*CELLULOSE CHEMISTRY AND TECHNOLOGY*

# COTTON CELLULOSE MODIFIED WITH UREA AND ITS DYEABILITY WITH REACTIVE DYES

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Cellulosic materials are reasonably strong, hydrophilic, insoluble in water, insoluble in organic solvents, safe to living organisms, reproducible, recyclable and biodegradable. Many technologies have been applied to produce modified cellulosic materials for our daily and industrial necessities. Dyeing of cotton cellulose is done mostly with reactive dyes, which form a strong covalent bond with the substrate. The reactive dyeing process requires a high amount of salt and alkali, with the main problem of low equilibrium exhaustion. Studies have been carried out to improve the exhaustion and reduce the use of salt and alkali by cationization of the substrate. This study focuses on carbamation of mercerized cotton cellulose for the purpose of preparing an alternative way of dyeing cotton fabric with Reactive Red HE3B dye in the absence of electrolyte. The carbamation process was performed by the pad-dry-cure technique. The effect of carbamation was qualitatively evaluated by FTIR spectroscopy. The optimal results were found to be the following: degree of substitution (DS) of 0.2829, warp-way tensile strength of 285.98N and weft-way tensile strength is 203.81N, with urea concentration of 400 g/L, temperature of 135 ºC and reaction time of 5 minutes. The carbamated cotton showed lower decomposition temperature than that of native cotton. The color strength, exhaustion, fixation and total dye utilization studies revealed good results, compared to dyeing conventional cotton fabric. Adsorption isotherms were also studied. Therefore, this modification of cotton cellulose will be beneficial for textile mills processing cotton and blends of cotton fabrics.

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

## INTRODUCTION

Cellulose is a chemically homogeneous linear polymer of up to 10,000 D-glucose molecules, which are connected by β-1,4 bonds.[1] Each glucose residue is tilted by 180° towards its neighbor; the structural subunit of cellulose is cellobiose. The chemical uniformity allows spontaneous crystallization of the cellulose molecules. Hydrogen bonding within and between multiple layers of parallel molecules results in the formation of tightly packed microfibrils in Cellulose II. It has been reported that, in the manufacturing of cellulose carbamate process, urea first decomposes into ammonia and isocyanic acid approximately at 135 ºC, whereas Fu *et al*. reported the decomposition of urea starts above its melting temperature 132.7 ºC, isocyanic acid (HNCO) reacts with cellulose hydroxyl (OH) groups to form cellulose carbamate.[2,3] The carbamate groups are substituted in the hydroxyl groups along the cellulose chain.[3,4-7] The reaction efficiency is dependent, among others, on the amount of urea, reaction conditions and raw material properties.[8,9]

Solventless carbamation has been carried out by heating (in an oven or oil bath) urea with MCC or alkali-swollen cotton linters at a urea/cellulose weight ratio of 1.5-4.0, and cellulose carbamate (CC) was produced by microwave heating.[6] Carbanilation has been carried out with native cellulose or its alkali-activated counterpart. Many of these reactions start as heterogeneous (suspension) and turn into homogeneous. Hearon *et al*. suspended cotton linters in refluxing pyridine, and were then subjected to reaction with phenyl isocyanate or a-naphthyl isocyanate to give the corresponding tricarbanilates; the reaction mixture became homogeneous after 36 and 40 h, respectively. The CC was precipitated from the reaction mixture.[10] Cellulose tricarbanilate was obtained by the reaction of a suspension of the biopolymer in DMF, with phenyl isocyanate in the presence of triethylenediamine as a catalyst, and CC films were cast directly from the reaction mixture.[11]

The reaction of cellulose with phenyl isocyanate in pyridine produced a clear solution (MCC) or was incomplete (a pulp). Precipitation of CC in methanol resulted in the loss of a low molecular weight fraction, whereas precipitation in a water/methanol mixture resulted in less or no product fractionation.[12,13] Incomplete carbanilation of fibrous cellulose was later avoided by pretreatment (activation) of the biopolymer with liquid ammonia. The reaction was carried out in pyridine, DMF or DMSO. Clear solutions of cellulose tricarbanilate were obtained in all cases (Evans *et al.*).[14]

Kenaf core cellulose was suspended in urea solutions and the mixture was stirred under normal and then reduced pressure – the latter to enhance urea penetration within the biopolymer fibers. The reaction was induced by MW heating (380 W power) for 10-30 min. The N% in the purified CC increased as a function of increasing the urea concentration in the solution and the reaction time.[15] Cellulose derivatization can be better controlled, and the reaction temperature reduced, when an activated biopolymer is employed, and the carbanilation is 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 fiber.[16] The simplest approach to prepare CC under homogeneous conditions is to derivatize 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 by the reaction of phenyl isocyanate with the biopolymer dissolved in DMAc/LiCl in the presence or absence of pyridine catalyst.[13]

The conditions employed for carbamate formation under homogeneous conditions may lead to the formation of side products.[17,18] The formation of side products was avoided by using anhydrous reaction conditions, low reaction temperature of 60-70 °C, and long reaction time of 24-48 h, as well as di(1-butyl)tin dilaurate as catalyst, a controlled amount of isocyanate (phenyl- and 1-butyl), and a product workup that did not include quenching with an alcohol. The reaction of MCC, cotton linters or partially silylated cellulose in DMAc started heterogeneously and then turned homogeneous. Good to high yields (65-94%) of products, with a DS of carbamate from 1.74 to 3.0, was obtained.[19] Chemical modifications to cationize cotton were reported to have beneficial effects in reactive dyeing.[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, thus the theoretical maximum DS is 3.0.[2] The properties that are most considerably affected by the degree of substitution are solubility, swelling and plasticity. Among others, one of the key factors governing the substitution of the prepared cellulose carbamate is the amount of urea in the manufacturing process.[8] The nitrogen content of a cellulosic material is often used to describe the substitution degree of cellulose carbamates. However, the nitrogen content indicates only the amount of nitrogen in the sample, not the exact degree of substitution. Also, the uniformity of the product, the evenness of the carbamate groups in the cellulose chains are a significant factor determining the cellulose carbamate quality and properties. However, the researchers reported that the uniformity of the substituted cellulose is challenging to determine.[8] Yin *et al.* and Guo *et al.* have reported that the carbamate group is stable in acidic media but in alkaline media, hydrolysis can take place. In alkaline media, the carbamate groups are irreversibly decomposed to carbonate and ammonia at a rate depending on NaOH concentration and temperature.[6,16]

The primary objective of this study has been to achieve high dye absorption of reactive dye by carbamation of pre-activated cotton cellulose with caustic mercerization with the specific objectives of determining the optimum values of the operating parameters, understanding the difference in the dyeing results of carbamated and uncarbamated cotton celluloses, and analyzing the adsorption properties of carbamated cotton cellulose fabric. Mercerisation leads to changes in cellulose microstructure and also to changes in the electrical charge (zeta potential) of the fibre, and the subsequent carbamation will definitely alter this potential depending on the degree of substitution, which will have its influence in dyeing. This will represent the scope of our future study.

## EXPERIMENTAL

### Materials

Plain weave cotton fabric (half-bleached), with the warp density of 26 ends/cm, weft density of 22 picks/cm, GSM of 150 g/m$^2$, warp and weft-way tensile strength of 319 N and 228 N, respectively, warp and weft yarn count of 20 Ne, was used throughout the work. Extrapure urea (Loba Chemie Pvt. Ltd., India), which decomposes at the temperature above its melting temperature, as a source of isocyanic acid, sodium hydroxide pellets – a strong alkali for mercerizing, and sodium carbonate powder were used to fix the reactive dye to the fiber. In this study, acetic acid was used for neutralizing the fabric after mercerizing, sodium sulphate – for exhaustion in conventional reactive dyeing of cotton (Alpha Chemika, India) and Reactive Red HE3B dye was used for dyeing.

The following research equipment was utilized in the present study: a Perkin Elmer TGA – to study the thermal decomposition properties of the carbamated material; a Perkin Elmer FTIR Spectrometer – to find the molecular fingerprint of the carbamated fabric; an oven dryer (Mesdan Lab, Italy) – for drying and curing purposes; a Tensolab 100 (Mesdan Lab, Italy) – to evaluate the mechanical strength of the carbamated fabric; a crock meter (Mesdan Lab, Italy) – to determine the resistance to fading of the dyed carbamated fabric by dry or wet rubbing; a light fastness solar box (Mesdan Lab, Italy) – for evaluating the resistance to fading of the dyed carbamated fabric when exposed to light; a Laundr-o-meter (Mesdan Lab, Italy) – for evaluating the resistance to fading of the dyed carbamated fabric by wet washing; a GretagMacbeth Color Eye 310 – for evaluating the color strength; a UV/VIS Spectrometer (Perkin Elmer Lambda 25, Singapore) – for determining the dye absorbance; an Eco-IR dyeing machine for dyeing (Ahiba, US); and a Padder Lab 300 (Mesdan Lab, Italy) – for applying the treatment to the mercerized fabric. The Kjeldahl method was used for determining the nitrogen content in the carbamated fabric to find the degree of carbamation.

### Methods

The experimental part was divided into three main sections.

i. First, the carbamation of the cotton cellulose (*i.e.*, that is first pretreated half-bleached fabric by mercerization for the purpose of enhancing the accessibility of the functional groups in cotton cellulose) was carried out with the objective of optimizing the main variables during manufacturing of cotton cellulose carbamate, which are temperature, time and concentration of urea. The properties of the cotton cellulose carbamate were studied, the major responses being the degree of substitution and tensile strength (warp and weft direction) of the fabric; the optimized fabric was analyzed by FTIR for determining the molecular fingerprint of the product, and by TGA studies.

ii. Secondly, the dyeing of the optimized carbamated and uncarbamated cotton was done with reactive dyes (*i.e.*, Reactive Red HE3B dye). The properties of the dyed cotton cellulose carbamate, in comparison with those of the dyed untreated cotton fabric, were evaluated. The tests were the degree of exhaustion, fixation, color strength (K/S), fastness to washing, fastness to light, and rubbing fastness.

iii. Thirdly, the modeling of the adsorption isotherm experiment was done by the Langmuir and Freundlich adsorption isotherms, to find the best model that can express the property of the carbamated cotton cellulose for dye adsorption.

The cellulose carbamate derivatives were prepared by following the steps given below:

a. Mercerization

Mercerization 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 mercerizing temperature of 20-25 °C. Then, the frame with the fabric still attached was transferred to a sink and rinsed with running water to remove the majority of the alkali. After detaching from the frame, the fabric was rinsed, neutralized with dilute acetic acid and air dried. As an indicator of the mercerization degree, the barium number of the mercerized cotton fabrics was determined according to the AATCC test method 89-2003 (AATCC, 2010).[25]

b. Carbamation

The mercerized cotton fabric (BAN = 141.2 ± 1.0) was subjected to carbamation using 100 g/L, 250 g/L and 400 g/L amounts of urea, by following the pad-dry-cure method. The prepared cotton fabric was impregnated using the 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 optimization were carried out using the response surface methodology (*i.e.*, three level factorial), the major responses being the degree of substitution of hydroxyl groups by carbamate groups, the warp -and weft-way tensile strength, as indicated in Table 1.

### Dyeing of untreated and treated 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 dye was performed according to the procedure recommended by the manufacturer; shade (% o.w.f.) 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 ºC, at a rate of 1.5 ºC/min. Before reaching 80 ºC, 40 g/L of electrolyte ($Na_2SO_4$) was added in two installments at 55 ºC and 65 ºC to each bath. After holding the temperature at 80 ºC for 10 min, 10 g/L of sodium carbonate was added. The bath was then held at 80 ºC for 50 min, cooled to 60 ºC, at a rate of 2.5 ºC/min, and then discarded (Fig. 1).[25]

The procedure for dyeing the carbamated cotton was the same as that for uncarbamated cotton, except that for carbamated cotton dyeing was done in the absence of electrolyte ($Na_2SO_4$), with the bath buffered at pH = 6 using acetic acid (Fig. 1 (b)).

Table 1
Experimental plan of cotton fabric carbamation

| | Factor 1 | Factor 2 | Factor 3 |
|---|---|---|---|
| Run | A: Concentration (g/L) | B: Temperature (ºC) | C: Time (min) |
| 1 | 250 | 185 | 3 |
| 2 | 250 | 135 | 1 |
| 3 | 400 | 135 | 3 |
| 4 | 100 | 135 | 3 |
| 5 | 400 | 185 | 5 |
| 6 | 400 | 185 | 3 |
| 7 | 250 | 160 | 3 |
| 8 | 100 | 135 | 1 |
| 9 | 250 | 185 | 5 |
| 10 | 250 | 135 | 3 |
| 11 | 100 | 135 | 5 |
| 12 | 400 | 160 | 3 |
| 13 | 400 | 160 | 5 |
| 14 | 250 | 160 | 1 |
| 15 | 100 | 185 | 3 |
| 16 | 400 | 135 | 1 |
| 17 | 250 | 160 | 5 |
| 18 | 400 | 135 | 5 |
| 19 | 100 | 160 | 5 |
| 20 | 100 | 185 | 1 |
| 21 | 250 | 185 | 1 |
| 22 | 100 | 185 | 5 |
| 23 | 100 | 160 | 3 |
| 24 | 250 | 135 | 5 |
| 25 | 400 | 160 | 1 |
| 26 | 100 | 160 | 1 |
| 27 | 400 | 185 | 1 |

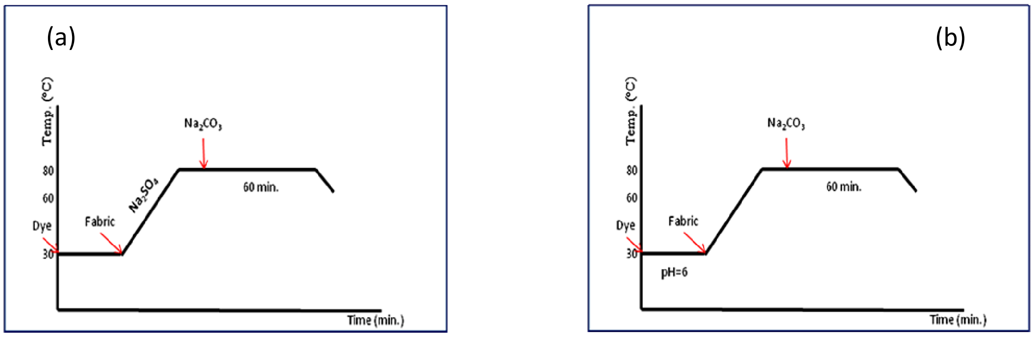


Figure 1: Dyeing cycle of (a) uncarbamated cotton fabric, (b) carbamated cotton fabric[26]

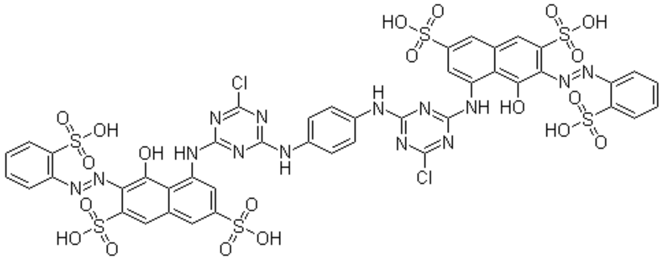


Figure 2: Reactive Red HE3B

The dye uptake of both the treated and untreated cotton 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 maximum absorption ($\lambda_{max}$ = 560) of the dye, using a UV-Visible spectrophotometer. The percent dye bath exhaustion, E%, was determined using Equation 1:

$$\mathbf{E\% = 100(1 - \frac{A_1}{A_0})} \quad (1)$$

where $A_0$ = absorbance of dye solution before dyeing and $A_1$ = absorbance of dye solution after dyeing.

The color strength of the dyed samples was determined as the K/S value, calculated from the sample reflectance (R) (Eq. 2):

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

The extent of dye fixation of the reactive dyes on all the treated and untreated cotton fabrics was determined by measuring the K/S values of the dyed samples before and after soaping, from which the extent of dye fixation was calculated using Equations 3 and 4:

$$\mathbf{F\% = \frac{C_2}{C_1} 100} \quad (3)$$

$$\mathbf{T\% = E\% \frac{C_2}{C_1}} \quad (4)$$

where T% = total dye fixed, $C_1$ = K/S value of dyed sample before soaping, $C_2$ = K/S value of dyed sample after soaping, and F% = degree of fixation of absorbed dye.

**Determination of 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 by the Kjeldahl method, using a sample mass of 10 ± 2 mg.

The degree of substitution was determined with the following Equation 5:

$$\mathbf{DS = \frac{162 \ast N}{(14 \ast 100) - (43 \ast N)}} \quad (5)$$

where N = specimen nitrogen content (%); 162 = molar mass (g/mol) of an anhydroglucose unit (AGU); 14 = molar mass of nitrogen (g/mol); 43 = 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**

The following tests were performed to assess the strength and color fastness of the fabric samples: the tensile strength test – according to the ASTM D5034-textile grab method, color fastness to laundering – according to the AATCC test method 61-2007, color fastness to light – in accordance with ISO 105-B02:1994, color fastness to rubbing – in accordance with the AATCC test method 8-2007.[26]

## RESULTS AND DISCUSSION

### Optimization of carbamation

The response surface methodology (RSM) was used to evaluate the degree of substitution of cotton cellulose hydroxyl groups by the carbamate groups, with a low impact on the weft and warp-way tensile strength. The results obtained in terms of the relationship between the variables (urea concentration, curing temperature and curing time) and the responses (degree of substitution and tensile strength) were explained through the experimental design used in the study. The 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 F-values were calculated to measure the extent of the effects (normal % probability *vs* residuals plots in Fig. 3).

Figure 4 (residual *vs*. predicted) shows the graph plots of the normality test of the residuals for the degree of substitution, warp-way tensile strength and weft-way tensile strength, respectively. It is observed that, in all the graphs, the residuals lie on the straight line, which indicates that the distribution of residuals for all the degrees of substitution, warp-way tensile strength and weft-way tensile strength is normal. The residual *vs*. predicted responses for the degree of substitution, warp-way tensile strength and weft-way tensile strength, respectively, are depicted in Figure 4. The graphs show that most of the points lie within the area of ±3.0. This indicates that the assumption of constant variance is confirmed, and thus, the suggested model is suitable.

Tables 2, 3 and 4 show the ANOVA results for the degree of substitution, warp-way tensile strength and weft-way tensile strength, respectively. The objective of finding the responses for degree of substitution, warp-way tensile strength and weft-way tensile strength is to visualize the optimal processing conditions with minimum loss of the warp-way and weft-way tensile strength and a higher degree of substitution.

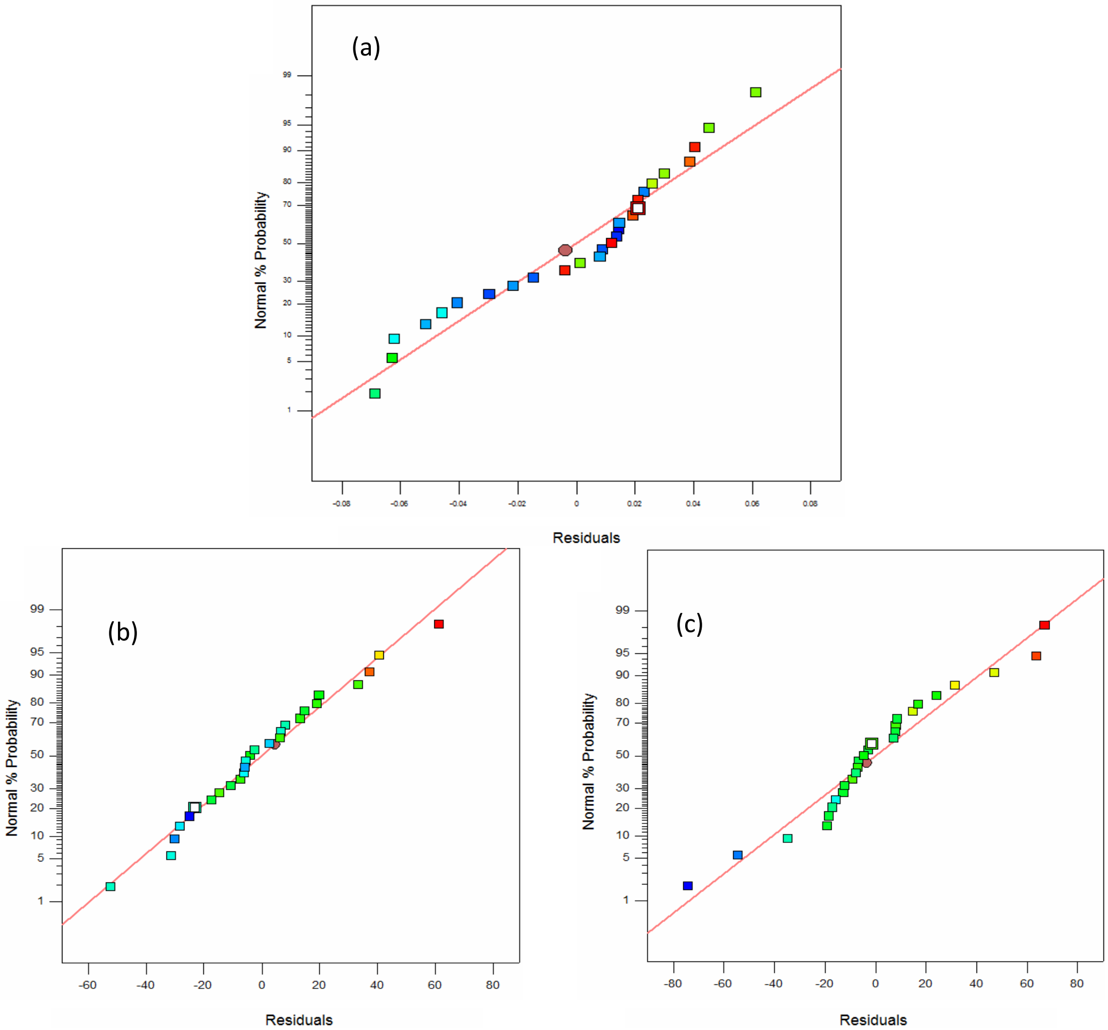


Figure 3: Normal % probability *vs*. residuals plots for (a) DS, (b) warp-way tensile strength, and (c) weft-way tensile strength

Table 4 shows that the model is not significant for weft-way tensile strength, which means it was not significantly affected by any of the factors. The two F-values of the degree of substitution and warp-way tensile strength models are 32.91 and 5.55, respectively, which implies that the two models are significant. In these two models, there is only a 0.0001% and 0.0051%, respectively, chance of getting a high F-value, due to the noise. The probabilities (P-value) for the degree of substitution model, terms A and C, and for the warp-way tensile strength model, term B, were significant because the values are less than 0.05. The F-value of weft-way tensile strength model is 0.50, which implies that the model is not significant. There is 68.55% chance that the F-value could occur. Therefore, this model is not used to navigate the design space. The output for optimal results was obtained by the Design Expert software 10, by 3D-plots (Fig. 5). It has been found that the optimum conditions with the criteria of minimum effect on the warp-way and weft-way tensile strength and maximum DS are the following: a concentration of 400 g/L, temperature of 135 ºC and time of 5 minutes.

It can be understood from Table 2 that DS increased significantly with increasing concentration of urea and increasing time, while there was no significant change in DS with varying temperature. Tensile strength in the warp direction was significantly affected when increasing the temperature, as can be noted in Table 3 and Figure 5, while there was no significant change caused by an increment in concentration and curing time. Tensile strength in the weft direction was not significantly affected by any of the factors (concentration, temperature and time), as may be observed in Table 4 and Figure 6. The desirability was found to be 0.7711 for the preferred criteria of optimization (*i.e.*, maximum DS, maximum warp tensile strength, and maximum weft tensile strength), with 0.2829 for DS, warp tensile strength of 285.98 N and weft tensile strength of 203.815. With these conditions, the warp tensile strength decreased by about 10.35% and the weft tensile strength decreased by about 10.61%, compared to the control half-bleached fabric.

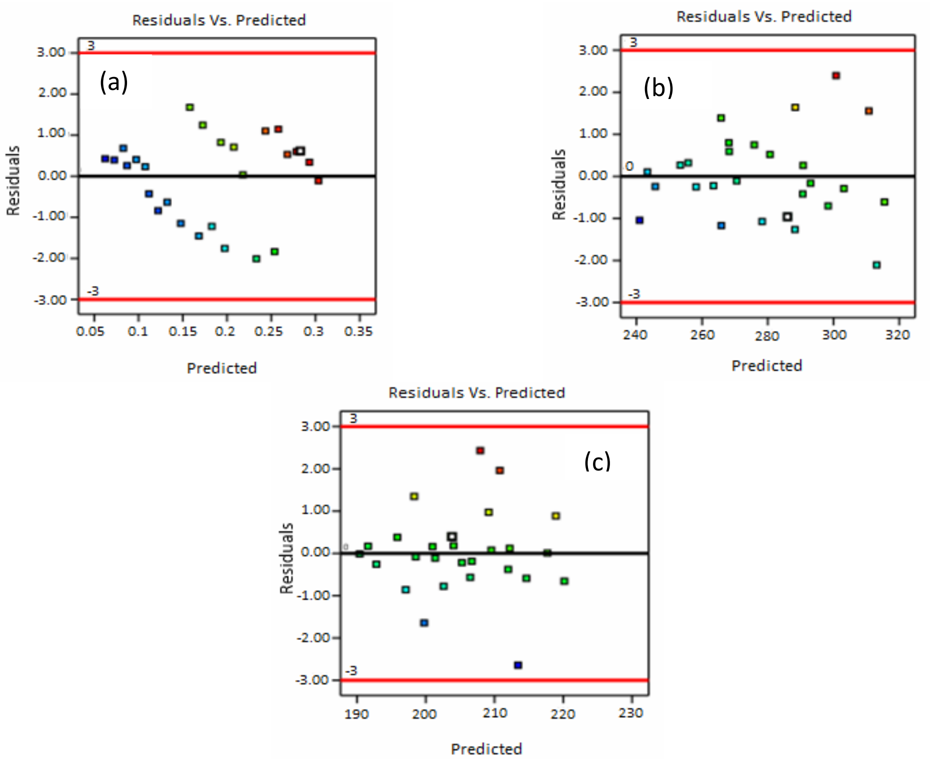


Figure 4: Residuals *vs*. predicted plots for (a) DS, (b) warp-way tensile strength, and (c) weft-way tensile strength

Table 2
ANOVA results for DS

| Source | Sum of squares | df | Mean square | F-Value | p-Value Prob > F | Significance |
|---|---|---|---|---|---|---|
| Model | 0.14 | 3 | 0.048 | 32.91 | 0.0001 | significant |
| A-Concentration | 0.13 | 1 | 0.13 | 89.85 | 0.0001 | - |
| B-Temperature | 1.895E-003 | 1 | 1.895E-003 | 1.29 | 0.2672 | - |
| C-Time | 0.011 | 1 | 0.011 | 7.58 | 0.0113 | - |
| Residual | 0.034 | 23 | 1.466E-003 | - | - | - |
| Cor. Total | 0.18 | 26 | - | - | - | - |

Table 3
ANOVA results for warp-way tensile strength

| Source | Sum of squares | df | Mean square | F-Value | p-Value Prob > F | Significance |
|---|---|---|---|---|---|---|
| Model | 11977.94 | 3 | 3992.65 | 5.55 | 0.0051 | significant |
| A-Concentration | 102.72 | 1 | 102.72 | 0.14 | 0.7090 | |
| B-Temperature | 9112.50 | 1 | 9112.50 | 12.67 | 0.0017 | |
| C-Time | 2762.72 | 1 | 2762.72 | 3.84 | 0.0623 | |
| Residual | 16547.24 | 23 | 719.45 | - | - | |
| Cor. Total | 28525.19 | 26 | - | - | - | |

Table 4
ANOVA results for weft-way tensile strength

| Source | Sum of squares | df | Mean square | F-Value | p-Value Prob > F | Significance |
|---|---|---|---|---|---|---|
| Model | 1771.89 | 3 | 590.63 | 0.50 | 0.6855 | not significant |
| A-Concentration | 26.89 | 1 | 26.89 | 0.023 | 0.8813 | - |
| B-Temperature | 544.50 | 1 | 544.50 | 0.46 | 0.5037 | - |
| C-Time | 1200.50 | 1 | 1200.50 | 1.02 | 0.3236 | - |
| Residual | 27131.30 | 23 | 1179.62 | - | - | -- |
| Cor. Total | 28903.19 | 26 | - | - | - | - |

The models that are used to predict the degree of substitution and warp-way tensile are presented by the equations below in terms of the actual factors:

$$\text{Warp\_way tensile strength} = 278.26 - 2.39 * A - 22.50 * B - 12.39 * C \tag{6}$$

$$DS = 0.18 + 0.086 * A + 0.010 * B + 0.025 * C \tag{7}$$

## FTIR analysis

Since the properties of cotton cellulose carbamates are one of the most significant factors contributing to the dyeability of the material, the differences between the cotton cellulose carbamate sample and uncarbamated cotton were evaluated to understand the chemical change that has taken place in carbamation (Fig. 6). Carbamates of cotton cellulose were characterized by means of FTIR to ensure the reaction of hydroxyl groups with urea. A typical loss in the transmittance band for the carbamated cotton is observed in the range from 3600 cm$^{-1}$ to 3300 cm$^{-1}$, which is assigned to the (NH$_2$) of the carbamate group.[27] The stretch is not as broad or strong as it appears for 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 signifies the large numbers of –OH groups in cotton.[28] Meanwhile, this band is not as broad in the carbamated cotton, which indicates a reduction in –OH groups, as they are replaced by the carbamate groups. The transmittance peak around 1100 cm$^{-1}$ observed for the uncarbamated cotton disappeared from the spectrum of the carbamated cotton, which is attributed to the loss of –OH vibration in the carbamated cotton fabric. Also, the reduction of the hydroxyl peak at 3250 cm$^{-1}$ represents strong evidence for the reaction of urea with the cotton samples.

## Thermogravimetric analysis

The TG curves of the cotton cellulose and its carbamate derivatives, with DS of 0.2829, are shown in Figure 7. The TG curves were separated into three sections. At first, the weight loss in the temperature range from 100 ºC to 150 ºC can be assigned to the evaporation of water and absorbed gas by cellulose. In the range from 150 ºC to 250 ºC, there appeared a minor thermal decomposition of the residues. Observing the TG curves, it has been found that all the major decompositions are located in the ranges from 300 ºC to 400 ºC and from 300 ºC to 375 ºC for the control cotton cellulose and the carbamated cotton cellulose, respectively.

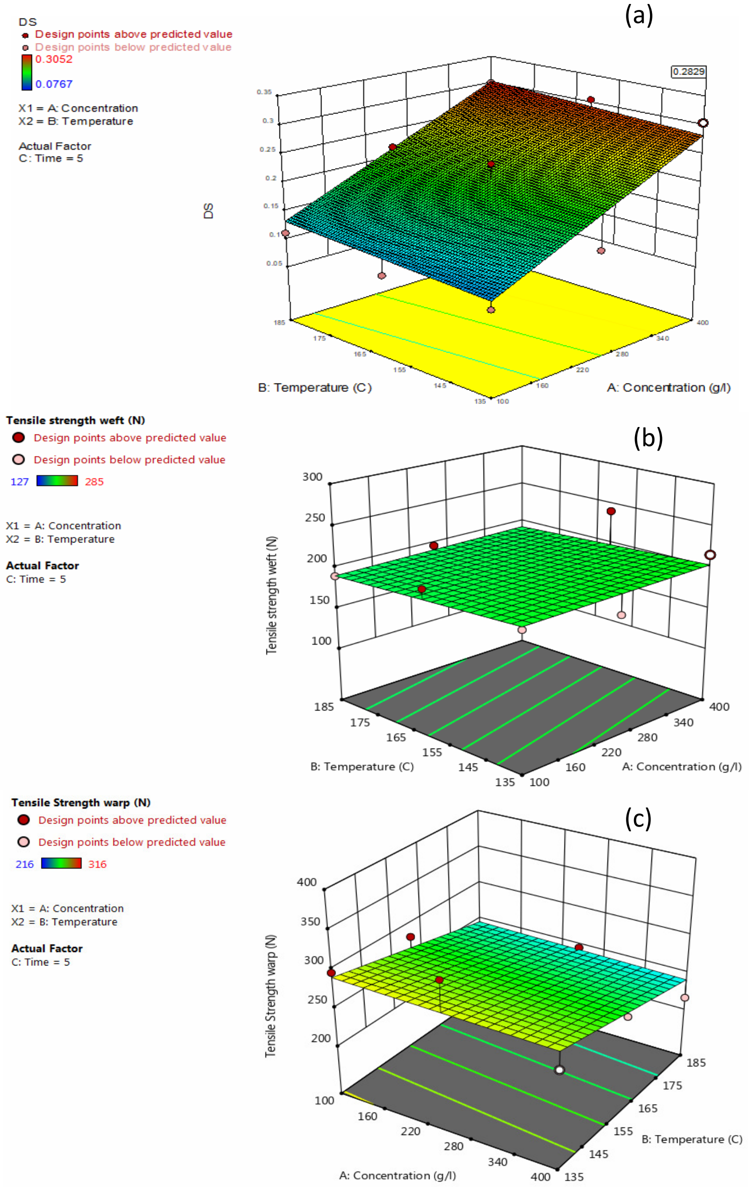


Figure 5: Response for (a) optimum carbamation, (b) weft-way tensile strength, (c) warp-way tensile strength

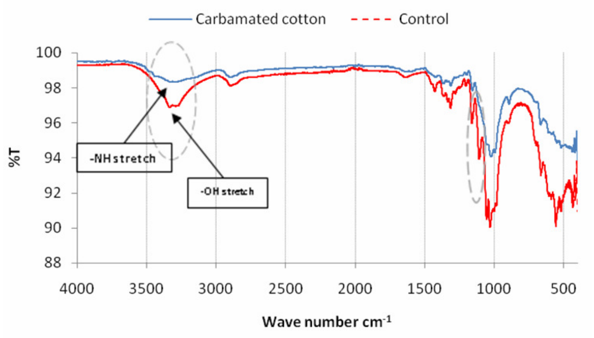


Figure 6: FTIR spectra of carbamated cotton and control fabric

### Dyeing results

The results for exhaustion, fixation and total dye utilized are presented in Table 5.

### *Determination of exhaustion*

Exhaustion was determined by measuring the absorbance of the dye bath before and after the dyeing process. The absorbance of the diluted solution was measured at the wavelength of maximum absorption ($\lambda_{max}$ = 543 nm), using a PerkinElmer λ-25 UV-Vis spectrophotometer. Maximum absorbance ($\lambda_{max}$) of the dye was determined from the calibration curve of a series of standard solutions. Figure 8 shows the calibration curve for Reactive Red HE3B. For the calibration curve, a dye stock solution of 0.5 g/L was prepared. By pipetting this stock solution, the concentrations of the calibration standard solutions, in the range from 0.05 g/L to 0.3 g/L, at 543 nm (*i.e.*, maximum absorbance) were measured and the calibration curve was drawn accordingly. The figure indicates that Reactive Red HE3B obeyed the Beer-Lambert's law,[29,30] with an $R^2$ value of 99.1%. Mathematically, the Beer-Lambert law is expressed as:

$$\mathbf{A = \varepsilon cl} \quad (8)$$

where A is the absorbance or optical density, *c* is the concentration of solute (dye) in solution, *l* is the path length radiation through the sample in centimeters (1 cm) and ε the molar absorptivity or extinction coefficient.

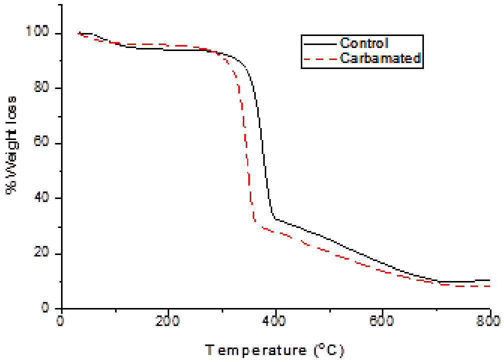


Figure 7: TG curves of cotton cellulose and carbamated cotton

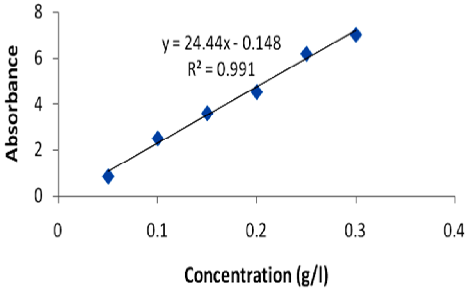


Figure 8: Calibration curve of Reactive Red HE3B

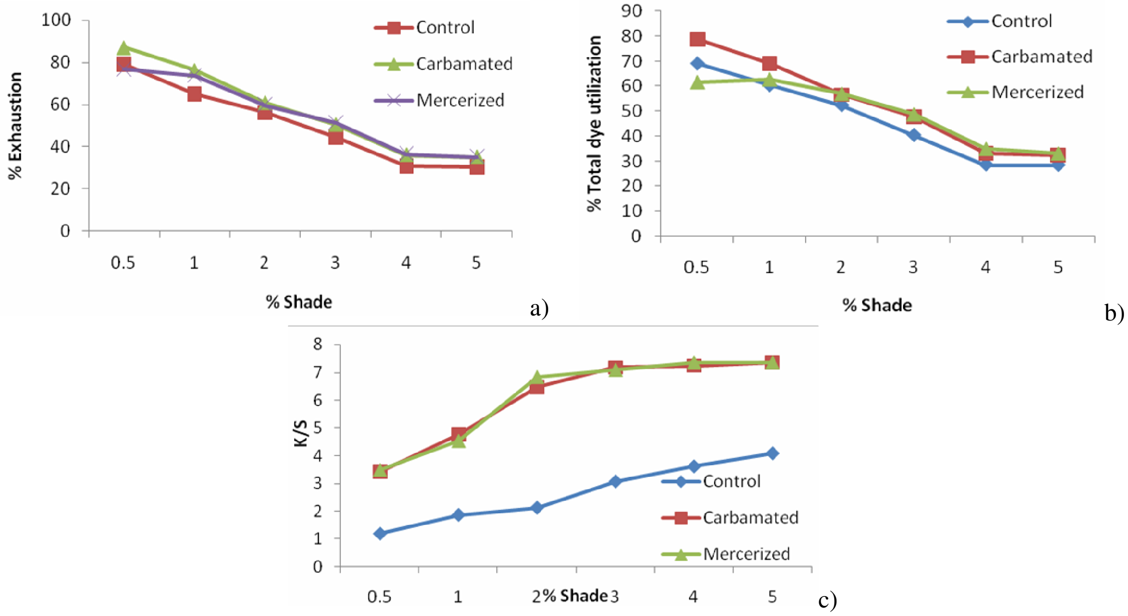


Figure 9: Percent exhaustion (a), total dye utilization (b) and K/S (c) of Reactive Red HE3B on carbamated, mercerized and control fabric

Table 5
Summary of dyeing properties of Reactive Red HE3B for carbamated, mercerized and control samples

| Shade (%) | Absorbency of dye solution before dyeing ($A_1$) | Material type | Absorbency of dye solution after dyeing ($A_2$) | K/S value | | Exhaustion (%) | Fixation (%) | Total dye utilized (%) |
|---|---|---|---|---|---|---|---|---|
| | | | | Before washing (C1) | After washing (C2) | | | |
| 0.5 | 6.2 | T | 0.80 | 3.80 | 3.44 | 87.10 | 90.48 | 78.81 |
| | | UT | 1.30 | 1.38 | 1.21 | 79.03 | 87.51 | 69.16 |
| | | M | 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 |

‘T’ stands for carbamated, ‘UT’ stands for control half-bleached fabric, ‘M’ stands for mercerized fabric

Reactive Red HE3B dye consumption when dyeing all the control, mercerized and carbamated samples decreased with increasing the dye bath concentration. The change percentage in dye consumption 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 (Fig. 9).

The color intensity (K/S) was employed to express the reduction ratio of light, owing to absorption and scattering, achieved based on reflectance. Figure 9 shows that the color strength of the carbamated cotton was much higher than that of the control half-bleached fabric and similar to the mercerized one. However, dyeing without using electrolyte is considered beneficial in carbamated cellulose. The carbamated cotton cellulose fabric was dyed with Reactive Red HE3B without utilization of electrolyte, rather the pH was slightly acidic (pH = 6) with the addition of acetic acid. The improved dye uptake of treated cotton fabric may be attributed to the generation of positive charges.

Also, the pretreatment of the fabric before carbamation (*i.e.*, caustic mercerized) could affect the dye adsorption, ensuring uniform introduction of the carbamate groups. In this study, very good leveling on the carbamated cotton cellulose samples was visually confirmed.

In dyeing carbamated cotton samples in an acid bath, it could be confirmed that there was strong attraction between the cationic dye sites on the carbamated cotton and the anionic. Reactive Red HE3B dye, which led to higher exhaustion rates, without addition of electrolytes to the dye bath. An enhancement in the color strength is expected when the dye concentration is increased, since 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 treated cotton is limited by its saturation adsorption value, which could be related to the amount of nitrogen introduced during pretreatment. The color strength of the carbamated cotton increased with increasing the dye concentration, but after the 4% shade the difference was very small. This indicates the fiber reached its saturation point, whereas the color strength of the control half-bleached fabric increased approximately linearly.

Table 6
Summary of color fastness results

| Con. (%) | Material type | Wash fastness | | | | | | | Rubbing fastness | | Light fastness |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Color change | Staining on white | | | | | | | | |
| | | | Ace | Co | Ny | Po | Acr | Wo | Dry | Wet | |
| 0.5 | Control | 4-5 | 4-5 | 4 | 4-5 | 5 | 4-5 | 5 | 5 | 4-5 | 4 |
| | CCC | 4-5 | 4 | 3-4 | 4-5 | 5 | 4-5 | 5 | 5 | 4-5 | 4 |
| | M | 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 |

‘Con.’ – initial concentration, ‘CCC’ – cotton cellulose carbamate, ‘Ace’ – Acetate, ‘Co’ – Cotton, ‘Ny’ –Nylon, ‘Po’ – polyester, ‘Acr’ – Acrylic, ‘Wo’ – Wool

Looking at the results, the color strength achieved by using the 5% shade of Reactive Red

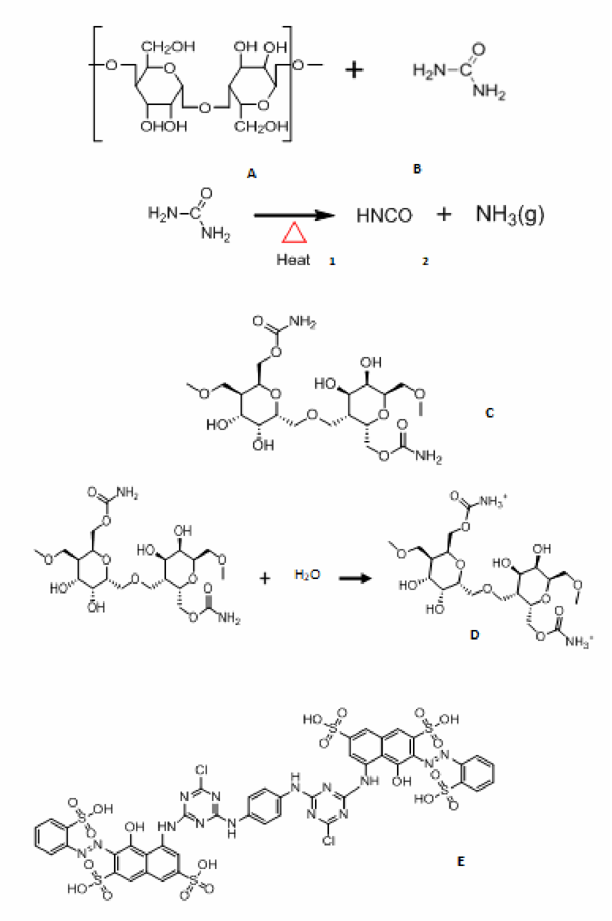
HE3B on the control half-bleached fabric could be obtained by using the 1% shade on the carbamated cotton fabric, increasing the dye consumption. In addition to that, excellent leveling was visually observed on the dyed carbamated cotton fabric. The overall results of the dyeing properties, in terms of fastness of Reactive Red HE3B, towards carbamated cotton and control half-bleached fabric are summarized in Table 6.

### *Fastness properties*

Table 6 shows that the wash fastness and rub fastness are not affected significantly. This may be due to the formation of strong ionic bond between the fiber and the dye, which is equally good as the covalent bond that normally links the dye and the fiber.

### *Reaction mechanism*

The scheme of the reaction mechanism is presented in Figure 10. Cotton fiber, a cellulosic fiber (A), was subjected to reaction with urea (B); beyond its decomposition temperature (135 ºC), urea is decomposed into isocyanic acid (1) and ammonia (2) in the gas form. Isocyanic acid (1) is capable of reacting with alcohol groups (-OH) as in the case of the production of polyurethane fibers. Cotton cellulose has three hydroxyl groups (one primary and two secondary) in one anhydroglucose unit. Depending on the relative reactivity, primary hydroxyl groups preferably react with isocyanic acid (1).



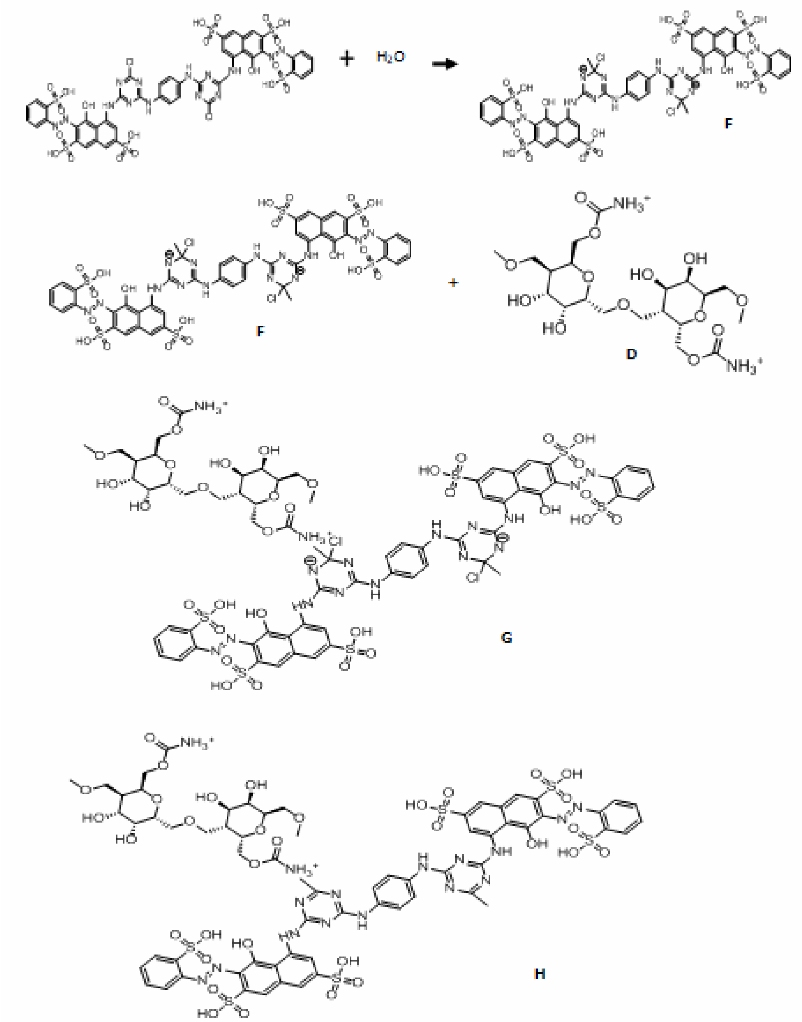


Figure 10: Schematic dyeing reaction mechanism

***Adsorption isotherm analysis***

For studying the adsorption property of Reactive Red HE3B dye on the carbamated cotton at constant temperature, a sample of carbamated cotton fabric was inserted into the bath buffered at pH = 6, with the dye, for two hours, at the temperature recommended by the manufacturer (*i.e.*, 80 ºC). The dye concentrations were in the range from 0.5% (owf) to 4% (owf) and the sample mass was 5 grams. The adsorption of Reactive Red HE3B dye by the carbamated cotton is shown in Figure 11. It is observed that the initial dye adsorption was fast and with a rise in concentration, the dye adsorption decreased. The profile obtained (Fig. 11) from the study was used to obtain Langmuir and Freundlich adsorption isotherms, by using the well-known adsorption isotherm equations. In both cases, linear plots were obtained, which reveals the applicability of these isotherms to the ongoing adsorption process. Figures 12 and 14 exhibit the Freundlich and Langmuir plots, respectively, for the adsorption of Reactive Red HE3B onto carbamated cotton. The Freundlich and Langmuir constants derived from these plots are presented in Table 7. However, it has been found that the Freundlich adsorption isotherm is the best fit for the system, with an $R^2$ value of 0.987 (Fig. 12), whereas with the Langmuir model, the fitting obtained is $R^2 = 0.963$ (Fig. 14).

Therefore, it can be concluded that the dyes not only attached to the available carbamate groups, but also formed layers. The result was not expected, because the carbamate groups, which ionize positively, should attract the negatively ionized Reactive Red HE3B dye particles, while the remaining $OH^-$ were not expected to adsorb the dye, as the hydroxyl group and the dye are negatively ionized, as a result, they should repel each other.

According to the results, the adsorption was mostly explained by the Freundlich adsorption isotherm, which assumes that the dye adsorption is not limited to the functional groups available in the material to be dyed. Therefore, an assumption was made that the introduced functional groups play a role in attracting not only a single molecule, but rather many molecules, which could be adsorbed onto the hydroxyl groups.

Figure 13 shows SEM images of carbamated and half-bleached control fabrics. It is visible that the surface roughness increased after carbamation, the fibers are deconvoluted, swollen, with a circular cross-section. Meanwhile, the fibers in the half-bleached control fabric are convoluted and surface roughness is not visible up to x500 magnification. The surface roughness may have improved the adsorption property of the carbamated fabric, since it is expected that only the carbamate groups will participate in the adsorption of the Reactive Red HE3B dye. Therefore, while most reported studies show the Langmuir adsorption isotherm explains better the adsorption on cationized cotton,[26,30-32] this is not the case in this study, which might be explained by the increased surface roughness of the carbamated cotton fabric.

The experimental data were also fitted to the Langmuir model and the linearized form is shown in Figure 14, which had a high correlation coefficient ($R^2 = 0.963$), thus, showing very good agreement with this model. The correlation coefficients also indicated a good agreement between the parameters and confirmed the functional adsorption of Reactive Red HE3B dye onto the carbamated fabric.

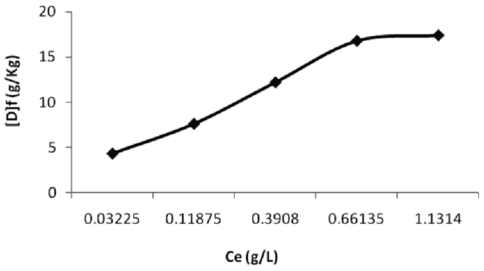


Figure 11: Effect of Reactive Red HE3B concentration on its adsorption onto the samples (temperature 80 ºC, pH 6, amount 5 g, time 2 h)

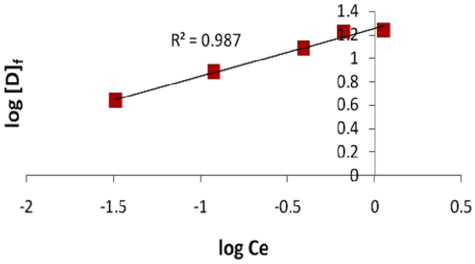


Figure 12: Freundlich adsorption isotherm for the Reactive Red HE3B–carbamated cotton system (temperature 80 ºC, pH 6, amount 5 g, time 2 h)

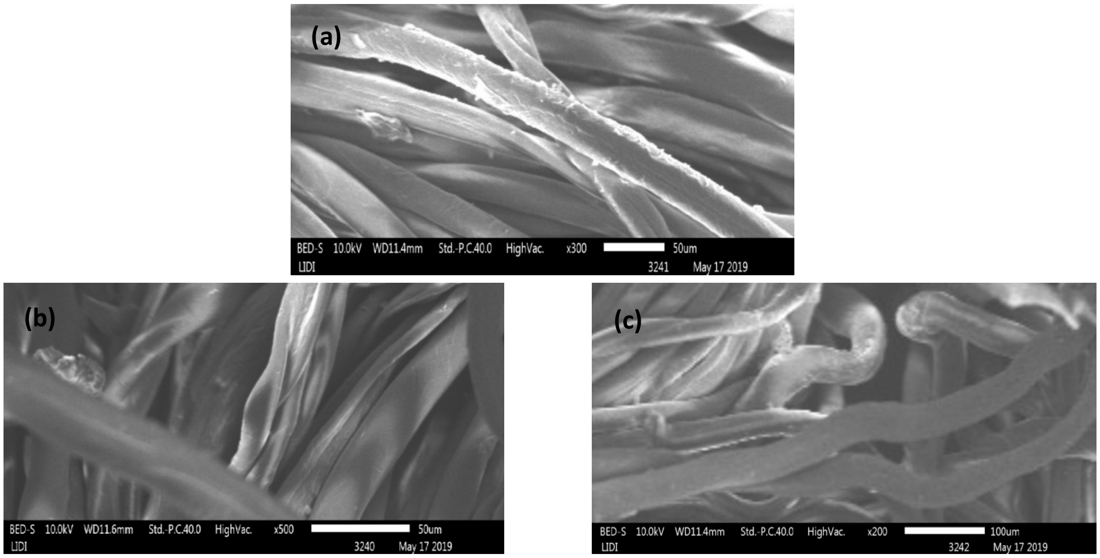


Figure 13: SEM images of (a) carbamated, (b) control, and (c) mercerized fabrics

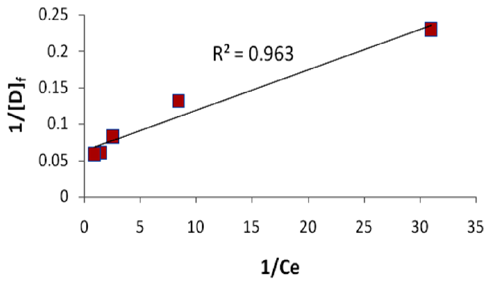


Figure 14: Langmuir adsorption isotherm for the Reactive Red HE3B–carbamated cotton system (temperature 80 ℃, pH 6, amount 5 g, time 2 h)

Table 7
Freundlich and Langmuir constants of Reactive Red HE3B adsorption onto carbamated cotton (temperature 80 ℃, pH 6, amount 5 g, time 2 h)

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

Interestingly, the dye has a better correlation ($R^2$ = 0.987) with the Freundlich model rather than with the Langmuir model. A conclusion concerning a Langmuir type interaction between anionic dyes and aminized cotton has been reported by Porter,[32-34] who stated that the sorption of dye from dye baths can be stopped when the amino groups of fiber have been saturated with dye molecules.[34] The results obtained in this study, indicating that a Freundlich type of interaction better describes the dye adsorption process in this case, may be explained by the interaction between the anionic Reactive Red HE3B dye and a positive functional site (-$NH_3^+$) of the cotton fabric, which first causes the adsorption of more dye molecules on the carbamated cotton. After the dyeing sites are fully occupied, the dyes might start to be adsorbed onto the rest of the surface by weak bonds. Therefore, this mechanism ensures improved dyeing, but the surface roughness of the carbamated cotton might play a crucial role.

## CONCLUSION

The problem of reactive dyes requiring a large amount of electrolyte in fabric dyeing could be reduced. The approach proposed in this study involves an additional pretreatment process after mercerization using urea to introduce a carbamate group in place of the hydroxyl group, to make the cotton fabric positively charged. It makes the Reactive Red HE3B dye, which is negatively charged, highly attracted towards the fiber. It can be concluded from this investigation that urea and the pad-dry-cure modification (*i.e.*, carbamation) can improve the dyeability of cotton fiber. The treatment of carbamation allowed the adsorption of Reactive Red HE3B dye molecules onto the cotton fibers and the reaction between the dye molecule and the cotton fiber without utilization of electrolyte. Optimum carbamation appeared to be achieved at the urea concentration of 400 g/L for the curing time of 5 minutes at 135 ºC. The degree of substitution was 0.2829, while the warp and weft-way tensile strength were not significantly affected.

The dyeing studies showed very good results on cotton with the DS of 0.2829. It was concluded that the introduction of a higher number of carbamate groups into cotton cellulose has an enhanced effect on its dyeability, without significantly affecting other physical properties. The method would have a significant potential for industrial application, as the pad-dry-cure procedure is a relatively clean and environmentally friendly technique, with low requirement of energy, water, time and resources, as the liquor could be reused. A special new system is required on the curing equipment, which can collect the ammonia gas released during the decomposition of urea (*i.e.*, which could be considered as an advantage, since the ammonia could be used as pre-activating agent for cotton cellulose, replacing caustic mercerization, or as a raw material for different chemical reactions), and care has to be given during the production of cotton cellulose carbamate.

The thermal analysis revealed that carbamated cotton fabrics degrade rapidly beyond the temperature of 300 ºC up to 370 ºC, whereas the control half-bleached fabric starts at the same temperature of 300 ºC and goes up to 400 ºC. 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 utilization percentage showed an improvement in comparison with the corresponding values of the control half-bleached fabric. The total dye utilization was 7-15% lower than that of the control half-bleached fabric. The dyeing basically happens between the negatively charged reactive red HE3B dye and the positively charged cotton cellulose due to the replacement of the hydroxyl groups with carbamate groups. The adsorption results showed good correlation with the Langmuir ($R^2 = 0.963$) and the Freundlich ($R^2 = 0.987$) models. The increment in the surface roughness, demonstrated by SEM, has a role in the dyeing process, and therefore the adsorption was best described by the Freundlich model.

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