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Effect of Chitosan and Mordants on Dyeability of Cotton Fabrics with *Ruellia tuberosa Linn*.

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ABSTRACT

Knitted cotton fabric was treated with chitosan at different concentrations to find a suitable concentration on dyeability with *Ruellia tuberosa Linn*. The influence of dyeing methods with mordants, i.e. pre-mordanting, meta-mordanting, and post-mordanting was determined. The light and wash fastness of chitosan-treated samples were measured compared with untreated samples. The results showed that the suitable chitosan concentration used in this research was 0.75%W/V. Chitosan-treated fabric improved both dyeability and fastness compared with untreated fabric. Each mordant gave different shades of color and mordant techniques affected to color intensity and fastness of fabric.

Keywords: *Ruellia tuberosa Linn*., natural dye, cotton, chitosan, mordant.

1. INTRODUCTION

Natural dyes can be anything that come from natural sources such as flowers, leaves, roots, insects, shells, and mineral substances [1,2]. They are used for food coloring [3], painting [4], and textile dyeing [5,6]. Using natural dyes in textile processing have been shown a greater interest because they are more-ecofriendly than synthetic dye and show a variety of colors from one natural dye depending on dyeing process and types of mordants [7-9]. There are a small number of companies that produce commercially natural dyes i.e. de la Robbia and Allegro natural dyes. However, natural dyes are less permanent and wash out easily so they need mordants to fix dye on fabric. Mordants can be divided into two groups: toxic metal salts such as aluminum potassium sulfate and stannous chloride and non-toxic mordants i.e. mud, blood, cream-of-tartar and tannic acid from leaves [1, 10]. Some examples of natural dyes are obtained from various sources such as tea leaves [11], lawsone, and burberine [12]. However, there is no work reported on the use of *Ruellia tuberosa Linn* as a natural dye in textile application.

Ruellia tuberosa Linn. known as popping pod or meadow weed is reported as a medical plant in some countries and as weed in some crop plantations because of its fast propagation ability. In folk medicine, the ethanol extraction of this plant has been used as diuretic, antidiabetic, antipyretic, analgesic, antihypertensive, thirst quenching, and antidotal agent [13-15]. This tropical plant is widely distributed in Southeast Asia. It can grow up to a height of 6.5 inches on moist and shady place. It can be found to flower abundantly in July-August. Flowers are light bluish purple in color that is due to anthocyanin, the common name of flavonoid pigments [16] with funnel-shaped, 5-lobed corolla. Fruits, a pod with 7-8 seeds, can be split when they get wet.

Most types of fibers can be dyed with natural dyes; nevertheless, the depths of color and fastness of dyed fabrics are varied. Generally, the vegetable fibers, for example cotton, flax, and linen are less suitable to dye with natural dyes than protein fibers such as silk and wool. To get higher color intensity of vegetable fabrics, they were modified with cationic agents.

Chitosan, one of cationic agents, is used as a plant growth enhancer in agriculture and used for removing oils, heavy minerals, and phosphorous from water in industrial company. It also can speed up blood clotting and provide antibacterial properties and used for fabric modification [17-20]. It is a deacetylated of chitin produced from prawn shells, shrimp shells, crab shells, fly larva shells and squid pens [21-23]. A number of investigators, including Davidson and Due [19] reported a better dyeability for treated wool by chitosan. Vakhitova and Safonov [20] found that using chitosan in acid dye bath increased intensity and strength of color. Houshyar and Amirshahi [18] observed cotton treatment with chitosan also increased the dye absorption of reactive dye.

In this study, the effect of chitosan and mordants on dyeing properties was studied. The results of fastness properties, shade, and depths of shade as affect by three different methods of dyeing, i.e. pre-mordanting, meta-mordanting, and post-mordanting were also studied.

2. MATERIALS AND METHODS

2.1 Materials

Blue-purple *Ruellia tuberosa Linn* flowers were collected from Rajamangala University of Technology Krungthep, Bangkok, Thailand. Knitted cotton fabric was donated from Nan Yang Knitting Factory Co., Ltd., Thailand. Chitosan (middle viscose) was purchased from Fluka, USA. Some mordants, lime and ash, were get from fresh-food market and burnt charcoal, Thailand, respectively. All other chemicals were of laboratory grade and used without further purification.

2.2 Extract Preparation

Flowers were dried with silica gel for overnight and ground in a grinding mill through mesh number 35. Fifteen grams of flower powder was dissolved in 85 ml of water in a beaker. The mixture was stirred at room temperature for 5 minutes. The dye solution was filtered for further use.

2.3 Pretreatment of Cotton Fabric

Cotton fabric was scoured and bleached with a solution containing hydrogen peroxide (50%) 6 g/L, sodium hydroxide 5 g/L, sodium silicate as a stabilizer 2 g/L, non-ionic wetting agent 1 g/L. The ratio of fabric to dyeing solution was 1:30 (W/V). The condition was used at 100^{o}C for 45 minutes. Then, the fabric was rinsed with hot and cold water for 15 minutes each, respectively. The fabric was tested water absorption according to AATCC Test Method 79-2000 before use. After scouring and bleaching process, the fabrics were cut into 5 g in weight in all experiment.

2.4 Preparation of Chitosan Solution

Chitosan solutions were prepared at 0.25, 0.5, 0.75, 1.0, and 1.5 % W/V. Each amount of chitosan was dissolved in 1 % V/V acetic acid and left overnight at room temperature. Then, the solution was filtered to remove any insoluble materials.

2.5 Treatment of Chitosan on Cotton Fabric and Dyeing Method

Each chitosan solution was padded on cotton fabrics by padding machine (model MU504A), Beijing Textile Equipment Institute, China. The chitosan-treated samples were dried at 100°C for 5 minutes in oven. After that, they were dyed with dye solution as mentioned earlier (section 2.2) at 50°C for 30 minutes with 1:20 (W/V) of fabric to dyeing solution ratio by using a UniDye Infra-red dyeing machine OD-501, Union TSL Limited, Thailand. The dyed fabric were washed with 2 g/L of soap solution at 50°C for 15 minutes, rinsed with tap water, squeezed, and dried at room temperature. Depth of color, expressed as K/S, was measured on the dyed fabric.

2.6 Dyeing with Mordants

Natural dyes require mordants to produce affinity between fabric and pigments. The three different methods of dyeing with mordants were pre-mordanting, meta-mordanting, and post-mordanting. Concentration of mordants was used at 5 g/L. For pre-mordanting, both untreated and chitosan-treated fabrics were immersed in a solution containing each studied mordant for 45 minutes at room temperature, then fabrics were dyed at 50°C for 30 minutes. Both a mordant and dye solution were mixed and dyed at 50°C for 30 minutes on untreated and chitosan-treated fabrics for meta-mordanting. For post-mordanting, the untreated and chitosan-treated fabrics were dyed and then followed by immersing dyed fabric in solution containing each mordant at room temperature for 45 minutes. All mordanted fabrics were washed with 2 g/L of soap solution for 15 minutes at 50°C, rinsed with tap water, squeezed, and dried at room temperature.

2.7 Color Measurement

The depth of color, color difference, and CIE L*a*b* values were determined by Datacolor Check II spectrophotometer, Datacolor, USA. The color strength (K/S value) was calculated from reflectance data using the Kubelka-Munk equation:

$$K/S = (1-R)^2/2R$$

where R is the reflectance of dyed fabric at maximum wavelength

2.8 Fastness Determination

Wash-fastness and light-fastness tests were carried out according to the ISO 105-CO2:1998(E) and AATCC method 16-1998, respectively. The color change and degree of staining were evaluated using grey scale.

3. RESULTS AND DISCUSSION

The results in Table 1 show that the color strength, K/S values, of all chitosan-treated fabrics had higher values than the untreated fabrics. The K/S values increased gradually with an increase in the concentration of chitosan. The results indicated that chitosan treatment on fabric provided more dye sites than untreated fabric. These can be explained that natural dyes contain unsaturated moiety bearing ionizable groups such as hydroxyl and carboxylic groups. In water with right pH value, they become water soluble due to their presence in anionic forms. Cotton by its nature is negatively charged in water, thus exhibiting poor absorption for natural dyes due to repulsion effect. The application of chitosan could help improve the absorption of natural dyes thanks to its cationic characteristic. It is well-known that chitosan is capable of forming ionic interaction with cotton cellulose,

Table 1. K/S values of chitosan-treated cotton fabric at different concentrations on dyed fabric.

Chitosan concentration (%)	Chitosan-treated fabric				Chitosan-treated fabric with dyeing			
	K/S at 400 nm	L*	a*	b*	K/S at 400 nm	L*	a*	b*
0	0	92.82	-0.03	4.44	1.00	79.95	2.35	14.55
0.25	0.01	92.51	-0.19	4.85	2.98	68.68	4.96	18.78
0.50	0.02	92.64	-0.15	5.40	3.29	66.19	5.19	17.28
0.75	0.03	92.18	-0.11	5.79	3.53	65.61	5.20	17.81
1.00	0.04	91.99	-0.15	5.76	3.69	65.44	4.03	17.20
1.50	0.09	89.08	-1.12	6.21	5.78	59.79	5.21	16.41

rendering cotton cellulose positive charged. As a result, chitosan treated cotton is anticipated to favorably absorb natural dyes through the ionic interaction between dye-anions and fiber-cations mechanism [18, 23]. However, treatment of chitosan affected to hand properties and color of fabrics. Chitosan made the fabric stiffer and a bit yellower than untreated fabrics. In this research, 0.75% chitosan concentration was used for padding on cotton fabric because of desirable stiffness fabric. The amount of chitosan can be adjusted depending on the end-used fabric; nevertheless, applied amount of chitosan was limited at high concentration because its high viscosity which caused un-uniform coating and color on fabric [24].

The effect of mordants on color intensity (K/S) of chitosan-treated and untreated fabric was examined by spectrophotometer. Table 2 and 3 show chitosan-treated fabric had higher K/S than those of untreated fabrics for all mordants. This result indicated that chitosan provided more dye site on fabric surface. In the case of dyeing techniques with mordants, post-mordanting showed higher K/S compared with other methods for untreated fabric. For fabrics treated with chitosan, K/S values of meta-mordanting and post-mordanting were higher than those of pre-mordanting. These results were explained that post-mordanting can form more stable dye-mordant complex than other methods in the case of untreated fabric, whereas chitosan-treated fabric can form more stable dye-mordant complex in meta-mordanting and post-mordanting than in pre-mordanting depending on used mordant. The difference of mordant types showed different in color of fabric expressed as CIE L*a*b*. Three values of CIE L*a*b* are L* (white-black), a* (red-green), and b* (yellow-blue). The increased values of L*, a*, and b* define whiter, more reddish, and more yellowish, respectively. Both untreated and chitosan-treated fabrics dyed with popping pod gave the same color in each mordant. However, when shade of fabrics were called the same such as pale yellownish brown, they were not exactly the same that the L*a*b* values can explain the difference in each shade.

For untreated dyed fabric, it can be seen that the post-mordanting method showed larger color difference (ΔE^*) values compared with the other two methods. The ΔE^* values mean the color difference between sample and reference which are the dyed fabric using mordant and no mordant, respectively in this study. The increased ΔE^* values mean the larger color difference. These results can be

Table 2. Effect of mordants on dye properties of dyed fabrics without chitosan treatment.

Mordant	K/S	ΔE*	CIE L*a*b*			Visual color description
			L*	a*	b*	
None	0.03	0	92.18	-0.11	5.79	Pale yellowish brown
Pre-mordanting						
$MnSO_4$	0.64	7.22	84.00	-0.15	13.4	Pale yellowish brown
$FeSO_4$	1.15	10.90	73.70	4.04	11.61	Pale reddish brown
$SnSO_4$	1.33	8.07	76.62	1.28	8.00	Pale yellowish brown
$CuSO_4$	3.04	17.80	79.49	-4.57	26.53	Pale yellowish green
NaCl	0.76	6.83	83.39	0.57	12.43	Very pale yellowish brown
Lime juice	0.68	6.32	81.69	0.74	10.19	Very pale yellowish brown
Ash	0.75	6.68	83.29	-0.04	12.16	Very pale yellowish brown
Meta-mordanting						
$MnSO_4$	1.85	11.49	75.06	-1.34	15.49	Pale yellowish brown
$FeSO_4$	3.93	18.60	56.74	5.04	10.21	Reddish brown
$SnSO_4$	1.45	6.95	81.22	0.52	11.21	Very pale yellowish brown
$CuSO_4$	5.86	18.95	68.03	-3.93	24.03	Pale yellowish green
NaCl	1.35	9.70	79.8	0.52	15.3	Very pale yellowish brown
Lime juice	1.29	8.05	82.79	0.66	14.1	Very pale yellowish brown
Ash	1.11	8.91	76.65	1.03	11.24	Very pale yellowish brown
Post-mordanting						
$MnSO_4$	2.81	16.67	70.87	2.50	21.94	Yellowish brown
$FeSO_4$	5.44	21.43	52.71	4.39	15.29	Reddish brown
$SnSO_4$	2.56	13.68	75.93	0.92	19.82	Yellowish brown
$CuSO_4$	6.81	21.83	68.35	-0.90	29.16	Yellowish green
NaCl	1.28	12.00	76.31	3.19	16.73	Pale yellowish brown
Lime juice	1.36	12.67	74.98	3.86	16.90	Pale yellowish brown
Ash	1.01	10.20	78.51	2.39	15.08	Pale yellowish brown

explained that more dye can form complex formation in post-mordanting than in other two methods. The stannous sulphate, manganese sulfate, sodium chloride, lime juice, and ash gave the yellowinsh brown similar to the shade of dyed fabric without mordants. Iron sulphate gave pale reddish brown, while copper sulphate gave pale yellownish green. Each mordant gave different colors on fabrics because the individual metal ions display unique complex formation. Briefly, metals have relatively low energy levels. The incorporation of the metal atoms into the delocalized electron system of the dye result in a lowering of the overall energy that affect to absorbance of dye-mordant complex known as chelate [25].

In the case of chitosan-treated fabric dyed with popping pod, the dyed fabric exhibited a yellowish brown color with using stannous sulphate, manganese sulphate, sodium chloride, lime juice, and ash as a mordant. They all gave the same shade of color compared with dyed fabric without mordant. Copper sulphate had yellownish green in all mordanting techniques. Iron sulphate resulted in reddish brown shade in pre-mordanting method, while it gave dark

Table 3. Effect of mordants on dye properties of dyed fabrics with chitosan treatment.

Mordant	K/S	ΔE*	CIE L*a*b*			Visual color description
			L*	a*	b*	
None	3.53	0	65.61	5.20	17.81	Yellowish brown
Pre-mordanting						
$MnSO_4$	5.87	2.78	61.10	5.57	20.82	Yellowish brown
$FeSO_4$	9.64	11.57	44.30	10.88	16.71	Reddish brown
$SnSO_4$	4.11	1.95	62.34	6.43	19.11	Yellowish brown
$CuSO_4$	8.55	7.71	64.45	1.63	30.50	Pale yellowish green
NaCl	4.35	1.64	62.33	5.32	17.90	Light brown
Lime juice	4.20	1.19	63.67	4.30	17.60	Light brown
Ash	4.99	1.89	62.58	6.46	19.32	Light brown
Meta-mordanting						
$MnSO_4$	5.83	3.52	58.78	5.54	19.37	Brown
$FeSO_4$	15.63	17.49	32.87	5.86	7.59	Dark brown
$SnSO_4$	4.67	2.99	60.19	5.89	20.11	Yellowish brown
$CuSO_4$	8.55	6.71	59.21	-1.62	21.54	Yellowish green
NaCl	5.71	2.16	61.90	6.04	19.71	Brown
Lime juice	5.24	2.62	61.72	6.98	20.43	Brown
Ash	6.21	3.75	58.40	6.26	19.34	Brown
Post-mordanting						
$MnSO_4$	6.62	4.78	62.53	3.43	25.35	Brown
$FeSO_4$	10.81	11.63	42.71	5.57	14.39	Dark brown
$SnSO_4$	5.12	4.55	67.22	0.71	22.17	Brown
$CuSO_4$	10.92	7.48	58.62	2.18	28.69	Yellowish green
NaCl	3.60	0.77	64.79	4.64	18.53	Brown
Lime juice	3.92	1.07	64.84	6.44	18.86	Brown
Ash	5.61	3.97	61.00	3.66	22.95	Brown

brown shade in meta-mordanting and post-mordanting methods. Stannous sulphate showed yellowish brown shade in pre-mordanting and meta-mordanting, and brown shade in post-mordatning. Once again, it can conclude that individual metal ions and different techniques exhibit unique complex formation resulting in the different shade of color. The color differences of these dyed fabrics with chitosan treatment were different in each technique depending on mordant.

The results of wash-fastness (WF) and light fastness (LF) of dyed fabric with and without chitosan are shown in Table 4. The fabrics were compared with grey scale to obtain the color change compared with fabric before testing. Grey scale has scale from 1 to 5 that scale 1 indicates the most color difference and scale 5 means no color difference. Both LF and WF of chitosan-treated fabrics showed higher scale than those of untreated fabric, indicating that chitosan can help to improve fastness in both methods. Using different techniques for dyeing affected to the fastness as well. For example, in the case of LF, most fabrics treated with chitosan can remain the same scale or improve LF as before testing. However, using sodium

Table 4. Fastness values for cotton fabrics dyed with popping pod.

Mordant	Fastness			
	Untreated fabric		Chitosan-treated fabric	
	LF	WF	LF	WF
None	3/4	4	4	4/5
Pre-mordanting				
$MnSO_4$	3/4	3/4	3/4	4/5
$FeSO_4$	4	2/3	4/5	2/3
$SnSO_4$	2/3	3	3	3/4
$CuSO_4$	4/5	2	4/5	3/4
NaCl	3/4	3/4	3	4/5
Lime juice	3	4	4	4/5
Ash	3/4	2	3/4	4/5
Meta-mordanting				
$MnSO_4$	3	2	4	4/5
$FeSO_4$	3	1/2	4	2
$SnSO_4$	3	3/4	3/4	4
$CuSO_4$	3	2/3	3	3
NaCl	3/4	3/4	3/4	4
Lime juice	3	3/4	4	4
Ash	3	3/4	3/4	4
Post-mordanting				
$MnSO_4$	3	4/5	3/4	4/5
$FeSO_4$	3	3	4	3
$SnSO_4$	3	4/5	3	4/5
$CuSO_4$	4/5	4	4/5	4/5
NaCl	3/4	4/5	3	4/5
Lime juice	4	4/5	3/4	4/5
Ash	4	4/5	2/3	4/5

chloride as a mordant, the results showed the chitosan-treated fabric decreased light-fastness in both pre-mordanting and post-mordanting, while LF scale remained the same as before testing in meta-mordanting technique. Moreover, LF of fabric treated with chitosan was decreased when using lime juice and ash in post-mordanting. Overall, the post-mordanting for WF and LF of chitosan-treated fabric showed a highest scale compared with other methods because of better fixing of dye on fabric. The explanation of these results is the metal ions can chelate several dye molecules together, thus creating a larger complex and providing a link between the dye and fiber [1]. These insoluble complexes form within the fiber resulting in increasing depth of shade and fastness of color [26].

The specimens of dyed fabrics were attached with multifiber fabric consisting of wool, polyester, polyamide, acrylic, cotton, and cellulose acetate. After WF test, the specimens were obtained color change and multifiber fabrics were observed the staining with grey scale as shown in Tables 5 and 6. The scale 5 means no staining on fabric, while scale 1 indicates the most staining on fabric. All dyed fabrics showed good to excellent results that were no staining or a bit staining on multifiber fabrics. In the case of fiber types, cotton was the greatest fibers that this dye attached. The most staining on multifiber fabric was occurred when using copper sulphate as mordant. However, sometimes the staining was not observed because the color of dyed fabrics was pale color.

Table 5. Staining degree of dyed fabrics without chitosan treatment.

Mordant	Staining					
	Wool	Polyester	Polyamide	Acrylic	Cotton	Cellulose acetate
None	5	5	5	5	5	5
Pre-mordanting						
$MnSO_4$	5	5	5	5	5	5
$FeSO_4$	5	5	5	5	5	5
$SnSO_4$	5	5	5	5	5	5
$CuSO_4$	5	5	5	5	4/5	5
NaCl	5	5	5	5	5	5
Lime juice	5	5	5	5	5	5
Ash	5	5	5	5	5	5
Meta-mordanting						
$MnSO_4$	5	5	5	5	5	5
$FeSO_4$	5	5	5	5	5	5
$SnSO_4$	5	5	5	5	5	5
$CuSO_4$	5	5	5	5	4/5	5
NaCl	5	5	5	5	5	5
Lime juice	5	5	5	5	5	5
Ash	5	5	5	5	5	5
Post-mordanting						
$MnSO_4$	5	5	5	4/5	5	5
$FeSO_4$	5	4/5	4/5	4/5	4/5	4/5
$SnSO_4$	5	5	5	5	5	5
$CuSO_4$	4	4	4	4	4	4
NaCl	5	5	5	5	5	5
Lime juice	5	5	5	5	5	5
Ash	5	5	5	5	5	5

Table 6. Staining degree of dyed fabrics without chitosan treatment.

Mordant	Staining					
	Wool	Polyester	Polyamide	Acrylic	Cotton	Cellulose acetate
None	5	5	5	5	5	5
Pre-mordanting						
$MnSO_4$	5	5	5	5	5	5
$FeSO_4$	5	5	5	5	5	5
$SnSO_4$	5	5	5	5	5	5
$CuSO_4$	4/5	4/5	4/5	4/5	4/5	4/5
NaCl	5	5	5	5	5	5
Lime juice	5	5	5	5	5	5
Ash	5	5	5	5	5	5
Meta-mordanting						
$MnSO_4$	5	5	5	5	4/5	5
$FeSO_4$	5	5	5	5	4/5	5
$SnSO_4$	5	5	5	5	5	5
$CuSO_4$	5	5	5	5	4	5
NaCl	5	5	4/5	4/5	4/5	4/5
Lime juice	5	5	4/5	4/5	4/5	5
Ash	5	4/5	4/5	4/5	4/5	4/5
Post-mordanting						
$MnSO_4$	5	5	5	5	5	5
$FeSO_4$	5	5	5	5	5	5
$SnSO_4$	5	5	5	4/5	4/5	5
$CuSO_4$	5	4/5	4/5	4/5	4	5
NaCl	5	5	5	5	5	5
Lime juice	5	5	5	5	5	5
Ash	5	5	5	5	5	5

4. CONCLUSIONS

The purpose of this study is to investigate the effects of chitosan, types of mordants, and dyeing methods on dyeing properties of cotton fabric dyed with popping pod. Chitosan can improve color intensity of cotton fabric because it provided more dye sites than of untreated fabric. In the case of fastness, chitosan-treated fabric showed better wash-fastness and light-fastness than untreated fabric dyed with popping pod. Using different mordants showed different dye shades. Moreover, mordanting methods affected to depth of shade. The explanation to this phenomenon is based on the fact that each metal-ion has a different ability to form complex form in different methods.

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