Using Chitosan for Improving the Dyeability of Cotton Fabrics with Mangosteen Rind Dye

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The study examined the influence of chitosan to improve dye absorption on cotton farbric using Mangosteen Rind. The results of this study concluded that the cotton fabrics treated with chitosan had better depth of shade than those of the untreated fabrics dyed with Mangosteen Rind. This may be because the chitosan treated cotton fabrics provided more dye sites than those present on the untreated fabric. The cotton fabrics treated with chitosan not only provided better depth of shade but also provided better wash fastness and light fastness than those of the untreated fabrics when dyed with Mangosteen Rind. The use of different mordants and mordanting methods affected the dye shade and depth of shade differently on the dyed fabrics both with and without chitosan. Only natural dyes can have their shades changed by using different mordants. This phenomenon cannot be observed in synthetic dyes. The cotton fabrics dyed with mordants had better wash fastness and light fastness than those of cotton fabrics dyed without mordant.

Key words: Natural dyes, chitosan, mangosteen rind and cotton fabrics.

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อิทธิพลของสารไคโตซานต่อการดูดซับสีย้อมบนผ้าฝ้ายที่ย้อมด้วยสีธรรมชาติที่สกัดจากเปลือกมังคุด

สิริวรรณ กิตติเนาวรัตน์ (2547)

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งานวิจัยนี้ศึกษาอิทธิพลของสารไคโตซานต่อการดูดซับสีย้อมบนผ้าฝ้ายซึ่งย้อมด้วยสีธรรมชาติที่สกัดได้จากเปลือกมังคุด ผลการทดลองสรุปได้ว่า การปรับสภาพผ้าก่อนย้อมด้วยไคโตซานลงไปบนผ้าฝ้ายช่วยให้การดูดซึมสีย้อมที่สกัดได้จากเปลือกมังคุดดีขึ้น มีผลทำให้ผ้าฝ้ายที่ย้อมด้วยสีเปลือกมังคุดมีค่าความเข้มของสีมากกว่าของผ้าที่ย้อมด้วยสีเปลือกมังคุดที่ไม่ได้ตกแต่งด้วยไคโตซาน นอกจากนี้สมบัติความคงทนของสีต่อแสงและต่อการซักของผ้าฝ้ายที่ย้อมด้วยสีเปลือกมังคุดที่ตกแต่งด้วยไคโตซานดีกว่าสมบัติทั้งสองของผ้าที่ไม่ได้ตกแต่งด้วยไคโตซาน การใช้มอแดนต์และวิธีการใช้มอแดนต์ มีผลกระทบโดยตรงต่อเฉดสีและความเข้มของสีย้อมบนผ้าฝ้ายที่ย้อมด้วยสีเปลือกมังคุด ทั้งของผ้าฝ้ายที่ตกแต่งและผ้าฝ้ายที่ไม่ตกแต่งด้วยไคโตซานแตกต่างกันออกไป การใช้มอแดนต์มีผลทำให้ผ้าฝ้ายที่ย้อมด้วยสีธรรมชาติมีเฉดสีที่หลากหลายซึ่งเป็นลักษณะพิเศษของสีย้อมธรรมชาติ ซึ่งลักษณะพิเศษนี้ไม่พบในสีสังเคราะห์ นอกจากนี้การใช้มอแดนต์ยังช่วยปรับปรุงสมบัติความคงทนของสีต่อแสงและต่อการซักของผ้าทั้งที่ตกแต่งด้วยไคโตซานและไม่ได้ตกแต่งด้วยไคโตซานให้ดีขึ้นกว่าของผ้าฝ้ายที่ย้อมด้วยสีเปลือกมังคุดที่ไม่ได้ใช้มอแดนต์

คำสำคัญ สีย้อมธรรมชาติ ไคโตซาน เปลือกมังคุด ผ้าฝ้าย

INTRODUCTION

Recently people have shown greater interest in the use of natural dyes in textile processing. This is because of people's increasing awareness of the environmental effects of water pollution and waste disposal. In addition, there are problems of toxic in and allergic reactions associated with synthetic dyes, while natural dyes exhibit fewer problems of toxicity, better biodegradability, and more compatibility with the environment. However, natural dyes have some drawbacks in their reduced fastness and intensity. There are some natural dyes such as Mangifera Indica Bark and Tea that could be used for dyeing cotton fabrics as reported in research articles.(1,2) There is not much work reported on the use of Mangosteen Rind as a natural dye in textile applications. Mangosteen is one of the local fruits of Thailand, and its rind has been used as a component in soaps and lotions. In addition, local people in Thailand have used Mangosteen Rind as a natural dye for cotton fabric since ancient times,(3) but its use not been well documented. This study looked at the colour depth and fastness of the natural dye extracted from Mangosteen Rind (*Gracinia Mangosatana L*).

Additionally of this research studied the influence of chitosan on the dyeing properties of Mangosteen Rind or cotton fabric. Chitosan is the deacetylated derivative of chitin and has been mainly(4-6) used in three textile applications: primary production of man-made fiber, textile fiber finishes and textile auxiliary chemicals.

The chemical structure of Mangosteen Rind is shown in Figure 1.(7) Mangosteen Rind's structure contains hydroxyl groups that render its affinity with cotton fiber through hydrogen bonding. When cotton fabrics are treated with chitosan, the treated cotton fabric should have more functional groups (amino and methylol groups) than are present on untreated fabrics. This phenomenon should provide more sites to attach dyes and form more hydrogen bonds to improve dying properties.

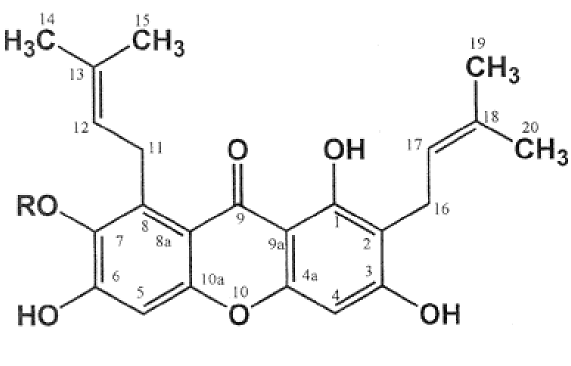

Figure 1. Chemical structure of Mangosteen Rind.

The hypothesis of this study is that the cotton fabric treated with chitosan should show an increase in the dye sites for attaching dye molecules to the fabric over the untreated fabrics. The study focuses on the effect of chitosan on the dyeing properties of cotton fabric with dye filtrate extracted from Mangosteen Rind. In addition, this study is also to investigates the fastness properties, shade and depths of shade as affect by three different methods of dyeing, i.e. pre-mordanting, meta-mordanting and post-mordanting.

EXPERIMENT

Materials

Mangosteen rind was dried and ground in a grinding mill through mesh number 35. Desized, scoured and bleached 65 x 60 plain cotton woven fabric weighing 137 g/m^2 was purchased from BekerTex Co., LTD. Chitosan purchased from Seafresh Chitosan (Lab) Company Limited with a molecular weight of 111,000 g/mol and 95% degree of deacetylation was used. Aluminium potassium sulphate dodecahydrate ($KAl(SO_4)_2.H_2O$), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), stannous chloride ($SnCl_2.2H_2O$) and copper sulphate pentahydrate ($CuSO_4.5H_2O$) were laboratory grade and used as mordants. All chemicals were purchased from suppliers in Bangkok.

Extract preparation

Aqueous extracts were prepared by adding Mangosteen Rind powder (2 to 12 g) to 100 ml. tap water in the flask. The mixture was stirred, heated and held at boiling point for 30 minutes. It was allowed to stand overnight at room temperature and then filtered. The filtrate was used for dyeing. The optimum Mangosteen Rind powder concentration was determined from various quantities of powder from 2 to 12 g. Optical density of the aqueous extract was used as the dye extracted. The optical density values were measured at wavelength 238 nm on Specord S 100 Spectrophotometer. The optical density value at this wavelength gave the maximum value of optical density, while the wavelength at visible region gave the value of optical density very low and unstable. The optical densities of aqueous extracts are given in Table 1. The results in Table 1 show that the optical density increased with an increase in the quantity of Mangosteen Rind and reached the maximum with 10 g of Mangosteen Rind powder for 100 ml. of tap water. The optical densities were not significantly increased with an increase in the quantity of Mangosteen Rind powder. Therefore, 2 g of Mangosteen Rind powder was used for aqueous extracts through out this study.

Table 1. Optimization of Mangosteen Rind powder concentration[a].

Mangosteen Rind Powder (g/100 ml of tap water)	Optical Density Value at 238 nm
2	2.90
4	2.90
6	2.92
8	2.95
10	2.96
12	2.95

[a] dilution ratio 1:20

Preparation of chitosan solution

Chitosan solutions were prepared at 0.1%, 0.25%, 0.50% and 1% concentration. Chitosan was dissolved in 1 % acetic acid and left overnight at room temperature.

Pretreatment chitosan on cotton fabric by padding

Each chitosan solution was padded on cotton fabric. The padded sample was dried at 100°C for 5 min. After that, the padded fabric was dyed with aqueous extract from 2 g of Mangosteen Rind powder/100 ml. of water by exhaustion method. The dyed fabrics were rinsed with tap water, squeezed and dried at room temperature. Depth of shade, expressed as K/S, was measured on the dyed fabric. The resulting K/S of the dyed fabrics treated with various concentrations of chitosan are reported in Table 2. The results in Table 2 show that the chitosan treated fabrics had a K/S value better than that of the untreated fabric. Higher concentrations of chitosan increased the K/S on dyed fabric. From the results, we concluded that the chitosan treated cotton fabrics have more dye sites to attach more dye molecules than that of the untreated fabrics. Although the chitosan treated cotton fabric took more dyes of Mangosteen Rind aqueous extract, the 1% chitosan treated fabric felt a little stiffer than the untreated fabric. The amount of chitosan used in treating the cotton fabric needs to be adjusted if stiffness is not desirable for the end fabric. For this study, the 1% chitosan concentration was used for padding on cotton fabric through out this work.

Table 2. K/S on dyed fabrics.

Chitosan concentrations	K/S, at 360 nm
0%	0.99
0.10%	1.07
0.25%	1.34
0.50%	1.54
1.0%	2.27

The fabric was dyed with aqueous extract from 2 g of Mangosteen Rind powder/100 ml. of water

Dyeing without a mordant

The untreated and 1% chitosan treated cotton fabrics were dyed with 2 g of dye extract at a liquor ratio of 35:1. The temperature of the dye bath was raised to 100°C and maintained at this temperature for 1 h. The dyeing was carried out in an AHIBA NUANCE dyeing machine. The dyed fabrics were rinsed with tap water, followed by soaping at a liquor ratio of 50:1 with sodium hydroxide 1 g/l at 50°C for 45 min. Finally, the fabric samples were washed with tap water, squeezed and dried.

Dyeing with mordants

The three different methods of dyeing employed were pre-mordanting, meta-mordanting and post-mordanting. Mordant concentration at 5 g/l was used.

Pre-mordanting, the untreated and chitosan treated fabrics were first immersed in a bath containing each studied mordant for 45 min. at 30°C. All the mordanted fabrics were dyed by the above method.

Meta-mordanting, the untreated and chitosan treated fabrics were immersed in a bath containing both a mordant and the dye extract and dyed by the above method.

Post-mordanting, the untreated and chitosan treated fabrics were first dyed at 100°C for 60 min., and then followed by mordanting in a separate bath containing each studied mordant at 30°C for 45 min. The mordanted fabrics were rinsed, soaped, washed with water, squeezed and dried.

Colour measurement

Colour values were evaluated by means of K/S and CIE L*, a*, b* colour difference values (illuminant D_{65}/10° observer) on Macbeth Color-eye 7000 spectrophotometer.

Fastness determination

Wash-fastness tests were carried out according to the ISO105-CO2:1998 (E) in AHIBA NUANCE dyeing machine. Light-fastness tests were carried out according to AATCC Method 16-1998 in Heraeus. The colour change of the sample was assessed against the grey scale and the blue wool references.

RESULTS AND DISCUSSIONS

Colours

Results in Tables 3 and 4 show the effect of mordants on K/S and colour differences of dyed fabrics treated with 1% chitosan and untreated. Comparison of the results in Tables 3 and 4 showed that the chitosan treated cotton fabrics had a higher depth of shade (K/S) than those of the untreated fabrics for all mordants. The effect of all mordant dyeing techniques on the depth of shade and colour differences was studied.

For the untreated dyed fabrics, the meta-mordanting dyeing method showed a higher depth of shade for three mordants compared with the fabrics dyed using the other two methods. The stannous chloride in the pre-mordanting dyeing method only provided better K/S value than that of the dyed fabrics using no mordant, while the stannous chloride in meta-mordanting and post-mordanting provided lower K/S values than that of the dyed fabric using no mordant. This may be due to less dye complex formation formed in meta-mordanting and post-mordanting than that formed in pre-mordanting. The meta-mordanting dyeing method showed higher colour difference (ΔE*) values for all mordants compared with the fabrics dyed using the other two methods. This means that all mordants used in meta-mordanting method provided the most colour differences in dye shade when compared with that of the dyed fabrics using no mordant. The ΔE* could be attributed to the difference in CIE L*, a*, b* values of the dyed samples. The L* value defines the white-dark range. The higher L* is whiter or lighter. The a* defines the red-green range. The higher a* is more reddish. The b* defines the yellow-blue range. The higher b* is more yellowish. The ferrous sulphate heptahydrate mordant gave a gray shade on dyed fabric. The copper sulphate pentahydrate gave a dark brown shade on dyed fabric. The stannous chloride and aluminum potassium sulphate gave a light brown shade on dyed fabric the same as on the dyed fabric without mordant. Although the shade of dye on those fabrics was called light brown, they were not exactly the same. The value of CIE L*, a*, b* were somewhat different. There were a few differences in each light brown shade.

Table 3. Effect of mordants on dye properties of dyed fabrics without treating chitosan.

Mordant	K/S	ΔE*	CIELAB			Visual colour description
			L*	a*	b*	
No mordant	1.19	0.00	74.94	7.86	17.92	Pale yellowish brown
Pre-mordanting						
$KAl(SO_4)_2 . H_2O$	1.31	0.87	74.31	7.82	18.52	Pale yellowish brown
$FeSO_4 . 7H_2O$	2.16	11.07	64.45	6.54	14.62	Pale brownish gray
$SnCl_2 . 2H_2O$	2.27	5.57	69.71	9.58	18.74	Pale reddish brown
$CuSO_4 . 5H_2O$	3.12	13.05	62.35	9.92	20.66	Brown
Meta-mordanting						
$KAl(SO_4)_2 . H_2O$	1.73	4.42	70.59	8.61	18.00	Pale yellowish brown
$FeSO_4 . 7H_2O$	3.01	20.36	56.11	5.33	10.60	Light brownish gray
$SnCl_2 . 2H_2O$	0.71	9.29	81.08	5.12	11.50	Very pale yellowish brown
$CuSO_4 . 5H_2O$	3.46	14.48	60.49	9.60	20.29	Brown
Post-mordanting						
$KAl(SO_4)_2 . H_2O$	1.00	3.23	75.61	6.80	14.94	Pale yellowish brown
$FeSO_4 . 7H_2O$	1.97	10.87	66.08	4.46	12.63	Pale brownish gray
$SnCl_2 . 2H_2O$	0.76	6.38	78.84	6.33	13.10	Very pale yellowish brown
$CuSO_4 . 5H_2O$	1.51	4.08	71.48	5.72	17.70	Pale yellowish brown

Table 4. Effect of mordants on dye properties of dyed fabrics treated by 1% chitosan.

Mordant	K/S	ΔE*	CIELAB			Visual colour description
			L*	a*	b*	
No mordant	3.17	0.00	60.68	10.76	20.58	Brown
Pre-mordanting						
$KAl(SO_4)_2 . H_2O$	2.89	2.20	62.48	10.30	19.40	Light brown
$FeSO_4 . 7H_2O$	6.78	19.19	43.96	7.10	11.89	Dark brownish gray
$SnCl_2 . 2H_2O$	6.61	8.25	53.69	14.27	23.20	Dark reddish brown
$CuSO_4 . 5H_2O$	6.28	9.33	51.46	11.81	21.55	Dark brown
Meta-mordanting						
$KAl(SO_4)_2 . H_2O$	3.47	1.82	62.27	11.27	21.31	Light brown
$FeSO_4 . 7H_2O$	7.20	20.94	42.67	6.22	10.91	Dark brownish gray
$SnCl_2 . 2H_2O$	1.06	19.35	78.10	6.29	13.43	Pale yellowish brown
$CuSO_4 . 5H_2O$	6.79	10.46	50.29	11.20	21.66	Dark brown
Post-mordanting						
$KAl(SO_4)_2 . H_2O$	3.02	2.63	60.30	10.35	18.01	Brown
$FeSO_4 . 7H_2O$	4.10	16.23	50.05	5.27	9.62	Brownish gray
$SnCl_2 . 2H_2O$	2.25	5.32	63.74	11.15	16.24	Reddish brown
$CuSO_4 . 5H_2O$	4.22	6.00	55.59	8.38	18.47	Brown

For the chitosan treated dyed fabrics, the meta-mordanting dyeing method showed the maximum depth of shade for three mordants compared with the fabrics dyed using the other two methods. The aluminium potassium sulphate dodecahydrate using the pre-mordanting dyeing method provided better K/S value than that of the dyed fabrics using no mordant, while the other methods of meta-mordanting and post-mordanting provided less K/S values than that of the dyed fabric using on mordant. The meta-mordanting dyeing method showed a higher colour difference (ΔE*) value for three mordants compared with the fabrics dyed using the other two methods. This means that the mordants used in the meta-mordanting method resulted in the most shade change as compared with that of the dyed fabrics using no mordant. The ferrous sulphate heptahydrate mordant gave the highest value of ΔE* because the shade of dyed fabric changed from brown to gray on the dyed fabric. The copper sulphate pentahydrate gave a dark brown shade on dyed fabric. The aluminum potassium sulphate gave a light brown shade on dyed fabric similar to the shade of the dyed fabric without mordant. The stannous chloride gave a light brown shade to the dyed fabric when using pre-mordanting and post-mordating techniques, but it gave a light yellow shade on dyed fabric when using meta-mordaing technique. This may be due to the less complex-forming ability of the metal ions with the dye molecules in this technique.[1,2]

According to the results in Tables 3 and 4, it can be concluded that each mordant and each mordant dyeing technique affected the K/S and CIE L* a* b* of the dyed fabrics differently. This may be due to the individual metal ions exhibiting unique dye complex formations, leading to different shades.

The K/S values of untreated and chitosan treated fabrics in the Tables 3 and 4 were different from those in Table 2. This is because the K/S values of dyed fabrics in Tables 3 and 4 were measured after the dyed fabrics passed the soaping step while those in Table 2 did not under go this soaping step. The dyed fabrics soaped with sodium hydroxide had a higher K/S value than those of un-soaped fabrics.

Fastness

Wash-fastness (WF) and light-fastness (LF) results of the dyed fabrics with and without chitosan treatment are indicated in Table 5. The dyed fabric treated with chitosan improved both the light-fastness by one unit on the standard blue wool scale and wash-fastness by one unit on the standard grey scale compared with the dyed fabric without chitosan. In addition, the results indicate that the use of mordants also improved the wash-fastness and light-fastness of the dyed fabrics in some cases, depending on the mordanting techniques used. For wash-fastness of both treated and untreated chitosan dyed fabrics, the improvement in wash-fastness was greatest with post-mordanting. This may be due to better fixing of dye onto the fiber by using the post-mordanting method and there were fewer dye molecules for fixing than those in the other two methods. The improvement in light-fastness was maximized with meta-mordanting. This may be due to the greater complex-forming ability of the metal ions with dye molecules than occurs in the other processes.

Table 5. Fastness values for cotton fabrics dyed with Mangosteen Rind.

Mordant	Fastness			
	Untreated chitosan fabric		Treated chitosan fabric	
	LF	WF	LF	WF
No mordant	2	3	3	4
Pre-mordanting				
$KAl(SO_4)_2 . H_2O$	2	3	3	3/4
$FeSO_4 . 7H_2O$	3	3	4	4
$SnCl_2 . 2H_2O$	3	4/5	4	4
$CuSO_4 . 5H_2O$	3	3	4	4/5
Meta-mordanting				
$KAl(SO_4)_2 . H_2O$	3	3	4	3/4
$FeSO_4 . 7H_2O$	4	3	4	4
$SnCl_2 . 2H_2O$	4	4/5	4	4
$CuSO_4 . 5H_2O$	4	¾	4	4/5
Post-mordanting				
$KAl(SO_4)_2 . H_2O$	3	4	3	4
$FeSO_4 . 7H_2O$	3	4	4	4
$SnCl_2 . 2H_2O$	3	4/5	4	4/5
$CuSO_4 . 5H_2O$	4	¾	4	4/5

CONCLUSIONS

The purpose of this project was to study the effect of chitosan on the dyeing properties of Mangosteen Rind on cotton fabric. The results of this study conclude the chitosan treatment of cotton fabric improved depth of shade on dyed fabrics. This may be because the chitosan treated cotton fabric provided more dye sties to attach more dye extraction than that of the untreated fabric. The cotton fabric treated with chitosan not only provided better depth of shade but also provided better wash-fastness and light-fastness than those of untreated fabric dyed with Mangosteen Rind. The use of different mordants and the mordanting methods affected the dye shade and depth of shade on the dyed fabrics differently. This may be due to the different complex-forming ability of metal ions and dye molecules in each combination mordant and mordanting technique. Cotton fabrics dyed with Mangosteen Rind with mordants had better wash and light fastness results than those of fabrics dyed without mordants.

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