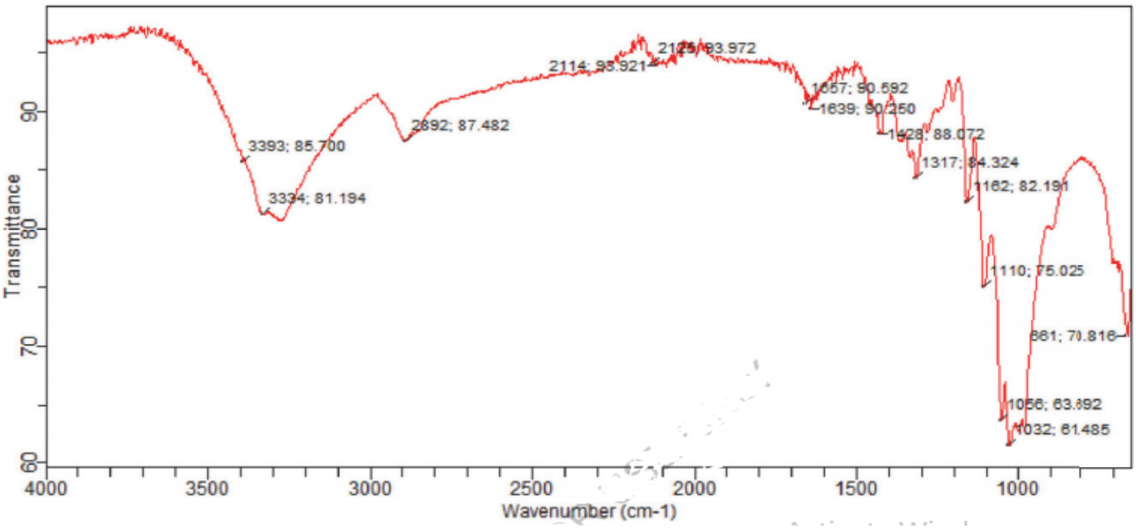

Fig. 2a: FTIR spectrum of unmodified cotton fabrics

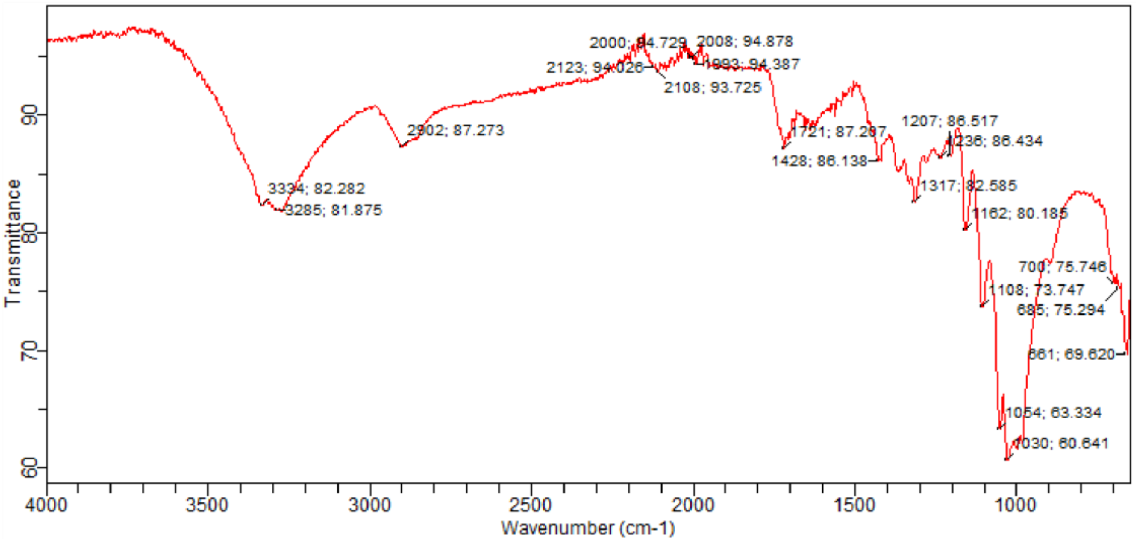

Fig. 2b:0.5% Chitosan modified cotton fabric

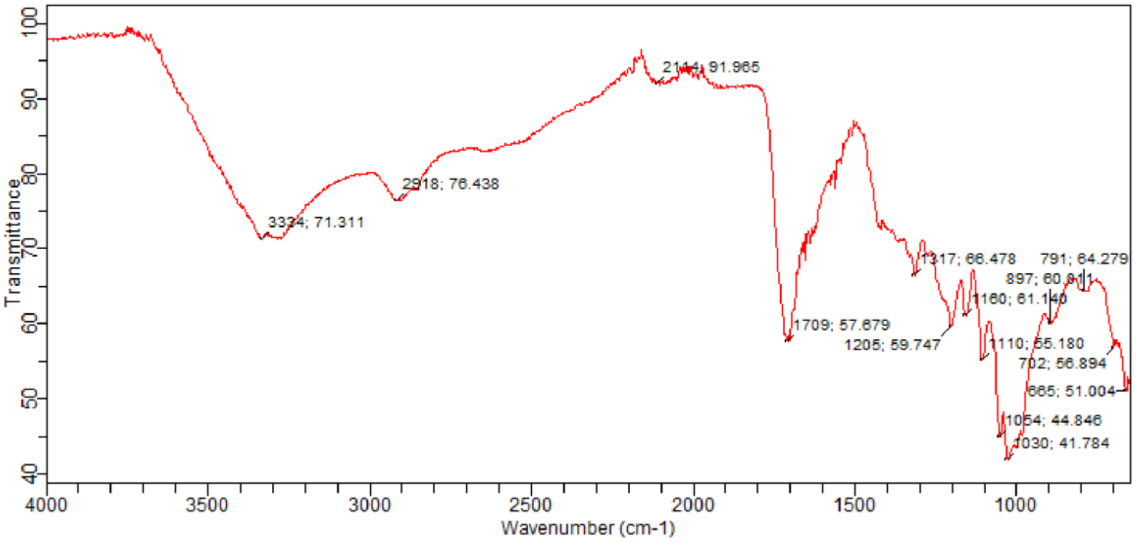

Fig. 2c: 1.0% Chitosan modified cotton fabric

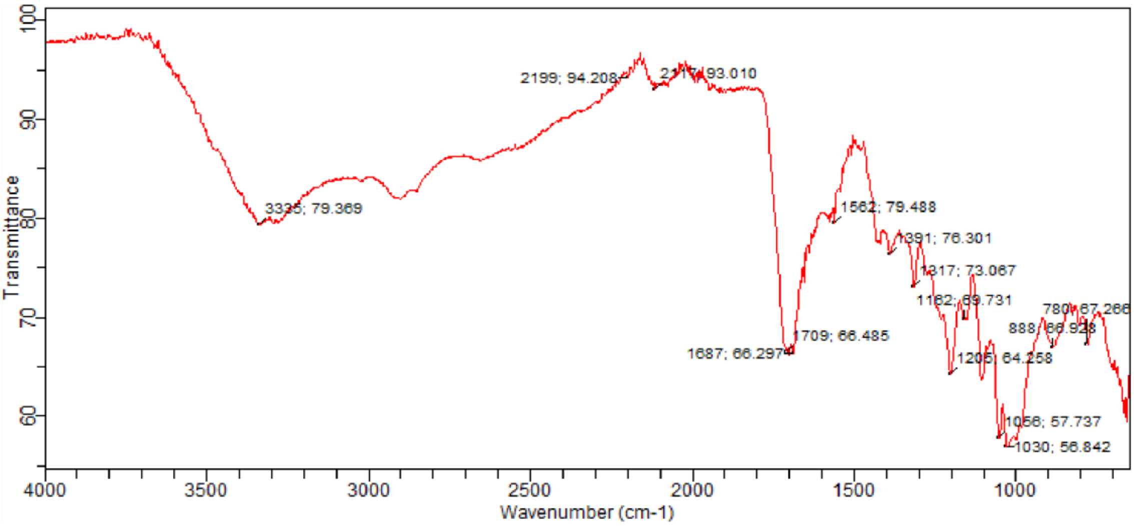

Fig. 2d: 1.5% Chitosan modified cotton fabric

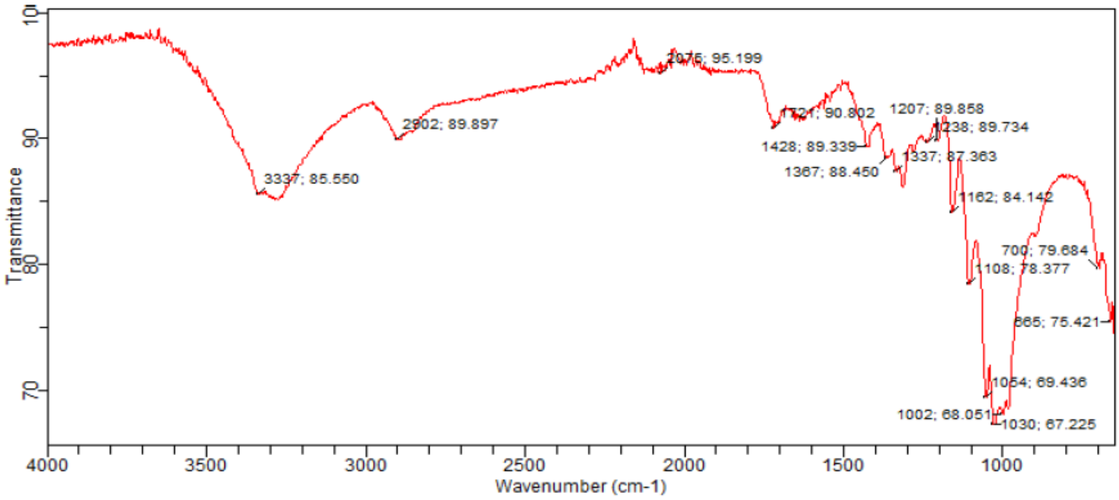

Fig. 2e: 2.0% Chitosan modified cotton fabric

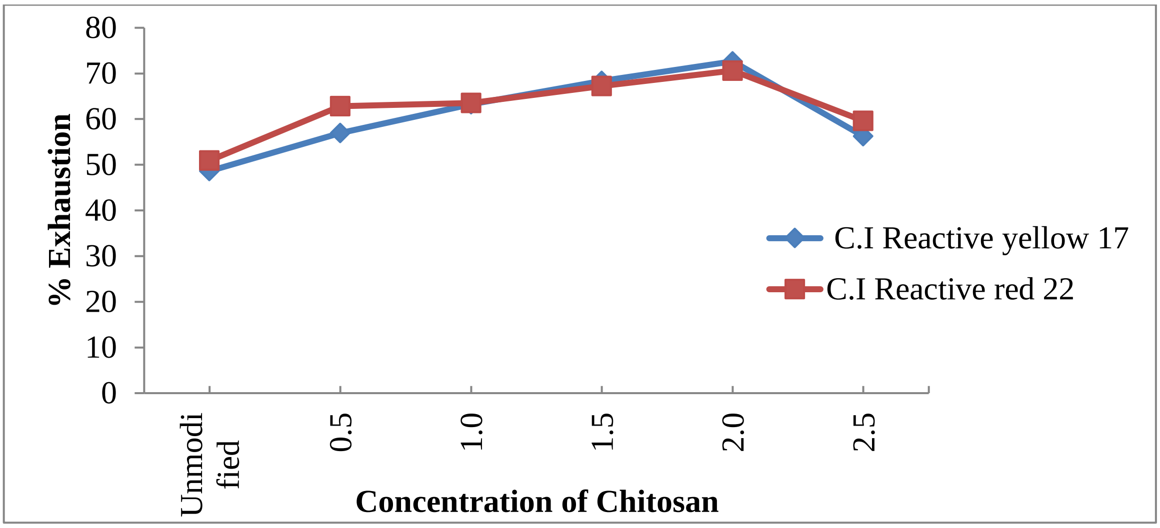

Fig. 3: Effect of Modifying Agent on dye exhaustion

Effect of dye concentration on dye exhaustion

To evaluate the influence of dye concentration on the dye exhaustion different dye shade were used as shown in Table 4 and Figure 4.

From Figure 4; It was observed that chitosan modified fabrics yield high exhaustion values for both remazol red B and remazol golden yellow G in concentration dependent manner of dye shade. The high exhaustion was due to the strong attraction between the cationic sites on the modified fabrics and the anionic dyes which lead to high exhaustion without the addition of electrolyte to the dye bath (Kunal *et al.*, 2012).

Effect of chotsan modification on the fastness properties of grey cotton fabrics

The colour fastness properties of cationized cotton fabrics using different chitosan concentration and then dyed with C.I. Reactive Red 22 was assessed for washing and light fastness. The results are shown in table 5.

From table 5, it was observed that all chitosan modified fabrics have shown very good fastness to both light and washing of comparable strength to the unmodified fabrics at lower concentration of chitosan. At higher concentration of chitosan, modified fabrics yield excellent fastness properties. This is due to the strength of the covalent bond that exist between the dye molecules and the cationic cotton fabrics (Rahman *et al.*, 2014).

Effect of Modification on Fastness Properties of Cotton fabrics dyed with C.I Reactive Yellow 17

The colour fastness properties of modified fabrics using variable concentration of chitosan and then dye with remazol golden yellow G (C.I reactive yellow 17) was assessed for their washing and light fastness, the results are depicted in table 4.

From table 6, It was observed that all chitosan modified fabrics have shown excellent fastness to both washing and light of comparable strength to the unmodified fabrics at lower concentration of chitosan. But yield higher fastness at higher concentration of the modifier. This might to be due to the strength of the covalent bond that exist between the dye molecules and the cationic cotton fabrics (Kunal*et al.*, 2012).

Table 4: Effects of dye concentration on dye exhaustion

Dye Concentration (%) (o.w.f)	**Dye Exhaustion (%)**	
	Remazol Red B	Remazol Golden Yellow G
1	47.85	45.96
2	58.68	50.92
4	65.20	63.82
6	69.90	65.98
8	80.23	80.02

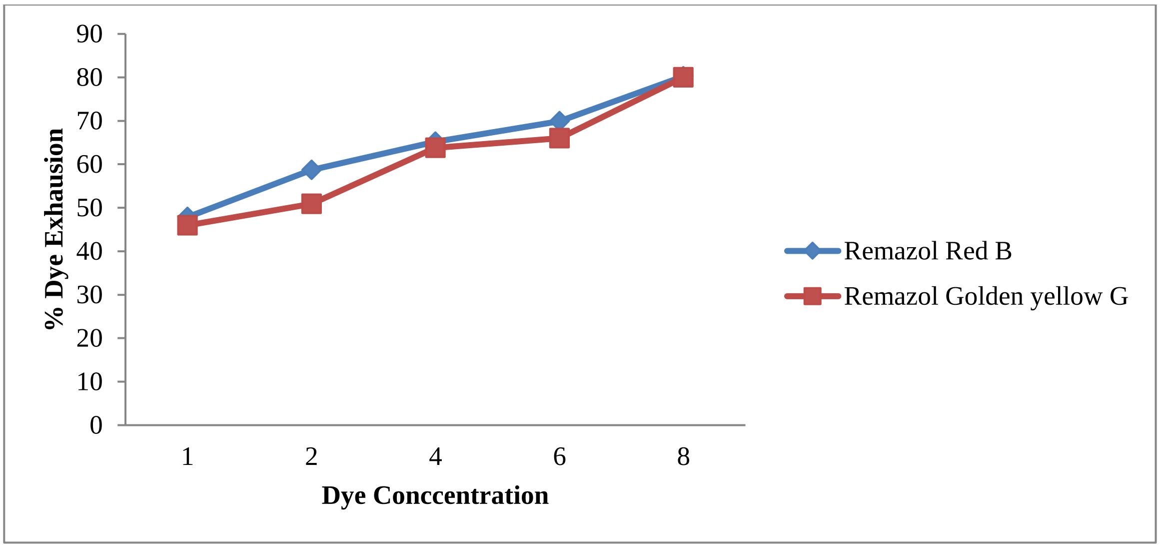

Fig. 4: Effect of dye concentration on dye exhaustion

Table 5: Colour fastness to light and washing for Remazol Red B

Fabrics Samples	Washing fastness										Light fastness				
	Colour change					Colour stain									
	Colour Shade (% o.w.f)														
	1	**2**	**4**	**6**	**8**	**1**	**2**	**4**	**6**	**8**	**1**	**2**	**4**	**6**	**8**
Unmodified	4/5	4/5	4/5	4	4	4/5	4	4	4	6	6	7	7	7	7
0.5% CHTM	4/5	4/5	4/5	4	4	4/5	4/5	4/5	4	4	6	6	6	7	7
1% CHTM	4/5	4/5	4/5	4	4	4/5	4/5	4/5	4/5	4/5	6	6	6	6	7
1.5% CHTM	5	5	5	5	5	5	5	5	5	5	7	7	7	7	7
2.0% CHTM	5	5	5	5	5	5	5	5	5	5	7	7	7	7	7
2.5% CHTM	4	4	4	4	4	4	4	4/5	4/5	4/5	7	7	7	7	7

Table 6: Colour fastness to light and washing for Remazol golden yellow G

Fabrics Samples	Washing fastness										Light fastness				
	Colour change					Colour stain									
	Colour Shade (% o.w.f)														
	1	**2**	**4**	**6**	**8**	**1**	**2**	**4**	**6**	**8**	**1**	**2**	**4**	**6**	**8**
Unmodified	4	4	4	4	4	4	4	4	4	4	6	6	6	7	7
0.5% CHTM	4	4	4	4	4	4	4	4	4	4	6	6	6	7	7
1% CHTM	4/5	4/5	4/5	4/5	4	4/5	4	4/5	4/5	4	6	6	6	7	7
1.5% CHTM	5	5	5	5	5	5	5	5	5	5	7	7	7	7	7
2.0% CHTM	5	5	5	5	5	5	5	5	5	5	7	7	7	7	7
2.5% CHTM	4	4	4	4	4	4	4	4	4	4	7	7	7	7	7

CONCLUSION

Modification of grey cotton fabrics using chitosan create cationic sites in the fiber polymer that results in higher absorption of reactive dyes. Varying the concentration of chitosan (from 0.5, 1.0, 1.5, 2.0 and 2.5 %) played an important role and noticeable effect on the dyeability of cotton with reactive dyes. In this work, we study the improvement of dyeing properties of grey cotton fabrics modified with chitosan in the presence of a cross linker (citric acid) without salt and alkali: the fastness properties are adequately good and comparable to the conventionally dyed samples.

Hence, Chitosan modification have shown overall suitability for dyeing cotton fabrics with reactive dyes without salt and alkali and thus hold promise for environment.

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