J. Cotton Res. Dev. **31** (1) 147-151 (January, 2017)

Effect of plasma and chitosan nanoparticles on cotton reactive dyeing

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ABSTRACT: Cotton textiles are dyed mostly with reactive dyes because they produce a wide gamut of bright colours with excellent colour fastness to washing. However, reactive dyeing requires considerable quantities of inorganic salt and alkali for efficient utilization and application of dyes. These salts and alkalis when drained to effluent generate heavy amounts of total dissolved solids leading to environmental pollution. Substantial remedies are being considered within the textile processing sector to reduce the effluent pollution and to fulfill the environmental regulations. This paper is a part of such efforts and presents results where cotton fabrics pretreated with plasma -nano chitosan and reactive dyeing carried out without salt. In this work, a plasma and chitosan nanoparticles was used for developing salt free ecofriendly dyeing. The effect of plasma and chitosan nanoparticles in colour strength (K/S value), colour difference, colour fastness to crocking and washing of the dyed cotton fabric was in-vestigated. The cotton fabric treated with plasma and 0.3 per cent nano chitosan had higher K/S values.

Key words : Chitosan nanoparticles, colour strength, cotton, plasma, reactive dye

Cotton fibers are widely applied in textile industry due to its excellent properties of hygroscopicity, air permeability, biodegradability, no static electricity, etc. The dyeing of these fibers are generally dyeing with reactive dyes due to its brilliancy, variety of hue, high wet fastness, convenient usage and high applicability. These reactive dyes contain a reactive group, that, when applied to a fiber in an alkaline dye bath, forms a chemical bond with hydroxyl 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 some problems, such as low dye utilization, large amount of electrolyte used and high volume of waste water discharged, always exist in the application of reactive dyes. The dyeing of one kg of cotton with reactive dyes demands from 70 to 150 l water, 0.6-0.8 kg NaC1 and from 30 to 60 g dyestuffs. Due to these problems this class of dyes is the most unfavorable one from the ecological point of view, these effluents produced gives high values of TDS and increases salinity of the rivers affects the delicate biochemistry of aquatic life. More than 80,000 t of reactive dyes are produced and consumed each year, making it possible to quantify the total amount of pollution caused by their use. Therefore, the better approach would be to improve the textile technologies and chemistry for reducing the discharge pollution. Plasma treatment of textiles has been investigated as an alternative wet chemical fabric treatment and pretreatment processes. Glow discharge plasma of oxygen, nitrogen, ammonia etc. introduces functional groups like hydroxyl, peroxides, and amines on polymer surface. The technique of plasma treatment is an effective surface modification method to save processing costs and to avoid environment 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 effect of plasma and chitosan nanoparticles on cotton reactive dyeing and possibilities to reduce the colourants and chemical auxiliaries in the dyeing effluents

MATERIALS AND METHODS

The grey cotton fabric for dyeing having the specification of 140 g/ m2, warp 34 threads /cm, yarn count 40/1, weft 33 threads/cm was used. Two reactive dyes namely; C.I. Reactive Red 66 and C. I. Reactive Black 5 were purchased. Chitosan was provided by Indian Sea Food Industry, Cochin. (Degree of deacetylation (DD) = 92.5 per cent, molecular weight=1000kD. All other reagents are commonly used laboratory reagent grade.

Low temperature plasma treatment : The cotton fabric was treated with using low pressure glow discharge plasma. The DC glow discharge was operated at a pressure of 0.5mbar air was admitted into the plasma chamber using needle valve to control the pressure. The distance between electrodes is 0.2 cm. The samples were placed between electrodes and treated on both sides, each side for 60s (60s x 2). In all treatments, a uniform glow discharge plasma system operating under atmospheric condition with air used as a processing gas, with a power of 450 W. Due to interactions between air and activated surface, plasma treated fabric was conditioned for 24 h at standard atmospheric condition as per ISO 139 test method.

Preparation of chitosan nanoparticles: Typically, chitosan was dissolved in a dilute aqueous acetic acid solution of 0.5 per cent (w/v), under magnetic stirring. Aqueous ammonia was then dropped into the chitosan solution to precipitate the chitosan. The obtained gellike 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 icewater bath. Finally, a milky emulsion was obtained.

Pretreatment of cotton with nano chitosan : Cotton fabrics were soaked for 15 min in the emulsions with different concentrations separately: 0.01, 0.05, 0.1, 0.3 and 0.5 per cent (w/v). The padding processes were then completed with pick up weight of around 80 per cent. Finally, the cotton fabrics were dried at 80 °C for 3 min and cured at 150 °C for 3 min.

Reactive dyeing : In a dye bath containing 3 per cent of CI Reactive Red 66 or CI Reactive Black 5 with liquor ratio 1:30, cotton fabric was added at 35 ºC and the temp is raised to 60 ºC and 80 ºC for RR 66, RB5, respectively, over 20 min. L.R 1:30 is used due to maximum depth of shade on fabric. After that time the dyeing is continued for 30 min. Then 5 g/l and 8 g/l of updated soda ash added portion wise and the dyeing is maintained for further 45 min. For comparison, conventional dyeing carried out in untreated cotton fabrics.

Evaluation of the dyed cotton fabrics : The colour 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.

RESULTS AND DISCUSSIONS

Colour strength : K/S value of a dyed material has a close relationship to the amount of dye absorbed by the fabric. K/S values of pretreated with nano chitosan cotton dyed samples with Reactive Red 66 and Reactive Black 5 are shown in Table 1. Regarding Table 1, it can be concluded that the K/S values of chitosan treated dyed fabrics are higher than that of untreated dyed samples. As the chitosan concentration increases, the dye uptake also increases (Shin and Yoo, 1998).

The pre treatment of cotton fabric with air plasma created more aldehyde groups on the fabric surface and the following reductive ammination with chitosan afforded stable C–N bonds between cellulose and chitosan chains. The attachment of chitosan to the fabric considerably improved dye uptake of reactive dyes resulting in greater dye exhaustion and the colour strength (K/S). The enhanced dye ability 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 involved in the adsorption of anionic chromospheres of reactive dyes. The improved dye ability is postulated due to the presence of amide groups available from the polyacrylamide which also tends to improve the reactivity of cellulosic substrate. 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 (Shahidi *et al.,* 2007).

Table 1. K/S values of dyed cotton pre treated with nano chitosan

Dyes	Chitosan concentration (%)	~E	K/S concent-ration (%)
	0	-	8.246
Reactive	0.01	0.943	8.996
Red 66	0.05	1.276	9.724
	0.1	1.510	10.967
	0.3	2.136	13.189
	0.5	2.0897	13.023
	0	-	5.985
	0.01	0.543	6.402
Reactive	0.05	0.786	7.045
Black 5	0.1	1.023	8.186
	0.3	1.563	9.095
	.3	.3	.95
	0.5	1.560	9.057

It can be concluded that colour strength value of cotton fabric has increased in plasmanano chitosan pretreatment.

Table 2. K/S values of dyed cotton pre treated with plasma nano chitosan

Dyes	Chitosan concent-ration (%)	~E	K/S concentration (%)
	0	-	8.246
Reactive	0.01	0.989	9.259
Red 66	0.05	1.376	9.924
	0.1	1.623	11.257
	0.3	2.316	13.789
	0.5	2.289	13.223
Reactive		-	5.895
Black 5		0.596	6.802
		0.875	7.243
		1.223	8.656
		1.633	9.205
		1.606	9.155

Fastness properties : Textiles are subjected to frequent treatments such as washing and exposure to light during their usage. As the durability of the finish applied on the textile material is extremely important in these conditions, it has been assessed and is given in Table 3 for both reactive dyes, respectively.

Table 3. Colour fastness properties

Dyes	Chitosan concentration (%)	Wash fastness		Wet rub fast ness	Light fastness
		Colour change	Staining on cotton		
	0	4	4-5	3-4	4
	0.01	4	4-5	4	4
Reactive	0.05	4	4-5	4	4
Red 66	0.1	4	4-5	4	4
	0.3	4	4-5	4	4
	0.5	4	4-5	4	4
	0	4	3-4	2-3	4
	0.01	4	4	3	4
Reactive	0.05	4	4	3	4
Black 5	0.1	4	4	3	4
	0.3	4	4	3	4
	0.5	4	4	3	4

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 also indicative through the fastness properties wash fastness. The fastness values of all such dyed samples are quite satisfactory and comparable with those of conventional dyed samples (Allegra, 2006).

Table 4. Physical properties of nano chitosan pre treated cotton dyed fabrics

Dyes	Chitosan concentration (%)	Tensile strength (N)	Air permeability ($l/m^2/s$)
	0	351.5	480.5
	0.01	347.4	367.5
Reactive	0.05	345.6	352.7
Red 66	0.1	342.2	345.2
	0.3	340.8	333.9
	0.5	339.9	331.7
	0	350.7	478.5
	0.01	347.9	356.5
Reactive	0.05	345.2	352.7
Black 5	0.1	344.2	343.2
	0.3	343.5	339.3
	0.5	341.9	338.2

Physical properties : It is inferred from the Table 4 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 (Di *et al.,* 2011.

It is also obvious from Table 5 that tensile strength loss is higher in plasmanano chitosan pretreated cotton dyed fabric. The loss of strength is mainly due to the oxidation of atmospheric plasma on cotton fabrics (Lili and Wei, 2009).

Table 5. Physical properties of plasma nano chitosan pre treated cotton dyed fabrics

Dyes	Chitosan concentration (%)	Tensile strength (N)	Air permeability ($l/m^2/s$)
Reactive Red 66	0	351.5	480.5
	0.01	330.5	349.5
	0.05	328.4	346.7
	0.1	326.9	342.1
	0.3	325.5	331.9
	0.5	324.3	330.7
Reactive Black 5	0	350.7	478.5
	0.01	329.1	348.5
	0.05	327.2	347.3
	0.1	326.4	342.6
	0.3	324.6	338.9
	0.5	323.8	338.0

Comparative effluent analysis : Data in Table 6 shows that resulted 65 per cent TDS reduction in the effluent of CI Reactive Red 66

Table 6. TDS of nano chitosan treated dyeing effluents

Dye (30g/l)	Sample	TDS
CI Reactive	Untreated sample[ams]	1360
Red 66	Chitosan treated[s]	510
CI Reactive	Untreated sample	1420
Black 5	Chitosan treated sample	595

Table 7. TDS of plasma nano chitosan treated dyeing effluents

Dye (30g/l)	Sample	TDS
CI Reactive Red 66	Untreated Sample	1360
	Chitosan Treated samples	450
CI Reactive Black 5	Untreated Sample	1420
	Chitosan Treated Sample	510

and 55 per cent reduction in the case of CI Reactive Black 5 in nano chitosan treated cotton dyeing.

Table 7 shows reduction of 68 per cent TDS in the effluent of CI Reactive Red 66 and 64 per cent reduction in the case of CI Reactive Black 5 in plasmanano chitosan treated cotton dyeing.

The lower per cent reduction in TDS for CI Reactive Black 5 was due to the higher concentration of alkali needed to obtain optimum colour fixation and ultimate colour yield (Di *et al.,* 2007).

CONCLUSION

In this research work, cotton fabrics were treated with plasma and different amounts of chitosan nanoparticles and reactive dyeing carried out without salt. It was found that for both reactive dyes, plasma nano chitosan pre treatment resulted significant colour yield of cotton fabric. Pre treatment of cotton with atmospheric plasma introduce functional group in cotton surface which enhance chitosan binding in cotton surface. Reactive dyes can be much more efficiently exhausted onto cellulosic fabrics under neutral conditions in absence of salt due to change of electro kinetic (zeta) potential of chitosan treated samples. Moreover, colorfastness properties to washing and wet crocking of the treated cotton samples with plasma and nano chitosan were improved. Dyeing effluent showed enormous reduction of total dissolved solid content (TDS) which is significance requirement for textile industry.

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Received for publication : May 2, 2015
Accepted for publication : December 19, 2015