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APPENDICES

APPENDIX A

Enhancement of reactive dye uptake on cellulose fabric with chitosan

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Abstract

The pretreatment of cotton fabrics with chitosan improved the reactive dyes uptake and lowered the concentration of salt required in the dyeing process. Oxidation of cotton fabric with KIO_4 followed by reductive amination with chitosan led to the highest chitosan content in the fabric analyzed by Kjeldahl nitrogen analysis technique. The %exhaustion and color yield (K/S) in the dyeing process with mono-chloro-triazine and vinyl sulphone reactive dyes showed that this method of fabric modification considerably improved dye uptake of the fabric. The chitosan-modified fabric had no discernable adverse color fastness properties. The improvement of dye uptake brought about an improved dyeing process in which the dye and salt used could be reduced by half and 14% respectively.

Keywords: Chitosan; Reactive dye; Dye uptake; Oxidation; Potassium periodate

1. Introduction

The modification of fabrics with chitosan is interested in this work because of chitosan is a natural biopolymer, has a combination of many unique properties such as nontoxic, biodegradability and cationic nature. Amino groups of chitosan increase the attraction between the fibers and anionic dyes. This method enhances dye uptake, reduces the amount of dye used and also contribute to reduce the amount of salt used in dyeing. Various uses of chitosan for textile dyeing and finishing were reviewed in several papers.

Modification of cotton fabrics to improve the reactive dyes uptake can increase the utilization rate of the dyes and reduce the concentration of salt required for dyeing. Considerable attention has focused on the introduction of cationic groups, commonly quaternized amino groups, by means of pre-treatment of the cotton fibers and cotton fabrics to increase the attraction between the fibers and anionic dyes and so enhance the dye-fibers substantivity (Lewis & Lei, 1991; Broadmann, 1999; Burkinshaw, Mignanelli, Froehling & Bide, 2000).

As a polycationic polymer, chitosan was investigated to improve the dyeability of cotton fibers with reactive dyes by pad and exhaust processes (Shin & Yoo, 1998; Tahlwy, 1999; Lim & Hudson, 2004; Smith, 2004). Chitosan was applied after oxidation by hydrogen peroxide and subsequently stabilized by reducing agent such as sodium cyanoborohydride and sodium borohydride showed improved dyeability with reactive dyes (Weltrowski & Masri, 1996). The modification by oxidizing the cellulose fiber with potassium periodate and subsequent Schiff's base formation is highly specific reaction to convert 1,2-dihydroxyl group to a pair of aldehyde groups without significant side reaction and is widely used in structural analysis of carbohydrates (Varma, Jamdade & Nadkarni, 1985; Varma & Chavan, 1995; Kim, Kuga, Wada, Okano & Kondo, 2000; Liu, Nishi, Tokura & Sakairi, 2001; Varma & Kulkarni, 2002; Fras, Johasson, Stenius, Laine, Stana-Kleinschek & Ribitsch, 2005). The chitosan content was determined from the nitrogen percentage (Rose Scientific Ltd, 2006).

This work relates to a method for improving the dyeability of cotton fabrics with reactive dyes by treatment of the fabric prior to dyeing with an aqueous solution of chitosan. The first step, bleached cotton fabrics were first oxidized by potassium periodate to give dialdehyde cellulose which would possess the ability to couple with an amino group of chitosan after reacting with a chitosan solution in acetic acid to provide the formation of a Schiff's base and then stabilizing with sodium borohydride.

2. Experimental

2.1 Materials and equipments

Chitosan ($M_v \approx 50{,}000$, %DD = 84) was purchased from a local supplier in Thailand. The viscosity-averaged molecular weight (M_v) was determined from intrinsic viscosity $[\eta]$ using Mark-Houwink equation; $[\eta] = KM_v^a$ (Shoemaker, Garland & Nibler, 1989) and the degree of deacetylation (%DD) was determined by colloidal titration with potassium polyvinylsulfate (Wako, Japan). Bleached knitted cotton fabrics were used throughout this work. All dyes and auxillaries used were commercial grade. The main dyes used in the study were Evercion Blue H-ERD (monochlorotriazine dyes, C.I. Reactive Blue 160) (Everlight, Taiwan) and Remazol Red RB133 (vinylsulphone dyes, C.I. Reactive Red 198) (Dystar, Germany). Potassium periodate and 2,4-dinitrophenylhydrazine were obtained from Fluka, Switzerland. Sodium borohydride was obtained from Labchem, Australia. Anionic surfactant (Multinal H/C) was obtained from Winimex, Taiwan. The reflectance was measured on a ColorQuest XE Spectrometer (Hunter Lab, USA) with CIE 1964 supplemental observer using D65 illuminant with specular component. Chitosan content in the fabrics was analysed by Kjeldahl nitrogen analysis (Kjeltec KD-02 Tecator, Sweden). Scanning Electron microscrope (JSM-5410LV JEOL, Japan) was used to study microstructure of fabrics. UV-Vis Spectrophotometer (Jasco V-570) was used by measuring %exhaustion. Test devise for colorfastness tests were obtain from Sumet Labtest,Co,Ltd, Thailand.

2.2 Procedures

2.2.1 Oxidation of cellulose fabrics with potassium periodate

Three pieces of bleached cotton knit fabric (0.5 g, 4X5 cm^2 unless specified otherwise) were immersed in an aqueous solution of potassium periodate (0.031 M, 100 mL) at pH 5. The solution was shaken at 55 °C for designated period. The cotton fabric samples were washed repeatedly with copious amount of water (10X100 mL) and squeezed. The oxidized fabrics were used for the next reaction without further drying.

2.2.2 Reductive amination with chitosan

A chitosan solution was prepared by dissolving chitosan (1.0 g, 6.2 mmole) in 1% aqueous acetic acid solution (30 mL) at 60 °C. The oxidized fabric samples(0.5 g, 4X5 cm^2 unless specified otherwise) were immersed in a chitosan solution (30 min, 1%AcOH, 30 mL) under constant shaking at 60 °C for 2 h and then washed repeatedly with water (10X100 mL) to remove unreacted chitosan. The iminic bonds between the aldehyde group of the oxidized cellulose and amino group of chitosan was reduced by sodium borohydride solution (0.2 M, 30 mL) at room temperature under constant shaking for 2 h. The fabrics were washed with copious amounted water (10X100 mL) to remove excess reductant. The chitosan treated fabrics were allowed to completely dry in the air prior to undergoing the dyeing process.

2.2.3 Dyeing process

The dyeings were carried out in a laboratory dyeing machine with a temperature control unit and 12 shaking units at a liquor ratio of 60:1. The samples of fabrics were dyed at 2% or 4% owf (on weight fabric) with Evercion Blue H-ERD dye and Remazol Red RB133 dye in the presence of varied amount of NaCl (the exact amount used is specified in the results). The dyebath was prepared by dissolving the dye and NaCl in distilled water. The fabrics were added to the dye bath at room temperature. The temperature was raised from room temperature to 80 °C for Evercion Blue H-ERD dye, or 60 °C for Remazol Red RB133 dye and held for 10 min. Sodium carbonate (5 g/L) and sodium hydroxide (0.8 g/L) (2.5 g/L for Remazol Red RB133 dye) were then added and the temperature was held for additional 45 min. The dyed fabrics were rinsed thoroughly in a soaped solution (1 g/L anionic surfactant Multinal H/C) at 100 °C for 20 min at a liquor ratio of 60:1. The fabrics were rinsed thoroughly with copious amount of water (10X100 mL) and air dried.

2.3 Analysis

2.3.1 Chemical test with 2,4-dinitrophenylhydrazine (2,4-DNP)

Preparation 2,4-DNP reagent (Shriner, Hermann, Morrill, Curtin & Fuson, 1989): Dissolve 3 g of 2,4-dinitrophenylhydrazine in 15 mL of concentrated sulfuric acid. This solution is then added, with stirring, to 20 mL of water and 70 mL of 95%ethanol. This solution is mixed thoroughly and filtered. Fabric samples were immersed into 2,4-dinitrophenylhydrazine reagent about 30 sec. Fabric samples were taken to compare the color of each piece after drying at room temperature 5 min.

2.3.2 Chitosan content in the fabrics

The chitosan contents in the fabrics were determined from the nitrogen percentages. The nitrogen percentages in the fabrics were analyzed by Kjeldahl nitrogen analysis method (Tecator instrument). Samples of fabrics (0.2 g) were suspended in concentrated sulfuric acid (15 mL) and then digested for 150 minutes at 350 °C and the suspension was allowed to cool to room temperature. Distilled water (~80 mL) and excess sodium hydroxide (40 %w/v) was added until the suspension was basic (pH $\approx$ 14). The mixture was heated under reflux until the solution distilled into a receiving flask containing boric acid (4%, 20 mL) and 4-5 drops of the indicator

(0.2% bromocresol green in ethanol 0.2% methyl red in ethanol at 5/1 v/v. The mixture in the receiving flask had blue color. A standardized solution of HCl (0.1 N) was added titrimetrically from a burette until the blue color changed into red color. The titration was performed in triplicate. The blank titration was performed with the same procedure but without the fabric sample. The analysis was done twice on different pieces of samples to obtain an average value. The nitrogen percentage (%N) was calculated from the following equation; $\%N = 1.4007[HCl] (V - V_{blank})/W$ where [HCl] is the molar concentration of HCl, V is the sample titration volumes (mL), V_{blank} is the blank titration volumes (mL) and W is the weight of fabric sample (g). The chitosan content was calculated from the nitrogen percentage using the following equation; chitosan content = $162(N-N_b)/14$ where N is the nitrogen percentage, N_b is the nitrogen percentage of bleached fabric used as a blank.

2.3.3 Microstructure of fabrics

Scanning electron microscope (SEM) was used to study the particle and surface morphology of chitosan coated cotton fabrics. The samples of fabrics were coated with gold by sputtering at room temperature. Scanning electron micrographs of fabrics were taken by scanning electron microscope (JSM-5410LV). The instrument was operated at 15 kv.

2.3.4 Color measurement

Dye uptake was studied by measuring %exhaustion of four types of fabrics in solution of Evercion Blue H-ERD dye and Remazol Red RB133 dye. The absorbance of the solution at 615 nm (Evercion Blue H-ERD dye) and 516 nm (Remazol Red RB133 dye) were measured and %exhaustion were calculated from $100(A_0-A)/A_0$ where A_0 is the absorbance before dyeing (in presence of sodium chloride) and A is the absorbance after dyeing (Cai, David, & Pailthorpe, 2000; Ahmed, 2005). The dyed fabric samples were measured the color yield (K/S) calculated from the reflectance (R) using the following equation: $(1-R)^2/2R$. The reflectance was measured on a ColorQuest XE Spectrophotometer.

2.3.5 Colorfastness test

The fastness tests of dyed fabrics were carried out according to ISO standard methods and sample size (10X4 cm). The specific tests were: color fastness to washing ISO 105-C06 (1994) Test No B1M, color fastness to water ISO 105-E01 (1994), color fastness to perspiration ISO 105-E04 (1994), color fastness to rubbing ISO 105-B02 (1994) and color fastness to light ISO 105-X12 (1993). The evaluation of color change and staining were made according to ISO 105-A02 and ISO 105-A03. The grey scale was used for color change and staining, giving color ratings from 1 to 5 in the step of 0.5 where grade 5 implies no color change.

2.3.6 Dye uptake in exhaustion step

Tested sample consist of chitosan powder, BF, RCOF, RCBF. Dye uptake as studied by measuring %exhaustion of various amount of tested samples in a solution of dye (0.007%w/v) in the absence and presence of sodium chloride salt (1.225 g/L) under constant shaking at room temperature (30 °C). After 1 h, the absorbance of the solution at 615 nm (for Evercion Blue H-ERD dye) or 516 nm (for Remazol Red RB 133 dye) was measured and %exhaustion was calculated from $100(A_0-A)/A_0$ where A_0 is the initial absorbance and A is the absorbance after 1 h. The effect of salt concentration on dye uptake was also investigated by varying the concentration of the sodium chloride salt. Dye uptake of chitosan powder was also studied in comparison to the cotton fabrics using similar procedure.

3. Result 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 (Fig. 1.).

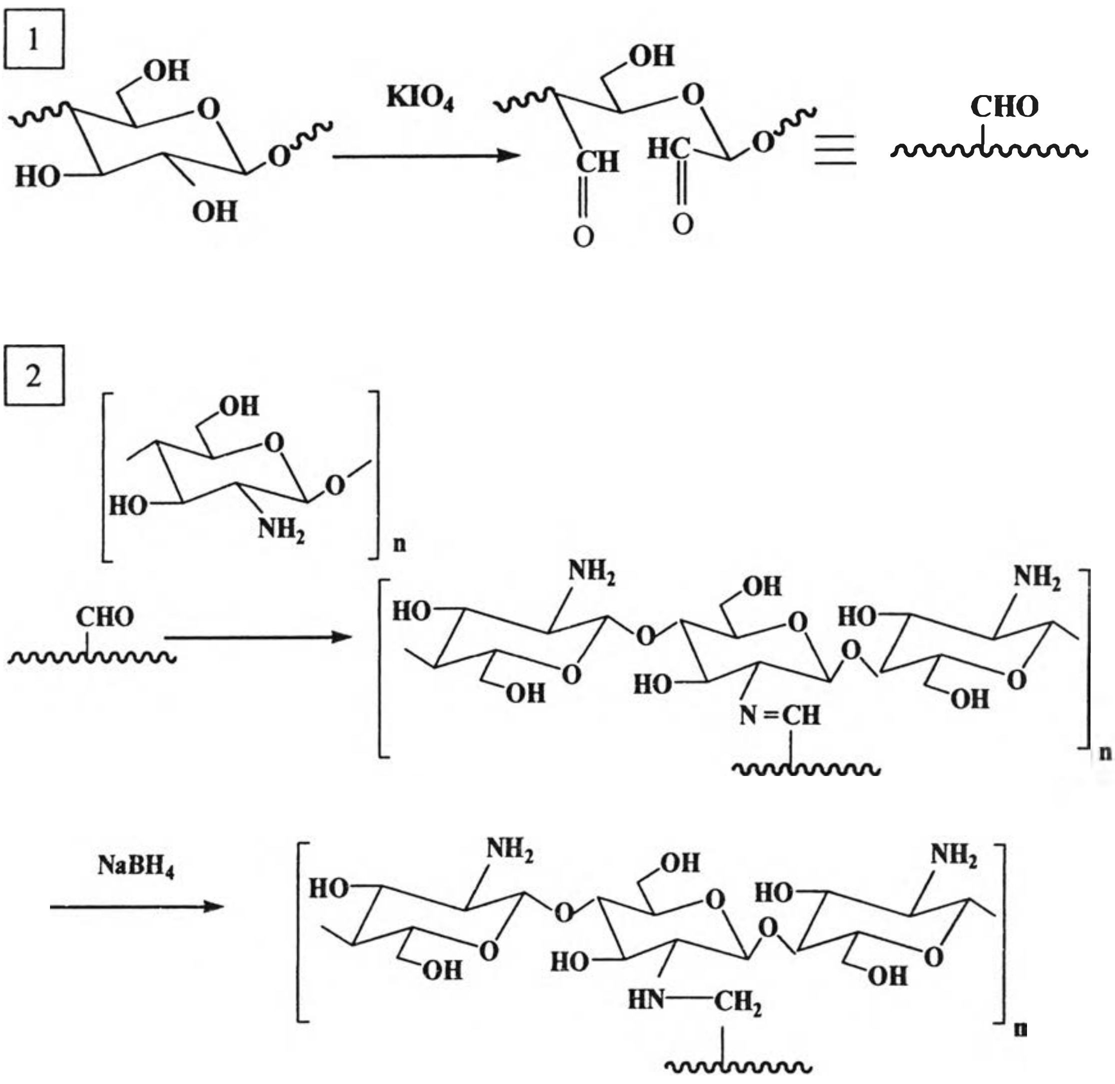


Fig. 1. Reaction series, (1) oxidation and (2) reductive amination, for surface modification of cotton fabric with chitosan.

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 1).

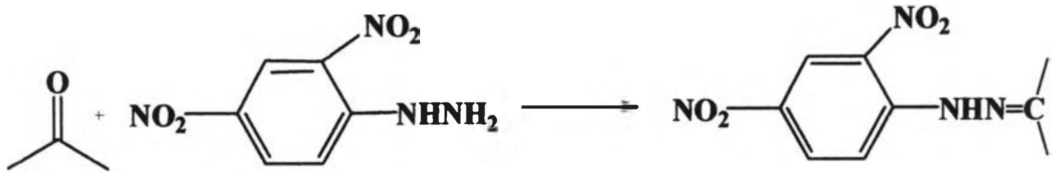
Table 1 Abbreviations for each fabric used in this work

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 (Fig. 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 (Fig. 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

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

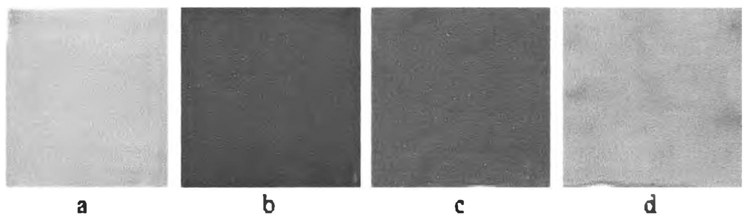


Fig. 3. Chemical test with 2,4-DNP on (a) BF, (b) OF, (c) RCOF and (d) RCBF

There have been literature reports on the oxidation of cellulose fabrics with H_2O_2 (Weltrowski & Masri, 1996) and KIO_4 (Varma, Jamdade & Nadkarni, 1985; Varma & Chavan, 1995; Kim, Kuga, Wada, Okano & Kondo, 2000; Liu, Nishi, Tokura & Sakairi, 2001; Varma & Kulkarni, 2002; Fras, Johasson, Stenius, Laine, Stana-Kleinschek & Ribitsch, 2005) 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 ~ 98,000, 79 %DD, 0.0154 M) 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 (Fig. 4.). Only KIO_4 was thus used as an oxidizing agent in the subsequent study.

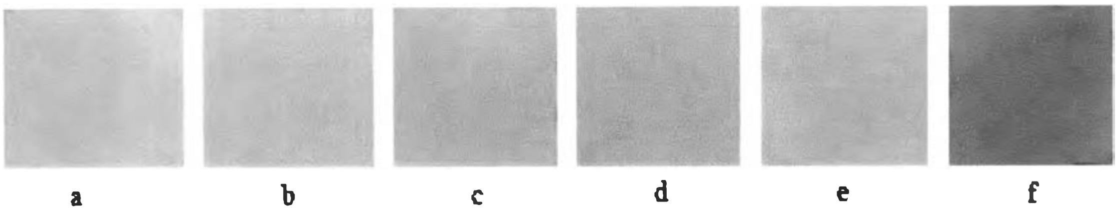


Fig. 4. Chemical test with 2,4-DNP on (a) BF, fabric oxidized by (b) H_2O_2 0.294 M, (c) by H_2O_2 1.765 M, (d) by H_2O_2 0.01 M, (e) by $Na_2S_2O_8$ 0.01 M, (f) by KIO_4 0.01 M.

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) 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 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) 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 (Weltrowski & Masri, 1996). 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 2). This 25% difference was proven to be important for improving dyeing efficiency discussed in the subsequent section.

Table 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 = $162(N-N_b)/14$ 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.

Table 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 = $162(N-N_b)/14$ where N is the nitrogen percentage, N_b is the nitrogen percentage of bleached fabric used as a blank.

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 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 2). CBF showed only slightly higher color yield (K/S) than that of BF in good agreement with the lost of chitosan content under dyeing condition observed in the previous section. OF showed even lower %exhaustion and color yield than that of BF indicate 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 (Fig. 5.).

Table 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.

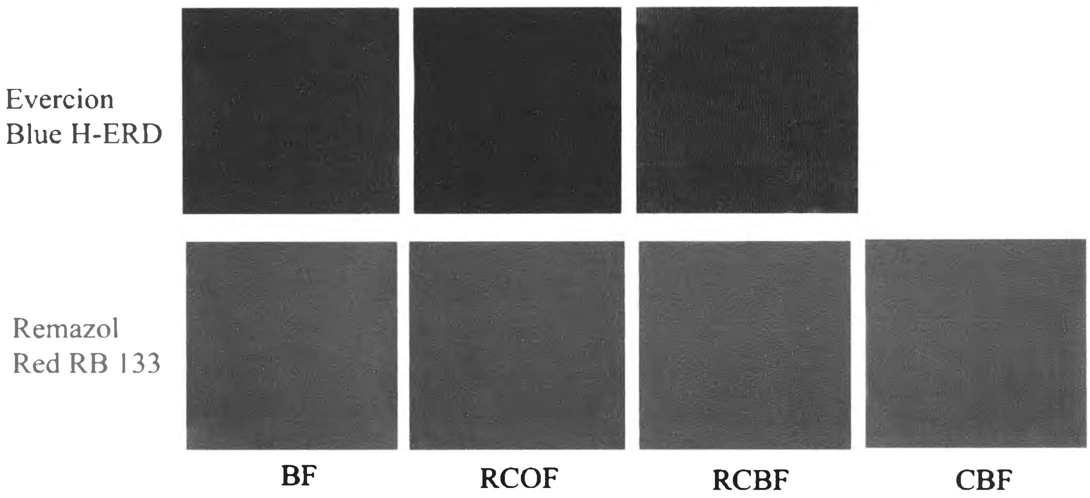


Fig. 5. Photographs of dyed fabrics show different intensity of the colors.

3.4 Colorfastness of dyed fabrics

The dyed fabrics were tested for colorfastness to washing, water, acid perspiration, alkaline perspiration (Table 5), rubbing (Table 6) and light (Table 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 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-tion	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
	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Alkaline perspira-tion	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
	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-tion	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
Alkaline perspira-tion	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
	RCBF	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Table 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 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 (Fig. 6.a and b) while that of OF was irregular (Fig.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(Fig. 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 (Fig. 6.g and h) coinciding with the higher amount of chitosan attached to the cotton fabric surface found in section 3.2.

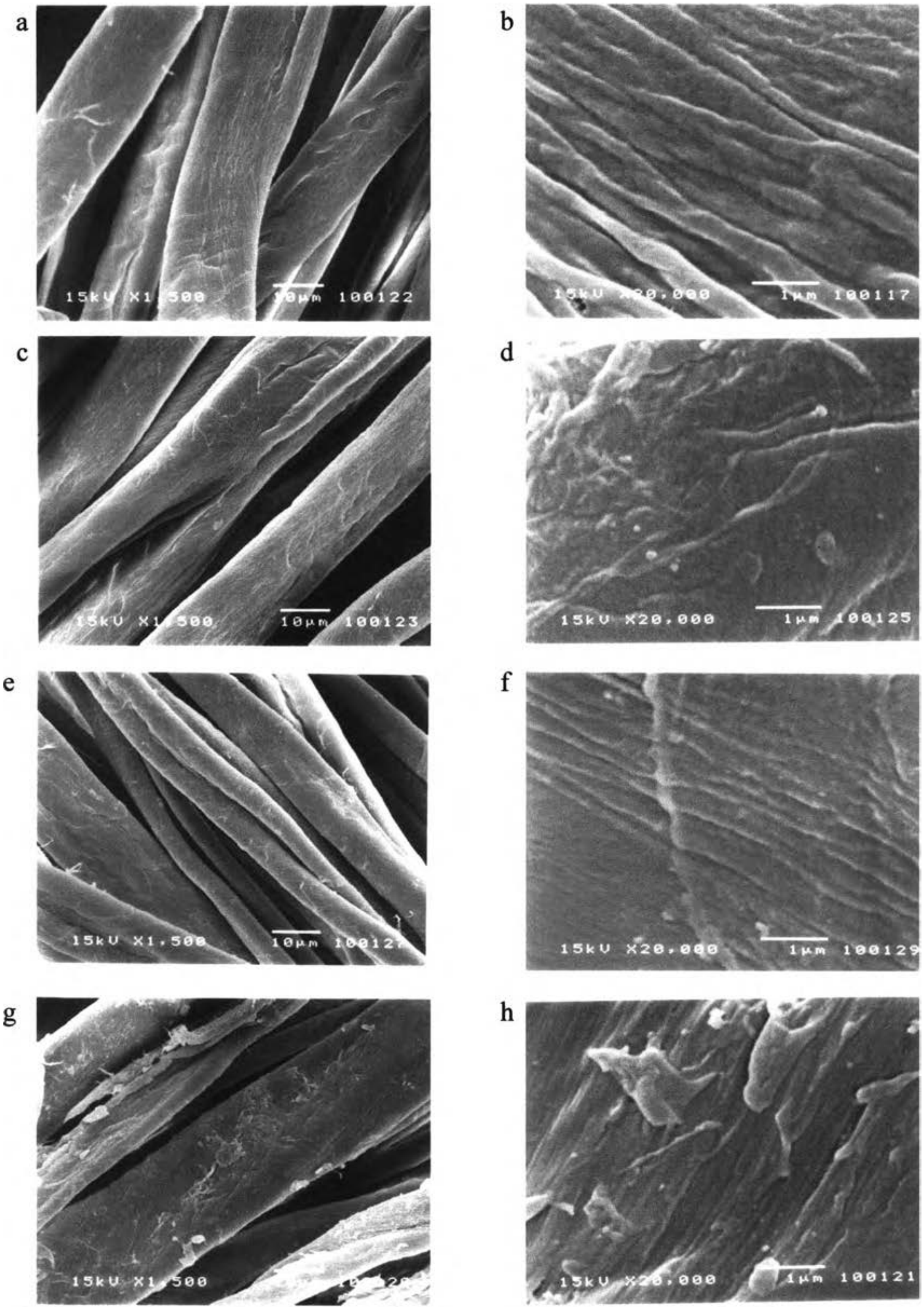


Fig. 6. SEM micrographs of BF (a and b), OF (c and d), RCBF (e and f), and RCOF (g and h).

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 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 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.

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 (Fig. 7.a). As expected, dye exhaustion of RCOF and RCBF were between those of chitosan and BF (Fig. 7.b). Dye adsorption of RCOF was also clearly higher than that of RCBF that is in good agreement with the chitosan contents dicussed 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 (Rattanaphani, Chairat, Bremner & V. Rattanaphani, 2005; Lewis & Lei, 1991; Brodmann, 1999; Burkinshaw, Mignanelli, Froehlings & Bide, 2000; Cai, David & Pailthorpe, 2000).

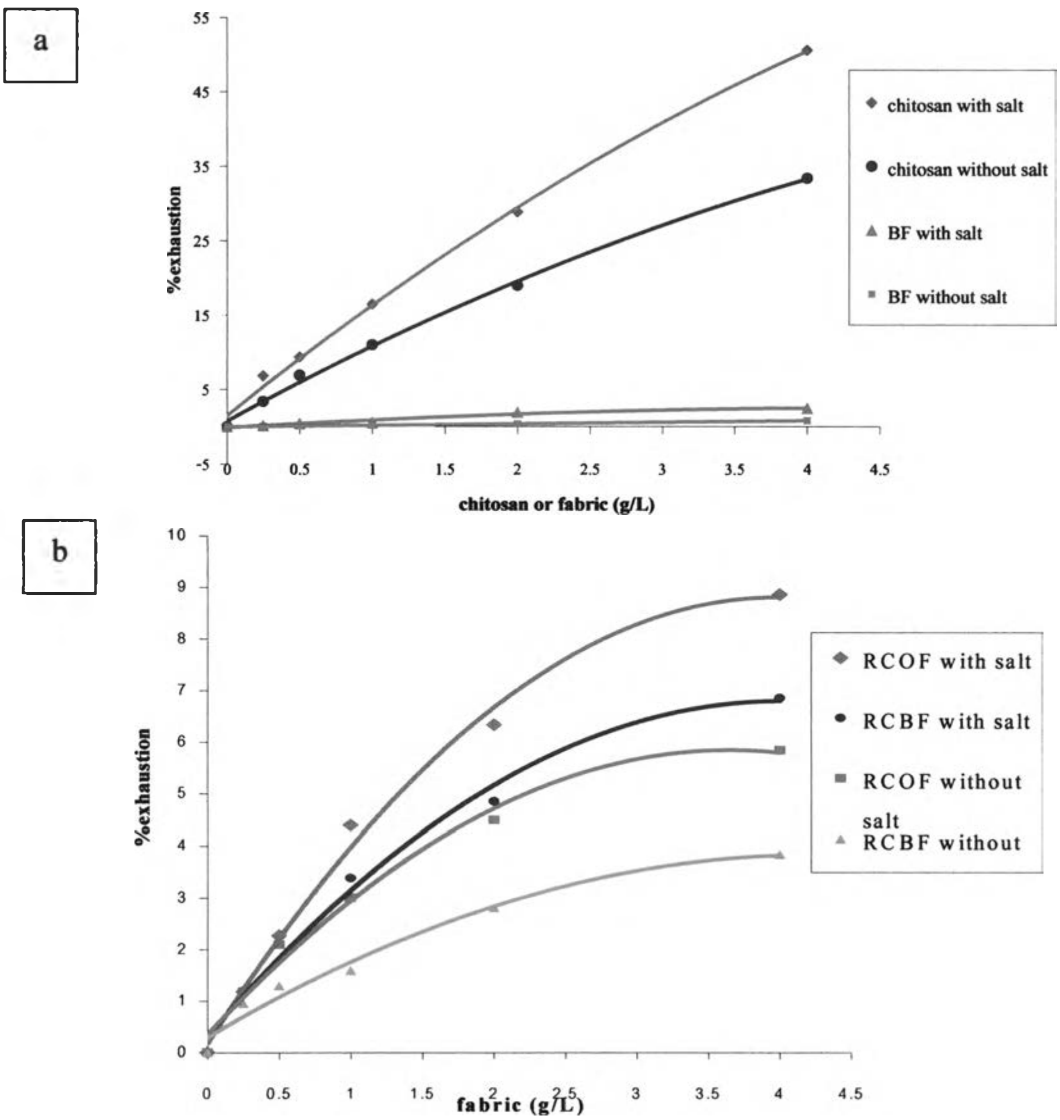


Fig. 7. %exhaustion of Evercion Blue H-ERD dye as a function of the absorbent weight comparing between (a) BF and chitosan powder; (b) RCOF and RCBF in the absence and presence of sodium chloride salt (1.225 g/L). Exhaustion condition: [dye] = 0.007% w/v, pH ≈ 6, Temp. = 30 °C, Time = 1 h, LR 60:1.

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 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 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 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.

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 10), (Fig. 8.). 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 10 The CIELAB measurements 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.

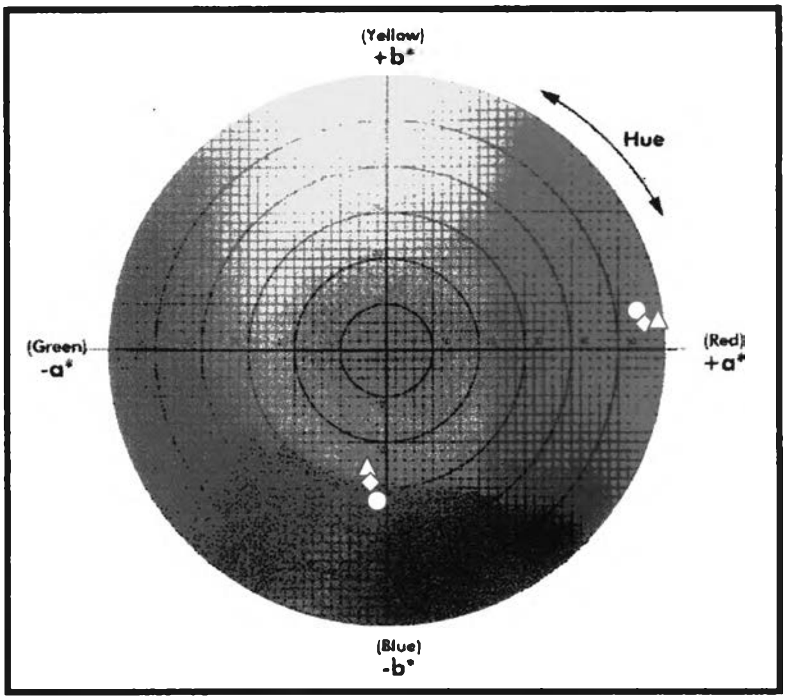


Fig. 8. CIELAB color space of (△) BF dyed with Blue H-ERD at 4%owf, (○) RCOF dyed with Blue H-ERD at 4%owf, (◇) RCOF dyed with Blue H-ERD at 2%owf and (△) BF dyed with Red RB133 at 4%owf, (○) RCOF dyed with Red RB133 at 4%owf, (◇) RCOF dyed with Red RB133 at 2%owf.

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 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 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		% exhaustion	Color yield (K/S)
		g/L	% reduction		
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.

4. Conclusions

The chemical modification of cotton fabrics with chitosan was achieved through a series of oxidation/reductive amination. Oxidation of cotton fabric with KIO_4 followed by reductive amination with chitosan led to the highest chitosan content in the fabric analyzed by Kjeldahl nitrogen analysis technique. The %exhaustion and color yield (K/S) in the dyeing process with mono-chloro-triazine and vinyl sulphone reactive dyes showed that this method of fabric modification considerably improved dye uptake of the fabric. The dyeability of the modified fabric with monochlorotriazine and vinylsulphone reactive dyes was clearly greater than those of original bleached cotton fabric. The reduction of repulsive force between the negatively charged cellulose and the anionic dye molecules by the more positively charged chitosan chains probably accounted for this greater dyeability. The modification of fabrics chitosan by this method did not post discernable colorfastness to the dyed fabric. The chitosan modified fabric can be dyed under improved dyeing condition in which the amount of dyes and sodium chloride salt used significantly lower without affecting the color yield. This improved dyeing condition can reduce the cost of dyes and salt used but also reduce the amount of dyes and salt remain in the dyeing house effluent.

Suggestion for future work

Fine tuning of this research work should be studied to bring about real application of the method into an industrial use. Oxidation condition, reductive amination condition and chitosan molecular weight are among the important parameters should be investigated to bring about the most economical and effective method for surface modification of chitosan. Antimicrobial activity of the chitosan-modified fabric is also an interesting property needed to be fully investigated to gain and claim added benefit from using chitosan as a modifying agent.

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APPENDIX B

Table B1 Recipe of bleach process for bleached fabrics

Chemicals	Concentration (g/L)
Hydrogen peroxide	3.0
Sodium hydroxide	4.0
Stabilizing agent (BK CONC)	0.3
Nonionic surfactant (Perlavin NEP)	0.5
Sequestering agent (Polyphos T)	0.5

Table B2 Nitrogen content in fabrics analyzed by Kjeldahl analysis

Fabrics	%Nitrogen			SDV
	1	2	AVG	
BF	0.097	0.091	0.094	0.004
OF	0.117	0.100	0.109	0.012
RCOF	0.239	0.240	0.240	0.001
RCBF	0.208	0.216	0.212	0.005
CBF	0.240	0.238	0.239	0.001

Table B3 Nitrogen content in fabrics, after undergoing dyeing condition without dye, analyzed by Kjeldahl analysis

Fabrics	%Nitrogen			SDV
	1	2	AVG	
BF	0.093	0.095	0.094	0.001
RCOF	0.210	0.206	0.208	0.003
RCBF	0.179	0.200	0.189	0.015
CBF	0.116	0.129	0.122	0.009

APPENDIX C

Table C1 %Exhaustion of fabrics dyed with Evercion Blue H-ERD at 4% owf and LR = 60:1 for 45 min

Fabrics	Absorbance			%Exhaustion			
	1	2	3	1	2	3	AVG
Blank (1:10)	0.5377	0.5374	0.5379	-	-	-	-
BF(1:10)	0.2091	0.2099	0.2094	61.1121	60.9416	61.0708	61.0416
OF(1:10)	0.2800	0.2801	0.2802	47.9264	47.8787	47.9085	47.9045
RCOF	0.4065	0.4055	0.4060	92.4400	92.4544	92.4521	92.4488
RCBF(1:10)	0.1528	0.1524	0.1524	71.5827	71.6226	71.6676	71.4500

Table C2 %Exhaustion of fabrics dyed with Remazol Red RB133 at 4% owf and LR = 60:1 for 45 min

Fabrics	Absorbance			%Exhaustion			
	1	2	3	1	2	3	AVG
Blank (1:20)	0.8018	0.8015	0.7994	-	-	-	-
BF(1:20)	0.4210	0.4216	0.4209	47.4931	47.398	47.3480	47.4132
OF(1:20)	0.4714	0.4714	0.4715	41.2073	41.1853	41.0183	41.1370
RCOF(1:20)	0.3065	0.3064	0.3069	61.7735	61.7717	61.6087	61.7180
RCBF (1:20)	0.4124	0.4128	0.4119	48.5657	48.4966	48.4739	48.5121

Table C3 The effect of oxidation time on %exhaustion of fabrics dyed with Evercion Blue H-ERD at 4% owf in the dyeing of RCBF and RCOF

Fabrics	time hour	Absorbance			%Exhaustion			
		1	2	3	1	2	3	AVG
Blank (1:10)	-	0.5377	0.5374	0.5379	-	-	-	-
RCBF (1;10)	3	0.1528	0.1525	0.1524	71.5827	71.6226	71.6676	71.4500
RCOF	1	0.5069	0.5064	0.5060	90.5728	90.5769	90.5930	90.5809
	3	0.4065	0.4055	0.4060	92.4400	92.4544	92.4521	92.4488
	10	0.2229	0.2220	0.2219	95.8546	95.8690	95.8747	95.8661

Table C4 The effect of oxidation time on %exhaustion of fabrics dyed with Remazol Red RB133 at 4% owf in the dyeing of RCBF and RCOF

Fabrics	time hour	Absorbance			%Exhaustion			
		1	2	3	1	2	3	AVG
Blank (1:20)	-	0.8018	0.8015	0.7994	-	-	-	-
RCBF (1:20)	3	0.4124	0.4128	0.4119	48.5657	48.4966	48.4739	48.5121
RCOF (1:20)	1	0.3656	0.3636	0.3640	54.4026	54.6351	54.4658	54.5012
	3	0.3065	0.3064	0.3069	61.7735	61.7717	61.6087	61.7180
	10	0.3007	0.2992	0.2998	62.4969	62.6700	62.4969	62.5546

Table C5 Absorbance (at λ=615 nm) and %Exhaustion of Evercion Blue H-ERD of BF without salt

BF (g/L)	Absorbance			%Exhaustion			
	1	2	3	1	2	3	AVG
0	0.7109	0.7108	0.7105	0	0	0	0
0.25	0.7105	0.7105	0.7100	0.0563	0.0594	0.0704	0.0620
0.50	0.7101	0.7101	0.7099	0.1127	0.0986	0.0844	0.0996
1.00	0.7097	0.7095	0.7092	0.1688	0.1829	0.1830	0.1782
2.00	0.7080	0.7078	0.7077	0.4079	0.4221	0.3941	0.4114
4.00	0.7051	0.7048	0.7048	0.8159	0.8441	0.8425	0.8348

Table C6 Absorbance (at λ=615 nm) and % Exhaustion of Evercion Blue H-ERD of chitosan without salt

Chitosan	Absorbance			%Exhaustion			
(g/L)	1	2	3	1	2	3	AVG
0	0.7005	0.7001	0.7005	0	0	0	0
0.25	0.6769	0.6765	0.6766	3.3690	3.3709	3.4118	3.3833
0.50	0.6522	0.6519	0.6519	6.8951	6.8847	6.9379	6.9059
1.00	0.6211	0.6266	0.6220	11.3347	10.4985	11.2063	11.0132
2.00	0.5677	0.5670	0.5670	18.9579	19.0116	19.0578	19.0091
4.00	0.4671	0.4665	0.4667	33.3191	33.3666	33.3762	33.3540

Table C7 Absorbance (at λ=615 nm) and %Exhaustion of Evercion Blue H-ERD of BF with salt

BF(g/L)	Absorbance			%Exhaustion			
	1	2	3	1	2	3	AVG
0	0.7000	0.7001	0.7000	0	0	0	0
0.25	0.6990	0.6995	0.6989	0.1429	0.0857	0.1571	0.1286
0.50	0.6970	0.6971	0.6969	0.4286	0.4285	0.4429	0.4333
1.00	0.6959	0.6960	0.6959	0.5857	0.5856	0.5857	0.5857
2.00	0.6878	0.6875	0.6844	1.7429	1.8000	2.2243	1.9524
4.00	0.6830	0.6825	0.6826	2.4286	2.5139	2.4857	2.4761

Table C8 Absorbance (at λ=615 nm) and % Exhaustion of Evercion Blue H-ERD of chitosan with salt

Chitosan (g/L)	Absorbance			%Exhaustion			
	1	2	3	1	2	3	AVG
0	0.6972	0.6969	0.6970	0	0	0	0
0.25	0.6499	0.6492	0.6493	6.7843	6.8446	6.8436	6.8242
0.50	0.6318	0.6319	0.6320	9.3804	9.3270	9.3257	9.3444
1.00	0.5819	0.5819	0.5821	16.5376	16.5017	16.4850	16.5081
2.00	0.4964	0.4960	0.4955	28.8009	28.8277	28.9096	28.8461
4.00	0.3450	0.3451	0.3448	50.5164	50.4807	50.5308	50.5093

Table C9 Absorbance (at λ=615 nm) and % Exhaustion of Evercion Blue H-ERD of RCOF without salt

RCOF	Absorbance			%Exhaustion			
(g/L)	1	2	3	1	2	3	AVG
0	0.7004	0.7008	0.7007	0	0	0	0
0.25	0.6931	0.6932	0.6934	1.0423	1.0845	1.0418	1.0562
0.50	0.6925	0.6920	0.6920	1.1279	1.2557	1.2416	1.2084
1.00	0.6800	0.6795	0.6790	2.9126	3.0394	3.0969	3.0163
2.00	0.6698	0.6690	0.6691	4.3689	4.5377	4.5098	4.4721
4.00	0.6601	0.6595	0.6590	5.7539	5.8933	5.9512	5.8661

Table C10 Absorbance (at λ=615 nm) and %Exhaustion of Evercion Blue H-ERD of RCBF without salt

RCBF	Absorbance			%Exhaustion			
(g/L)	1	2	3	1	2	3	AVG
0	0.6989	0.6985	0.6989	0	0	0	0
0.25	0.6922	0.6920	0.6921	0.9586	0.9162	0.9730	0.9493
0.50	0.6900	0.6897	0.6895	1.2734	1.2598	1.3450	1.2927
1.00	0.6885	0.6877	0.6870	1.4880	1.5462	1.7027	1.5790
2.00	0.6790	0.6795	0.6794	2.8473	2.7201	2.7901	2.7858
4.00	0.6721	0.6719	0.6718	3.8346	3.8082	3.8775	3.8401

Table C11 Absorbance (at λ=615 nm) and % Exhaustion of Evercion Blue H-ERD of RCOF with salt

RCOF	Absorbance			%Exhaustion			
(g/L)	1	2	3	1	2	3	AVG
0	0.6980	0.6977	0.6975	0	0	0	0
0.25	0.6895	0.6895	0.6897	1.2178	1.1753	1.1183	1.1705
0.50	0.6780	0.6785	0.6770	2.8653	2.7519	2.9390	2.8521
1.00	0.6675	0.6685	0.6680	4.3700	4.1852	4.4195	4.3249
2.00	0.6539	0.6534	0.6532	6.3181	6.3494	6.3513	6.3396

Table C12 Absorbance (at λ=615 nm) and %Exhaustion of Evercion Blue H-ERD of RCBF with salt

RCBF	Absorbance			%Exhaustion			
(g/L)	1	2	3	1	2	3	AVG
0	0.6980	0.6978	0.6979	0	0	0	0
0.25	0.6901	0.6895	0.6896	1.1318	1.1895	1.1751	1.1655
0.50	0.6840	0.6835	0.6837	2.0057	2.0493	2.0206	2.0252
1.00	0.6743	0.6745	0.6748	3.3954	3.3391	3.2961	3.3435
2.00	0.6650	0.6645	0.6645	4.7278	4.7721	4.7721	4.7573

Table C13 Effect of salt on dye uptake of BF, Absorbance at λ=615 nm of Evercion Blue H-ERD dyes

BF (g/L)	Absorbance			%Exhaustion			
	1	2	3	1	2	3	AVG
0	0.7062	0.7060	0.7061	0	0	0	0
1.75	0.6858	0.6856	0.6859	2.8887	2.8895	2.8608	2.8791
3.50	0.6725	0.6726	0.6724	4.7720	4.7309	4.7727	4.7585
5.25	0.6613	0.6615	0.6610	6.3580	6.3030	6.3872	6.3494
7.00	0.6521	0.6525	0.6523	7.6607	7.5779	7.6193	7.6193

Table C14 Effect of salt on dye uptake of chitosan, Absorbance at λ=615 nm of Evercion Blue H-ERD dyes

Chitosan	Absorbance			%Exhaustion			
(g/L)	1	2	3	1	2	3	AVG
0	0.5404	0.5403	0.5401	0	0	0	0
1.75	0.5209	0.5210	0.5207	3.6084	3.5721	3.5919	3.5908
3.50	0.5045	0.5040	0.5044	6.6432	6.7185	6.6099	6.6572
5.25	0.4820	0.4818	0.4821	10.8068	10.8273	10.7388	10.7910
7.00	0.4649	0.4648	0.4645	13.9711	13.9737	13.9974	13.9807
8.75	0.4395	0.4392	0.4390	18.6714	18.7118	18.7188	18.7007

Table C15 The colour measurement of dyeing RCOF with reduced amount of salt and dye compared with BF

Dyed with Evercion Blue H-ERD dyes

Dye % owf	Fabric	NaCl (g/L)	Absorbance 1	Absorbance 2	Absorbance 3	%Exhaustion 1	%Exhaustion 2	%Exhaustion 3	%Exhaustion AVG
4	Blank	0(1:10)	0.5876	0.5875	0.5874	-	-	-	-
		35(1:10)	0.5790	0.5789	0.5788	-	-	-	-
		70(1:10)	0.5377	0.5374	0.5379	-	-	-	-
4	BF	70(1:10)	0.2091	0.2099	0.2094	61.1121	61.7603	61.8145	61.8288
4	RCOF	0(1:10)	0.4700	0.4698	0.4699	20.0136	20.0034	20.0034	20.0068
		35(1:10)	0.1532	0.1528	0.1525	73.5406	73.6051	73.6523	73.5993
		70	0.4065	0.4055	0.4060	92.4400	92.4544	92.4521	92.4488
2	Blank	0(1:10)	0.3221	0.3181	0.3190	-	-	-	-
		35(1:10)	0.3171	0.3167	0.3165	-	-	-	-
		60(1:10)	0.3002	0.3003	0.3003	-	-	-	-
2	RCOF	35	0.9489	0.9465	0.9450	70.5402	70.2452	70.3762	70.3802
		52.5	0.6514	0.6506	0.6500	79.4576	79.4569	79.5261	79.4802
		60	0.0185	0.0185	0.0186	99.3874	99.3879	99.3806	99.3840

Table C16 The colour measurement of dyeing RCOF with reduced amount of salt and dye compared with BF

Dyed with Remazol Red RB133 dyes

Dye % owf	Fabric	NaCl (g/L)	Absorbance 1	Absorbance 2	Absorbance 3	%Exhaustion 1	%Exhaustion 2	%Exhaustion 3	%Exhaustion AVG
4	Blank	0(1:20)	0.8288	0.8280	0.8285	-	-	-	-
		30(1:20)	0.8134	0.8130	0.8130	-	-	-	-
		60(1:20)	0.8018	0.8015	0.7994	-	-	-	-
4	BF	60(1:20)	0.4210	0.4216	0.4209	47.4931	47.3986	47.3480	47.4132
4	RCOF	0(1:20)	0.6095	0.6122	0.6104	26.4599	26.0628	26.3247	26.2825
		30(1:20)	0.4209	0.4227	0.4210	48.2542	48.0074	48.2165	48.1594
		60(1:20)	0.3065	0.3064	0.3069	61.7735	61.7717	61.6087	61.7180
2	Blank	30(1:10)	0.7632	0.7630	0.7630	-	-	-	-
		45(1:10)	0.7403	0.7402	0.7400	-	-	-	-
		50(1:10)	0.7200	0.7202	0.7200	-	-	-	-
2	RCOF	30(1:10)	0.3801	0.3822	0.3834	50.1965	49.9083	49.7510	49.9519
		45(1:10)	0.3167	0.3171	0.3165	57.2200	57.1602	57.2297	57.2033
		50(1:10)	0.2693	0.2698	0.2690	62.5972	62.5382	62.6389	62.5914

Table C17 The colour measurement of dyeing RCOF with reduced amount of salt and dye compared with BF

Dyed with Evercion Blue H-ERD dyes

Dye % owf	Fabric	NaCl (g/L)	Absorbance 1	Absorbance 2	Absorbance 3	%Exhaustion 1	%Exhaustion 2	%Exhaustion 3	%Exhaustion AVG
4	Blank	70(1:40)	0.9309	0.9308	0.9311	-	-	-	-
	BF	70(1:10)	0.4477	0.4480	0.4479	87.9767	87.9673	87.9739	87.9726
	RCOF	70(1:5)	0.2690	0.2692	0.2690	96.3879	96.7348	96.3887	96.3871
2	Blank	60(1:20)	0.9218	0.9218	0.9217	-	-	-	-
	RCOF	60	0.7033	0.7012	0.7015	96.1852	96.1966	96.1945	96.1921
2	Blank	52.5(1:10)	0.9951	0.9953	0.9954	-	-	-	-
	RCOF	52.5	0.7914	0.7883	0.7872	96.0235	96.0399	96.0458	96.0364

Table C18 The colour measurement of dyeing RCOF with reduced amount of salt and dye compared with BF

Dyed with Remazol Red RB133 dyes

Dye % owf	Fabric	NaCl (g/L)	Absorbance 1	Absorbance 2	Absorbance 3	%Exhaustion 1	%Exhaustion 2	%Exhaustion 3	%Exhaustion AVG
4	Blank	60(1:80)	0.8261	0.8258	0.8257	-	-	-	-
	BF	60(1:20)	0.8239	0.8214	0.8212	75.0666	75.1332	75.1362	75.1120
	RCOF	60(1:20)	0.2302	0.2299	0.2295	93.0335	93.0400	93.0514	93.0416
2	Blank	50(1:40)	0.7457	0.7439	0.7440	-	-	-	-
	RCOF	50(1:10)	0.2495	0.2490	0.2495	91.6354	91.6319	91.6163	91.6279
2	Blank	45(1:40)	0.7732	0.7729	0.7730	-	-	-	-
	RCOF	45(1:10)	0.3166	0.3168	0.3165	89.7633	89.7529	89.7639	89.7600

APPENDIX D

Table D1 Time of chitosan A solution traveling through the Ubbelohde Viscometer

C g/L	Time				η_{rel}	η_{sp}	η_{sp}/C
	t1	t2	t3	t			
0.000	91.65	91.28	91.18	91.37	-	-	-
3.375	133.54	134.01	133.79	133.78	1.4642	0.4642	138
2.813	125.51	125.65	125.70	125.62	1.3748	0.3748	133
2.413	117.81	117.95	117.75	117.84	1.2897	0.2897	120
1.688	108.25	108.10	108.15	108.17	1.1839	0.1839	109
1.534	106.20	106.35	106.20	106.25	1.1629	0.1629	106
1.406	104.60	104.80	104.87	104.76	1.1465	0.1465	104

Table D2 Time of chitosan B solution traveling through the Ubbelohde Viscometer

C g/L	Time				η_{rel}	η_{sp}	η_{sp}/C
	t1	t2	t3	t			
0.000	91.65	91.28	91.18	91.37	-	-	-
3.375	116.75	116.86	116.78	116.80	1.2783	0.2783	82
2.813	111.30	111.30	111.27	111.30	1.2181	0.2181	78
2.413	107.20	107.15	107.26	107.20	1.1733	0.1733	72
1.688	100.90	100.99	101.00	100.96	1.1050	0.1050	62
1.534	99.89	99.97	100.00	99.95	1.0939	0.0939	61
1.406	99.20	99.10	99.10	99.11	1.0847	0.0847	60

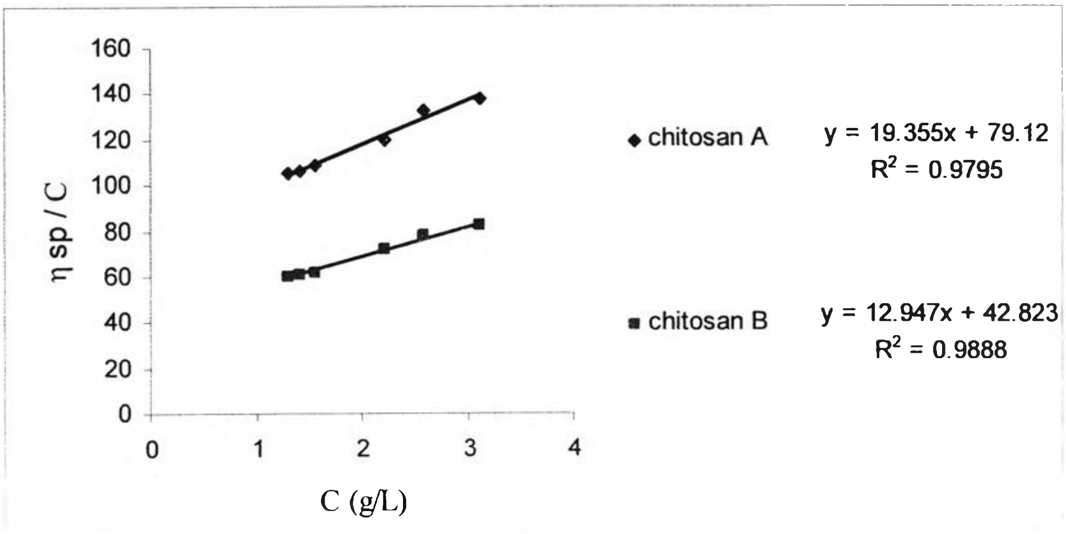

Figure D1 Plots of η_{sp} / C against C and molecular weight of the various types of chitosan.

Table D3 Molecular weight of chitosan A and B calculated from $[\eta] = KM_v^a$ ($K = 1.8 \times 10^{-3}$, $a = 0.93$)

Chitosan	$[\eta]$	log M_v	M_v
A	79.12	4.992	98,282
B	42.82	4.706	50,781

APPENDIX E

Table E1 Volumes of the PVSK solution for blank and CPC titration

Time	PVSK (mL)	
	CPC Titration	Blank Titration
1	3.45	0.1
2	3.50	0.1
3	3.50	0.1
AVG.	3.48	0.1

Table E2 Volumes of the PVSK solution for titration of chitosan A and B

Chitosan	Weight (mg)	PVSK (mL)				%DD
		1	2	3	AVG.	
A	8.4	3.10	3.00	3.10	3.07	79
B	8.7	3.40	3.40	3.50	3.43	84

VITAE

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