CHAPTER III

RESULTS AND DISCUSSION

In this work, the method for enhancement of reactive dye uptake of cotton fabrics with chitosan was investigated. Chitosan was fixed onto the fabrics through series of reactions, oxidation and reductive amination before dyeing (**Figure 3.1**).

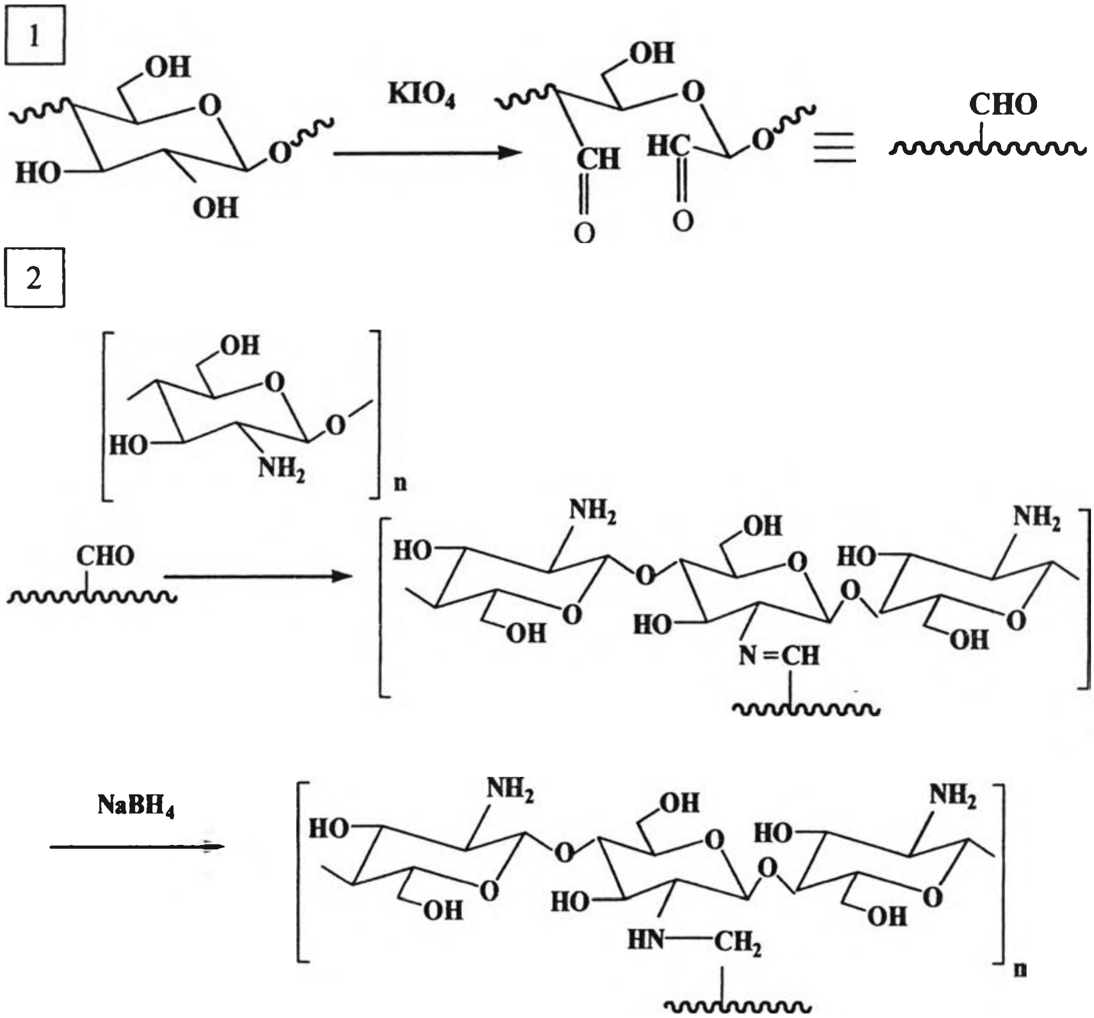


Figure 3.1 Reaction series, (1) oxidation and (2) reductive amination, for surface modification of cotton fabric with chitosan.

The first step was the oxidation of the bleached fabric (BF) with potassium periodate under acidic conditions to give oxidized fabric (OF) containing aldehyde groups which was confirmed by a chemical test with 2,4-DNP. In the subsequent step, the aldehyde groups in the OF were allowed to react with amino groups of chitosan to form iminic Schiff base followed by a reduction with sodium borohydride to generate secondary amine linkage between cellulose and chitosan in the chitosan reductive aminized oxidized fabrics (RCOF). The chitosan contents in the fabrics were determined from the nitrogen percentages obtained from Kjeldahl analysis. The changes in micro structure of the fabric surface were examined with scanning electron microscope. Bleached fabric soaked with chitosan solution (CBF) and bleached fabric reductive aminized with chitosan (RCBF) were also studied for comparison (**Table 3.1**).

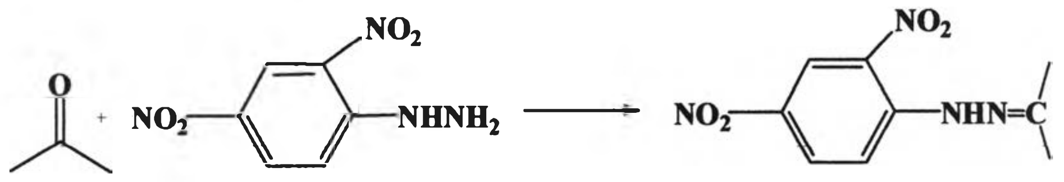
Table 3.1 Abbreviations for each fabric used in this thesis

Treatment on fabric	Abbreviation for fabric
bleaching	BF
oxidation with KIO_4 after bleaching	OF
reductive aminized with chitosan after oxidation	RCOF
reductive aminized with chitosan after bleaching	RCBF
soaking in chitosan solution after bleaching	CBF

3.1 Oxidation of cotton fabric

The early attempt to verify the conversion of cellulose to aldehyde cellulose utilized infrared (IR) spectroscopy. Neither the transmittance spectra obtained from KBr ground sample nor the reflectance (ATR-IR) spectra obtained directly from the fabric sample showed significant difference between the oxidized and unoxidized fabrics. The four different samples of fabrics, BF, OF, RCOF and RCBF generally gave almost identical IR spectra. We speculated that the unsuccessful analysis by IR-spectroscopy was probably due to the oxidation occurred only on the surface and the surface of fabrics was probably too rough to be suitable for the ATR-IR analysis. The low degree of oxidation on the surface comparing to the bulk quantity of the fabric also did not allow any observable change in the transmittance IR-spectra.

The analysis of aldehyde groups was opted to use a qualitative chemical testing method, treating the fabric samples with 2,4-dinitrophenylhydrazine reagent. The reaction of aldehydes and ketones with 2,4-dinitrophenylhydrazine to form the 2,4-dinitrophenylhydrazone probably represents the most studied and most reliable of all qualitative tests for the presence of carbonyl groups **(Figure 3.2)**. The deep orange color of 2,4-dinitrophenylhydrazone is very typical and easy to be observed. Both OF and RCOF clearly gave the positive orange color of the hydrazone while the BF and RCBF gave only light yellow color of the hydrazine reagent **(Figure 3.3)**. Interestingly, the test also showed deeper orange color for OF comparing to that for RCOF confirming the loss of some aldehyde groups on the fabrics upon reductive amination with chitosan.



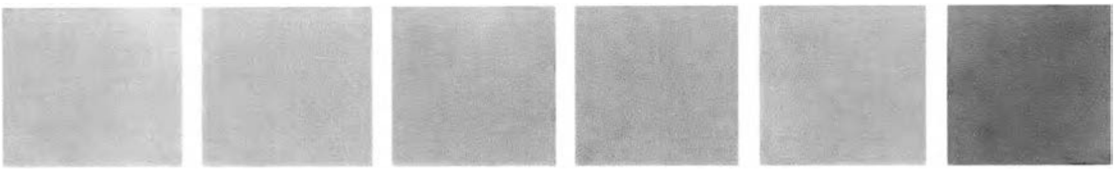
carbonyl group   2,4-dinitrophenylhydrazine   2,4-dinitrophenylhydrazone

Figure 3.2 The reaction of carbonyl groups with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazone.

a b c d

Figure 3.3 Chemical test with 2,4-DNP on (a) BF, (b) OF, (c) RCOF and (d) RCBF.

There have been literature reports on the oxidation of cellulose fabrics with H_2O_2 [18] and KIO_4 [19-24] to increase aldehyde groups on the fabric surface prior to the treatment with chitosan. The attempt to use hydrogen peroxide at 0.294 and 1.765 M to oxidize the cotton fabric followed by reductive amination with chitosan A ($M_v \sim$ 98,000, 79 %DD, 0.0154 M) (See Appendix D and E for analysis data of chitosan) by padding method. Chemical testing method was used to determine the formation of the aldehyde group. The fabric oxidized by H_2O_2 at various concentration and by $Na_2S_2O_8$ gave yellow color similar to the ordinary bleached fabric (BF) while the fabric oxidized by KIO_4 gave the positive orange color of the hydrazone **(Figure 3.4)**. Only KIO_4 was thus used as an oxidizing agent in the subsequent study.



a b c d e f

Figure 3.4 Chemical test with 2,4-DNP on (a) BF, fabric oxidized by (b) H_2O_2 0.294 M, (c) by H_2O_2 1.765 M, (d) by H_2O_2 0.01 M, (e) by $Na_2S_2O_8$ 0.01 M, (f) by KIO_4 0.01 M.

3.2 Reductive amination with chitosan

After oxidation with KIO_4, the cotton fabric was treated with chitosan B (M_v ~50,000, 84 %DD, 0.20 M) (See Apendix D and E for analysis data of chitosan) and $NaBH_4$ in an aqueous solution to create covalent linkages between cellulose and chitosan by reductive amination. The amount of chitosan attached to the surface of the fabric was determined from the nitrogen content using Kjeldahl analysis.

The nitrogen contents in five types of fabrics, namely, BF, OF, RCOF, RCBF and CBF were analyzed by Kjeldahl method **(Table 3.2)**. The chitosan contents were calculated from the nitrogen percentage using BF as a blank. RCOF, RCBF and CBF had significantly higher nitrogen contents than that of OF and BF confirming the presence of chitosan on the fabrics after the treatment of the fabric with chitosan solution. Only few percentages of chitosan observed suggested that the chitosan resided only on the surface of the fabrics.

To investigate on what type of interactions holding the chitosan chains to the cellulose surface, the fabrics were subjected to an alkaline solution (pH $\approx$ 11.0) at elevated temperature (60 °C), similar to the dyeing condition, and the nitrogen contents were reevaluated. RCOF and RCBF retained most of their nitrogen contents upon subjecting to the alkaline condition of the dyeing while CBF lost most of its nitrogen content **(Table 3.3)** indicating that the reduction step was necessary for keeping chitosan intact in such condition. It is thus reasonable to hypothesize that chitosan in CBF was probably attached to the fabric through iminic bonds and the reduction converted the iminic bonds into the more stable amine bonds in RCOF and RCBF. According to this hypothesis, some aldehyde groups must be present in the

BF. The presence of aldehyde groups in ordinary bleached fabric have been noted previously in literatures.[18] The oxidation of BF with KIO_4 prior to the treatment with chitosan under reductive amination increased the chitosan content in RCOF by 25% comparing to RCBF **(Table 3.2)**. This 25% difference was proven to be important for improving dyeing efficiency discussed in the subsequent section.

Table 3.2 Nitrogen and chitosan content in fabrics analyzed by Kjeldahl analysis

Fabric	Nitrogen content % w/w	Chitosan content % w/w
BF	0.094 (± 0.004)	0
OF	0.109 (± 0.012)	NA
RCOF	0.240 (± 0.001)	1.69
RCBF	0.212 (± 0.005)	1.37
CBF	0.239 (± 0.001)	1.68

The chitosan content = $162(N\text{-}N_b)/14$ where N is the nitrogen percentage, N_b is the nitrogen percentage of bleached fabric used as a blank. NA = not applicable as there was no treatment with chitosan; See Table B2 in Appendix B for analysis data of each sample.

Table 3.3 Nitrogen and chitosan contents in fabrics, after undergoing dyeing condition without dye, analyzed by Kjeldahl analysis

Treatment of fabric	Nitrogen content % w/w	Chitosan content % w/w
BF	0.094 (± 0.001)	0
RCOF	0.208 (± 0.003)	1.28
RCBF	0.189 (± 0.015)	1.06
CBF	0.122 (± 0.009)	0.29

The chitosan content = $162(N\text{-}N_b)/14$ where N is the nitrogen percentage, N_b is the nitrogen percentage of bleached fabric used as a blank. See Table B3 in Appendix B for analysis data of each sample.

3.3 Dye uptakes of fabrics in dyeing process

Dye uptakes of the fabrics were evaluated by using %exhaustion and color yield (K/S) was used to indicate the fixation performance of exhausted dyes. Two types of dyes, Evercion Blue H-ERD (a mono-chloro-triazine dye) and Remazol Red RB133 (a vinyl sulphone dye) were used in the dyeing. Among five types of fabrics, the RCOF had the highest %exhaustion and color yield **(Table 3.4)** indicated that the treatment of cotton fabric by KIO_4 oxidation and reductive amination with chitosan was the most effective way to enhance the dye uptake of the fabric. The RCBF also showed significant improvement in dye uptake comparing to BF but not as high as the RCOF due to its 25% lower chitosan content (see **Table 3.2**). CBF showed only slightly higher color yield (K/S) than that of BF in good agreement with the loss of chitosan content under dyeing condition observed in the previous section. OF showed even lower %exhaustion and color yield than that of BF, indicating the reduction of dye uptake of the fabric upon oxidation with KIO_4. Lower numbers of hydroxyl groups required for the reaction with the dye molecules may be the main reason for this decrease of the dye uptakes. The color intensity of dyed RCBF observed by eyes was clearly deeper than the other fabrics **(Figure 3.5)**.

Table 3.4 %Exhaustion and color yield K/S of fabrics dyed with Evercion Blue H-ERD and Remazol Red RB133

Fabrics	Evercion Blue H-ERD		Remazol Red RB133	
	%exhaustion	Color yield (K/S)	%exhaustion	Color yield (K/S)
BF	61.0	3.66	47.4	3.62
OF	47.9	2.38	41.1	3.20
RCOF	92.4	6.88	61.7	7.11
RCBF	71.5	4.68	48.5	5.00
CBF	-	-	48.0	3.90

Amount of dye = 4% owf, dyeing time = 45 min and LR = 60:1. Other dyeing condition for Evercion Blue H-ERD: [NaCl] = 70 g/l pH ≈ 10.5, Temp. = 80 °C and for Remazol Red RB133: [NaCl] = 60 g/l, pH ≈ 11.0, Temp. = 60 °C. See Table C1-C2 in Appendix C for the unprocessed data.

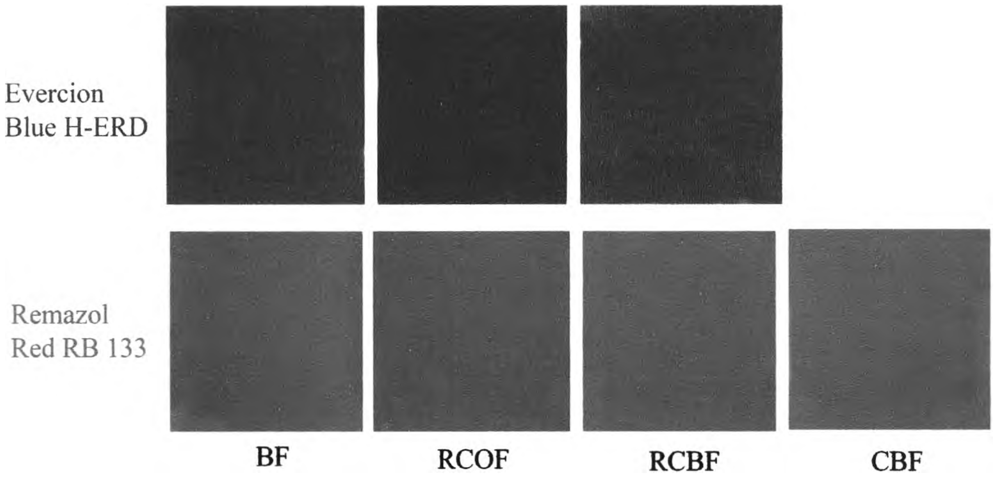


Figure 3.5 Photographs of dyed fabrics show different intensity of the colors.

3.4 Colorfastness of dyed fabrics

The dyed fabrics were tested for colorfastness to washing, water, acid perspiration, alkaline perspiration **(Table 3.5)**, rubbing **(Table 3.6)** and light **(Table 3.7)**. Generally, the colorfastness of the dyed RCOF and RCBF were comparable to that of BF with some slight differences observed in the tests of fastness to alkaline perspiration and wet rubbing where RCOF and RCBF showed slightly lower fastness resistance. The test results indicated that surface modification of cotton fabrics with chitosan through reductive amination prior to dyeing with reactive dyes did not posted discernable problem on colorfastness to the dyed fabrics.

Table 3.5 The tests for colorfastness of the dyed fabrics to washing, water, acid perspiration and alkaline perspiration

Fabrics dyed with Evercion Blue H-ERD

Color fastness	Fabrics	Color change	Color staining					
			acetate	cotton	nylon	polyester	acrylic	wool
Washing	BF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCOF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Water	BF	4-5	4-5	4	4	4-5	4-5	4-5
	RCOF	4-5	4-5	4	4-5	4-5	4-5	4-5
	RCBF	4-5	4-5	4	4-5	4-5	4-5	4-5
Acid perspira-	BF	4-5	4-5	4	4	4-5	4-5	4-5
	RCOF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
tion	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Alkaline perspira-	BF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCOF	4-5	4-5	4	4-5	4-5	4-5	4-5
tion	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Fabrics dyed with Remazol Red RB133

Color Fastness	Fabrics	Color change	Color staining					
			acetate	cotton	nylon	polyester	acrylic	wool
washing	BF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCOF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
water	BF	4-5	4-5	4	4-5	4-5	4-5	4-5
	RCOF	4-5	4-5	4	4-5	4-5	4-5	4-5
	RCBF	4-5	4-5	4	4-5	4-5	4-5	4-5
Acid perspira-	BF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCOF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
tion	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Alkaline perspira-	BF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	RCOF	4-5	4-5	4	4-5	4-5	4-5	4-5
tion	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Table 3.6 The tests for colorfastness of the dyed fabrics to rubbing

Dyeing with	Fabrics	Color staining			
		Warp direction		Weft direction	
		Dry	Wet	Dry	Wet
Evercion Blue H-ERD	BF	4-5	4	4-5	4
	RCOF	4-5	3-4	4-5	3-4
	RCBF	4-5	3-4	4-5	3-4
Remazol Red RB 133	BF	4-5	4	4-5	4
	RCOF	4-5	3-4	4-5	3-4
	RCBF	4-5	3-4	4-5	3-4

Table 3.7 The tests for colorfastness of the dyed fabrics to light

Dyeing with	Fabrics	Color change
Evercion Blue H-ERD	BF	3-4
	RCOF	3-4
	RCBF	3-4
Remazol Red RB 133	BF	3-4
	RCOF	3-4
	RCBF	3-4

3.5 Surface morphology

Different surface roughness patterns were observed among the SEM micrographs of the fabrics. The rifts appeared on the fibers of BF was rather uniform lying in one direction (**Figures 3.6**a and b) while that of OF was irregular (**Figures 3.6**c and d) signifying the surface oxidation. The treatment of BF with reductive amination with chitosan, without undergoing oxidation, to produce RCBF possessing fibers with less rifts and roughness with few submicron-sized crumbs(**Figures 3.6**e and f) suggesting a partial coverage of the cellulose fiber surface with chitosan. In RCOF, numerous submicron-sized crumbs clearly observed on the fibers surface (**Figures 3.6**g and h) coinciding with the higher amount of chitosan attached to the cotton fabric surface found in section 3.2.

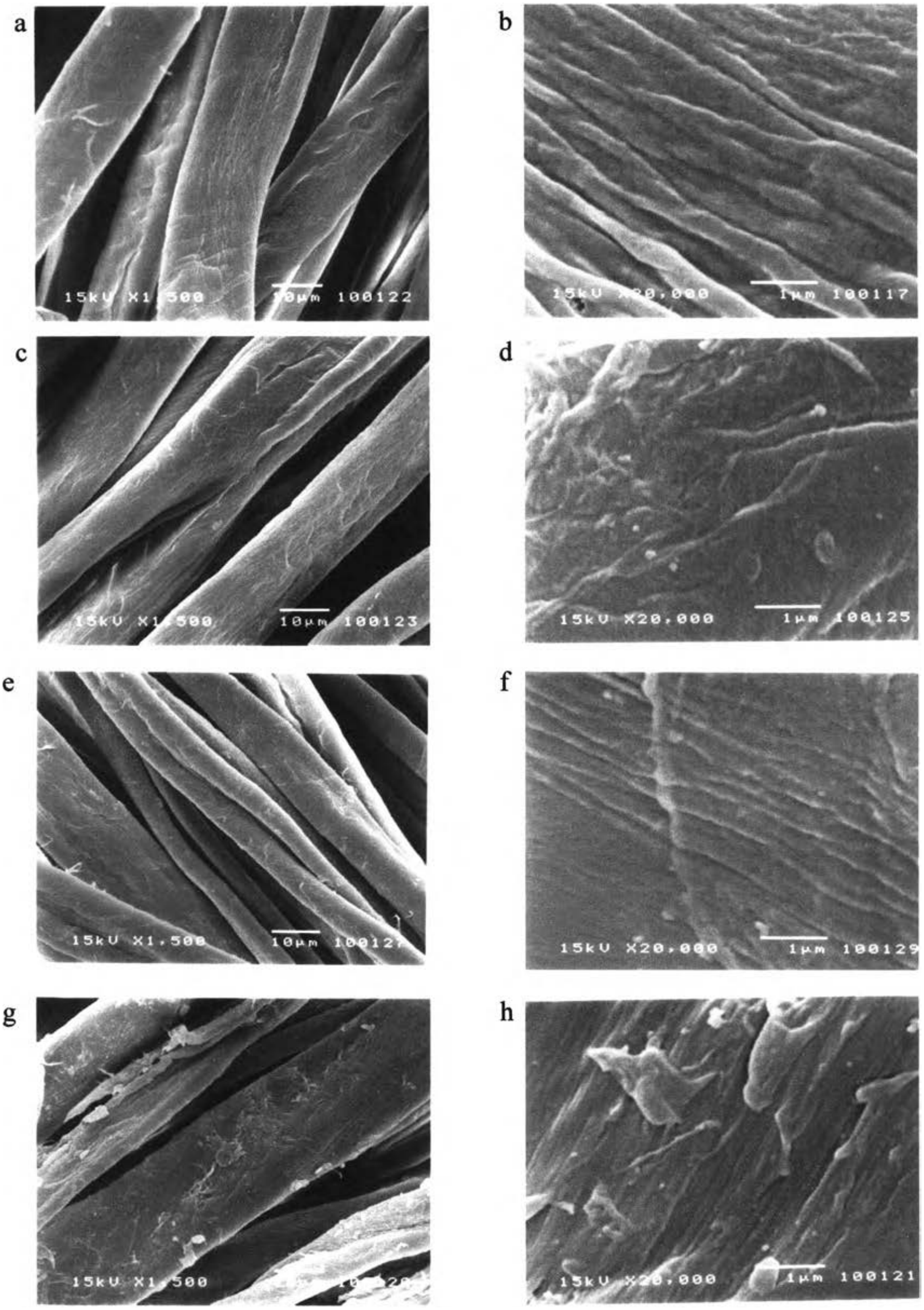


Figure 3.6 SEM micrographs of BF (a and b), OF (c and d), RCBF (e and f), and RCOF (g and h).

3.6 Effect of oxidation time on the dye uptake

The effect of oxidation time used for preparation of chitosan-modified cotton fabric on the dye uptakes was studied by using two indicative parameters, %exhaustion and color yield, obtained from the results of dyeing process. Both parameters clearly showed that the dye uptake of RCOF was greater than that of RCBF and the increase in oxidation time resulted in even greater dye uptake (**Table 3.8**). The results confirmed the generation of more aldehyde groups on the bleached fabric through KIO_4 oxidation resulting in the increase of chitosan attachment of the fabric and thus the dye uptake.

Table 3.8 The effect of oxidation time on %exhaustion and color yields in the dyeing of RCBF and RCOF

Fabric	Oxidation time (hours)	Evercion Blue H-ERD		Remazol Red RB133	
		% exhaustion	Color yield K/S	% exhaustion	Color yield K/S
RCBF	0	71.5	4.68	48.5	5.00
RCOF	1	90.6	5.31	54.5	5.59
RCOF	3	92.4	6.88	61.7	7.11
RCOF	10	95.9	10.26	62.6	9.45

Amount of dye = 4% owf, dyeing time = 45 min and LR = 60:1. Other dyeing condition for Evercion Blue H-ERD: [NaCl] = 70 g/l pH ≈ 10.5, Temp. = 80 °C and for Remazol Red RB133: [NaCl] = 60 g/l, pH ≈ 11.0, Temp. = 60 °C. See Table C3-C4 in Appendix C for the unprocessed data.

3.7 Effect of chitosan on dye adsorption in the exhaustion step

A hypothesis for the improvement of dyeability of the fabrics by the surface modification with chitosan lies on the theory that positively charged chitosan chain should increase the dye adsorption in the exhaustion step prior to the fixation step in the reactive dyeing process. To validate the hypothesis, the %exhaustion of Evercion Blue H-ERD dye by BF and by chitosan were compared. Chitosan powder indeed showed much higher dye exhaustion than the BF both in the absence and in the presence of NaCl (**Figures 3.7**a). As expected, dye exhaustion of RCOF and RCBF were between those of chitosan and BF (**Figures 3.7b**). Dye adsorption of RCOF was also clearly higher than that of RCBF that is in good agreement with the chitosan contents discussed in section 3.2. Dye adsorptions of chitosan and all the fabrics were higher in the presence of NaCl salt due to the reduction of charge repulsion between the fabric surface and the dye molecules by the increasing ionic strength. [3,10-12,28]

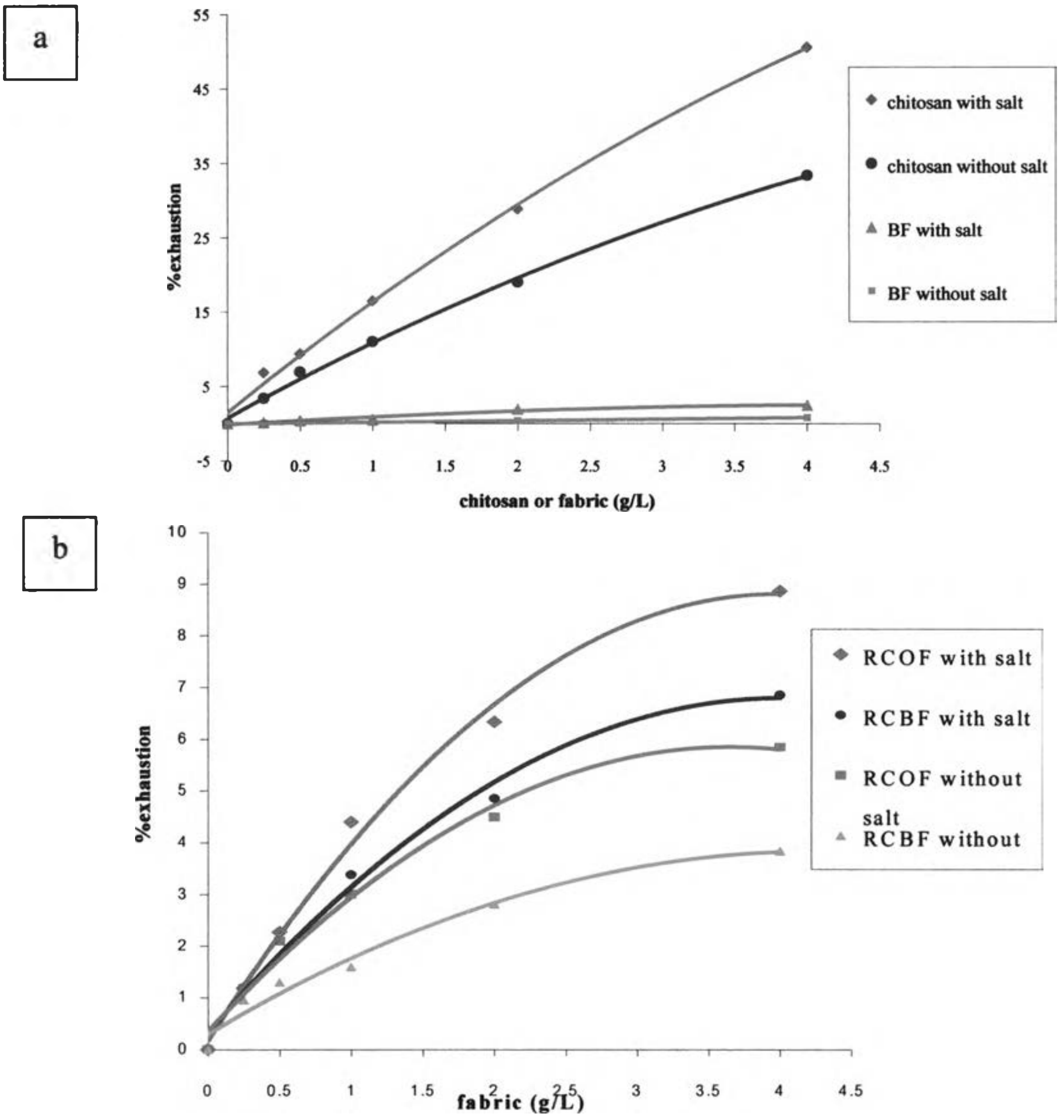


Figure 3.7 %exhaustion of Evercion Blue H-ERD dye as a function of the absorbent weight comparing between (a) BF and chitosan powder; (b) RCOF and RCBF in the absence and presence of sodium chloride salt (1.225 g/L). Exhaustion condition: [dye] = 0.007% w/v, pH ≈ 6, Temp. = 30 °C, Time = 1 h, LR 60:1. See Table C5-C12 in Appendix C for the unprocessed data.

Percent exhaustion of the dye by chitosan powder and cotton fabric (BF) in the presence of various amounts of sodium chloride salt showed that dye adsorption increased with the salt concentration **(Figure 3.8)**. The increased salt concentration affected the dye adsorption of chitosan slightly greater than the cotton fabrics (BF) as the slightly steeper slope was observed in the plot of %exhaustion againt the salt concentration for chitosan. The increase of dye adsorption in the higher concentration of salt was due to the reduction of dye solubility in water and the charge repulsion between the chitosan (or cellulose) and dye molecules.

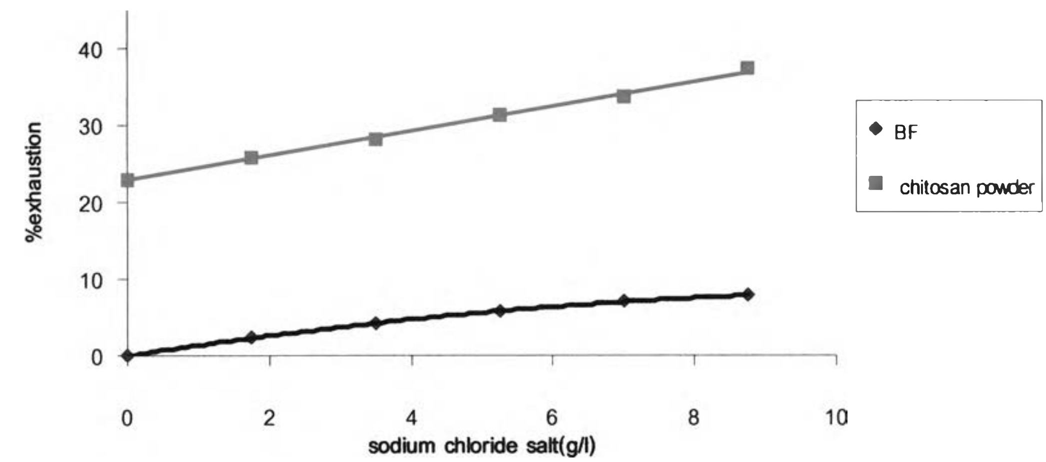


Figure 3.8 Effect of salt concentration on dye adsorption by chitosan powder and BF. Adsorption condition: [chitosan powder] and [BF] = 2 g/L, [dye] = 0.007%w/v, pH≈6, room temp, 1 h, LR 60:1. See Table C13-C14 in Appendix C for the unprocessed data.

3.8 Improved dyeing process

3.8.1 Dyeing RCOF with reduced amount of salt

RCOF dyed with Evercion Blue H-ERD and Remazol Red RB133 behaved similarly. Dyed RCOF had higher color yield (K/S) than that of dyed BF when using equal amount of salt. Dyeing under the condition with 50% reduction of salt on RCOF still gone slightly higher color yield (K/S) than that of dyed BF, but without salt (0 g/L NaCl) the color yield (K/S) of dyed of RCOF was very less than dyed BF **(Table 3.9)**. The higher %exhaustion was also observed for the dyeing process of RCOF when using equal of salt.

3.8.2 Dyeing RCOF with reduced amount of dye and salt

When the amount of dyes used in the dyeing process reduced by half and varying the reduced amount of salt, Evercion Blue H-ERD and Remazol Red RB133 gave similar results. RCOF dyed with either dyes at 14% reduction of salt or 50% reduction of dyes color yields (K/S) with those of dyed BF **(Table 3.9).** The results indicate that chitosan can improve the dyeing process in terms of lower amount of dyes and salt required and left in the waste water.

Table 3.9 The color measurement of dyeing RCOF with reduced amount of salt and dye compared with BF

Dyeing with	Fabrics	The amounts of sodium chloride		% exhaustion	Color yield (K/S)
		g/L	%reduction		
Blue H-ERD 4% owf	BF	70	-	61.8	3.66
Blue H-ERD 4% owf	RCOF	0	100	20.0	0.73
		35	50	73.6	4.45
		70	0	92.4	6.88
Blue H-ERD 2% owf	RCOF	35	50	70.4	2.61
		52.5	25	79.5	3.37
		60	14	99.4	3.70
Red RB133 4% owf	BF	60	-	47.4	3.62
Red RB133 4% owf	RCOF	0	100	26.3	0.88
		30	50	48.2	4.53
		60	0	61.7	7.11
Red RB133 2% owf	RCOF	30	50	50.0	2.51
		45	25	57.2	3.30
		50	14	62.6	3.68

Dyeing condition: [Evercion Blue H-ERD]= 2-4% owf, [NaCl]= 0-70 g/l, pH ≈ 10.5, 80 °C, 45 min and for Remazol Red RB133= 2-4% owf, [NaCl] = 0-60 g/l, pH ≈ 11.0, 60 °C, 45 min and LR 60:1, See information in Appendix C, Table C15-C16.

3.8.3 CIELAB measurement

As RCOF gave the most promising dyeing results, it was tested for CIELAB measurement. RCOF dyed with either Evercion Blue H-ERD and Remazol Red RB133 gave comparable L* a* b* values to the dyed BF **(Table 3.10), (Figure 3.9)**. The result clearly indicated that the chitosan-modified fabric can be dye at lower salt and dye concentration to give industrially acceptable color depth and hue.

Table 3.10 The CIELAB measurement of dyeing RCOF with reduced amount of salt and dye compared with BF

Dyeing with	Fabric	The amounts of sodium chloride		CIELAB		
		g/L	%reduction	L*	a*	b*
Blue H-ERD 4%owf	BF	70	0	41.77	-2.54	-29.29
Blue H-ERD 4%owf	RCOF	70	0	33.17	-0.39	-30.54
Blue H-ERD 2%owf	RCOF	60	14	40.27	-1.99	-29.56
Red RB133 4%owf	BF	60	0	46.98	59.64	4.53
Red RB133 4%owf	RCOF	60	0	40.02	58.95	7.78
Red RB133 2%owf	RCOF	50	14	47.51	59.17	3.87

Dyeing condition: [Evercion Blue H-ERD]= 2-4% owf, [NaCl]= 0-70 g/l, pH ≈ 10.5, 80 °C, 45 min and for Remazol Red RB133= 2-4% owf, [NaCl] = 0-60 g/l, pH ≈ 11.0, 60 °C, 45 min and LR 60:1.

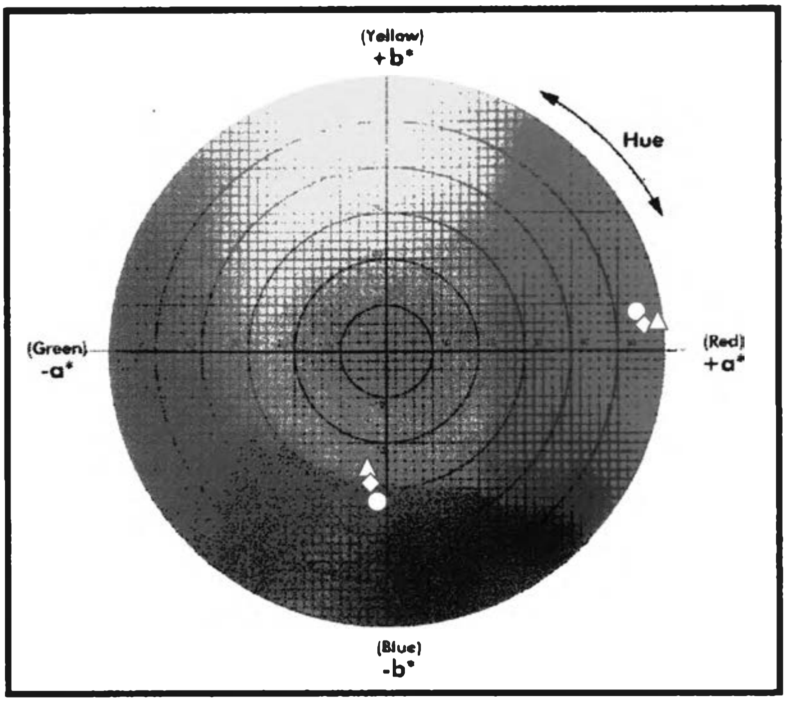


Figure 3.9 CIELAB color space of (△) BF dyed with Blue H-ERD at 4%owf, (○) RCOF dyed with Blue H-ERD at 4%owf, (◇) RCOF dyed with Blue H-ERD at 2%owf and (△) BF dyed with Red RB133 at 4%owf, (○) RCOF dyed with Red RB133 at 4%owf, (◇) RCOF dyed with Red RB133 at 2%owf.

3.9 Application of improved dyeing process under industrial dyeing condition

The fabrics were dyed under industrial dyeing condition whereas the liquor ratio was 10:1. Dyeing with Evercion Blue H-ERD and Remazol Red RB 133 gave similar results. Dyed RCOF had higher color yield (K/S) and %exhaustion than dyed BF when using equal amount of salt **(Table 3.11)**. When amount of dyes used in the dyeing process was reduced by half and the amount of salt was reduced by 14% RCOF still gave color yield (K/S) compared to that of dyed BF. The higher %exhaustion also indicates that lower amount of dyes remained in the waste water.

Table 3.11 The color measurement of dyeing RCOF with reduced amount of salt and dye compared with BF by using industrial condition.

Dyeing with	Fabrics	The amounts of sodium chloride g/L	The amounts of sodium chloride % reduction	% exhaustion	Color yield (K/S)
Blue H-ERD 4% owf	BF	70	-	87.97	4.06
Blue H-ERD 4% owf	RCOF	70	-	96.39	7.92
Blue H-ERD 2% owf	RCOF	52.5	25	96.04	3.46
		60	14	96.19	3.98
Red RB133 4% owf	BF	60	-	75.11	4.11
Red RB133 4% owf	RCOF	60	-	93.04	8.05
Red RB133 2% owf	RCOF	45	25	89.76	3.82
		50	14	91.63	4.01

Dyeing condition: [Evercion Blue H-ERD]= 2-4% owf, [NaCl]= 0-70 g/l, pH ≈ 10.5, 80 °C, 45 min and for Remazol Red RB133= 2-4% owf, [NaCl] = 0-60 g/l, pH ≈ 11.0, 60 °C, 45 min and LR 10:1, See information in Appendix C, Table C17-C18.