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Chemical Modification of Cotton Cellulose by Carbamation with Urea and its Dyeability with Reactive Dyes without the use of Electrolytes

Kemična modifikacija bombaža s karbamiranjem s sečnino in njegova obarvljivost z reaktivnimi barvili brez uporabe elektrolita

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Abstract

Cotton cellulose is primarily dyed with reactive dyes that form a strong covalent bond with the substrate. The reactive dyeing process requires a high amount of salt and alkali. Studies have been conducted to improve exhaustion and reduce the use of a high amount of salt and alkali through the cationisation of the substrate. This study focuses on the carbamation of mercerised cotton cellulose for the purpose of preparing an alternative way of dyeing cotton fabric with reactive dye in the absence of electrolytes. The effect of carbamation was shown qualitatively using FTIR spectroscopy where the optimal results were achieved using a urea concentration of 400 g/l, a temperature of 135 ºC and a time of 5 minutes. The carbamated cotton demonstrated a lower decomposition temperature than that of native cotton. Colour strength, exhaustion, fixation and total dye utilisation studies demonstrated good results compared to the dyeing of conventional cotton fabric.

Keywords: cotton, carbamation, urea, pad-dry-cure technique, dyeing, Reactive Red HE3B, adsorption isotherm

Izvleček

Barvanje bombažne celuloze poteka večinoma z reaktivnimi barvili, ki tvorijo močno kovalentno vez s substratom. Proces barvanja z reaktivnim barvilom zahteva veliko količino soli in alkalij. Opravljene so bile raziskave s kationizacijo substrata za izboljšanje izčrpanja in zmanjšanje uporabe velikih količin soli in alkalij. Študija se osredotoča na karbamiranje mercerizirane bombažne celuloze z namenom priprave alternativnega načina barvanja bombažne tkanine z reaktivnim barvilom v odsotnosti elektrolita. Učinek karbamiranja je bil kvalitativno viden na spektrih FTIR, kjer so bili optimalni rezultati doseženi pri koncentraciji sečnine 400 g/l, temperaturi 135 °C in času 5 min. Karbamirani bombaž je imel nižjo temperaturo razgradnje od nemodificiranega bombaža. Jakost obarvanja, izčrpanje, fiksiranje in celotna uporaba barvil je pokazala dobre rezultate v primerjavi z barvanjem konvencionalne bombažne tkanine.

Ključne besede: bombaž, karbamiranje, sečnina, impregnirno-fiksirni postopek, barvanje, Reactive red HE3B, adsorpcijska izoterma

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1 Introduction

Cellulose is a chemically homogeneous linear polymer of up to 10,000 anhydroglucose units that are connected by β-1,4 bonds [1]. Each glucose unit is tilted by 180° towards its neighbour. The structural subunit of cellulose is cellobiose. Chemical uniformity facilitates the spontaneous crystallisation of cellulose molecules. Hydrogen bonding within and between multiple layers of parallel molecules results in the formation of tightly packed microfibrils. It has been reported that, in the manufacturing of cellulose carbamate, urea first decomposes into ammonia and isocyanic acid at approximately 135 °C [2], while Fu et al. reported that the decomposition of urea starts above its melting temperature of 132.7 °C [3]. Isocyanic acid (−HNCO−) reacts with cellulose hydroxyl (−OH) groups to form cellulose carbamate. The carbamate groups are substituted in the hydroxyl groups of the cellulose chain [4–7]. Reaction efficiency depends, *inter alia*, on the amount of urea, reaction conditions and raw material properties [8, 9]. The processes for synthesizing carbamated cellulose materials are explained in the following sections.

Solventless carbamation has been reported by heating (in an oven or oil bath) urea with a mercerised, carbamated cotton/cellulose (MCC) or alkali-swollen cotton linters in the temperature range of 110–185 °C for 3–9 hours, with an urea/cellulose weight ratio of 1.5–4.0, followed by microwave heating (255 W power) for 2–5 minutes [9]. Cellulose carbanilation performed through the reaction of cellulose, with phenyl isocyanate mostly in dimethyl sulfoxide (DMSO) or pyridine as the solvents, has been used widely for determining the analytical parameters of celluloses through gel permeation chromatography (GPC) in organic solvents, such as tetrahydrofuran (THF) or N,N-dimethylacetamide (DMAc) [10]. Carbanilation was performed using native cellulose or its alkali-activated counterpart. Many of these reactions start heterogeneously (suspension) and turn homogeneously. Hearon et al. carried out work through the suspension of cotton linters in refluxing pyridine, while reaction was conducted using phenyl isocyanate or a-naphthyl isocyanate to give the corresponding tricarbanilates. The reaction mixture became homogeneous after 36 and 40 hours, respectively. The CC was precipitated from the reaction mixture [11]. Cellulose tricarbanilate was obtained through the reaction of a suspension of biopolymer in DMF, using phenyl isocyanate in the presence of triethylenediamine as a catalyst at 95–100 °C. The suspension turned homogeneous within 30–60 minutes CC films were cast directly from the reaction mixture [12].

The reaction of cellulose with phenyl isocyanate in pyridine at 80 °C for 2 days produced a clear solution (MCC) or was incomplete (a pulp). The precipitation of CC in methanol resulted in the loss (5–26% (w/w)) of a low molecular weight fraction, while precipitation in water/methanol mixture (volume ratio 30/70) resulted in less [13] or no product fractionation [14]. Incomplete carbanilation of fibrous cellulose (bisulfite pulp; 86.3–97.1% α-cellulose; decrystallized cotton linters) was later avoided through the pretreatment (activation) of the biopolymer with liquid ammonia. The reaction was carried out for 2 days at 80 °C in pyridine, DMF or DMSO. Clear solutions of cellulose tricarbanilate were obtained in all cases [4].

Kenaf core cellulose was suspended in urea solutions [0.9–4.5% (w/w)] and the mixture was stirred under normal and then reduced pressure, the latter to enhance urea penetration within the biopolymer fibres. The reaction was induced by MW heating (380 W power) for 10–30 minutes. The N% in the purified CC increased as a function of increasing the urea concentration in the solution and the reaction time [15]. Cellulose derivatisation can be better controlled, and the reaction temperature reduced, e.g. to 100–130 °C, where an activated biopolymer was employed and carbanilation was carried out in the presence of a solvent. Another approach to obtaining CC under heterogeneous conditions is to use SC–CO_2 as a solvent to introduce urea into the biopolymer fibres [16]. The simplest approach to prepare CC under homogeneous conditions is to derivatise the hydroxyl groups of the AGU of a cellulose derivative. Cellulose tricarbamate from MCC, cotton linters, sulfate pulp, and cellulose obtained from wheat straw and hardwood by steam explosion was obtained through the reaction of phenyl isocyanate with the biopolymer dissolved in DMAc/LiCl for 2 hours, at 60–80 °C, in the presence or absence of a pyridine catalyst [14].

The conditions employed for carbamate formation under homogeneous conditions may lead to the formation of by-products [17, 18]. The formation of these by products was avoided by using anhydrous reaction conditions, a low reaction temperature

60–70 °C and a longer time period of 24–48 hours, and by using di(1-butyl) tin dilaurate as catalyst, a controlled amount of isocyanate (phenyl- and 1-butyl) and product workup that did not include quenching using an alcohol. The reaction of MCC, cotton linters or partially silylated cellulose in DMAc started heterogeneously and then turned homogeneously. Good to high yields (65–94%) of products with DS of carbamate from 1.74 to 3.0 were obtained [19]. Chemical modifications to cationise cotton have been reported to have beneficial effects in dyeing with reactive dyes [20–23].

In cellulose carbamate, the hydroxyl groups in the cellulose repeating unit are partially substituted with carbamate groups. The degree of substitution indicates the average amount of substituted hydroxyl groups per anhydroglucose unit. The theoretical maximum DS is thus 3.0 [2]. Properties that are affected most by the degree of substitution are solubility, swelling and plasticity. One of the key factors governing the substitution of the prepared cellulose carbamate is the amount of urea in the manufacturing process [24]. The nitrogen content of cellulosic material is often used to describe the substitution degree of cellulose carbamates. However, nitrogen content only indicates the amount of nitrogen in the sample, not the exact degree of substitution. Moreover, the uniformity of the product and the evenness of the carbamate groups in the cellulose chains are significant factors in determining cellulose carbamate quality and properties. However, researchers have reported that it is challenging to determine the uniformity of the substituted cellulose[11, 25]. Guo et al. and Yin et al. reported that the carbamate group is stable in acidic media, but that hydrolysis can take place in alkaline media. In alkaline media, the carbamate groups are irreversibly decomposed to carbonate and ammonia at a rate dependent on NaOH concentration and temperature [6, 17].

2 Materials and methods

2.1 Materials

Plain weave cotton fabric (half-bleached) with a warp density of 26 ends/cm, a weft density of 22 picks/cm, mass per unit area of 150 g/m^2, warp and weft-way tensile strength of 319N and 228N respectively, and a warp and weft yarn count of 50 tex (20 Ne) were used throughout the work. Urea extra pure (Loba Chemie Pvt. Ltd., India), which decomposes at temperature above its melting temperature as a source for isocyanic acid, sodium hydroxide pellets, which is a strong alkali for mercerising, sodium carbonate powder to fix the reactive dye to the fibre, acetic acid to neutralise the fabric after mercerising, sodium sulphate for exhaustion in the conventional reactive dyeing of cotton (Alpha Chemika, India) and reactive dye of the class of HE (Reactive Red HE3B) for dyeing were utilised throughout this study.

The following instruments were used in this study: Perkin Elmer TGA instruments to study the thermal decomposition properties of the carbamated material, a Perkin Elmer FTIR spectrometer to identify the molecular fingerprint of the carbamated fabric and a Tensolab 100 (Mesdan Lab, Italy) to evaluate the mechanical strength of the carbamated fabric. Also used were: a crock meter (Mesdan Lab, Italy) to evaluate the resistance to fading of the dyed carbamated fabric to dry or wet rubbing, a lightfastness solar box (Mesdan Lab, Italy) to evaluate the resistance to fading of the dyed carbamated fabric while exposed to light and Laundr-o-meter (Mesdan Lab, Italy) to evaluate the resistance to fading of the dyed carbamated fabric to wet washing. A Gretagmacbeth Colour Eye 310 was used to evaluate colour strength, while a UV/VIS spectrometer (Perkin Elmer Lambda 25, Singapore) was used to determine dye absorbance. The machines used in this study were an eco-IR dyeing machine for dyeing (Ahiba, US), a Padder Lab 300 (Mesdan Lab, Italy) for the application of treatments application to the mercerised fabric and an oven dryer (Mesdan Lab, Italy) for drying and curing purposes. The Kjeldahl method was used to determine the nitrogen content in the carbamated fabric to determine the degree of carbamation.

2.2 Methods

The experimental part of this study was divided into three main sections.

i. First, the carbamation of the cotton cellulose (i.e. the initial pre-treatment of half-bleached fabric through mercerization for the purpose of enhancing the accessibility of the functional groups in cotton cellulose) was carried out with the objective of optimisation. The main variables during the manufacturing of cotton cellulose carbamate were temperature, time and the concentration of urea. The properties of the cotton cellulose carbamate were studied, with major responses being the degree of substitution and the tensile strength (warp and weft direction) of the fabric. The optimised fabric was analysed using FTIR to determine the molecular fingerprint of the product, while TGA studies were also performed.

ii. Secondly, the optimised carbamated and uncarbamated cotton was dyed using reactive dyes (i.e. Reactive Red HE3B dye). The properties of the dyed cotton cellulose carbamate were evaluated against the dyed uncarbamated cotton fabric. The tests carried out were: the degree of exhaustion, fixation, colour strength (K/S), fastness to washing, fastness to light and rubbing fastness.

iii. Thirdly, the modelling of an adsorption isotherm experiment was performed using Langmuir and Freundlich adsorption isotherms to find the best method to express the property of the carbamated cotton cellulose for dye adsorption.

Preparation of cellulose carbamate derivatives

a. Mercerisation

The mercerisation of half-bleached cotton fabric (i.e. sinking time < 3 seconds) was performed manually using a setup of a non-adjustable pan and frame. A piece of fabric was fixed to the pins of the steel frame with a tension of 3% and submerged into the concentrated (300 g/l) NaOH solution for 60 seconds with a mercerising temperature of 20–25 °C. The frame with the fabric still attached was then transferred to a sink and rinsed with running water to remove the majority of the alkali. After detaching the fabric from the frame, was rinsed, neutralised with dilute acetic acid, rinsed/washed with water and air dried. As an indicator of the degree of mercerisation, the barium number of the mercerised cotton fabrics was determined according to the AATCC test method 89-2003 [26].

b. Carbamation

The mercerised cotton fabric (barium activity number = 141.2 ± 1.0) was subjected to carbamation using 100 g/l, 250 g/l and 400 g/l amounts of urea by following pad-dry-cure method. The prepared cotton fabric was impregnated using a padding liquor in a laboratory padding mangle. The samples were then pre-dried for 5 minutes at 60 °C using an oven dryer, and then cured at 135 °C, 160 °C and 185 °C for 1, 3 and 5 minutes. The prepared carbamated samples were washed thoroughly with distilled water to purify them from the remains of urea and finally air dried.

The experiment and optimisation were carried out using the response surface methodology (i.e. three-level factorial), with the major responses being the degree of substitution of carbamate groups in place of hydroxyl groups, warp- and weft-way tensile strength.

Dyeing of uncarbamated and carbamated cotton

Dyeing of untreated (uncarbamated) and carbamated cotton fabrics was carried out using a laboratory eco-IR dyeing machine. Dyeing of uncarbamated cotton with Reactive Red HE3B (Figure 1) dye was performed according to the procedure recommended by the manufacturer, in which a shade (% o.w.f.) of Reactive Red HE3B (C.I. Reactive Red 120) dye was added to a room temperature dyebath. The fabric samples were then added and each bath was heated to 80 °C at a rate of 1.5 °C/minute. Before reaching 80°C, electrolyte (Na_2SO_4) of 40 g/l was added in two instalments at 55 °C and 65 °C to each bath. After holding the temperature at 80 °C for 10 minutes, 10 g/l of sodium carbonate was added. The bath was then held at 80 °C for 50 minutes, cooled to 60 °C at a rate of 2.5 °C/minute and then discarded (Figure 2 (a)) [27].

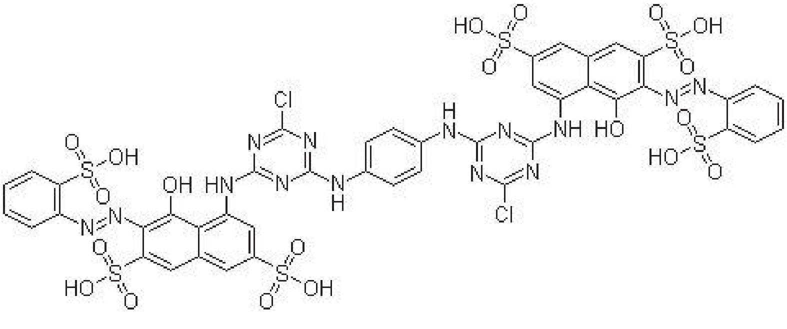


Figure 1: Reactive Red HE3B

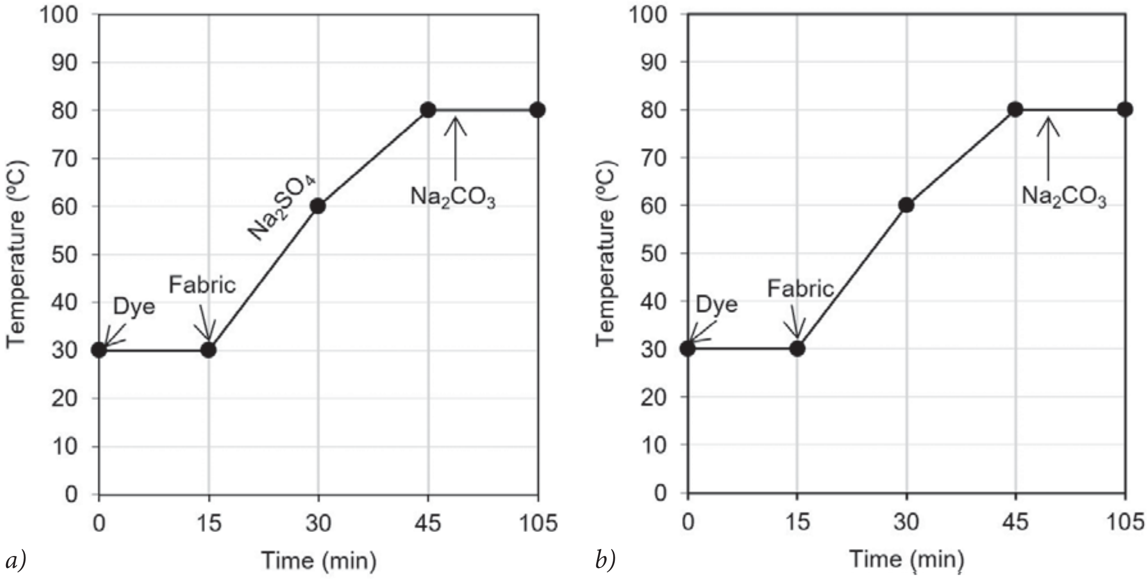


Figure 2: Dyeing cycle of (a) uncarbamated cotton fabric, (b) carbamated cotton fabric

The procedure for dyeing the carbamated cotton was the same as that for uncarbamated cotton, except that the dyeing of carbamated cotton was done in the absence of electrolytes (Na_2SO_4), with the bath buffered at pH 6 using acetic acid (Figure 2 (b)). Dye uptake of both the carbamated cotton without sodium sulphate and uncarbamated cotton with sodium sulphate, was measured by sampling the dye bath before and after the dyeing process. The absorbance of the diluted dye solution was measured at the wavelength of the maximum absorption ($\lambda_{max} = 560$) of the dye using a UV-visible spectrophotometer. Percent dye bath exhaustion E% was determined using equation 1.

$$E = 100\left(1 - \frac{A_1}{A_0}\right)\ (\%) \qquad (1),$$

where A_0 represents the absorbance of the dye solution before dyeing and A_1 represents the absorbance of the dye solution after dyeing. The colour strength of the dyed samples was determined as the *K/S* value calculated from the sample reflectance (*R*) (equation 2):

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

The extent of the dye fixation of the reactive dyes on all the carbamated and uncarbamated cotton fabrics were determined using measurements of the *K/S* values of the dyed samples taken before and after soaping, from which the extent of dye fixation was calculated using equation 3 and 4.

$$F = \frac{C_2}{C_1}\ 100\ (\%) \qquad (3),$$

$$T = E\ \frac{C_2}{C_1}\ (\%) \qquad (4),$$

where *T* represents total dye fixed (%), C_1 represents the *K/S* value of dyed sample before soaping, C_2 represents the *K/S* value of dyed sample after soaping and *F* represents the degree of fixation of absorbed dye.

Determination of the degree of substitution

The percentage of nitrogen present in the cotton fabric was measured in duplicate and used as an indicator of the level of carbamation. The analysis was conducted according to the Kjeldahl method using a sample mass of 10 mg ± 2 mg.

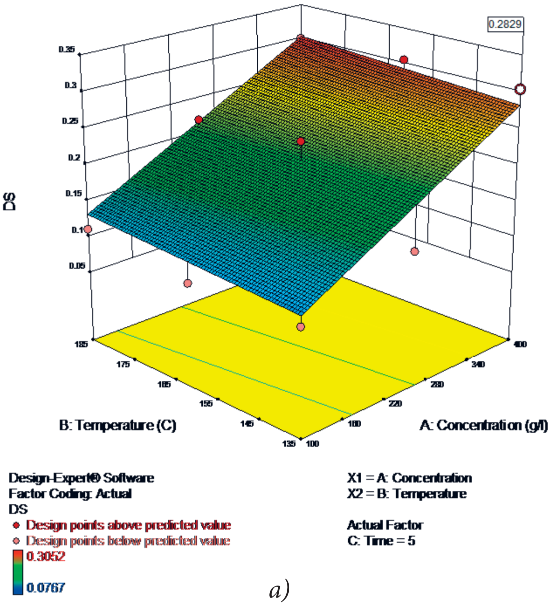
The degree of substitution (DS) was determined using equation 5 below:

$$DS = \frac{162 \times N}{(14 \times 100) - (43 \times \mathrm{N})} \qquad (5),$$

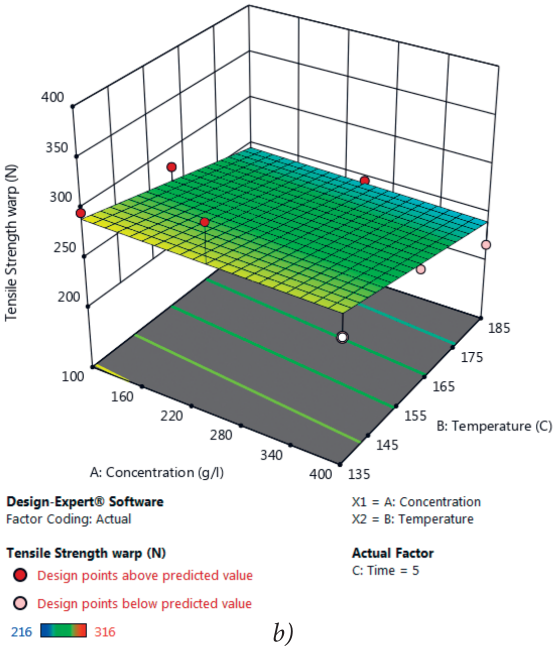
where *N* represents specimen nitrogen content (%), 162 represents the molar mass (g/mol) of an anhydroglucose unit (AGU), 14 represents the molar mass of nitrogen (g/mol) and 43 represents the net increment in molar mass (g/mol) of an AGU on substitution of a hydroxyl (–OH) by a carbamate (–$OCONH_2$) group.

Tensile strength and fastness testing

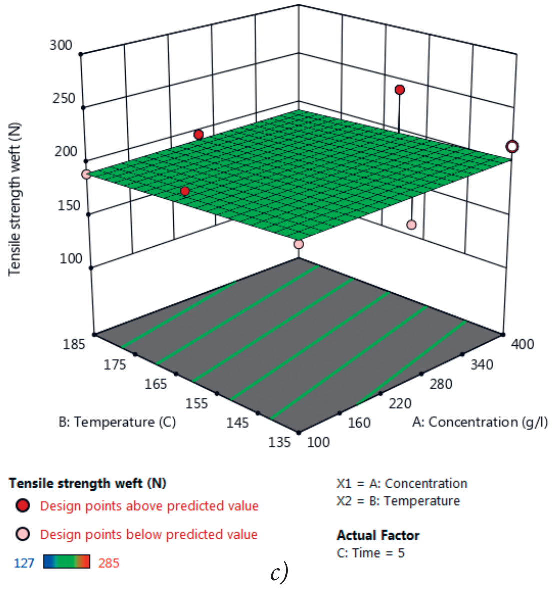
Tensile strength was tested according to the ASTM D5034 textile grab method [28], colourfastness to laundering according to the AATCC test method 61-2007 [26], colourfastness to light in accordance with the ISO 105-B02:1994, and colourfastness to rubbing in accordance with the AATCC test method 8-2007 (AATCC, 2010).



a)



b)



c)

Figure 3: Response for (a) optimum carbamation, (b) weft-way tensile strength and (c) warp-way tensile strength

3 Results and discussion

3.1 Optimisation of the carbamation

The response surface methodology (RSM) was used to evaluate the degree of the carbamate group that has been substituted in place of the hydroxyl group of cotton cellulose, with less effect on the weft- and warp-way tensile strength. The design was also used to study the relationship between the variables (urea concentration, curing temperature and curing time) and the responses (degree of substitution and tensile strength). Analysis of variance (ANOVA) was used to test whether the variables (urea concentration, curing temperature and curing time) significantly affect the response values (degree of substitution, warp-way tensile strength and weft-way tensile strength). The results are presented in Figure 3.

The effects of the factors are concentration, curing temperature and curing time, while responses are the degree of substitution, DS and tensile strength. It could be understood from the results that DS increased significantly by increasing the concentration of urea and increasing time, while there was no significant change in DS due to the varying of temperature. Tensile strength in the warp direction was affected significantly by increasing the temperature, while there was no significant change due to increment in concentration and curing time. Tensile strength in the weft direction was affected significantly by all the factors (concentration, temperature and time). The desired results were found to be: DS of 0.283, tensile strength in warp of 285.98 N and weft of 203.82 N. Under these conditions, the warp tensile strength decreased by 10.35%, while the weft tensile strength decreased by 10.61% relative to the control half-bleached fabric.

3.2 FTIR analysis

Bands due to the stretching of OH groups of crystalline and amorphous modifications of cellulose in terms of celluloses I and II on account of mercerisation and carbamation have been reported in literature [3, 31]. Because the properties of cotton cellulose carbamate material are one of the significant factors that contribute to the dyeability of material, differences between the mercerised cotton cellulose carbamate sample and mercerised, uncarbamated cotton were evaluated to understand the chemical change that took place in carbamation (Figure 4). Carbamates of cotton cellulose were characterised by means of FTIR to confirm the reaction of hydroxyl groups with urea. A typical loss in the transmittance band for the carbamated cotton was observed in the range of 3600 cm^{-1} to 3300 cm^{-1}, which is assigned to the ($-NH_2$) [31] of the carbamate group. The stretch is not as broad or strong as it appeared in the uncarbamated cotton (–OH stretch) in this region. The transmittance band from 3300 cm^{-1} to 3000 cm^{-1} is very broad in the uncarbamated cotton, which indicates the large numbers of –OH groups in the cotton [3, 31], while this band is not as broad in the carbamated cotton, which indicates a reduction in –OH groups that are replaced by the carbamate group.

The transmittance peak at around 1100 cm^{-1} observed on uncarbamated cotton disappeared on the carbamated cotton. This can be attributed to the loss of –OH vibration in the carbamated cotton fabric. The reduction of hydroxyl peak at 3250 cm^{-1} represents strong evidence for the reaction of urea with the cotton samples.

3.3 Thermogravimetric analysis

The TG curves of the mercerised cotton cellulose and its carbamate derivatives with DS of 0.2829 are shown in the Figure 5. The TG curves were separated into three sections. At the initial stage, the weight loss observed in the temperature range of 100 °C to 150 °C could be attributed to the evaporation of water and gas absorbed by the cellulose. In the range of 150 °C to 250 °C, there appeared a minor thermal decomposition of residues. In the TG curves, it was found that all the major decompositions are located in the range of 300 °C to 400 °C and 300 °C to 375 °C for control cotton cellulose and carbamated cotton cellulose, respectively. When comparing the samples, it was discovered that the major decomposition temperature of control cotton fabric was higher than carbamated cotton cellulose. From the FTIR (Figure 4), it was observed that the carbamation of cotton showed the diminished intensity of hydrogen bonding in the range of 3600 cm^{-1} to 3300 cm^{-1}, as the decrease in intensity had a visible effect on

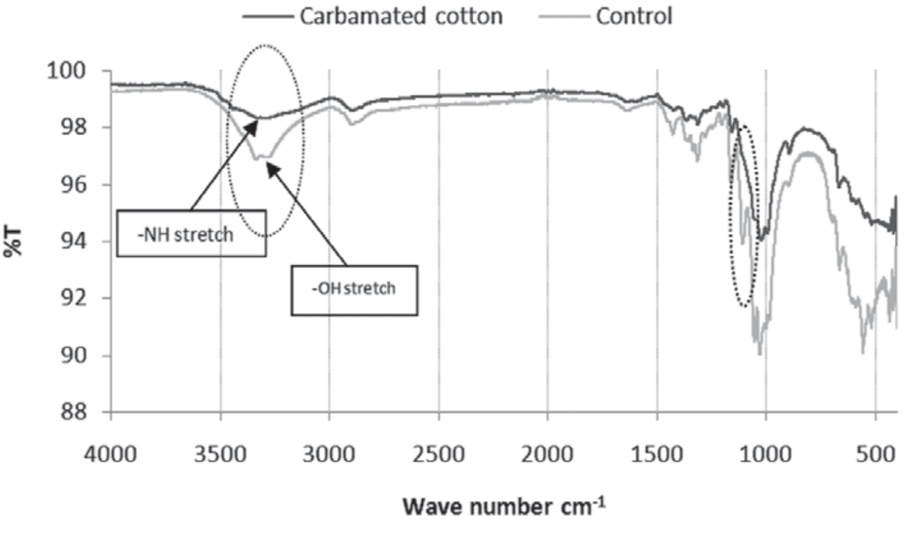


Figure. 4: FTIR spectra of carbamated and control fabric

the TG curve (Figure 5) and on the decomposition temperature of the materials.

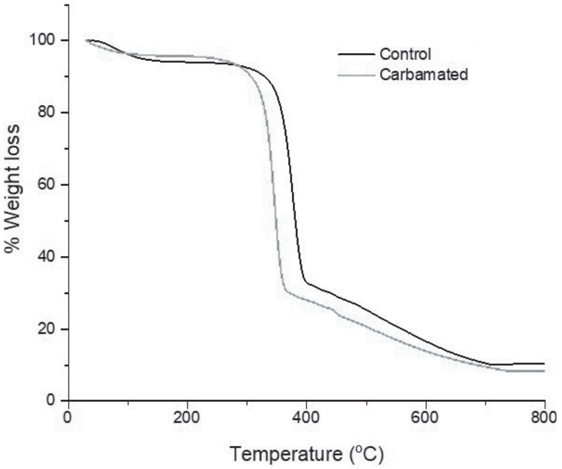


Figure 5: TG curves of cotton cellulose and carbamated cotton

3.4 Dyeing results

Exhaustion, fixation and dye utilised

The results of exhaustion, fixation and dye utilised are presented in Table 1. Exhaustion was determined by measuring the absorbance of the dye bath before and after the dyeing process at the wave length of maximum absorption (λ_{max} = 543 nm). The exhaustion percentage of the carbamated and mercerised cotton was higher than that of the control half-bleached fabric. For all fabrics, the exhaustion decreased by increasing the initial dye bath concentration. This can be attributed to the increment in affinity of the dye to the fibre. The dye utilisation of Reactive Red HE3B on all the control, mercerised and carbamated samples decreased by increasing the dye bath concentration. The exhaustion and dye utilisation are presented in Figures 6 and 7. The change percentage in dye utilisation was 12%, 13%, 7%, 15%, 14% and 10% for the shade depths of 0.5%, 1%, 2%, 3%, 4% and 5%, respectively, between the control and carbamated fabric.

Table 1: Summary of the dyeing properties of Reactive Red HE3B for carbamated, mercerised and control samples

Shade (%)	Absorbance of dye solution before dyeing (A_1)	Material type	Absorbance of dye solution after dyeing (A_2)	K/S value		Exhaustion (%)	Fixation (%)	Total dye utilised (%)
				Before washing (C1)	After washing (C2)			
0.5	6.2	T[a]	0.80	3.80	3.44	87.10	90.48	78.81
		UT[b]	1.30	1.38	1.21	79.03	87.51	69.16
		M[c]	0.90	3.90	3.50	85.48	89.74	76.72
1	8	T	1.90	5.27	4.78	76.25	90.58	69.06
		UT	2.80	2.02	1.88	65.00	92.93	60.40
		M	2.10	5.34	4.54	73.75	85.08	62.75
2	8.7	T	3.40	6.98	6.48	60.92	92.90	56.59
		UT	3.80	2.30	2.14	56.32	93.14	52.46
		M	3.50	7.17	6.83	59.77	95.29	56.96
3	9.3	T	4.10	7.59	7.19	55.91	94.68	52.94
		UT	4.70	3.39	3.07	49.46	90.59	44.81
		M	5.00	7.46	7.08	51.46	94.84	48.80
4	9.9	T	5.60	7.89	7.25	43.43	91.90	39.92
		UT	6.20	3.93	3.62	37.37	92.15	34.44
		M	7.54	7.68	7.35	36.64	95.70	35.06
5	10.8	T	6.30	8.00	7.37	41.67	92.07	38.36
		UT	6.80	4.38	4.09	37.04	93.43	34.60
		M	8.23	7.91	7.35	35.70	92.92	33.18

[a]carbamated, [b]control half-bleached fabric, [c]mercerised fabric

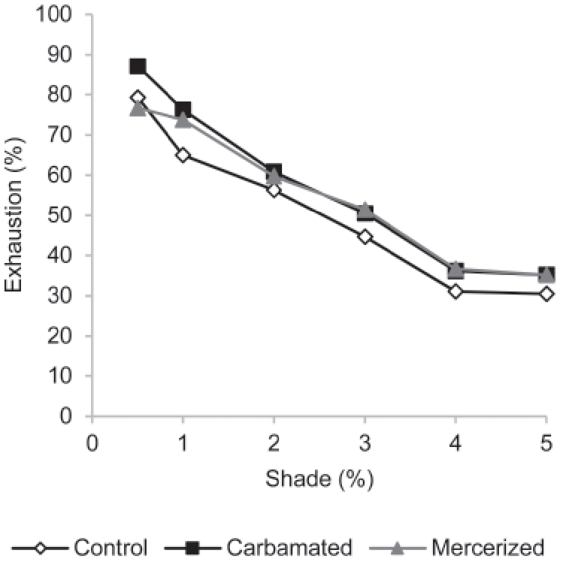


Figure 6: Percent exhaustion of Reactive Red HE3B on carbamated, mercerised and control fabric

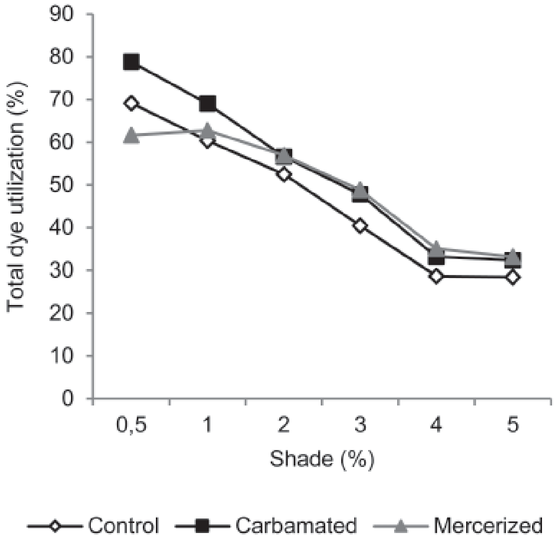


Figure 7: Total dye utilisation of carbamated, mercerised and control samples

Colour intensities (*K/S*) were employed to express the reduction ratio of light owing to absorption and scattering achieved based on reflectance. Figure 8 shows that the colour strength of the carbamated cotton dyed without sodium sulphate was much higher than that of the control half-bleached fabric. The carbamated cotton cellulose fabric was dyed with Reactive Red HE3B without using electrolytes; pH was instead made slightly acidic (pH = 6) through the addition of acetic acid. The improved dye uptake of carbamated cotton fabric may be attributed to the generation of positive charges, while the treatment fabric before carbamation (i.e. caustic mercerised) could also affect the dye adsorption, with the carbamate groups introduced. Very good levelling on the carbamated cotton cellulose samples was visually confirmed in this study.

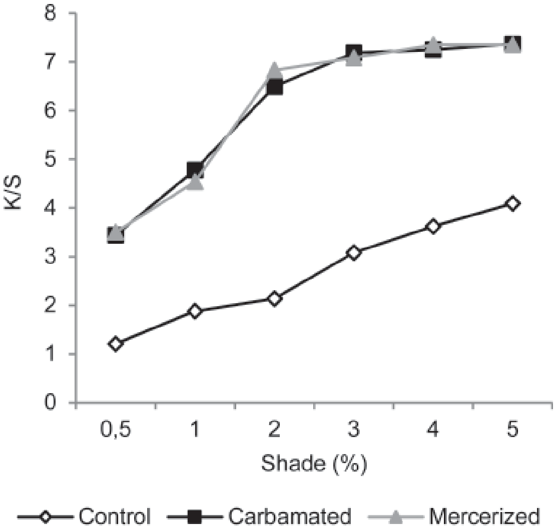


Figure 8: K/S values of carbamated, mercerised and control dyed samples

In the dyeing of carbamated cotton samples using an acid bath, it was confirmed that there was a strong attraction between the cationic dye sites on the carbamated cotton and the anionic Reactive Red HE3B dyes, which led to the achievement of higher exhaustion rates, without the addition of electrolytes to the dye bath. An enhancement of the colour strength is expected when the dye concentration is increased, as a greater number of dye molecules would be available in the vicinity of the cotton cellulose at higher concentrations. Unlike uncarbamated cotton, however, the dye build-up on the carbamated cotton is limited by its saturation adsorption value, which could be related to the amount of nitrogen introduced during pretreatment. The colour strength of the carbamated cotton increased by increasing the dye concentration, but the difference was very small at a 4% shade. This indicates that the fibre reached its saturation point, while the control half-bleached fabric colour strength increased in a fairly linear fashion. Looking at the results, the colour strength achieved by using a 5% shade of Reactive Red HE3B on the control half-bleached fabric could be obtained by using a 1% shade on the carbamated cotton fabric, thus increasing the dye utilisation. Moreover, excellent levelness was visually observed on the dyed carbamated cotton fabric.

Fastness properties

The overall result of dyeing properties in terms of the fastness of Reactive Red HE3B towards carbamated cotton and control half-bleached fabric is summarised in Table 2. The result shows that wash fastness and rub fastness were not affected significantly. This may be due to the formation of a strong ionic bond between the fibre and the dye because it is equally good as the covalent bond that normally links the dye and the fibre.

Adsorption isotherm analysis

In order to study the adsorption property of Reactive Red HE3B dye on the carbamated cotton at a constant temperature, a sample of fabric was placed in a dye bath buffered at pH 6 and dyed for two hours at the temperature recommended by the dye manufacturer (i.e. 80 °C) [25]. The adsorption of Reactive Red HE3B dye by mercerised, carbamated cotton as a function of concentration is shown in Figure 9. It was observed that the initial dye adsorption was fast, and decreased with a subsequent increase in the concentration the dye.

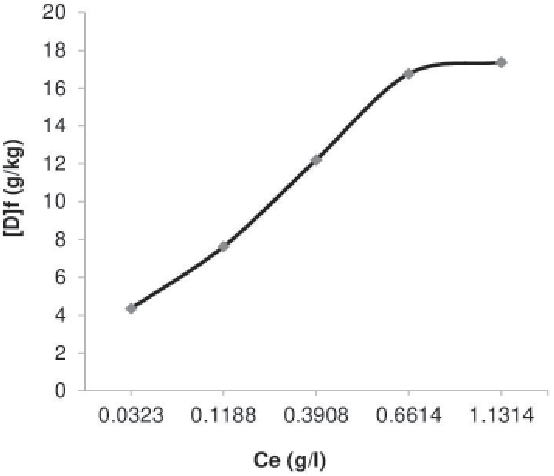


Figure 9: Effect of concentration on the adsorption of Reactive Red HE3B: temperature 80 °C; pH 6; amount is 5 g; time is 2 hours

Table 2: Summary of colourfastness results

Con. (%)	Material type	Wash fastness							Rubbing fastness		Light fastness
		Colour change	Staining on white								
			CA	CO	PA	PES	PAN	WO	Dry	Wet	
0.5	Control	4–5	4–5	4	4–5	5	4–5	5	5	4–5	4
	CCC[a]	4–5	4	3–4	4–5	5	4–5	5	5	4–5	4
	M[b]	4–5	4–5	4	4–5	5	4–5	5	5	4–5	5
1	Control	4–5	4–5	4	4–5	5	4–5	4–5	5	4–5	4
	CCC	4–5	4	3–4	4	5	4–5	4–5	4–5	4–5	4
	M	4–5	4–5	4	4–5	5	4–5	4–5	5	4–5	5
2	Control	4–5	4–5	4	4–5	5	4–5	4–5	5	4–5	5
	CCC	4	4	3–4	4	4–5	4–5	4–5	4–5	4–5	5
	M	4–5	4–5	4	4–5	5	4–5	4–5	5	4–5	5
3	Control	4–5	4–5	4	4	4–5	4–5	4–5	4–5	4–5	5
	CCC	4	4	3–4	3–4	4–5	4	4	4	4	5
	M	4–5	4–5	4	4	4–5	4–5	4–5	4–5	4–5	5
4	Control	4	4–5	4	4	4–5	4–5	4–5	4–5	4–5	5
	CCC	3–4	4	3–4	3–4	4–5	4	4	4	4	5
	M	4	4–5	4	4	4–5	4–5	4–5	4–5	4–5	5
5	Control	4	4	3–4	3–4	4–5	4–5	4	4	4	5
	CCC	3–4	3–4	3	3–4	4	3–4	3–4	4	4	5
	M	4	4	4	4	4–5	4–5	4	4	4	5

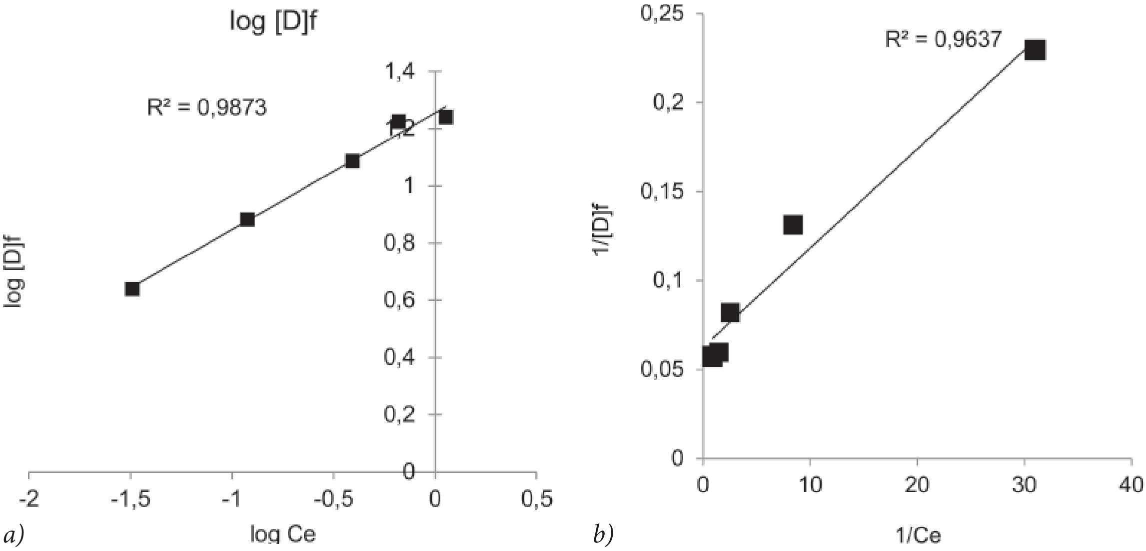
[a] carbamated cotton cellulose; [b] mercerised; CA: acetate; CO: cotton; PA: nylon, PES: polyester; PAN: acrylic; WO: wool

The profile obtained (Figure 9) from the study was utilised to plot Langmuir and Freundlich adsorption isotherms using well-known adsorption isotherm equations. In both the cases, linear plots were obtained and reveal the applicability of these isotherms on the ongoing adsorption process. Figures 10 (a) and 10 (b) illustrate Freundlich and Langmuir plots respectively for the adsorption of Reactive Red HE3B on mercerised carbamated cotton, while different Freundlich and Langmuir constants derived from these plots are presented in Table 3. However, the best fit for the system is found with a Freundlich adsorption isotherm with an R^2 value of 0.987 (Figure 10 (a)), while with Langmuir, the fit obtained is $R^2 = 0.963$ (Figure 10 (b)). It can thus be concluded that the dyes are not only attached to the available carbamate groups, but that they also form layers. In normal situations, with the dye used, the formation of layers is not particularly surprising because the dye molecule is essentially linear, similar to a direct dye. It would, therefore, be expected to show a tendency to form layers, with hydrogen bonding between appropriately placed groups on the dye and the fibre, and between dye molecules and other dye molecules. In this study, however, this kind of result was not expected because the carbamate groups that ionize (positively) should attract the negatively ionized Reactive Red HE3B dyes, while the remaining –OH were not expected to adsorb, as the hydroxyl group and the dye are negatively ionized and should thus repel one another. However, from the results, the adsorption was mostly explained with the Freundlich adsorption isotherm, which assumes that the dye adsorption is not limited to the functional groups available in the material to be dyed. The assumption was therefore made that the introduced functional groups play the role of attracting not only a single molecule, but rather many molecules that could be adsorbed on the hydroxyl groups.

Table 3: Freundlich and Langmuir constants of Reactive Red HE3B over carbamated cotton: temperature 80 °C; pH 6; amount 5 g; time 2 hours

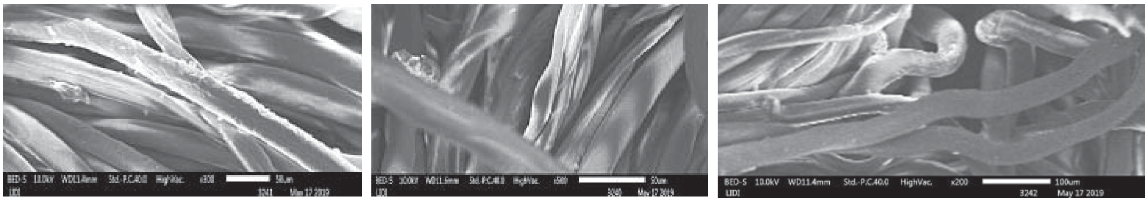
Freundlich constants	n	0.407
	K	1.254
Langmuir constants	$[S]_f$ (g/l)	15.97
	K (l/g)	0.0056

Figure 11 shows the SEM image of half-bleached control, mercerised and carbamated fabrics. It is evident that surface roughness increased after carbamation, better than the deconvoluted, swollen and circular cross section of mercerised fibres. The fibres in the half-bleached control fabric are convoluted; surface roughness is not visible up to a magnification of 500-x. Surface roughness may have improved the adsorption property of the carbamated fabric, since it is expected that only the carbamate groups will be involved in the adsorption of the Reactive Red HE3B dye. The fact that most studies



a) b)

Figure 10: Adsorption isotherm for Reactive Red HE3B carbamated cotton system: temperature of 80 °C; pH 6; amount is 5 g; time is 2 hours; (a) Freundlich; (b) Langmuir



a) b) c)

Figure 11: SEM image of (a) carbamated; (b) control and (c) mercerised fabric

[29–31] of adsorption isotherm on cationised cotton provide a better explanation of the Langmuir adsorption isotherm (which is not the case in this study) might be because the surface roughness of the carbamated cotton fibre increased. The experimental data were fitted to the Langmuir model, with the linearised form presented in Figure 10 (b), which had high correlation coefficient ($R^2 = 0.963$), and demonstrated a very good correlation with the aforementioned model. The correlation coefficients also indicated a good correlation between parameters, and confirmed the functional adsorption of Reactive Red HE3B dye onto the carbamated fabric. Interestingly, the carbamated cotton with the selected dye fits the Freundlich model of adsorption isotherm, showing an even better correlation ($R^2 = 0.987$), as indicated in Figure 10 (b). A conclusion concerning a Langmuir-type interaction between anionic dyes and aminised cotton was already reported by Porter [32]. It was described that the sorption of dye from dye baths can be stopped when the amino groups of fibres have been saturated with dye molecules. According to the results obtained (which a Freundlich type of interaction explains better), the process could be because of the interaction between the anionic Reactive Red HE3B dye and a positive functional site ($-NH_3^+$) of the cotton fabric, which first causes the sorption of more dye molecules on the carbamated cotton. After the dyeing sites are fully saturated, dyes might begin to be adsorbed on the surface by weak bonds. The dyeing process will thus be improved with the mechanism explained, while the surface roughness of the carbamated cotton might play a crucial role.

4 Conclusion

The problem of reactive dyes requiring a large amount of electrolytes could be mitigated through an additional pretreatment process after mercerisation using urea to introduce a carbamate group in place of hydroxyl groups to make the cotton fabric positively charged. This makes the Reactive Red HE3B dye, which is negatively charged, highly attracted to the fibre. It can be concluded from the investigated report that urea, pad-dry-cure modification (i.e. carbamation) can improve the dyeability of cotton fibre. The treatment of carbamation allowed the adsorption of Reactive Red HE3B dye molecules onto cotton fibres and the reaction between the dye molecule and the cotton fibre without the utilisation of electrolytes. The procedure for optimum carbamation appeared to be at a urea concentration of 400 g/l for a curing time of 5 minutes at 135 °C. The degree of substitution was 0.2829, while warp- and weft-way tensile strengths were affected significantly. Dyeing studies show very good results with DS of 0.2829, The method would have great potential for industrial application, as pad-dry-cure is a relatively clean, environmentally friendly technique, with less energy, water, time and resources required, as the liquor could be reused. An entirely new system is required on curing equipment, which can collect the ammonia gas released during the decomposition of urea (which could be considered an advantage and could be used as a pre-activating agent for cotton cellulose, replacing caustic mercerisation, or as a raw material for different chemical reactions), while care must be given during the production of cotton cellulose carbamate.

The thermal analysis showed carbamated cotton fabrics have a very rapid degradation property above a temperature of 300 °C up to 370 °C, where the control half-bleached fabric starts at the same temperature of 300 °C and goes up to 400 °C. The dyeing results were good, with satisfactory fastness properties. The visual levelness of the dyed fabric was also good. The exhaustion, fixation and total dye utilisation percentage showed improvement compared with control half-bleached fabric. The change in total dye utilisation was in the range of 7–15% than that of control half-bleached fabric.

Dyeing basically happens between the negatively charged Reactive Red HE3B dye and the positively charged cotton cellulose due to the replacement of the hydroxyl group with the carbamate group. The adsorption isotherm demonstrated a good correlation with Langmuir (R^2 = 0.963) and Freundlich (R^2 = 0.987), while the increment in the surface roughness studied by SEM played a role in dyeing and in explaining the isotherm as Freundlich.

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