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OPTIMIZATION OF REACTIVE DYEING PROCESS FOR CHITOSAN TREATED COTTON FABRIC

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The colour of textiles plays an important role in the marketability of fabrics, due to its psychological and eye-catching effects on consumers. Synthetic dyes are widely used in the textiles industry due to their ability to reproduce different colours and shades, easy application method and huge production to fulfill the demands of ever-increasing population. Reactive dyes are most commonly used for cotton fabric, due to their brilliant colours and good washing fastness. However, the major problem with reactive dyes is that they consume huge amounts of alkali or salts as mordant for the fixation of dyes on cotton fabric. Most of the commercial dyeing units and textile export houses have started seeking possibilities to use safe synthetic dyes for dyeing different textiles for targeting the niche market. For that purpose, appropriate standardized scientific dyeing techniques and procedures need to be adopted. In the present study, the use of chitosan as mordant, instead of alkali or salt, was investigated for dyeing cotton fabric with reactive red dye, and the dyeing variables were optimized to attain the maximum colour strength value. The results of study showed that higher percent dye absorption (78.90%), colour strength (18.72) and good wash fastness rating (4/5) were achieved for the chitosan treated dyed fabric, compared to the alkali treated dyed sample (68.36% and 13.03, respectively).

Keywords: reactive dye, cotton, chitosan, textiles, dyeing

INTRODUCTION

The interest in eco-friendly textile wet processing techniques has been increasing in recent years due to the increased awareness of environmental issues throughout the world. The main challenge the textile industry faces is to modify production at a competitive price by using safe dyes and chemicals, as well as by reducing treatment costs. The global consumption of textiles is estimated to grow at the rate of 3 percent per annum. The colouration of this huge quantity of textiles requires about 700,000 tonnes of dyes, which cannot be covered by natural dyes only. Only a certain portion of coloured textiles can be complemented and managed by eco-safe natural dyes.[1] Therefore, the use of eco-safe synthetic dyes is the need of the hour.

Dyes as coloured unsaturated organic molecules must have affinity for fibers to be effectively applied. The dyes are physically bound to the fiber by one or more physical forces. According to Broadbent, cotton and other cellulosic fibres can be dyed with direct, sulphur, vat, reactive or azoic dyes – more types of dyes than for any other fibre. Each of these classes of dyes has its own application methods, dyeing characteristics, costs, fastness properties and colour range, and therefore its own particular advantages and disadvantages.[2] Direct dyes generally cannot meet today's more stringent washing fastness requirements for apparel and linens. In recent years, their share of the market has gradually declined in favour of reactive dyes.

Reactive dyes have become very popular due to their brilliancy, variety of hues, high wet fastness, convenient usage and high applicability. Nowadays, reactive dyes maintain the largest annual consumption in the world, among the dyes used for cellulosic fibres, which establishes their important status in the dye manufacturing industry. For dyeing of one kilogram of cotton textile with reactive dyes, about 70 to 150 L of water, 600-800 g of sodium chloride and 30 to 60 g of dyestuff are required. In the application of reactive dyes, the use of large amounts of

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electrolytes, unfixed dye and high volumes of wastewater discharge create environmental problems. Thus, reactive dyes are the most unfavorable class of dyes, from the ecological point of view, because the effluents produced give very high values of biological oxygen demand (BOD), chemical oxygen demand (COD) and increase the salinity of river water, which affects the delicate biochemistry of aquatic life. More than 80,000 tonnes of reactive dyes are produced and consumed every year, making it impossible to quantify the total pollution caused by their use. The best approach would obviously be to modify the textile processing technologies and chemistry to reduce the effluent discharge produced during dyeing. Thus, most researchers focus on introducing salt-free/low-salt dyeing technology for reactive dyes.

When cotton fibres are immersed in an aqueous dye bath, the fibre surface acquires an initial negative charge that is referred to as zeta potential. Anionic dyes are usually sulphonated to provide aqueous solubility and possess a negative charge in the aqueous dye bath. Therefore, there is an electrostatic repellency for the dyes to diffuse through the fibre-water interface. The only widely used method of overcoming this barrier is the addition of large quantities of inorganic electrolyte, such as sodium chloride or sodium sulphate.[3] Cationization is one of the most important modifications for cotton to improve its affinity toward anionic substances, such as dyes, in conventional textile processing, and metal ions or unfixed dyes in effluent treatment. Cationic modification agents have two functional characteristics, namely, multiple functional groups that could react with cotton under alkaline conditions and cationic amino groups that could reduce the negatively charged barrier between fibre and dye.

Modification is also possible with the help of biopolymers, an environmentally benign route. It is well known that biopolymers are capable of forming ionic interactions with cotton cellulose by rendering positive charge and provide other functional properties to the fibre. Biopolymers can thus replace the salts, such as alum, ferrous sulphate, sodium sulphate, sodium carbonate and sodium chloride, which have been widely used for dyeing of cotton with natural and synthetic dyes to improve the fastness properties and absorption of dye. Biopolymers offer the complete elimination of electrolytes (salts), requiring low water consumption during the wash off process and providing maximum dye absorption and colour strength, which significantly contributes to reducing process costs. It has been reported that chitosan can be used in the production of man-made fibers and textile wet processing. Its potential can be utilized in dyeing to improve the dyeability, in finishing fabrics as antimicrobial agent and in printing as natural thickener in printing paste.[4] Sundar *et al.* reported that chitosan is a very useful and interesting bioactive polymer due to its availability, biocompatibility, bioactivity, cost-effectiveness, non-toxicity and biodegradability. It has many amino side groups, which offer possibilities of chemical modifications, the formation of a large variety of useful derivatives that are commercially available or can be made available via graft reactions and ionic interactions. The unique characteristics of chitosan in providing bio-adhesion, sorption and antimicrobial properties are the major reasons for its multiple applications.[5]

For successful application of more eco-friendly dyeing approaches for any particular type of fibres, for achieving acceptable colour fastness behaviour and reproducible colour yield, appropriate standardized dyeing techniques and procedures need to be adopted. Thus, relevant scientific studies and their output on the optimization of dyeing methods, process variables, dyeing kinetics and analysis of compatibility of selected synthetic dyes have become very significant, but scarce. Hence, the present study was undertaken to utilize salt free dyeing on cotton using reactive dye, which will contribute to minimizing the pollution load on the environment. Moreover, the application of chitosan to replace the salts is considered a promising approach that also provides multi-functionality to cotton fabric.

EXPERIMENTAL

Materials

Pure cotton fabric intended for apparel purposes was purchased from a local market of Hisar city of Haryana. For increasing the absorbency of the cotton fabric, enzymatic desizing treatment was performed using Americos Amylase 543 and enzymatic scouring – with Palkoscour APCL. Americos Amylase 543 was purchased from Alps Industries Ltd., Ghaziabad (Uttar Pradesh) and Palkoscour APCL was purchased from Maps Enzyme Ltd., Ahmadabad.

Chitosan, of off-white colour and a degree of deacetylation (DA) >85%, was purchased from India Sea Foods, Kochi, Kerala. Citric acid and sodium hypophosphite of minimum 99.5%, with M.W. 210.14, and 99% with M.W. 105.99, were purchased from S.D. Fine-Chem Limited and Hi Media, from a local supplier in Hisar (Rajesh Trading Company), respectively. Acetic acid, of minimum 99.6%, with molecular weight 60.5, was purchased from S.D. Fine-Chem Limited, from a local supplier (Rajesh Trading Company), Hisar.

Reactive red 120 dye (Reactive Brilliant Red HE38, C.I.292775, Hot Brand) was used in the study for dyeing of cotton fabric and optimization of the dyeing process.

Procedures

The methods used for treating, dyeing and testing the fabrics, accoding to specific standards, are described below.

Preparation of the cotton fabric

To ensure complete wetting and uniform absorbtion of the extracts during padding, the fabric must undergo preparatory processes. Therefore, the woven cotton fabric was subjected to desizing and scouring treatments to remove foreign materials before applying the finish.

Enzymatic desizing: The cotton fabric was subjected to a desizing treatment using 2 mL/L of Americos Amylase 543, at 60 °C temperature for 60 minutes with 1:20 material to liquor ratio, maintaining pH 7. The treatment liquor was drained out and the fabric was given one hot rinse, a cold wash and then dried.[6]

Enzymatic scouring: Desized cotton fabric was scoured in a bath containing 1.5% (owf) Palkoscour APCL enzyme, at 60 °C for 60 minutes at material to liquor ratio 1:15, maintaining pH 7.0. The fabric was rinsed in hot and cold water, and dried.[7]

Dyeing with reactive red dye with alkali treatment

The samples were dyed using an aqueous bath containing one percent Cibacron® Red LS-B (C.I. Reactive Red 270) reactive dye, 15 g/L sodium sulphate, 10 g/L sodium carbonate with a material to liquor (M:L) ratio of 1:50. The temperature of the dyeing bath was gradually raised from 30 to 60 °C for 160 minutes. The dyed fabric was rinsed with hot water, followed by cold water, and finally dried at room temperature.[8]

Application of biopolymer treatment prior to dyeing with reactive red dye

The biopolymer treatment was applied to cotton fabric using a standard test method. Cotton fabric was first impregnated in a solution containing chitosan (2.5%), citric acid (4%) and sodium hypophosphite (5%), keeping the 1:30 material to liquor ratio and pH 5.0, at 90 °C for 60 minutes. The impregnated fabric was pressed between the squeezing rollers of the padding mangle machine, maintaining the pressure of 2 kg/cm and achieving 70-75% expression. The biopolymer (chitosan) treated samples were dried at 100 °C for 7 minutes and cured for 3 minutes at 150 °C before dyeing with reactive red dye.[9]

Optimization of dyeing process

The dyeing process was optimized for biopolymer (chitosan) treated fabric. Experiments were undertaken to optimize dye concentration, dyeing pH, dyeing temperature, dyeing time and material to liquor ratio, on the basis of dye absorption, colour strength (K/S) and wash fastness properties. The dyeing parameters were optimized as described below.

Dye concentration

Five different concentrations of the selected synthetic dye, *i.e.* 1.0, 1.5, 2.0, 2.5, 3.0 percent, were used (owf) for dyeing the samples in five different beakers, while the other conditions were kept constant (pH: 5.0, treatment time: 45 minutes, M:L ratio: 1:30). The biopolymer treated samples were first wetted out in water for 10 minutes, and then transferred into the corresponding beaker containing the dye liquor and kept in water bath. The dyeing process was started at the temperature of 50 °C, which was gradually raised to 60 °C. The dyed samples were rinsed with warm water, followed by a cold water rinse, and finally dried in shade. Before and after the dyeing process, 2 mL of dye solution from each beaker was taken out, and optical density was measured on a spectrophotometer at 400 nm wavelength and percent dye absorption was calculated. The concentration of the dye corresponding to the dyed material exhibiting maximum dye absorption and wash fastness grade was selected as the optimum dye concentration.

Dyeing pH

For the optimization of pH, the dye bath was adjusted to pH 3.5, 4.0, 4.5, 5.0 and 5.5 with glacial acetic acid. The biopolymer treated samples were dyed with the optimum dye concentration, while the other variables were kept constant (treatment time: 45 minutes, M:L ratio: 1:30). The dyeing process was started at the temperature of 50 °C, which was gradually raised to 60 °C. The pH value that led to maximum dye absorption and wash fastness value was selected as the optimum dyeing pH for the selected synthetic dye.

Material to liquor ratio

The material to liquor ratio is another important parameter that influences the exhaustion of dye. The effect of the material to liquor ratio on the absorption of the selected dye onto the biopolymer treated cotton fabric was investigated varying the values as follows: 1:20, 1:30, 1:40 and 1:50, while using the optimized dye concentration, dyeing pH, and keeping treatment time at 45 minutes. The dyeing process was started at 50 °C, and the temperature was gradually raised to 60 °C. The material to liquor ratio that yielded the maximum dye absorption and wash fastness was taken as the optimum for dyeing biopolymer treated cotton fabric.

Dyeing temperature

The biopolymer treated cotton samples were dyed in dye baths containing the optimized concentration of synthetic dye, at optimized pH and M:L ratio, keeping dyeing time constant. The dyeing temperature was varied, *i.e.* 50, 60, 70 and 80 °C. The temperature at which maximum dye absorption and wash fastness were obtained was taken as the optimum dyeing temperature.

Dyeing time

The biopolymer treated fabrics were dyed with the selected dye for different durations: *i.e.* 15, 30, 45, 60 and 75 minutes, using the optimum values of the other dyeing parameters. The optimum dyeing time was selected on the basis of the maximum percent dye absorption and wash fastness value.

Dyeing with Reactive red 120 dye using standardized method

The scoured cotton fabric treated with biopolymer (chitosan) was dyed with reactive red dye (Hot Brand), using the exhaust method of dyeing, using the optimized values of dye concentration (2.5%), pH (5.0), M:L ratio (1:30), at 80 °C for 45 minutes.

Measurements of percent dye absorption

The percent dye absorption of differently dyed fabric samples was measured using optical density (OD). The exhaustion values of the dye bath were measured by taking the absorbance of the dye liquor (before and after dyeing) using a UV-visible spectrometer.

$$\text{Dye absorption (\%)} = \frac{\text{OD before dyeing} - \text{OD after dyeing}}{\text{OD before dyeing}} \qquad (1)$$

Colour measurement

The methods of measuring colour numerically were established by CIE in 1931 and 1976. The following equation was used to predict the colour value:

$$K/S = (1-R)^2/2R \qquad (2)$$

where K = constant of light absorption of dyed fabric; S = constant of light scattering of dyed fabric; R = reflectance of dyed fabric, expressed in fractional form.

The CIE Lab colour space uses L*, a* and b* scales to describe colour. L* is a measure of darkness/lightness of colour of an object and ranges from 0 (black) to 100 (white), a* – of redness (+ve a*) or greenness (-ve a*), b* – of yellowness (+ve b*) or blueness (-ve b*), C* – of dullness/brightness and H* is a measure of hue.

The whiteness index, yellowness index, and brightness index values of enzymatically desized and enzymatically scoured cotton fabric samples were measured using Premier Colorscan (SS5100A).

CIE whiteness index equation was used to assess the whiteness of enzymatically desized and scoured cotton fabric. Under D65 illuminant and CIE 1964 standard observer, the whiteness is given by:

$$W_{CIE} = Y + 800\,(x_n - x) + 1700\,(y_n - y) \qquad (3)$$

where Y shows the tristimulus value; x and y are coordinates; x_n and y_n are coordinates of MgO. For D65/10°, the values of x_n and y_n are 0.3138 and 0.3309, respectively.

The yellowness index was calculated by the ASTM method E313, using the following formula:

$$YIE313 = \frac{100\,(C_x X - C_z Z)}{Y} \qquad (4)$$

where X, Y and Z are the CIE tristimulus values, and the coefficient depends on the illuminant and observer. For D65/10°, the values of C_x and Y_x are 1.3013 and 1.1498, respectively.

The brightness index (ISO-2470-1977) was calculated using the following formula:

$$\text{Brightness Index} = \frac{\text{reflectance value of substrate at 475nm}}{\text{reflectance value of white tile at 475nm}} X100 \qquad (5)$$

Testing of fastness properties to different external influences

The fastness properties of dyed samples were studied against different influences, such as washing, sunlight, rubbing and perspiration.

Fastness to washing

Wash fastness tests were carried out as per the recommendation of IS: 3361-1979 method (BIS, 1979). The dyed samples were placed between two pieces of bleached fabrics measuring 10 cm x 4 cm (in parallel lengths). The composite specimen was weighed and the required quantity of soap solution at the rate of 5 g/L of water was prepared, keeping the material to liquor ratio at 1:50. The specimen was treated for 45 min at 50±2 °C in a Launder-Ometer, then was removed and rinsed with cold water. The changes in colour of the dyed samples were assessed with grey scale no. 1, as per the recommendation of the ISO 105 method.

Fastness to sunlight

The fastness to sunlight was determined according to IS: 686-1985 method (BIS, 1985). The samples were exposed to daylight in an exposure rack, every day from sunrise to sunset, keeping the exposure rack at an angle of 45° and the total exposure time being of 48 hours. The changes in colour of the exposed portion were compared with those of the unexposed portion using the grey scale.

Fastness to perspiration

The fastness to perspiration was tested using the IS: 971-1983 method, recommended by the Bureau of Indian Standards (BIS, 1983). Acidic and alkaline test liquor was prepared. The test specimens were soaked in the acidic and alkaline test solutions separately, at the material to liquor ratio of 1:50 for 40 minutes at room temperature. The loaded apparatus was kept in a hot air oven for four hours at 37±2 °C. The test samples were removed from the oven and air dried at a temperature not exceeding 60 °C. The numerical grading for colour change of the test pieces and for staining of two adjacent pieces was done using the grey scale.

Fastness to rubbing

Fastness to rubbing means the resistance of textile material to every type of rubbing and staining from the textiles in actual use. The fastness to rubbing was carried out according to IS: 776-1986 method (BIS, 1988).

FTIR analysis

Fourier transform infrared spectroscopy (FTIR) was carried out to characterize the chitosan treated reactive red dyed cotton fabric in terms of chemical composition and interactions of functional groups. FTIR analysis was performed by the potassium bromide (KBr) method at SAIF, IIT Madras.

RESULTS AND DISCUSSION

Effect of enzymatic desizing and scouring on whiteness and brightness indices

The effect of enzymatic desizing and scouring treatment on the whiteness and brightness indices of cotton fabric is presented in Figure 1. It was observed that, after enzymatic desizing of cotton fabric, the whiteness index increased from 81.27 to 83.19, and the brightness index – from 70.11 to 70.80, whereas the yellowness index decreased from -10.87 to -12.03. It can also be noticed from the figure that, after enzymatic scouring, the whiteness index increased from 81.27 to 85.40, the brightness index – from 70.11 to 72.63, as the yellowness index decreased from -10.87 to -12.31. The reason may be that the amylase plays an important role in the hydrolysis of starch, whereas the pectinase hydrolyzes the wax and vegetative impurities. The removal of starch and vegetative impurities enhances the whiteness and brightness indices and decreases the yellowness index of pretreated cotton fabric. At the same time, the treatment allows the cotton to achieve superior hydrophilicity, without fiber deterioration. The result of the study is also supported by Vigneswaran *et al*., who reported that the highest whiteness index and the lowest yellowness index were noticed for bioscoured organic cotton fabric with pectinase. The bio-preparation of cotton fabric is a valuable and environmentally friendly alternative for preparing cotton to the harsh alkaline chemicals. Pectinases have proved to be the most effective and suitable enzymes for cotton bioscouring.[6]

Optimization of various dyeing parameters in reactive red dyeing

The optimization of reactive red dyeing process was performed to attain the optimum results and the conditions of dyeing for different parameters are described below.

Optimization of dye concentration

Five different dye concentrations, *viz.* 1.0, 1.5, 2.0, 2.5 and 3.0 percent, were used to obtain the optimum dye absorption and colour strength on the cotton fabric. It evident from Table 1, as the concentration of dye increased from 1.0 to 3.0 percent, dye absorption increased from 56.44 to 78.64 percent and colour strength value from 6.20 to 18.76, but L* value registered a decrease from 50.28 to 47.77, indicating an increase in the darkness of shade. The hue angle (H*) was found between 270^o and 360^o, with positive a* and negative b* values at all pH values, which depicted a reddish blue (magenta) colour of samples. The wash fastness rating was found fairly good (3/4) at 1 percent, good (4) at 1.5 percent and very good (4/5) at 2.0, 2.5 and 3.0 percent of dye concentration.

The dye concentration of 2.5 percent was selected as the optimum, with dye absorption of 78.13 percent and colour strength value of 18.73, along with very good (4/5) wash fastness rating, as no remarkable difference was noticed between the results obtained for 2.5 and 3.0 percent dye concentration. This might be explained by the fact that, as the dye concentration increased, the availability of the dye molecules in the dye bath also increased, hence more dye molecules could attach to the fiber. More fixation of dye molecules on the fabric will enhance the colour strength of the fabric and ionic interaction between the dye anions and cationic cotton will improve the wash fastness of the dyed fabric. The findings of study are supported by Haggag et al. who found that an increase in dye concentration led to an increase in the colour strength (k/s) value.10 Ibrahim and Reda found that in the exhaust dyeing process, most of the reactive dyes were easily absorbed and diffused into modified cotton by opposite charges attraction. The absorption could greatly increase the concentration of reactive dyes inside treated cotton, which enhanced dye-fiber fixation reaction in the dye-fixation process.[11]

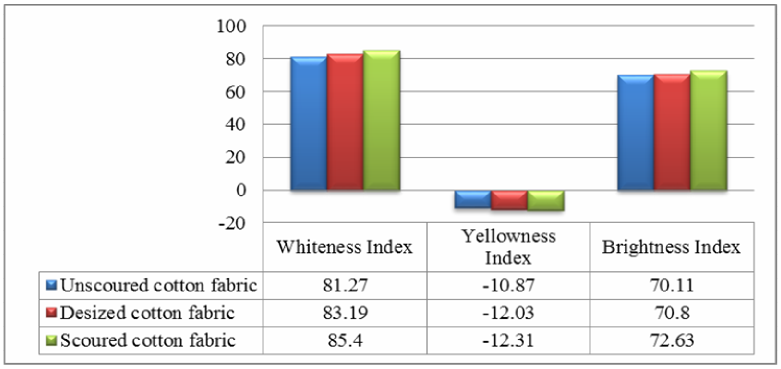

Figure 1: Effect of enzymatic preparatory processes on whiteness and brightness of cotton fabric

Table 1
Optimization of dye concentration on the basis of colour properties of reactive red dye

Dye concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (K/S)	Wash fastness grades
		L*	a*	b*	C*	H*		
1.0	56.44	50.28	23.54	-1.89	23.62	355.41	6.20	3/4
1.5	69.47	49.55	25.40	-1.85	25.47	355.82	10.65	4
2.0	77.09	48.95	26.07	-2.26	26.16	355.04	12.66	4/5
2.5	**78.13**	**47.94**	**26.84**	**-2.96**	**27.00**	**353.70**	**18.73**	**4/5**
3.0	78.64	47.77	27.18	-3.31	27.38	353.05	18.76	4/5

Optimization of dyeing pH

Five different pH values, *i.e.* 3.5, 4.0, 4.5, 5.0 and 5.5, were tested to find out the effect of the dyeing solution pH on the dyeing results. It is clear from Table 2 that, as the pH increased from 3.5 to 5.0, the reactive red dye absorption also increased from 67.63 to 78.26 percent, and the colour strength (K/S) value – from 9.74 to 14.75, whereas the L* value decreased from 58.00 to 52.99, indicating increased darkness of shade. However, further increase in pH from 5.0 to 5.5 led to a decrease in dye absorption from 78.26 to 75.63 and colour strength (K/S) from 14.75 to 10.13, while the L* value increased from 52.99 to 53.96, denoting lower darkness. The wash fastness rating was fairly good (3/4) at pH 3.5 and 4.0, good (4) at pH 4.5 and 5.0, and very good (4/5) at pH 5.0. The chroma (C*) value was the highest (38.56) at pH 5, followed by pH 4.5 (36.69), pH 4.0 (36.54), pH 5.5 (34.75) and pH 3.5 (33.82), indicating the brightness of the dyed samples. The highest percent dye absorption (78.26), colour strength value (14.75), with very good (4/5) wash fastness rating, were found at pH 5.0, hence this values was selected as the optimum pH for dyeing chitosan treated cotton fabric with reactive red dye. The reason may that the pH plays an important role in achieving the dye equilibrium. The percent dye absorption accelerated till equilibrium, then the hydrolysis of dye started, which caused a decline in wash fastness and colour strength values because of lower dye absorption. Another reason could be that the dye that was deposited on the fabric surface got hydrolyzed, thus the wash fastness decreased. Samanta and Agarwal used a different technique, in which a mixture of chitosan and PEG was used to pre-treat cotton muslin fabric, which allowed a salt-free reactive dyeing in acid bath.[1]

Optimization of material to liquor ratio (M:L ratio)

Table 3 reveals that, with the increase in M:L ratio from 1:20 to 1:30, there was an increase in dye absorption from 76.00 to 76.38 percent and in colour strength (K/S) value – from 14.77 to 17.43, but the L* value decreased from 66.26 to 65.67, depicting higher darkness of shade. However, further rising the M:L ratio from 1:40 to 1:50 led to a decrease in dye absorption from 76.02 to 75.86 percent and in colour strength values – from 16.84 to 16.30, whereas the L* value increased from 65.20 to 65.93, denoting lightness of shade. The wash fastness rating was observed to be fairly good (3/4) at M:L ratios 1:20 and 1:50, good (4) at 1:40 and very good (4/5) at 1:30 M:L ratio. The chroma (C*) value was the highest (29.87) for 1:40 M:L ratio, followed by 1:50 (29.18), 1:30 (28.00) and 1:20 (18.82), indicating brightness of the sample.

It can be concluded from the data in the table that the optimum M:L ratio is 1:30, when the highest percent dye absorption of 76.38, colour strength (K/S) value of 17.43 and very good wash fastness rating (4/5) were achieved. This might be explained by the fact that the 1:30 M:L ratio of the dye bath was sufficient for providing complete exhaustion of the dye uniformly inside the fabric structure, which provided maximum fixation of dye molecules onto the chitosan treated cotton fabric. On the contrary, a too low M:L ratio, *i.e.* 1:20, was insufficient for complete wetting of the cotton and the dye got adsorbed on the surface unevenly, which showed low absorption, uneven dyeing and low wash fastness, while 1:40 and 1:50 M:L ratios were too high, which allowed the dye remain more disperse and it took a very long time for it to get absorbed, causing slightly less dye absorption, but still higher than for the 1:20 ratio. Sharmila *et al.* also used the 1:30 material to liquor ratio for reactive dyeing, using the required amount of dyestuff.[12]

Table 2
Optimization of dyeing pH on the basis of colour properties of dyed cotton samples

pH	Dye absorption (%)	Colour coordinates					Colour strength (K/S)	Wash fastness grades
		L*	a*	b*	C*	H*		
3.5	67.63	58.00	27.85	-19.18	33.82	325.45	9.74	3/4
4.0	77.81	53.92	31.62	-18.30	36.54	329.95	12.26	3/4
4.5	78.18	53.26	31.20	-19.31	36.69	328.26	14.27	4
5.0	**78.26**	**52.99**	**32.37**	**-20.95**	**38.56**	**327.10**	**14.75**	**4/5**
5.5	75.63	53.96	29.88	-17.74	34.75	329.31	10.13	4

Table 3
Optimization of material to liquor ratio on the basis of colour properties of dyed cotton samples

M:L ratio	Dye absorption (%)	Colour coordinates					Colour strength (K/S)	Wash fastness grades
		L*	a*	b*	C*	H*		
1:20	76.00	66.26	18.75	-1.59	18.82	355.15	14.77	3/4
1:30	**76.38**	**65.67**	**27.86**	**-2.75**	**28.00**	**354.35**	**17.43**	**4/5**
1:40	76.02	65.20	29.66	-3.51	29.87	353.25	16.84	4
1:50	75.86	65.93	29.03	-2.90	29.18	354.28	16.30	3/4

Table 4
Optimization of dyeing temperature on the basis of colour properties of dyed cotton samples

Dyeing temperature (°C)	Dye absorption (%)	Colour coordinates					Colour strength (K/S)	Wash fastness grades
		L*	a*	b*	C*	H*		
50	74.90	48.03	32.96	-6.42	33.58	348.98	14.92	4
60	77.09	47.46	32.54	-2.01	32.60	356.45	15.76	4
70	78.18	46.41	31.28	-1.89	31.34	356.53	18.32	4/5
80	**78.54**	**45.66**	**30.66**	**-2.24**	**30.37**	**355.81**	**18.41**	**4/5**

Table 5
Optimization of dyeing time on the basis of colour properties of dyed cotton samples

Dyeing time (min)	Dye absorption (%)	Colour coordinates					Colour strength (K/S)	Wash fastness grades
		L*	a*	b*	C*	H*		
15	70.54	58.71	19.95	-16.54	25.92	320.36	10.49	3/4
30	71.63	51.12	33.79	-22.30	40.49	326.58	17.18	4
45	**72.36**	**50.94**	**32.97**	**-19.71**	**38.42**	**329.13**	**17.87**	**4/5**
60	72.72	50.76	40.35	-33.03	52.28	320.84	17.92	4/5
75	72.76	50.36	30.36	-21.32	37.10	324.93	17.02	4

Optimization of dyeing temperature

Table 4 demonstrates that, as the dyeing temperature rose from 50 to 80 °C, the dye absorption increased from 74.90 to 78.54 percent and colour strength (K/S) value – from 14.92 to 18.41, whereas the L* value decreased from 48.03 to 45.66, displaying a more pronounced darkness of shade. The wash fastness rating was found to be good (4) at 50 and 60 °C, very good (4/5) at 70 and 80 °C. It is thus envisaged that the dyeing temperature of 80 °C showed maximum dye absorption (78.54%) and colour strength value (18.41), as well as very good (4/5) wash fastness rating, hence it was selected as the optimum.

It is clear that higher dyeing temperature leads to better dyeing results. The reason might be that the increase in dyeing temperature enhanced the movement of dye molecules in the dye liquor and anionic dye molecules were attracted towards the cationic charged chitosan treated fabric, consequently the dye absorption and colour strength increased. Arif *et al.* revealed that higher temperature increased the kinetic energy of the dye molecules and thereby enhanced the rate of penetration of the dye into the vicinity of the substrate. The increase in dyeing temperature increased the molecular vibrations both in the fiber and in the dye, which induced favorable fixation kinetics.[13]

Optimization of dyeing time

Table 5 elucidates that with the increase in dyeing time from 15 to 75 minutes, the reactive red dye absorption onto the chitosan treated cotton fabric increased from 70.54 to 72.76 percent, the colour strength (K/S) rose from 10.49 to 17.02, whereas the L* value showed a decline from 58.71 to 50.36, depicting increased darkness of shade. The wash fastness rating was noticed to be fairly good (3/4) for 15 minutes, good (4) for 30 and 75 minutes and very good (4/5) for 45 and 60 minutes of dyeing time, respectively. The chroma (C*) value decreased from 52.28 for 60 minutes dyeing duration to 25.92 for 15 minutes, indicating brightness of the dyed samples.

The wash fastness rating after 45 and 60 minutes of dyeing time was very good (4/5), with negligible variation in dye absorption and colour strength, hence 45 minutes was selected as the optimum dyeing time, at which the dye absorption of 72.36 percent, the colour strength (K/S) value of 17.87 and very good (4/5) wash fastness rating were achieved. These data suggest that, while the rising dyeing temperature increased the molecular vibrations in the fiber and in the dye, and led to favorable fixation kinetics, an increase in the duration of dyeing was necessary to enhance dye exhaustion. The availability of an appropriate reaction time for adsorption ensured good fixation of the dye from the solution to the fabric. An increase in the dying time above the peak limits led to the hydrolysis of dye and caused a slight decrease in dye absorption. Alam *et al.* reported that the reactive dye absorption onto cotton fabric increased linearly with dyeing time and reached the maximum at 60 minutes, producing bright and even shades.[14]

Assessment of colour properties of reactive red dyed cotton fabric

Dye absorption and colour strength

The results regarding the colour properties of dyed fabrics are presented in Table 6. As can be noted, the percent dye absorption (78.90) and colour strength value (18.72) were higher for the chitosan pretreated reactive red dyed fabric than for the alkali pretreated dyed fabric – 68.36 and 13.03, respectively. The lower L* value (36.48) depicted that the chitosan pretreated reactive dyed sample was darker in colour than the alkali treated dyed fabric, for which the L* value was higher (54.76). The a* and b* values indicated that both alkali and chitosan treated reactive red dyed samples had redder and bluer tones, but more pronounced red and blue tones were observed for the chitosan pretreated dyed sample. The results of the study are in line with the findings of Bhuiyan *et al.*, who revealed that the chitosan present in the cotton fabric enhanced the number of dye sites, causing deeper shade.[15] Singha *et al.* also treated cotton with chitosan and found that it enhanced the dyeing results with various commercial reactive dyes, while the fastness properties were also found adequate and quite comparable with those of conventionally dyed samples. Dyeing of cotton with reactive dyes using chitosan with a cross-linker in the dye bath improved the dyeability of cellulosic fabrics with reactive dye in the absence of salt.[16]

Colour fastness properties

The data regarding the colour fastness properties, *viz.* wash, light, perspiration and rubbing fastness, of the reactive red dyed samples pretreated with alkali and chitosan separately are presented in Table 7.

Table 6
Dye absorption, colour coordinates and colour strength results of dyed fabrics

Reactive red dyed samples	Dye absorption (%)	Colour coordinates					Colour strength (K/S)
		L*	a*	b*	C*	H*	
Alkali treated	68.36	54.76	20.38	-16.25	26.07	321.44	13.03
Chitosan treated	78.90	36.48	43.15	-10.53	44.42	346.30	18.72

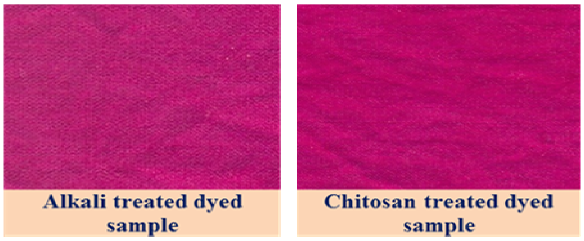
Alkali treated dyed sample
Chitosan treated dyed sample

Figure 2: Alkali and chitosan treated dyed samples

Table 7
Colour fastness grades of dyed fabrics

Reactive red dyed samples	Colour fastness grades																
	Wash		Light (days)							Perspiration				Rubbing			
										Alkaline		Acidic		Dry		Wet	
	CC	CS	1st	2nd	3rd	4th	5th	6th	7th	CC	CS	CC	CS	CC	CS	CC	CS
Alkali treated	4	4	4/5	4/5	4/5	4/5	4	4	4	4	4	4	4	4/5	4/5	4/5	4/5
Chitosan treated	4/5	4/5	4/5	4/5	4/5	4/5	4	4	4	4	4	4	4	4/5	4/5	4/5	4/5

CC = colour change, CS = colour staining

The reactive red dyed samples pretreated with chitosan showed very good (4/5) wash fastness rating for both colour change (CC) and colour staining (CS), compared to the dyed sample pretreated with alkali. The light fastness rating was found to be very good (4/5) for the reactive dyed samples pretreated with alkali and chitosan separately for first four days, followed by good results from the 4th to the 7th day. The perspiration fastness was found to be good (4) in terms of colour change and colour staining for the chitosan and the alkali treated dyed samples. The rubbing fastness was found to be 4/5 (very good) for both (alkali and chitosan) treated dyed fabrics in terms of colour change and colour staining. Overall, it can be concluded from the obtained data that the reactive red dyed samples pretreated with chitosan showed better wash fastness properties over the alkali treated ones, but comparable results in terms of light, perspiration, and rubbing fastness. The findings are in line with the results of Karthikeyan and Ramachandran, who reported that colour fastness properties to washing and wet crocking of the treated cotton samples improved after chitosan treatment of the fabric.[17]

FTIR analysis of chitosan treated reactive dyed cotton fabric

The FTIR spectrum of the chitosan treated cotton fabric dyed with reactive red dye is presented in Figure 3, while Table 8 lists the assignments of the peaks found in the spectrum.

The appearance of a strong broad band at 3276.62 cm^{-1} indicates the characteristics of hydroxyl groups (H-bonded OH stretching), whereas the small peaks at 2895.70 cm^{-1} and 2297.36 cm^{-1} are characteristic of alkanes and cyano compounds, distributed alkynes. Further intensification of a weak band at 2108.00 cm^{-1} corresponded to the carbon-carbon triple bond stretch and that at 1636.30 cm^{-1} to C=C stretch, primary amine and N-H bend. The characteristic band of organic sulphates was found at 1426.98 cm^{-1}, the **-**OH bending and aromatic primary amine stretching at 1314.73 cm^{-1} and 1363.66 cm^{-1}. The tertiary amine, –CN- stretch, and secondary amine, –CN- stretch, were noticed at 1202.68 cm^{-1} and 1105.15 cm^{-1} (and 1157.03 cm^{-1}), respectively. The peaks at 1024.85 cm^{-1}, 702.71 cm^{-1}, 663.84 cm^{-1}, 608.17 cm^{-1} and 555.32 cm^{-1} illustrated the existence of -C-C- stretching, skeletal –C-C- vibrations, aliphatic bromo compounds and -C-I- stretching, correspondingly.

The FTIR spectrum of chitosan treated cotton fabric dyed with reactive red dye shows evidence of the presence of various functional groups. The presence of tertiary and secondary amine groups was due to the chitosan treatment of the fabric performed before the dyeing process. These groups got protonated under acidic conditions, producing a positively charged cotton surface, and thus contributed to the attachment of anionic reactive red dye molecules to the cotton fabric, enhancing the dyeability without alkali and salt treatment. The results of the study are in line with the data reported by Chattopadhyay, who revealed that pretreatment of cotton with polyamide epichlorohydrin (PAE) polymer resulted in excellent exhaustion of reactive dye from the dye bath in acidic condition, in the absence of salts, but the exhaustion and fixation reached the maximum at 2.0% (owf).[18]

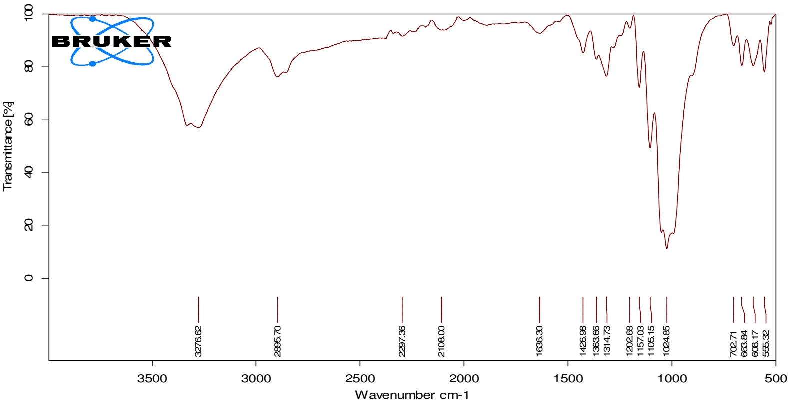

Figure 3: FTIR spectrum of chitosan treated reactive red dyed cotton fabric

Table 8
FTIR analysis of chitosan treated reactive red dyed cotton fabric

Peak ranges (cm^{-1})	Peaks	Functional groups
3200-3300	3276.62	Hydroxyl group (H-bonded–OH- stretch)
2800-2900	2895.70	C-H stretching, O-H stretching – Alkanes (CH; CH2; CH3), carboxylic acids
2200-2300	2297.36	Cyano compounds, disubstituted alkynes
2100-2200	2108.00	C-triple bond-C-stretch
1600-1700	1636.30	-C-double bond-C stretch, primary amine, N-H bend
1400-1500	1426.98	organic sulphates
1300-1400	1314.73 1363.66	-OH bend, aromatic primary amine stretching
1200-1300	1202.68	Tertiary amine, –CN- stretch

1100-1200	1105.15 1157.03	Secondary amine, –CN- stretch
1000-1100	1024.85	-C-C- stretch
700-800	702.71	Skeletal –C-C- vibrations
600-700	663.84 608.17	Aliphatic bromo compounds
500-600	555.32	-C-I- stretching

CONCLUSION

The exhaustion of reactive dyes on a cellulosic substrate is determined by a number of factors, the most important being the pH of the dye bath, the temperature of dyeing, the concentration of electrolyte, the dyeing time and the material to liquor ratio. The present study aimed to optimize the reactive red dyeing parameters for chitosan treated fabric. The findings have shown that the 2.5% dye concentration, pH 5.0, 80 °C dyeing temperature, 60 minutes dyeing time and 1:30 M:L ratio were the optimum conditions for dyeing the chitosan treated cotton. It was observed that with an increase in dye concentration, dyeing temperature and time, the dye absorption and colour strength values increased. As for the pH and M:L ratio, the dye absorption increased up to a specific threshold, beyond which it started declining. The percent dye absorption (78.90) and colour strength value (18.72) were higher for the chitosan pretreated reactive red dyed fabric than for the alkali pretreated dyed fabric, with corresponding values of 68.36 and 13.03, respectively, under the same conditions. The reactive red dyed samples pretreated with chitosan showed very good (4/5) wash fastness rating in terms of both colour change (CC) and colour staining (CS), compared to the dyed sample pretreated with alkali.

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