ADSORPTION OF REACTIVE DYES ON COTTON FABRICS TREATED BY CHITOSAN

TranThi Minh Kieu, Son-TaeWon, Cho-JinWon, Kim-TaeSon, and *Kwon-OhKyung

Yeungnam University, Korea; *Shun Pung Textile Co,Ltd, Korea

INTRODUCTION

Chitosan is the deacetylated derivation of chitin that is the second most abundant polysaccharide found on the earth, a main component in the shells of crustaceans. Because of chitosan's valuable properties, chitosan has been applied in and many fields, in textile industry with wet processing that includes dyeing and finishing cotton fabrics with reactive dyes and other fabrics and materials with variety of dyestuff[7,11,12] Reactive dyes, in the one hand, they are widely used for dyeing cotton fabrics because of their complete color range and ease of application as much as the brilliancy and high wet fastness properties. A reactive dye has at least one functional group that can covalently bond to the hydroxyl groups of the cellulose polymer, thereby fixing the dye molecule to the substrate. In the other hand, they are low affinity between dyes and fibers which leads to weak medium exhaustion, and the existence of some limitations in complete fixation of dyes[1,2] such hydrolysis of dyes during dyeing process, incomplete reaction between fibers and dye. Recently, many researches have focused on the application of chitosan as an auxiliary step in dyeing and finishing of textile materials. As going along, this paper examines different Chitosan concentrations padding on different weight of cotton fabrics and their color yield resulted by reactive dye.

EXPERIMENTAL

Materials: We used 2 types of cotton fabric weighted variety, they are: 189.97g/m^2 (cotton A: lighter but denser woven), and 248.46g/m^2(cotton B: heavier but looser woven). Fabrics were used without further treatment. A commercial grade Chitosan 12.6 cps obtained from TaeHun company was used. Levafix Golden Yellow E G 150% gran (no C.I. number), Levafix Royal Blue E FR(no C.I number). All reactive dyestuffs are in the commercial grade and supplied by DyStar - Korean. Other reagents used were of laboratory grade.

PROCEDURES

Fabric preparation: Chitosan(12.6 cps) solution treatments were prepared in different concentration of Chitosan as: 0.1%, 0.3%, 0.6%, 0.9%, 1.2%, 1.5%, and 1.8% Chitosan in the appropriated Acetic Acid. Those chitosan solutions were totally solute after 24 hours under stirring condition. Then each solution was filtered to remove any insoluble material.

The fabric samples were padded by processing in the laboratory.

Dyeing: The dye structure of this monofunctional dyestuff was not revealed, the dyeing temperature and electrolyte salt added was adjust as the supplier recommendation. All dyeing procedure was carried out at the liquor ratio of 1:50. From the room temperature, water in dye bath was raised to 50^0C and kept constant during the reactive dyeing process. The samples were wetted before added into dye bath. After a dyeing time, each sample was rinsed thoroughly in warm water till clear, and air dried.

Measurement of the dyebath exhaustion (%E): At the end of each dyeing time controlled dye bath, the fabric was squeezed to return surplus dye liquor to the dye bath and the dye bath then allowed to cool to room temperature. The absorbance spectra of an appropriately diluted aliquot of the cool, residual dyebath was measured using Carry 5000UV Vis NIR Spectrophotometer at the $\bullet_{max}$ of the dye. We can calculate the dye uptake as the following formula:

$$\text{Dye uptake } (\%E) = (A_0 \quad A)/A_0 * 100 \qquad (1).$$

(Ao is the absorbance of the original dye bath prior to dyeing, A is the absorbance of the residue dye bath after dyeing).

Color measurement of dyed fabrics:

The reflectance value (K/S) of each dry, dyed sample was measured by the CCM (Computer Color Matching) model X Rite 8200, wherein the CIE tristimulus values were obtained under CIE illuminant and observer conditions of D65/10^o. The fabric sample was folded in such way four layers of material were realized; four different measurements were made on the same side of the sample. We can calculate the K/S value of dyed fabrics (is the directly proportional to the concentration of colorant present in the substrate) using Kubleka Munk equation:

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

(R is reflectance value at $\bullet_{max}$ of each dye at which the reflectance value is the lowest, K is Absorption Coefficient; S is Scattering Coefficient)

RESULTS AND DISCUSSION

Cotton fabric does not absorb dye uniformly and creates small light colored or white spots[11], this is the result of the small groups of immature cotton fibers known as neps. The application of chitosan can improve the dyeability of these cotton fabrics. Lim[11] and other author[3] postulated that the affinity of chitosan to cotton would be by Van der Waals' forces between them because of the similar structures of chitosan and cotton[12].

Doctor Lim also mentioned for the binding chitosan to cellulose was crosslinking by formation of Schiff base between cellulose's reducing end(CO H) and the amino group of chitosan, in addition to the important role of hydrogen bonding. Though the application of chitosan by pad dry method was the most effective method in term of color yield achievement in reactive dye[3,4,5,11], it is still some unevenness dyeing on the fabris because of the migration of the chitosan during drying.Chitosan treatment on cotton using

pad dry method is the most efficient one[3,13]. The dye binding properties of chitosan has been studied and it is reported that chitosan has an extremely high affinity for many classes of dyes including reactive dyes[12]. Chitosan can easily absorb anionic dyes such as direct, acid, and reactive dyes by electrostatic attraction due to its cationic nature in an acidic condition. In addition, it was suggest that[11] the Amino groups of chitosan reacted with reactive group in the dye and the fixation was further improved. In the dyeing bath condition, reactive dyes could form a covalent bond with cellulose to form:

$$\text{Dye} \quad \text{X (leaving group)} + \text{HO} - \text{Cell} \rightarrow \text{Dye} - \text{O} - \text{Cell} + \text{HX} \quad \text{(i)}$$

At the same time, reactive dyes undergo hydrolysis with water to form:

$$\text{Dye} \quad \text{X (leaving group)} + \text{HO H} \rightarrow \text{Dye} - \text{OH} + \text{HX} \quad \text{(ii)}$$

All samples were individually dyed with 1.5% Levafix blue and yellow dyes. The K/S of the dried dye samples, were calculated by the equation(2). K/S values were made for all samples at different dyeing time. Results in figure[1] showed the highest K/S value for reactive blue dye was at 60 minute dyeing time, while 30 minute dyeing time for golden yellow. Concentration of chitosan treatment onto cotton had much effect through K/S values, the highest value achieved was major at 1.5% - 1.8%, some was peak at 1.2% or 0.9% chitodan treatment. The values showed there was a comparable of cotton treated by chitosan to untreated cotton as in table[1]. Result also faced that the denser the fabric, the lower K/S value calculated.

	royal blue								yellow							
	40'A	40'B	50'A	50'B	60'A	60'B	70'A	70'B	10'A	10'B	20'A	20'B	30'A	30'B	40'A	40'B
No cs	19.67	18.86	18.60	21.63	18.62	22.48	18.54	22.96	9.38	12.68	10.16	11.81	10.44	11.65	10.11	12.35
0.1%cs	20.11	23.10	19.93	24.14	20.75	23.64	19.09	23.64	10.03	13.55	10.11	13.34	10.44	12.35	11.11	13.55
0.3%cs	20.56	23.64	20.75	25.05	21.94	25.75	20.47	25.19	11.61	13.94	12.64	13.85	11.33	14.08	10.97	13.59
0.6%cs	20.84	24.78	20.94	25.05	22.05	24.14	21.13	25.75	11.65	14.69	12.46	13.85	12.64	14.17	11.61	15.14
0.9%cs	22.71	25.61	22.93	25.05	22.05	25.6	22.60	25.19	11.98	14.35	13.22	13.76	12.35	14.35	11.97	15.41
1.2%cs	22.48	24.92	21.03	25.75	22.70	25.46	23.52	26.33	12.98	15.35	13.14	16.96	13.26	14.64	12.32	16.25
1.5%cs	22.38	28.25	23.04	27.74	23.28	27.26	24.40	26.48	12.39	17.88	14.12	16.09	13.34	17.42	13.34	18.69
1.8%cs	23.52	27.10	22.94	26.79	24.39	28.77	22.48	28.60	12.64	16.01	13.68	16.37	13.34	16.74	12.30	18.02

Table 1: K/S values measured of dyed samples at the dyeing time which approximately high adsorption achieve

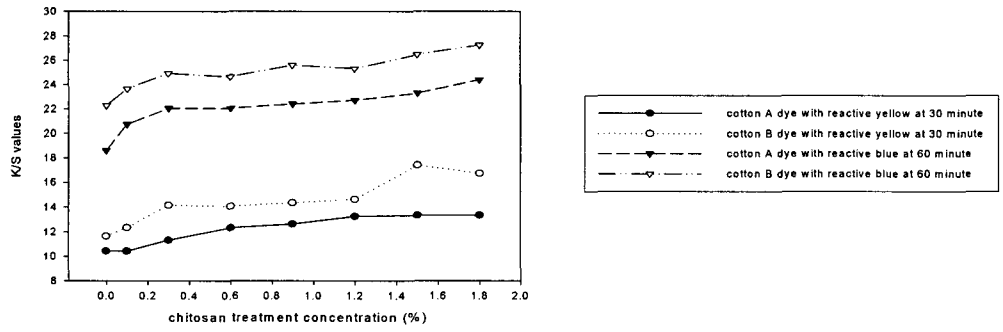

Figure 1: K/S value of dyed samples with reactive yellow and blue

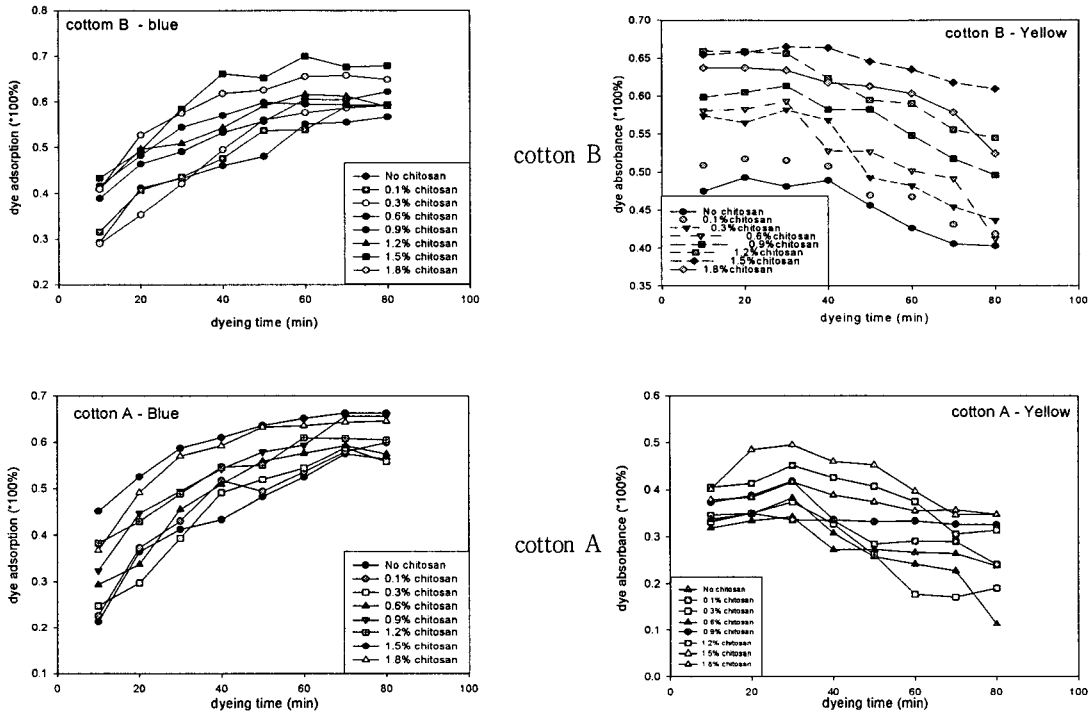

Figure 2: adsorption of treated and untreated cotton according to dyeing time

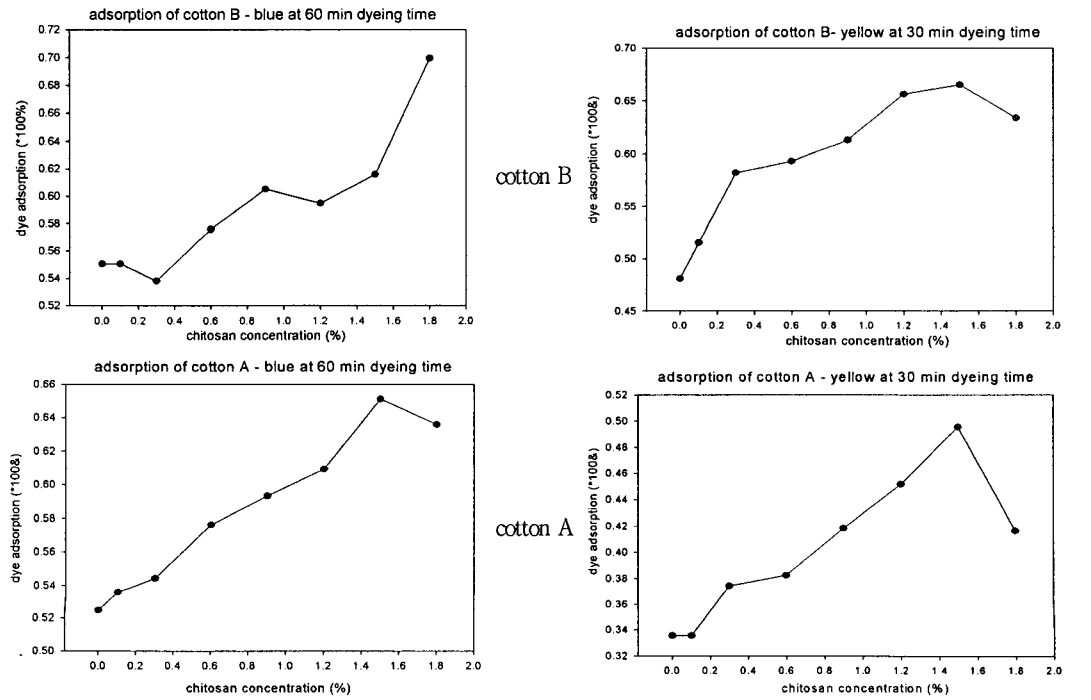

Figure 3: dye adsorption at the peak dyeing time of each reactive dye according to chitosan concentration

	10'	20'	30'	40'	50'	60'	70'	80'
No cs	0.889	0.86	0.892	0.768	0.734	0.74	0.712	0.743
0.1%cs	0.74	0.746	0.814	0.674	0.65	0.633	0.638	0.595
0.3%cs	0.714	0.71	0.728	0.640	0.573	0.618	0.522	0.534
0.6%cs	0.678	0.658	0.634	0.587	0.540	0.574	0.425	0.480
0.9%cs	0.653	0.582	0.55	0.557	0.504	0.514	0.437	0.47
1.2%cs	0.565	0.580	0.533	0.496	0.509	0.483	0.377	0.434
1.5%cs	0.56	0.515	0.519	0.498	0.511	0.488	0.407	0.43
1.8%cs	0.545	0.51	0.513	0.476	0.512	0.516	0.403	0.441

cotton B – Blue

	10'	20'	30'	40'	50'	60'	70'	80'
No cs	0.66	0.618	0.53	0.527	0.505	0.43	0.434	0.78
0.1%cs	0.638	0.607	0.547	0.524	0.49	0.43	0.43	0.775
0.3%cs	0.65	0.6	0.52	0.511	0.18	0.43	0.42	0.734
0.6%cs	0.64	0.62	0.54	0.503	0.52	0.47	0.422	0.769
0.9%cs	0.58	0.667	0.63	0.594	0.52	0.5	0.445	0.786
1.2%cs	0.72	0.67	0.65	0.626	0.56	0.51	0.458	0.811
1.5%cs	0.747	0.71	0.68	0.639	0.6	0.558	0.480	0.808
1.8%cs	0.75	0.73	0.7	0.74	0.63	0.57	0.49	0.821

cotton B– yellow

	10'	20'	30'	40'	50'	60'	70'	80'
No cs	0.988	0.977	0.946	0.888	0.85	0.776	0.69	0.795
0.1%cs	0.799	0.788	0.883	0.833	0.695	0.717	0.596	0.639
0.3%cs	0.738	0.716	0.762	0.654	0.635	0.642	0.519	0.54
0.6%cs	0.713	0.607	0.639	0.616	0.575	0.570	0.49	0.512
0.9%cs	0.650	0.636	0.604	0.554	0.529	0.565	0.457	0.462
1.2%cs	0.597	0.58	0.573	0.532	0.511	0.491	0.438	0.457
1.5%cs	0.53	0.528	0.517	0.512	0.432	0.493	0.423	0.448
1.8%cs	0.548	0.504	0.556	0.534	0.432	0.496	0.424	0.445

cotton A – Blue

	10'	20'	30'	40'	50'	60'	70'	80'
No cs	0.85	0.822	0.84	0.833	0.787	0.748	0.748	0.456
0.1%cs	0.83	0.818	0.818	0.819	0.77	0.737	0.737	0.456
0.3%cs	0.82	0.835	0.786	0.776	0.73	0.689	0.689	0.46
0.6%cs	0.95	0.836	0.846	0.870	0.835	0.722	0.722	0.48
0.9%cs	0.914	0.899	0.929	0.933	0.84	0.745	0.745	0.486
1.2%cs	0.921	0.891	1.03	0.953	0.838	0.785	0.786	0.5
1.5%cs	0.924	0.892	1.04	0.970	0.846	0.872	0.872	0.53
1.8%cs	0.958	0.954	1.017	1.11	0.846	0.862	0.862	0.598

cotton A – yellow

Table 2: UV spectraphotometer of residue dye liquor

The residue dye liquor(table 2) was calculated by formula(1) to get the dye adsorption, at different concentration of chitosan, the value of dye adsorption at dyeing time were different. Reactive blue dye residue liquor was lowest after 60 minute of dyeing process, while, the reactive yellow was achieved at dyeing time of 30 minute. The comparison between the cotton fabric and chitosan treated samples were the percentage of dye adsorption as in figure 3 . The 1.2%, 1.5%, 1.8% chitosan were taking turn to be the best choice with the line almost placed overtop in all plots, though, .5%chitosan treatment should be recommended for the best results for both fabrics and colors

CONCLUSION:

This study examines the color rate of adsorption with reactive dye on cotton fabric treated by Chitosan. For understanding how chitosan effects on different fabric, 100% woven cotton fabrics in two different weights were pretreated with chitosan by pad dry method, then after, different concentrations of Chitosan were used in order to achieve the suitable concentration that can apply on cotton fabric. There is no doubt that the dey adsorption of reactive dye on cotton treated Chitosan is greater than that on untreated cotton, and the higher concentration of chitosan, the possible better value. As the results ranged 1.5%cs were the most effect concentration of chitosan applied on cotton fabric. Another notice that the denser the fabric the lower effect in color adsorption as well as K/S values.

REFERENCE

1. Z. Bahrini, S.M. Burkinshaw. "A study of the Dyeing of Cotton with commercial Dichlorotriazyl Reactive Dyes". *Dyes and Pigments*, 27 (3), 1995,169-182

2. Marija G. "Dye-fibre bond stabilities of some reactive dyes on cotton". *Dyes and Pigments* 40 1999, 225-233
3. Shadi Houshyar, S. Hossein A."Treatment of cotton with Chitosan and its effect on Dyeability with Reactive dyes". *Iranian Polymer Journal*, 11 (5), 2002, 295-301
4. Sang-Hoon Lim, Samuel M Hudson, " Application of a fiber-reactive chitosan derivative to cotton fabric as a zero-salt dyeing auxiliary", *Color. Technol.*, 120, 2004, 108-113
5. Min-Ji Kim, " crosslinking of cotton fabric and chitosan by Epicholohydrin in a Mercerizing Process", Book of paper: *Proceedings of the first International conference on clothing and textiles, Teagu -Korea 2004*, 99-102
6. Yasuyo Okada, Fumiko F. "Environmental effects of oxygen on the fading of Monochlorotriazinyl Reactive dyes on cotton fabrics", *Dyes and Pigments*, 37(1) 1998, 169-182
7. MR Julia, E Pascual, "Influence of the molecular mass of chitosan on shrink-resistent and dyeing properties of chitosan treated wool", JSDC, 116, 2000, 62-67
8. Mehmet kanik, Peter J Hauser, "printing of cationised cotton with reactive dyes", *Color. Technol.*, 118, 2002, 300-306
9. S.M. Burkinshaw & D. Katsarelias, "the wash-off of Reactive Dyes on Cellulosic Fibers. Part 4: The use of different alkalis with Monocholotriazyl Dyes on cotton", *Dyes and Pigments*, 35(3) 1997, 249-259
10. Younsook Shin, "Use of Chitosan to improve Dyeability of DP-Finished cotton (II)", *Journal of Applied Polymer Science*, 67, 1998, 1515-1521
11. Lim Sang-Hoon, "Synthesis of a fiber-reactive chitosan derivative and its application to cotton fabric as an antimicrobial finish and a dyeing-improving agent", PhD dissertations, 2003
12. Majeti N.V. Ravi Kumar, "A review of chitin and chitosan applications", *Reactive and functional polymers* 46 ,2000, 1-27
13. Sang-Hoon Lim, Samuel M Hudson, " Application of a fiber-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish", C*arbohydrate Polymers* 56, 2004, 227-234