PROPERTIES OF SILK FABRIC DYED WITH EUCALYPTUS, QUERCETIN, RUTIN AND TANNIN USING PADDING TECHNIQUES

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Abstract Natural dyes from eucalyptus leaf extract, quercetin, rutin and tannin were applied to silk fabric by the padding techniques, namely the pad-batch and pad-dry techniques under different condition. In this experiment, ferrous sulfate was used as a mordant. The dyeing properties were evaluated by measuring K/S values and CIELAB. The different fastness properties were evaluated. The effect of dyes at different concentration levels with respect to their colour strength was also studied.

Keywords: natural dyes, eucalyptus, quercetin, rutin, tannin, pad-batch, silk, dyeing

1. Introduction

Natural dyes are known for their use in colouring of food substrate, leather, wood as well as natural fibers like wool, silk, cotton and flax as major areas of application since ancient times. Natural dyes may have a wide range of shades, and can be obtained from various parts of plants including roots, bark, leaves, flowers, and fruit [1]. Dyeing with natural dyes, however, normally requires the use of mordants, which are metallic salts of aluminum, iron, chromium, copper, among others, for ensuring a reasonable fastness of the colour to sunlight and washing [2]. The metal ions of these mordants can act as electron acceptors for electron donors to form coordination bonds with the dye molecules, making them insoluble in water. Lately, there has been increasing interest in natural dyes, as the public is becoming more aware of the ecological and environmental problems related to the use of synthetic dyes. The use of natural dyes cuts down significantly on the amount of toxic effluent resulting from synthetic dye processes. Natural dyes have also been used for antimicrobial [3-7] and for printing [8 - 11]. It is reported that some natural (vegetable) dyes not only dye with unique and elegant colours, but they also provide antibacterial and UV protective functions to fabrics [12-15]. Thus, these natural dyes are applied on fibres or fabrics of cotton, wool, silk, and flax.

Eucalyptus is one of the most important sources of natural dye that gives yellowish-brown colourants. The colouring substance of eucalyptus has ample natural tannins and polyphenols varying from 10% to 12% [16]. The major colouring component of eucalyptus bark is quercetin, which is also an antioxidant. It has been used as a food dye with high antioxidant properties [17]. Eucalyptus leaves contain up to 11% of the major components of tannin (gallic acid and ellagic acid) and flavonoids (quercetin, and rutin, etc.) as minor substances [18-20]. Tannins and flavonoids are considered very useful substances during the dyeing process because of their ability to fix dyes within fabrics. The structures of selected important colouring components of eucalyptus leaves are given in Figure 1.

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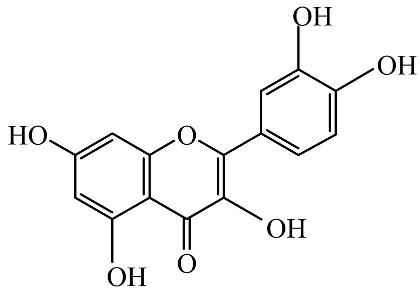
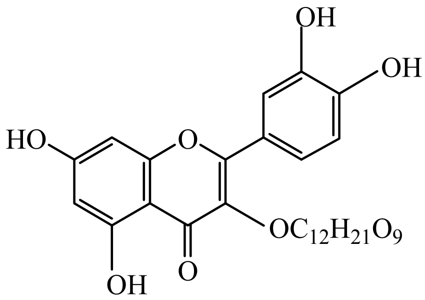
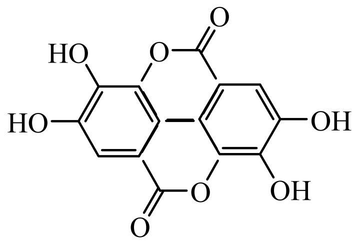


Quercetin (C.I. 75670)



Rutin (C.I. 75730)



Ellagic acid (C.I. 75270)

Figure 1. Colour composition of eucalyptus leaf extract dye.

Vegetable tannin extracts contain a variety of amorphous materials including polyphenolic tannins of large relative molecular mass (M_r), such as hydrolysable gallotannin, and tannic acid, as well as a less-complex of non-tannins, such as flavones and gums [21]. Because tannins have a large M_r and are water-soluble phenolic compounds, they undergo typical phenolic reactions, notably the chelation of metal ions. Tannins have been used in textiles for several hundreds of years, as exemplified by the dyeing of cotton and silk with dyewoods, in which the tannin is 'fixed' by a metal salt (e.g., $CuSO_4$) employed as a mordant for the dye [22]. Perkin [23] used tannins as mordants to increase the uptake of cationic dyes (e.g., Mauvein) onto cotton by firstly applying tannin to the cotton, followed by the 'fixing' of tannin by the application of metal (Fe, Al, Cu, Pb, or Sn) salt.

Flavonoids (polyphenolic pigments) are widely present in plants. Rutin (3,3',4',5,7-pentahydroxyflavone-3-rhamnoglucoside) and quercetin (3,3',4',5,7- pentahydroxyl-flavone) are phenolic compounds derived from hydroxyl substitutions on a flavone chromophore. Flavone-based compounds are known to form stable complexes with metal cations (Fe, Cu, Al and Cr) [24]. Flavonoids and tannins are two of the most interesting natural phenolic compounds.

Our interest lies in the colour that these compounds impart when added to silk fabric by the pad-batch dyeing technique, whereby a cloth is "padded" mechanically, applied by rapid passage through a small padding trough, followed by intensive squeezing between expression rollers and then dye fixation by batch at room temperature. After the dye fixation, the samples are thoroughly rinsed and air-dried.

Pure quercetin, rutin, and tannin were used in this study because they are the most common and effective. They are abundant in eucalyptus leaves. $FeSO_4.7H_2O$ mordant was also used in this work. This study also investigated the *CIELAB* and *K/S* values of the dyeing, as well as the fastness properties.

2. Experiment

2.1 Materials and chemicals

The eucalyptus leaves (Eucalyptus camaldulensis) used in this study were collected in Thailand. Quercetin dehydrate, 98% purity ($C_{15}H_{10}O_7.2H_2O$, M_W = 338.80), rutin hydrate, 95% purity ($C_{27}H_{30}O_{16}.xH2O$, M_W = 610.52), and tannin Ph. Eur. 5 ($C_{76}H_{52}O_{46}$, M_W = 1701.20) were purchased from Sigma, Fluka and Lachner, respectively. A commercially produced plain-weave silk fabric (thickness 0.15 mm, weight 67 g/m^2, fabric count per inch 96 x 80) was scoured and bleached (supplied by Chul Thai Silk Co., Thailand). The mordant used was ferrous (II) sulfate heptahydrate ($FeSO_4.7H_2O$). The anion wetting agent - Altaran S8 (Sodium alkylsulfate) and soaping agent- Syntapon ABA were supplied by Chemotex Děčin, Czech Republic.

2.2 Instrumentation

The mordanting and dyeing were carried out in a two-bowl padding mangle machine (Mathis, type number HVF.69805). A spectrophotometer (Datacolor 3890) was used to measure the colour strength. The colour strength, in terms of *K/S* values, was calculated using the Kubelka-Munk equation, $K/S = (1-R)^2/2R$, where R is reflectance of the dyed fabric; K is the sorption coefficient, and S is the scattering coefficient.

2.3 Dye extraction from eucalyptus leaves

Fresh eucalyptus leaves (Eucalyptus camaldulensis) were dried in sunlight for one month and crumbled using a blender and then were used as the raw material for dye extraction, which was achieved by the reflux technique: 70 g of crumbled eucalyptus leaves was mixed with 1 l of distilled water and refluxed for 1 h. It was then filtered and the dye solution was separated into two parts: (a) one for evaporating under reduced pressure (rotary evaporator), and (b) one for dyeing. The rotary evaporator provided a crude dye extract of eucalyptus leaves. Then, it was crumbled with a blender and used for obtaining the standard calibration curve. The dilution of the eucalyptus leaf extract gives a relatively clear solution system with a linear dependence on the concentration absorbance, an absorption peak (λ_{max}) at 262 nm [25]. The concentration of 20 g/l was calculated from a standard curve of concentrations of the eucalyptus leaf extract dye solution versus absorbance at the wavelength mentioned.

2.4 Mordanting and pad-dyeing

A simultaneous padding process was used in this study. To study the effect of dye concentration, three concentrations of the eucalyptus leaf extract, quercetin, rutin, and tannin dyes were chosen: 1 and 5 g/L. Ferrous sulfate mordant was used at concentration of 5 g/L for each dye concentration and 1 g/L of an anionic wetting agent (Altaran S8) was added to the dye solution. The pH of the dyeing solution (mixed with an acetic acid solution) was adjusted to 4. This pH condition has been optimised in the previous study [15, 26-27]. The fabric was then immersed in the dye solution at room temperature and padded on a two-bowl padding mangle at 80% pick up. After padding for 2 seconds, the samples were dried at 90 °C for 3 min for the pad-dry technique. Under the cold pad-batch dyeing technique, the padded fabric was rolled on a glass rod with a plastic sheet wrapped around the rolled fabric. Then, it was kept at room temperature for 24 hours. The samples were then washed in 1 g/L of the soaping agent, Syntapon ABA, at 80 °C for 5 min and air-dried at room temperature.

2.5 Evaluation of colour strength and fastness properties

The colour strength (*K/S*) and *CIELAB* of the dyed samples were evaluated using a spectrophotometer (Datacolor 3890). All samples measured showed a λ_{max} value of 400 nm The colour fastness to washing, light and rubbing of the dyed samples was determined according to ISO 105-C06 A1S: 1994, ISO 105-B02: 1994, and ISO 105-X12: 2001, respectively.

3. Results and Discussion

3.1 Effect of dyeing on CIELAB and K/S values

The colour value results are presented in Tables 1 and 2. Silk fabric dyed with eucalyptus leaf extract and tannin dye showed a pale yellowish-grey shade, while those dyed with ferrous sulfate showed a dark greyish-brown colour. Silk fabric dyed with quercetin without a mordant had a yellowish green colour. Silk mordanted with ferrous sulfate produced a dark yellowish-brown shade. Silk substrates dyed with rutin gave a pale yellowish-green, while those dyed with ferrous sulfate had a yellowish-brown colour.

Table 1 Colour value of silk fabric dyed with eucalyptus leaf extract and quercetin dyes by using simultaneous mordanting and padding techniques

Type of dye	Concen-tration	Pad-batch					Pad-dry				
		K/S	*L**	*a**	*b**	Dyed Sample	*K/S*	*L**	*a**	*b**	Dyed sample
Euca-lyptus	1 g/L Dye (without mordant)	0.59	86.5	2.0	-3.6		0.58	86.4	2.1	-3.8	
	5 g/L Dye (without mordant)	0.71	85.8	1.4	-1.4		0.66	86.2	1.5	-1.2	
	1 g/L Dye + 5 g/L $FeSO_4$	1.54	56.9	2.1	-1.8		1.48	60.9	2.3	-1.6	
	5 g/L Dye + 5 g/L $FeSO_4$	1.75	69.1	2.4	-1.2		1.63	58.2	1.9	-1.1	

Table 1 Colour value of silk fabric dyed with eucalyptus leaf extract and quercetin dyes by using simultaneous mordanting and padding techniques (Continue)

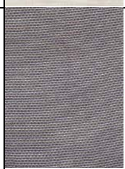
Type of dye	Concen-tration	Pad-batch					Pad-dry				
		K/S	*L**	*a**	*b**	Dyed Sample	*K/S*	*L**	*a**	*b**	Dyed sample
Querce-tin	1 g/L Dye (without mordant)	1.17	85.4	-2.2	6.0		1.09	86.3	-1.6	5.1	
	5 g/L Dye (without mordant)	1.58	86.3	-3.4	10.2		1.38	87.0	-3.0	8.2	
	1 g/L Dye + 5 g/L $FeSO_4$	4.55	46.9	3.5	20.1		4.30	51.9	1.7	15.2	
	5 g/L Dye + 5 g/L $FeSO_4$	8.03	36.7	1.4	14.9		7.61	39.8	2.9	16.8	

From Tables 1 and 2, it is clear that the colour shade of the fabrics dyed with tannin (a major constituent of eucalyptus leaves) is colourimetrically and visually observed to be very similar to that using eucalyptus leaf extract dye. The colours obtained with the various dyes vary in their tone due to the fact that when the different dyes (eucalyptus leaf extract, quercetin, rutin, and tannin) are combined with ferrous sulfate to form dye-ferrous complexes, different shades are then attained.

Figures 2 and 3 show the colour strength (*K/S*) values of silk fabric dyed with eucalyptus leaf extract, quercetin, rutin and tannin, respectively. It can be observed that the *K/S* values increase with an increase in dye concentrations. Silk fabric dyeing by pad-batch technique showed higher *K/S* values than using the pad-dry technique.

It can be concluded that silk fabrics can be successfully dyed with eucalyptus leaf extract dye, quercetin, rutin and tannin due to the formation of ferrous coordination complexes. Ferrous sulfate readily chelated with the dyes. As the coordination number of ferrous sulfate is 6, some coordination sites remain unoccupied when they interact with the fiber, which allows functional groups, such as amino and carboxylic acid, on the fiber to occupy these unoccupied sites. Thus ferrous can form a ternary complex on one site with the fiber and on another site with the dye [28].

Table 2 Colour value of silk fabric dyed with rutin and tannin dyes by using simultaneous mordanting and padding techniques

Type of dye	Concen-tration	Pad-batch					Pad-dry				
		K/S	*L**	*a**	*b**	Dyed Sample	*K/S*	*L**	*a**	*b**	Dyed sample
Rutin	1 g/L Dye (without mordant)	0.71	87.5	0.05	0.1		0.65	87.4	0.8	-1.6	
	5 g/L Dye (without mordant)	0.83	86.1	-0.4	2.0		0.76	87.0	-0.1	1.1	
	1 g/L Dye + 5 g/L $FeSO_4$	4.10	60.1	1.5	20.0		2.30	69.4	3.3	19.7	
	5 g/L Dye + 5 g/L $FeSO_4$	4.73	56.4	1.2	19.2		3.00	63.1	2.3	19.0	
Tannin	1 g/L Dye (without mordat)	0.58	86.2	2.0	-3.4		0.56	86.7	2.4	-4.1	
	5 g/L Dye (without mordant)	0.78	84.7	0.9	-1.0		0.67	86.8	1.3	-1.0	
	1 g/L Dye + 5 g/L $FeSO_4$	2.04	53.0	2.3	-1.8		1.77	54.5	2.1	-2.1	
	5 g/L Dye + 5 g/L $FeSO_4$	2.96	40.1	2.9	-4.4		2.81	41.6	4.1	-6.4	

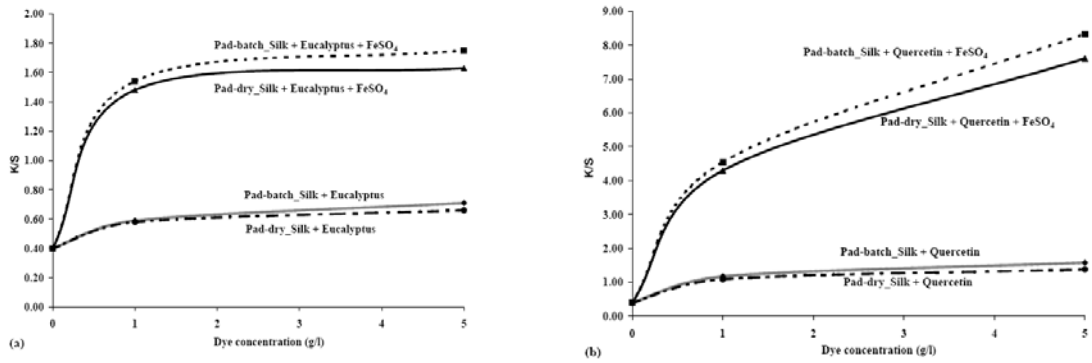


Figure 2. *K/S* values of silk fabric dyed with 1 *g/L* and 5 *g/L* ; eucalyptus leaf extract dye solutions (a) and quercetin (b) with 5 *g/L* $FeSO_4$, using pad-batch and pad-dry techniques

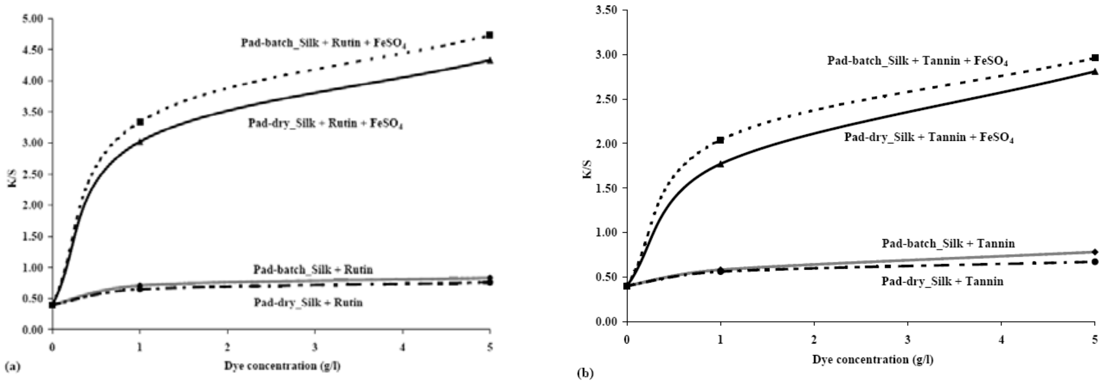


Figure 3. *K/S* values of silk fabric dyed with 1 *g/L* and 5 *g/L* ; rutin (a) and tannin (b) with 5 *g/L* $FeSO_4$, using pad-batch and pad-dry techniques

3.2 The colour fastness properties

The fastness ratings of silk fabric dyed with and without mordants at a dye concentration of 5 *g/L* and ferrous sulfate (5 *g/L*) are presented in Tables 3 to 5. Table 3 indicates that the washing fastness rating of silk fabric dyed with eucalyptus leaf extract, quercetin, rutin and tannin is very good (4 to 4-5). A probable explanation for the good fastness property is that tannin and flavonoids (quercetin and rutin) can form metal chelates with the ferrous mordant. Hence, after mordanting, the tannin and flavonoids are insoluble in water, thereby ultimately improving the washing fastness.

As seen in Table 4, a light fastness in the range of 3-4 (fair) can be observed in the silk fabric, except for that dyed with quercetin without mordant, whose rating was 2 (poor). This is attributed to the fact that the presence of 3-hydroxy groups in quercetin reduces the light fastness due to lower photostability [29]. However, silk dyed with tannin with or without a mordant, which shows to be in the range of 4 to 4-5 (good).

Table 3. Colour fastness to washing at 40°C (ISO 105-C06 A1S: 1994)

Dyeing and mordanting conditions	Colour change	Colour staining of multifibers					
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Pad-batch							
Eucalyptus	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Eucalyptus + Fe	4	4-5	4	4-5	4-5	4-5	4
Quercetin	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Quercetin + Fe	4	4-5	4	4	4-5	4-5	4
Rutin	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Rutin + Fe	4	4-5	4-5	4-5	4-5	4-5	4-5
Tannin	4-5	4-5	4-5	4-5	4-5	4-5	4
Tannin + Fe	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Pad-dry							
Eucalyptus	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Eucalyptus + Fe	4	4-5	4-5	4-5	4-5	4-5	4
Quercetin	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Quercetin + Fe	4	4-5	4	4-5	4-5	4-5	4-5
Rutin	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Rutin + Fe	4	4-5	4	4-5	4-5	4-5	4-5
Tannin	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Tannin + Fe	4	4-5	4	4-5	4-5	4-5	4

Note: Fe = $FeSO_4$

Table 4. Colour fastness to light (ISO 105-B02: 1994)

Dyeing and mordanting conditions	Colour change	
	Pad-batch	Pad-dry
Eucalyptus	3-4	3-4
Eucalyptus + $FeSO_4$	3-4	3-4
Quercetin	2	2
Quercetin + $FeSO_4$	3-4	3-4
Rutin	3	3
Rutin + $FeSO_4$	3-4	3-4
Tannin	4	4
Tannin + $FeSO_4$	4-5	4-5

From Table 5, very good (4-5) rubbing fastness can be observed in silk fabric dyed with eucalyptus leaf extract, quercetin, rutin and tannin, except for those mordanted with ferrous sulfate, whose ratings were 3 to 4 (fair to good). However, the fabrics dyed with eucalyptus, tannin and ferrous sulfate show a rating of 2 to 3 (poor to fair). This is attributed to a difference in the extent to which the low aqueous solubility ferrous-tannate complexes were able to diffuse within the dyed fiber. For the large molecular size complex that was formed within the dyeing bath, it could be anticipated to display very low diffusional behaviour and, therefore, to deposit mostly on the periphery of the dyed fiber, resulting in a low rubbing fastness [21].

Table 5. Colour fastness to rubbing (ISO105- X12: 2001)

Dyeing and mordanting conditions	Pad-batch				Pad-dry			
	Warp direction		Weft direction		Warp direction		Weft direction	
	Colour staining		Colour staining		Colour staining		Colour staining	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Eucalyptus	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Eucalyptus + Fe	3	2-3	3	2-3	3	2-3	3	2-3
Quercetin	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Quercetin + Fe	3-4	3-4	3-4	3-4	3-4	3-4	4	3-4
Rutin	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Rutin + Fe	4	4	4	4	4	4	4	4
Tannin	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Tannin + Fe	3	2-3	3	2-3	3	2-3	3	2-3

Note: Fe = $FeSO_4$

4. Conclusion

Silk fabrics dyed with eucalyptus leaf extract, quercetin, rutin and tannin by using pad-batch show higher colour strength than pad-dry technique. Tannins are considered as a main material in dyeing processes not only because of the shade similarities of eucalyptus leaves and tannin dyed on silk fabric. The colour fastness to washing shows very good results, whereas the colour fastness to rubbing was fair to good, except for silk fabric dyed with tannin and eucalyptus with ferrous sulfate as the mordant, whose rating was poor when subjected to wet rubbing. The light fastness property of the silk fabric mordanted with ferrous sulfate shows a fair to good result, but in the case of the silk fabric dyed with quercetin without mordant, whose rating was poor fastness. The application of natural dyes on silk fabric by the pad-dry technique can be considered to be an effective eco- option; hence the technique could be considered to be the most suitable for small scale industries or for the cottage dyeing of natural dyes.

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