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Properties of Wool and Cotton Fabrics Dyed with Eucalyptus, Tannin and Flavonoids

Abstract
Fabrics made from wool and cotton were dyed with eucalyptus leaf extract, rutin, querecetin and tannin dyes by the pad-dry technique. 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 also evaluated. The effect of dyes at different concentration levels with respect to their colour strength was also studied.

Key words: *natural dyes, eucalyptus leaves, quercetin, rutin, tannin, flavonoid, pad-dry dyeing.*

Introduction

Eucalyptus is a member of the evergreen hardwood genus, endemic to Australasia. There are approximately nine hundred species and sub-species. Eucalyptus has also been successfully ground in many parts of the world, including southern Europe, Asia and the west coast of the United States [1]. Eucalyptus leaves contain up to 11% of the major component - tannin (gallic acid [3,4,5-trihydroxybenzoic acid], with ellagic acid [2,3,7,8-tetrahydroxy (1) benzopyrano (5,4,3-cde) (1) benzopyran-5,10-dione]) and flavonoids (quercetin and rutin) as the minor components [2, 3]. The structures of selected important colouring components of eucalyptus leaves are given in ***Figure 1***.

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 [4]. 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 [5]. Perkin [6] 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) [7].

Silk dyed with an aqueous extract of eucalyptus leaves possessing a mordant compound displays a yellowish-brown colour. An exception is that when the fabric is dyed with a ferrous mordant, the fabric shade becomes dark brownish-grey. In such cases, the colour fastness to washing, water and perspiration is at a good to very good level, whereas the colour fastness to light and rubbing exhibits fair to good levels [8 - 10].

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 wool and cotton fabrics by the pad-dry 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 hot air while drying. After the dye fixation, the samples are thoroughly rinsed and air-dried. The process of padding is continuous and very rapid.

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.

Experimental

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 ($C_{27}H_{30}O_{16}.xH_2O$, 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. Commercially produced wool fabric (298 g/m^2, twill weave) was washed with a nonionic surfactant at 45 °C for 30 minutes. Then it was thoroughly rinsed and air dried at room temperature. The plain weave cotton fabric used was a mill-scoured and bleached cotton fabric of 135 g/m^2. 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.

Instrumentation

The mordanting and dyeing were carried out in a two-bowl padding mangle machine (Mathis, type number HVF.69805). A drying machine (Mathis Labdryer, type number LTE-2992) was used for drying the dyed fabrics. 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 the reflectance.

2.3 Dye extraction from eucalyptus leaves

Fresh eucalyptus leaves (*Eucalyptus camaldulensis*) were dried in sunlight for one month and crumbled using a blender, after which they were used as raw material for dye extraction, achieved by the

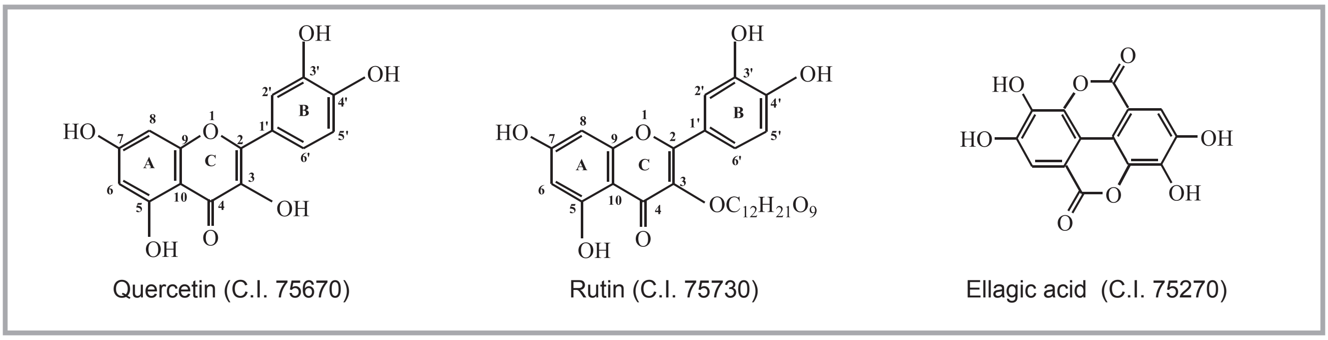


Figure 1. *Colour composition of eucalyptus leaf extract dye.*

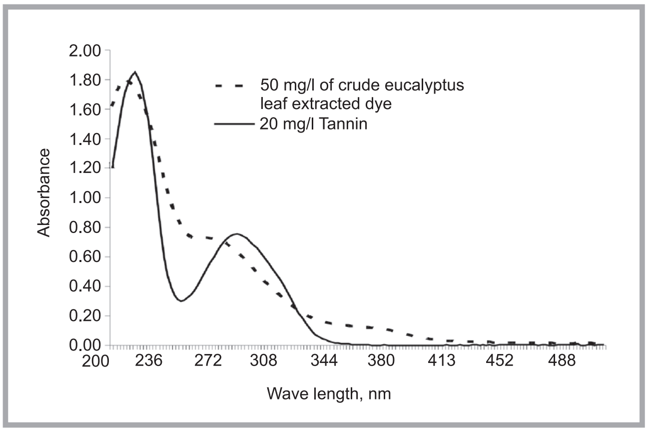


Figure 2. *UV-VIS spectra of 50 mg/l crude eucalyptus leaf extract dye and 20 mg/l tannin in distilled water.*

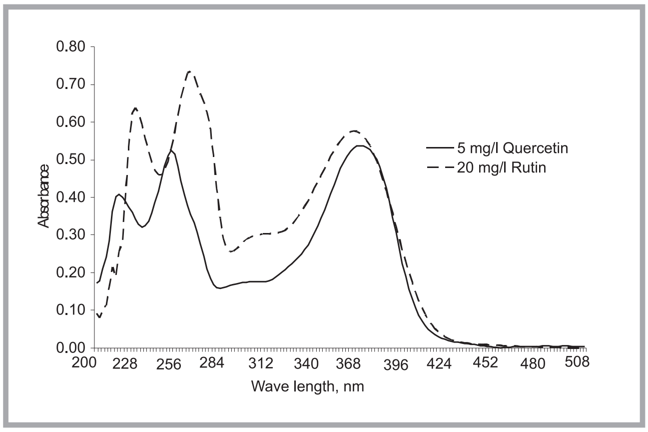


Figure 3. *UV-VIS spectra of 5 mg/l quercetin and 20 mg/l rutin in methanol.*

reflux technique. 70 grams of the crumbled eucalyptus leaves was mixed with 1 litre of distilled water and refluxed for 1 hour. The sample was then filtered and the dye solution separated into two portions, one for evaporating under reduced pressure (rotary evaporator), and the other for dyeing. A crude dye extract of eucalyptus leaves obtained from the rotary evaporator was crumbled with a blender and used for obtaining a standard calibration curve. The dilution of the eucalyptus leaf extract gave a relatively clear solution with a linear dependance on the concentration absorbance relation at an absorption peak (λ_{max}) of 262 nm [11]. A concentration of 20 g/l was calculated from a standard curve of concentrations of the eucalyptus leaf extract dye solutions versus the absorbance at the wavelength mentioned.

Identification of eucalyptus leaf extract dye, quercetin, rutin, and tannin

The crude eucalyptus leaf extract dye, quercetin, rutin, and tannin were characterised by UV-visible spectroscopy. The crude extraction solution (50 mg/l) and tannin (20 mg/l) were prepared by dissolution in distilled water, and the Quercetin (5 mg/l) and rutin (20 mg/l) were prepared by dissolution in methanol. The spectrophotometer scanned from 190 nm to 820 nm to obtain the UV-visible spectra.

Mordanting and pad-dyeing

A simultaneous padding process was used. To study the effect of dye concentration, 2 and 5 g/l concentrations of dyes (eucalyptus leaf extract, quercetin, rutin, and tannin) were chosen. Ferrous sulfate was varied at 2, 5 and 10 g/l for each concentration of the dye, and an anion wetting agent, Altaran S8 (1 g/l), was added to the solution. 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 ºC for 5 minutes. The samples were then washed in a 1 g/l solution of a soaping agent, Syntapon ABA, at 80 °C for 5 minutes and then air-dried at room temperature.

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.

Results and discussion

UV-visible spectra

The UV spectra of the crude eucalyptus leaf extract dye and tannin (in an aqueous solution) are presented in ***Figure 2***. The characteristic spectra show absorptions in the 200 nm to 220 nm and 250 nm to 285 nm regions. Absorption in the 200 nm to 220 nm region is attributed to various chromophores including the C=C bond of various compounds, the C=O bond of carbonyl compounds, and the benzene ring [12]. Absorption in the 250 nm to 285 nm region is attributed to the electronic transition of benzene [12].

The UV spectral characteristics of quercetin and rutin show three absorption maxima in the ranges of 200 nm to 230 nm, 240 nm to 280 nm and 300 nm to 400 nm. The absorption range of 240 nm to 280 nm is referred to as band II and the range of 300 nm to 400 nm as band

I. (The results are shown in ***Figure 3***). Absorption band II is considered to originate from the π→π* transitions in the A ring for the benzene system in ***Figure 1***, whereas absorption band I is attributed to transitions in the B ring for the cinnamoyl system [13 - 15].

Effect of dyeing on *CIELAB* and *K/S* values

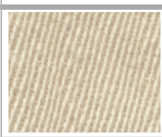
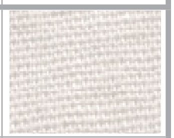
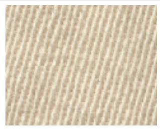
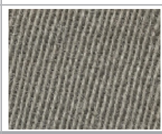
The colour value results are presented in ***Tables 1*** and ***2***. Wool and cotton dyed with eucalyptus leaf extract and tannin dye showed a pale yellowish-grey shade, while those dyed with ferrous sulfate showed a dark greyish-brown colour.

Wool and cotton fabrics dyed with quercetin without a mordant had a yellowish green and pale yellowish green colour, respectively. Wool and cotton mordanted with ferrous sulfate produced a dark yellowish-brown and greenish-yellowish brown shade, respectively.

Wool and cotton substrates dyed with rutin gave a pale yellowish-green and very pale yellowish-cream colour, respectively, while those dyed with ferrous sulfate had a yellowish-brown colour for wool and a grayish-pale yellow for cotton.

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.

Table 1. *Colour values of wool and cotton fabrics, with and without ferrous sulfate, dyed with various concentrations of eucalyptus leaf extract dye and quercetin.*

Dyeing and mordanting condition	Wool fabric				Cotton fabric			
	L*	a*	b*	Colour obtained	L*	a*	b*	Colour obtained
2 g/l Eucalyptus	74.3	3.0	11.3		83.8	0.8	3.3	
2 g/l Eucalyptus + 10 g/l $FeSO_4$	55.9	1.3	6.8		70.4	0.7	1.9	
5 g/l Eucalyptus	75.6	2.5	11.8		83.6	0.9	3.8	
5 g/l Eucalyptus + 10 g/l $FeSO_4$	45.6	1.2	3.2		60.7	1.1	1.2	
2 g/l Quercetin	74.3	-2.1	28.1		82.3	-3.5	16.6	
2 g/l Quercetin + 10 g/l $FeSO_4$	45.3	3.3	17.4		70.3	1.1	14.5	
5 g/l Quercetin	73.7	-2.3	30.5		81.0	-3.2	16.3	
5 g/l Quercetin + 10 g/l $FeSO_4$	37.4	2.4	14.4		64.3	1.2	15.6	

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 4 & ***5*** show the colour strength (*K/S*) values of wool and cotton fabrics 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 and ferrous sulfate concentrations for wool fabric as

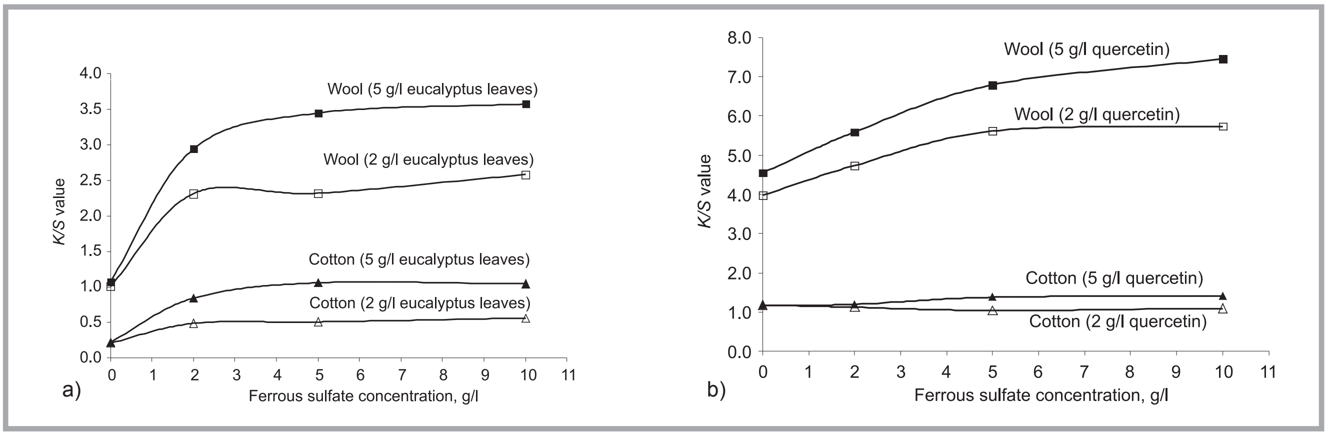
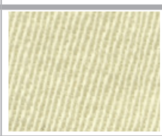
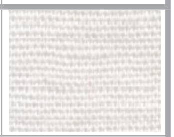
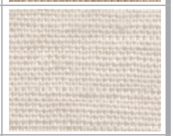
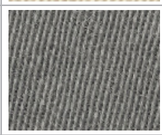
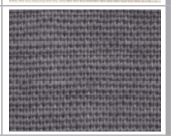
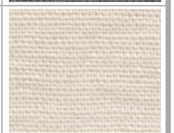
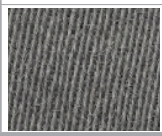


Figure 4. *K/S values of wool and cotton fabrics dyed with 2 g/l and 5 g/l; eucalyptus leaf extract dye solutions (a) and quercetin (b) with varying ferrous sulfate concentrations.*

Table 2. *Colour values of wool and cotton fabrics, with and without ferrous sulfate, dyed with various concentrations of rutin and tannin .*

Dyeing and mordanting condition	Wool fabric				Cotton fabric			
	L*	a*	b*	Colour obtained	L*	a*	b*	Colour obtained
2 g/l Rutin	78.9	-1.8	16.0		86.6	0.1	2.2	
2 g/l Rutin + 10 g/l $FeSO_4$	52.7	3.3	19.4		73.5	0.4	14.7	
5 g/l Rutin	78.0	-1.6	15.9		86.3	0.1	1.8	
5 g/l Rutin + 10 g/l $FeSO_4$	47.7	2.2	15.9		73.5	0.6	14.9	
2 g/l Tannin	76.3	2.4	9.4		86.8	0.2	1.9	
2 g/l Tannin + 10 g/l $FeSO_4$	41.6	1.7	-2.5		50.0	2.8	3.0	
5 g/l Tannin	76.3	2.1	9.6		85.4	0.1	2.5	
5 g/l Tannin + 10 g/l $FeSO_4$	38.9	1.9	-3.0		40.8	2.8	-3.9	

well as cotton fabric dyed with eucalyptus leaf extract and tannin. In the case of cotton fabric dyed with quercetin and rutin, it can be clearly observed (***Figures 5.a*** and ***5.b***) that when the concentrations of dye and ferrous sulfate were increased, the *K/S* values slightly increased.

It can be concluded that wool 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 fibre 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 [16]. Quercetin and rutin have a lower affinity to cotton fabric than tannin. Tannin has many carboxylic (-COOH) and hydroxyl (-OH) groups which are able to bind with cellulose macromolecules. It also possesses excellent possibilities for complexing with ferrous sulfate.

The colour fastness properties

The fastness ratings of wool and cotton fabrics dyed with and without mordants at a dye concentration of 5 g/l and ferrous sulfate (10 g/l) are presented in ***Tables 3*** to ***5. Table 3*** indicates that the washing fastness rating of wool and cotton fabrics 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 to 4-5 (fair to good) can be observed in the wool fabric, except for that dyed with quercetin, 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 [17]. However,

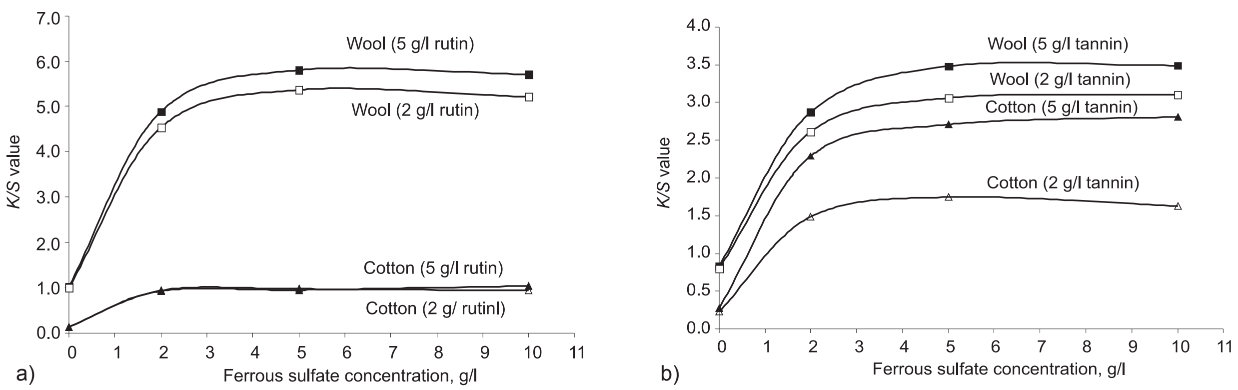


Figure 5. *K/S values of wool and cotton fabrics dyed with 2 g/l and 5 g/l rutin (a) and tannin (b) with varying ferrous sulfate concentrations.*

Table 3. *Colour fastness to washing at 40 °C (ISO 105-C06 A1S: 1994).* ***Note****: Fe =* $FeSO_4$*.*

Dyeing and mordanting conditions		Colour change	Colour staining of adjacent fibers					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Wool fabric	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
Cotton fabric	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

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

Dyeing and mordanting conditions	Colour change	
	Wool fabric	Cotton fabric
Eucalyptus	3-4	3
Eucalyptus + $FeSO_4$	4	3
Quercetin	2	2
Quercetin + $FeSO_4$	5	2-3
Rutin	3-4	2
Rutin + $FeSO_4$	5	2-3
Tannin	4-5	4
Tannin + $FeSO_4$	5	4-5

Table 5. *Colour fastness to rubbing (ISO105- X12: 2001).* ***Note****: Fe =* $FeSO_4$

Dyeing and mordanting conditions	Wool fabric				Cotton fabric			
	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	4	3-4	4	3-4	3-4	3	3-4	3
Quercetin	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Quercetin + Fe	3-4	3	3-4	3	4	3	4	3
Rutin	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Rutin + Fe	4	3-4	4	3-4	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	2	3	2	3	2

a rating of 4 to 5 (good) can be seen in the wool fabric mordanted with ferrous mordant. Poor light fastness (2-3) can be clearly observed for cotton dyed with dyes with or without the ferrous mordant, except for the cotton dyed with tannin with or without a mordant, which shows to be in the range of 4 to 4-5 (good). From these results, it can be concluded that cotton consisting of cellulose fibers fades due to the photo-oxidation process, while wool, bearing amino acids, retards photo-oxidation by the reductive process [17].

From ***Table 5***, very good (4-5) rubbing fastness can be observed in wool and cotton fabrics 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 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 [4].

Conclusions

Wool fabrics dyed with eucalyptus leaf extract, quercetin, rutin and tannin show higher colour strength than cotton fabrics. Tannins are considered as a main material in dyeing processes not only because of the shade similarities of eucalyptus leaves and tannin dyed on wool and cotton fabric but also because of the *K/S* and absorption spectra similarities of eucalyptus leaf extracts and tannin solutions. The colour fastness to washing shows very good results, whereas the colour fastness to rubbing was fair to good, except for wool and cotton fabrics dyed with tannin with ferrous sulfate as the mordant, whose rating was poor when subjected to wet rubbing. The light fastness property of the wool fabric mordanted with ferrous sulfate shows a fair to good result, but in the case of the cotton fabric, poor fastness was obtained, except for cotton fabric dyed with tannin, whose rating was fair to good.

Natural dyes from eucalyptus leaf extract, quercetin, rutin and tannin cannot be used as simple alternatives to synthetic dyes and pigments. They do, however, have potential for application in specific areas to reduce the consumption of some of the more highly polluting synthetic dyes. They also have potential to replace some of the toxic, sensitising and carcinogenic dyes and intermediates. The application of natural dyes on wool and cotton fabrics 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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