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INFLUENCE OF CHITOSAN NANOPARTICLES ON REACTIVE DYEING OF COTTON FABRICS

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ABSTRACT: Cotton textiles are dyed mostly with reactive dyes because they produce a wide range of bright colors with excellent colour fastness to washing. However, the reactive dyeing requires considerable quantities of inorganic salt and alkali for efficient utilization and application of dyes. These inorganic salts when drained to effluent generate huge amounts of total dissolved solids leading to serious environmental pollution. Considerable remedies are being measured within the textile processing industry to reduce the effluent pollution and to fulfill the environmental regulations. This work is a part of such efforts and presents results where cotton fabrics pretreated with chitosan nanoparticles and reactive dyeing carried out without salt. In this work, chitosan nanoparticle was used for developing salt free eco-friendly reactive dyeing. The effect of chitosan nanoparticles in color strength (K/S value), color difference, color fastness to crocking and washing of the cotton fabric was investigated. The cotton fabric treated with 0.5 (w/v) chitosan nanoparticles had higher K/S values.

Keywords: Cotton, chitosan nanoparticles, colour strength, fastness, reactive dye

INTRODUCTION

Eco-friendly textile wet processing techniques have been increasing in recent years due to the increased awareness of environmental issues throughout the world. Now-a-days consumers in developed countries are demanding bio-degradable and eco-friendly textiles. In dyeing of textiles, ecological restrictions are strictly followed from raw material selection, processing and water management to the final product. Cotton fibers are widely applied in textile industry due to its excellent properties of moisture regain, permeability of air, bio-degradability, no static electricity, etc.

The dyeing of these fibers is generally done with reactive dyes due to its variety of hue, high fastness, convenient usage and range of applicability. These reactive dyes contain a reactive group i.e. vinyl sulphone or triazine , that, when applied to a fiber in an alkaline dye bath, forms a chemical bond with hydroxyl (OH) group on the cellulosic fiber.

In recent years, reactive dyes maintain the largest annual consumption in the world among the dyes used for which establishes its important status in the dye manufacture industry. But important problems, such as low dye substantivity to cotton require large amount of electrolyte used and high volume of wastewater discharged, always exist in the application of reactive dyes. The dyeing of cotton with reactive dyes demands from 70 to 150 liter water, 0.6-0.8 Kg NaC1 and from 30 to 60 g dyestuffs. Due to these important problems, reactive dyes is the most unfavorable one from the ecological point of view, these effluents produced high values of Total Dissolved Solids and increases salinity of the rivers affects the delicate of aquatic life. Tons of reactive dyes are produced and

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consumed each year, making it possible to intensify the total amount of pollution caused by their use. Therefore, the better approach would be required to improve the textile processing in the discharge of pollution. The unique characters of nanoparticles for their small size and quantum size effect supposedly promised chitosan nanoparticles to exhibit superior dye ability improvement. The main objective of this research is to study influence of chitosan nanoparticles on cotton reactive dyeing and possibilities to reduce the colorants and chemical auxiliaries in the dyeing effluents.

2. MATERIALS AND METHODS

The grey cotton fabric for dyeing having the specification of 140 g/ m^2, warp 34 threads/cm, Yarn count 40/1, weft 33 threads/cm was used. Reactive dyes namely C.I. Reactive Red 6 was purchased. Chitosan was provided by Indian sea food industry, Cochin. (Degree of deacetylation (DD) = 92.5%, Molecular Weight=1000kD. All other reagents are commonly used laboratory reagent grade.

2.1 Preparation of chitosan nanoparticles

Chitosan was dissolved in a dilute aqueous acetic acid solution of 0.5 % (w/v) using microwave. Aqueous ammonia was then dropped into the chitosan solution to precipitate the chitosan. The obtained gel-like swollen chitosan was washed to neutral with DI water, and was then transferred into a 25 mL volumetric flask. The total volume of liquid was added to 25 mL with DI water. An ultrasound processor with a probe of 6 mm diameter was used. The ultrasound probe was put into the volumetric flask and was kept at 1 cm below the water level. Ultrasound treatment was conducted under an ice-water bath. Finally, a milky emulsion was obtained.

2.2 Pre-treatment of cotton with nano chitosan

Pre-washed cotton fabrics were soaked for 15 minutes in the emulsions with different concentrations separately: 0.01%, 0.05%, 0.1%, 0.3% and 0.5% (w/v). The padding processes were then completed with pick up weight of around 80%. Finally, the cotton fabrics were dried at 80 °C for 3 min and cured at 150 °C for 3 min and finally rinsed with warm water (40 ºC) for 1 min. Finally fabric rinsed with running cold water and dried again.

2.3 Reactive Dyeing

In a dye bath containing 3% of CI Reactive Red 6 with liquor ratio 1:30, cotton fabric was added at 35 ºC and the temperature is raised to 80 ºC over 20 min. Liquor ratio 1:30 is used due to maximum depth of shade on fabric. After which time the dyeing is continued for 30 min. Then 5 g/l soda ash added portion wise and the dyeing is maintained for further 45 min. For comparison, conventional dyeing carried out in untreated cotton fabrics. Dyed samples were thoroughly washed in hot water at 60°C, then washing with a solution containing 4g/l nonionic detergent and 1g/l sodium carbonate at 30°C for 15 min. and finally rinsing with cold water then air dried.

2.4 Evaluation of the dyed cotton fabrics

The color strength (K/S) of the treated sample using the untreated samples as blank was determined using X-rite spectrophotometer, Model colour- i5 equipped with integrated sphere according to Kubelka- Munk equation.

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

R: Decimal fraction of the reflectance of dyed samples,
K: Absorption coefficient,
S: scattering coefficient

3. RESULTS AND DISCUSSION

3.1 Colour Strength

K/S value of a dyed material has a close relationship to the amount of dye absorbed by the yarn. K/S values of pretreated with nano chitosan cotton dyed samples with Reactive Red 6 are shown in *Table 1*. It can be concluded that the K/S values of 0.5% chitosan treated dyed fabrics are higher than that of untreated dyed samples. As the chitosan concentration increases, the dye uptake also increases.

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Table 1 K/S Values of dyed fabrics

Dyes	Chitosan concentration (%)	ΔE	K/S
Reactive Red 6	0	-	8.246
	0.01	1.546	7.254
	0.05	1.454	7.374
	0.1	1.310	7.523
	0.3	1.012	7.975
	0.5	0.654	8.256

The enhanced dyeability of the modified fabric is likely resulted from the reduction of the coulombic repulsion between the fabric surface and the anionic dye molecules in the presence of the positively charged chitosan on the surface. The cationic charged amino groups may be involved in the adsorption of anionic chromospheres of reactive dyes. The improved dye ability is due to the presence of amine groups available from the chitosan which also tends to improve the reactivity of cellulosic substrate.

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3.2 Fastness Properties

The attachment of the dye molecules onto the partially-modified cellulosic substrate is by covalent bonding since no dyes strips out from the dyed sample. This is indicative through the fastness properties. Table 2 shows the fastness values of all such dyed samples are quite satisfactory and comparable with those of conventional dyed samples.

Table 2 Colour Fastness Properties

Dyes	Chitosan concentration (%)	Wash Fastness		Crock Fastness		Light Fastness
		Colour change	Staining on cotton	Dry	Wet	
Reactive Red 6	0	4	4-5	4-5	3-4	4
	0.01	4	4-5	4-5	3-4	4
	0.05	4	4-5	4-5	3-4	4
	0.1	4	4-5	4-5	3-4	4
	0.3	4	4-5	4-5	3-4	4
	0.5	4	4-5	4-5	3-4	4

3.3 Physical Properties

It is inferred from the Table 3 that there is a change in air permeability of the nano-chitosan treated cotton fabric as compared to the untreated one. It is perhaps due to the attachment of chitosan to all over the whole structure of the fabric. The slight losses of air permeability in the pretreated fabrics have not affected intact breathability of the cotton fabrics. There is no apparent change in tensile strength of dyed fabrics.

Table 3 Physical Properties of dyed fabrics

Dyes	Chitosan concentration (%)	Tensile Strength – Warp (N)	Air Permeability ($l/m^2/s$)
Reactive Red 6	0	351.5	480.5
	0.01	347.4	465.5
	0.05	345.6	463.7
	0.1	344.2	461.2
	0.3	343.9	458.4
	0.5	343.5	456.7

3.4 Dyeing Effluent Analysis

Table 4 shows that new method of eco friendly dyeing (0.5% chitosan treated) provided around 72% Total Dissolved Solids reduction in the effluent of CI Reactive Red 6.

Table 4 TDS of dyeing effluents

Dye	Effluent samples (Dyebath recipes diluted 100 times)	TDS (mg/l)
Reactive Red 6	Untreated Sample	1360
	Chitosan Treated Sample	380

4. CONCLUSION

The cotton fabrics were treated with different amounts of chitosan nanoparticles and reactive dyeing carried out without salt. It was found that reactive dye by increasing in chitosan concentration, there was a significant improvement in color strength (K/S). Pretreatment of cotton with chitosan nanoparticles enhances the possibility of dyeing cotton with reactive dyes without addition of salt. Reactive dyes can be much more efficiently exhausted onto cellulosic fabrics under neutral conditions in the absence of salt due to change of electrokinetic potential of chitosan treated samples. Moreover, the fastness values of all such dyed samples are quite satisfactory and comparable with those of conventional dyed samples. Dyeing effluent showed enormous reduction of Total Dissolved Solid content (TDS), which is essential requirement for textile industry.

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