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FAKULTA TEXTILNÍ

Dye Extraction From Eucalyptus Leaves And Application For Silk And Wool Fabrics Dyeing

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Chapters:

1. Introduction to natural dyes and eucalyptus leaves

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]. Since the advent of widely available and cheaper synthetic dyes in 1856 having moderate to excellent colour fastness properties, the use of natural dyes having poor to moderate wash and light fastness has declined to a great extent. However, recently there has been revival of the growing interest on the application of natural dyes on natural fibers due to worldwide environmental consciousness [2]. Although this ancient art of dyeing with natural dyeing with natural dyes withstood the ravages of time, a rapid decline in natural dyeing continued due to the wide available of synthetic dyes at an economical price. However, even after a century, the use of natural dyes never erodes completely and they are still being used. Thus, natural dyeing of different textiles and leathers has been continued mainly in the decentralized sector for specialty products along with the use of synthetic dyes in the large scale sector for general textiles owing to the specific advantages and limitations of both natural dyes and synthetic dyes.

The use of non-toxic and ecofriendly natural dyes on textiles has become a matter of significant importance because of the increased environmental awareness in order to avoid some hazardous synthetic dyes. However, worldwide the use of natural dyes for the colouration of textiles has mainly been confined to craftsman, small scale dyers and printers as well as small scale exporters and producers dealing with high valued ecofriendly textile production and sales [2-4]. Recently, a number of commercial dyers and small textile export houses have started looking at the possibilities of using natural dyes for regular basis dyeing and printing of textiles to overcome environmental pollution caused by the synthetic dyes [5]. Natural dyes produce very uncommon, soothing and soft shades as compared to synthetic dyes. On the other hand, synthetic dyes are widely available at an economical price and produce a wide variety of colours; these dyes however produce skin allergy, toxic wastes and other harmfulness to human body.

There are a small number of companies that are known to produce natural dyes commercially. For example, de la Robbia, which began in 1992 in Milan, produces water extracts of natural dyes such as weld, chlorophyll, logwood, and cochineal under the Eco-Tex certifying system, and supplies the textile industry. In USA, Allegro Natural Dyes produces natural dyes under the Ecolour label for textile industry [6]. Aware of the Toxic Substance Act and the Environmental Protection Agency, they claim to have developed a mordant using a non-toxic aluminium formulation and biodegradable auxiliary substance. In Germany, Livos Pflanzenchemie Forschungs and Entwicklungs GmbH marked numerous natural products. In France, Bleu de Pastel sold an extract of woad leaves. Rubia Pigmenta Naturalia is The Netherlands company, which manufactures and sells vegetable dyes. There are several small textile companies using natural dyes. India is still a major producer of most natural dyed textiles [4].

1.1 Natural dyes

Generally the colouring matters from plants, insect and animals are referred to as natural dyes of which plant and insect dyes find their application in dyeing textiles, wood and leather [7-8]. Non-toxic dyes of plant and insect origin are also used in food and cosmetic industries. The colourants from minerals are known as pigments, which are commonly used in paints for wall surfaces, cloth and paper. The chemical classification and the source and application of colourants is discussed below. Organic natural colourants can be nitrogenous

and non-nitrogenous. Based on the carbon skeleton and the chromophores they contain, the broad classification can be made as shown in Table 1 [7].

Table 1 Natural dyes and pigments

Skeleton type	Common colourants
Organic non-nitrogenous molecules	
a) Flavonoids	i. Flavones, flavonols, flavonones, isoflavones ii. Chalcones, aurones iii. Anthocyanins iv. Anhydrobases v. Xanthones vi. Tannins
b) Quinonoids	Benzoquinones, naphthoquinones, anthraquinones, extended anthraquinones.
c) Polyenes/ carotenoids	Bixin, crocin, β-carotene, capsorubin
Organic nitrogenous molecules	
a) Pyrrole	Porphyrins (chlorophyll, haeme, bilirubin)
b) Pyrimidine	The pterins
c) Alkaloids	Indigo, betaine

A brief description of some of the common natural dyes is given below

(a) Flavone Derivatives: Flavone is colourless organic compound. Most of the natural yellow colours are hydroxy and methoxy derivatives of flavones and isoflavones. It is obtained from as dust on flowers and seeds of various primulas, in buds of various varieties of polar, in yellow dahlias, in weld (Reseda luteola) and dyer's broom (*Genista tinctoria*) [4].

(b) Tannins

Tannins are constitutive polymeric polyphenols and fairly recently were also found to be induced by damage. They have relatively high molecular mass with a typical aromatic ring structure with hydroxyl substituents. These chemically reactive components easily form conjugations with other biomolecules via their hydroxyl moieties. In plants two different groups of tannins are found: hydrolysable tannins (HT) and proanthocyanidins (syn. Condensed tannins, CT) [3]. Hydrolysable tannins compounds are hydrolysable either by acids or by enzymes such as tannase, they are known as hydrolysable tannins. They are formed by the combination of several molecules of gallic acid and ellagic acid through ester-linkages to central glucose molecule. Such esters of gallic acid are known as gallo-tannins and the esters of ellagic acid are termed of ellagic-tannins. The condensed tannins, which are polymeric proanthocyanidins, form a major group of phenolic natural products occurring in woody and some herbaceous plants. Their accumulation in exceptionally large quantities in certain trees has resulted in their commercial exploitation of these tannins for tanning leather [4].

(c) Indigoid dyes: This is the most important group of natural dyes. The dyestuff is extracted from *Indigofera tinctoria*, a bush pea family. The dye was used pre-historically in India, where it probably originated. The word is derived from "Indican".

(d) Anthraquinone dyes: Some of the most important red dyes are based on the anthraquinon structure. They are obtained both from plants and insects. These dyes are characterized by good fastness to light. They form complexes with metal salts and the resultant metal-complex dyes have good wash fastness.

(e) Napthoquinones: The most prominent member of this class of dyes is lawsone. It is obtained from *Lawsonia inermis*.

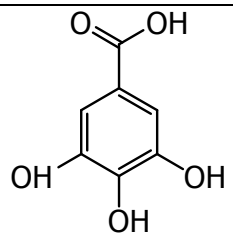
(f) Anthocyananidins: The naturally occurring members of this class include carajurin, obtained from the leaves of *Bignonia chica*. It dyes silk in blue shade.

(g) Carotenoids: The class name carotene is derived from the orange pigment found in carrots. Carrots are considered to be the richest sources of β-carotene. In these the colour is due to the presence of long conjugated double bond. Annatto and saffron are examples of this.

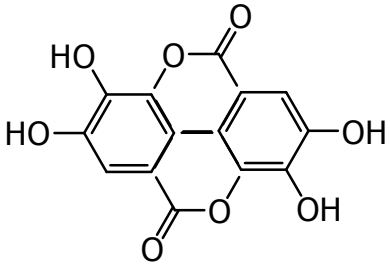
1.2 Natural organic dyes from eucalyptus

The eucalypts are members of an evergreen hardwood genus endemic to the Australasian region embracing approximately nine hundred species and sub-species. Eucalypts are represented across the Australian continent in all but the harshest of the arid interior regions, although they can be found in desert areas marking the positions of soaks and watercourses [9]. Eucalypts have successfully colonized many other parts of the world including southern Europe, Asia and the west coast of the United States.

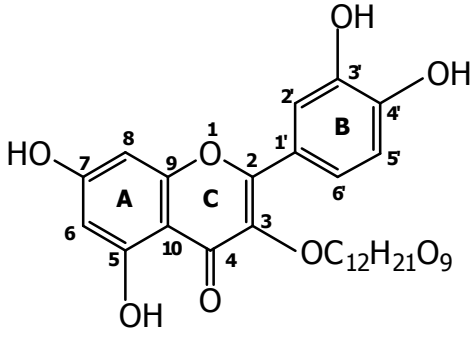
Eucalyptus is one of the most important sources of natural dye that gives yellowish-brown colourants. The colouring substance of eucalyptus has ample natural tannins and polyphenols varying from 10 % to 12 % [10]. The major colouring component of eucalyptus bark is quercetin, which is also an antioxidant. It has been used as a food dye with high antioxidant properties [11]. 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 [12-14]. (The structures of the colouring components found in eucalyptus leaves are given in Figure 1. Tannins and flavonoids are considered very useful substances during the dyeing process because of their ability to fix dyes within fabrics. Silk dyed with an aqueous extract of eucalyptus leaves and bark possessing a mordant compound displays a yellow-brown colour. An exception is a fabric being dyed with ferrous mordant, which results in a shade of dark brownish-grey. Colour fastness to water, washing, and perspiration is at good to very good levels, whereas colour fastness to light and rubbing exhibited fair to good levels [15-16].



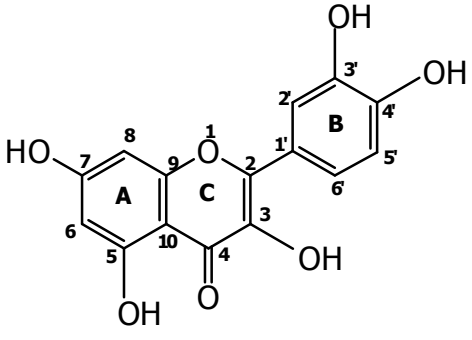
Gallic acid



Ellagic acid (C.I. 75270)



Rutin (C.I. 75730)



Quercetin (C.I. 75670)

Figure 1 The colour components of eucalyptus leaves

1.3 Using natural dyes

Currently, application of natural dye incorporates new technology not only to exploit traditional techniques but also to improve the rate, cost and consistency production. It therefore, requires some special measurement to ensure evenness in dyeing. The processes of natural dyes for textile dyeing are as follows:

1.3.1 Extraction

Efficient extraction of the dyes from plant material is very important for standardization and optimization of vegetable dyes, utilizing a) soxhlet b) supercritical fluid extraction c) subcritical water extraction and d) sonicator method.

1.3.2 Dyeing

Normally, one technique used for dyeing with natural dye; exhaustion dyeing (conventional dyeing, sonicator dyeing and microwave dyeing). Exhaustion dyeing is using lot of water as shown in "Liquor Ratio (ratio between water and goods)". Producers immerge the goods in dye for extended periods for complete penetrate. This produces excessive waste water compared to a continuous process.

1) Conventional dyeing is carried out by boiling the fabric in dye bath for 4-hours and often the dye uptake is still not completed. Enormous amount of heat is consumed in terms of heating the dye bath [4].

2) Sonicator Dyeing: Utilization of ultrasound energy to aid wet processing of fabrics. The process of increasing dye transfer from the dye-bath to fabric using ultrasound energy is a function of the acoustic impedance characteristics of the fabrics [4, 17-18].

3) Microwave dyeing take into account only the dielectric and the thermal properties. The dielectric property refers to the intrinsic electrical properties which affect dyeing by dyeing by dipolar rotation of the dye and the influence of microwave field upon dipoles. The aqueous solution of dye has two components, which are polar. In the high frequency microwave field, oscillating at 2450 MHz; it influences the vibrational energy in the water molecule and the dye molecules [18].

1.3.3 Mordanting

In the actual dyeing process, there are four ways of using mordant [3, 19] as follows:

(a) Mordanting before dyeing, or pre-mordanting;

(b) Mordanting and dyeing at the same time, called stuffing or simultaneous;

(c) Mordanting after dyeing, or after-mordanting or post-mordanting;

(d) A combination of pre-mordanting and after-mordanting.

2. Theoretical, ecological and economical aspects of dyeing with natural dyes

2.1 Theoretical presuppositions of natural dyes to dyeing

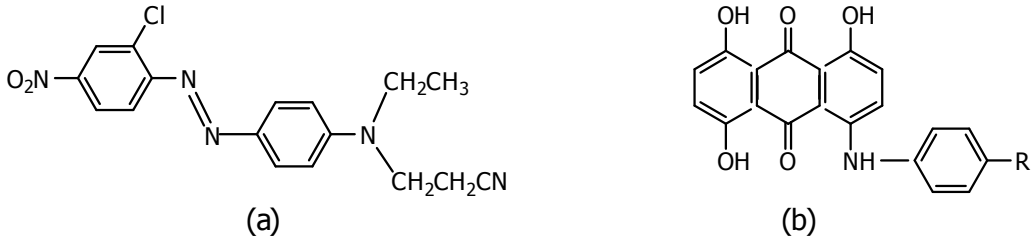
Achieving a good, or at least a relatively good, water solubility using natural dyes is rather exceptional. No chemical group is capable of electrolytic dissociation or ionization in a molecule; an interesting and important exception is the *anthocyanins*, for example, pelargonidine, cyanidine, and betanidine are slightly cationic dyes and, therefore, also have relatively good solubility in water.

The "conditional solubility" of indigoid natural dyes, which in their original form are entirely insoluble, presents a quite special principle. In fact, indigo has been imitated to a great extent; synthetic indigo and their derivatives were produced on an industrial scale at the end of the nineteenth century as a forerunner of the latter large group of *vat dyestuffs*. The alkali reductive conversion of this fully insoluble compound in a proper soluble sodium salt of

leucocompound with affinity to fibers and their oxidation after dyeing with the primary insoluble vat dye, which is finely dispersed in the fiber, is well known.

What do the majority of natural dyes have in common? The chemical constitution (and corresponding physical properties) of indigo and other anthocyanin dyes has remarkable similarity with the modern synthetic *disperse dyes*: the solubility of more or less elongated molecules of chromogen is due to the presence of several polar groups (mainly –OH) on aromatic rings. No groups are capable of electrolytic ionization (with the exception of the anthocyanin and betanin). From this follows that they only have low solubility in water. Empirically, it is known that it is impossible to strengthen dyeing of cotton with natural dyes, but it can be done by adding neutral electrolytes (sodium chloride or sulfate) as *substantive dyes*. And bath acidifying, while having a significant effect on the so-called *acid dyes* (coloured sodium salts of sulfonic acids), has a negligible effect on the natural dyes.

The structure of the flavonoid-colouring components of eucalyptus leaves and tannin (Figure 1) is compared with the typical azo and anthraquinone disperse dye (Figure 2).



C.I. Disperse Red 50

R = H (C.I. Disperse Blue 27)

R = CH3 (C.I. Disperse Blue 72)

Figure 2 Chemical constitution of typical disperse dyes. (a) Azo dye and (b) anthraquinone dyes

Assume that most natural dyes are, on the basis of modern dyeing science, the disperse dyes. But what are the dyes for wool, silk, cotton, and flax? Consider that each fiber type in dyeing has already been studied, and it has become apparent that the disperse dyes are not good dyes for the aforementioned fibers. On the contrary, the synthetic disperse dyestuffs were developed for dyeing acetyl cellulose and synthetic fibers (i.e., hydrophobic fibers), and they have a low affinity for wool, silk, cotton, and other such fibers that are mainly hydrophilic. Though low, the indispensable affinity of disperse dyes makes them very undesirable for the staining of wool or cotton component by the dyeing of fiber mixtures, namely with polyester fiber (which is dyeable only in disperse dyes). This imperfect colouration-staining must be rather difficult to remove from wool or cotton component after dyeing because of its poor wet fastness and mostly unpleasant shade, which can be different from the shade of the same dye on polyester.

However, the above-mentioned majority of natural dyes are providing only inexpressive wet fastness on wool and cotton fibers, and the mordanting by salts of suitable metals is also needed to improve wet fastness (not only to deepen but also to intensify the colour).

A lower affinity results in the low dye exhaustion after the dye bath on the fiber. This can also be observed in the dyeing of natural fibers with natural dyes, such as the indigoid and anthocyanin dyes.

2.2 Ecological and economical aspects of dyeing with natural dyes

If we carry out the dyeing process with natural dyes in a slightly large manufacturing unit or a factory rather than in a household unit, we can surpass the limits of historic methods of dyeing and material pretreatments, which are lengthy and uneconomical procedures. The old methods (likely transmitted without facing critical evaluation), consist of various actions that do not address modern requirements, and do not take into account the new possibilities offered by the modern textile chemistry. The number and duration of baths seem to be too high (at least for European standards and customs) and are non-productive. For example, the required 3–5 hours wetting of material with water before dyeing could be greatly reduced by wetting in a bath by specially made wetting agent, and this or another agent could also be added into the dyeing bath.

The ineffective use of natural dyes was already discussed above. The majority of dyes ceases as effluents in sewer. The mordanting salts do not have affinity to the fibers and therefore only a small part of them is bounded with fibers, and after dyeing and final rinsing all the remnants are carried off by water.

What about the idea of storing the mordanting baths for future use? While logical, the number and volume of stock reservoirs (and place in dye house) make it an unpractical possibility. Naturally, serious conception-questions follow from this. Should "natural dyeing" remain as something principally untouchable whose traditional originality must be safe-guarded at any costs, or are we going to consider this natural raw-material source as an ecologically favorable supplement to synthetic colourants? Or, can we synthesize the methodologies of "natural dyeing" with the research and application processes of modern dyeing technology?

Nevertheless, both natural dyeing and modern dyeing technology can coexist. In any case, we are trying to explore the second of the following:

- the consequent minimization of concentration of natural dyes and mordants,
- the shortening of operating times, i.e., to save energy and productivity, and
- the maximal efficient use of dye and mordanting baths.

All these can be assured by the *padding* (pad) technologies, in which the *liquor ratio* (weight of textiles: bath) is about one order lower (≤1:1) than the common exhaustion (bath or batch) dyeing methods.

The *padding technologies* are particularly advantageous to dyeing with the low-affinity products, because the dye affinity to fiber by padding is unnecessary (in phase of the dye deposition on the fabric). The dye bath is cloth "padded": mechanically applied by the rapid passage through the small padding trough, the intensive squeezing between expression rollers follows immediately. The process of padding is continuous and very rapid. It depends on the arrangement of the following dye fixation if the total procedure is continuous or semi continuous.

The dye bath by padding is about one order higher than by the common dyeing from the "long bath" (the so-called *exhaustion methods*), in which the dyestuff *exhausts* on the fiber in consequence to its affinity to the fiber. The higher padding bath concentration results in more rapid dye diffusion in fiber during the next fixation operation. Much smaller bath volume (related to the fiber unit) causes the higher dye exploitation (see also Agarwal and Patel) [20].

In the case of natural dyes, the dye fixation is based on the reaction with the salts of complex-forming metals-mordants in the same or next bath-or the textile can be *pre-metalized* with mordant (this *pre-mordanting* is carried out from the long bath-the large non-effectiveness is mentioned above. Therefore, we also experimented with pad-dry principle at this operation).

In semi continuous dyeing technology, several methods of dye fixation are known. The following two principles are important for our purpose:

(a) *fixation by drying,* the so-called *pad-dry* method, the process is rapid but requires a reliably functional drying device (an excellently even -drying effect breadth-ways and cross-ways in the fabric is necessary, otherwise it may result in colour depreciation and unevenness),

(b) *fixation by batching* of the padded goods at room or slightly increased temperature, now known as the *pad-batch* method. The padded and rolled goods are wrapped up in an airtight plastic sheet so that no selvedge drying occurs during storage, which lasts 8–24 hours.

After both dye fixation methods water rinsing follows repeatedly.

2.3 Potential of eucalyptus leaves dye

2.3.1 Potential commercial applications

Natural dyes cannot be used as simple alternatives to synthetic dyes and pigments. They do, however, have the potential for application, in specified areas, to reduce the consumption of some of the more highly polluting synthetic dyes. They also have the potential to replace some of the toxic, sensitizing and carcinogenic dyes and intermediates [21]. Eucalyptus leaves, as natural dye, has greater potential because it is grown already on an industrial scale. It also shows good fastness on silk and wool substrates.

2.3.2 Potential effluent problems

The effluent problems of synthetic dyes occur not only during their application in the textile industry, but also during their manufacture, and possibly during the synthesis of their intermediates and other raw materials. The application of synthetic dyes also requires metal salts for exhaustion, fixation, etc [21]. Natural dyes, like eucalyptus leaves do not cause damage the environment by their extraction and many could be used satisfactorily without mordants, although it is true that the use of mordant improves the depth of shade for natural dyes. These mordants are normally metal salts and hence damage to the environment is still possible, albeit to a smaller extent than for synthetic dyes in textile applications. The research in this field has already identified a few “natural mordant”, such as *Entada spiralis Ridl* [22] and harda (*Chebulic myrabolan*) [21]. The avoidance of metal-based mordants, or their replacement by natural mordants, may assist in the preservation of the environment.

3. Our experimental works

Most research on natural dyes has been focused on the fundamental aspects of natural dyes by exhaustion process [6, 10, 23-26]. Little attention has been give to the continuous process such as pad-batch and pad-dry techniques [20]. The aim of this research is to apply eucalyptus leaf extract on natural fibers, wool and silk, using pad-batch and pad-dry techniques since there was little information on dyeing fabrics with natural colorants using eucalyptus leaves [10,26]. In this study, we observed the various parameters in dyeing with metal irons. The adsorption isotherm of eucalyptus leaves extract onto silk was also to be investigated. In addition, a determination of the amount of flavonoids in eucalyptus leaf extract by liquid chromatography-mass spectrometry. Finally, we study the effect of UV-Protection properties of wool and silks fabrics dyed with eucalyptus leaves. The following is the description of the aforementioned experimental work.

3.1 Determination of colour component in eucalyptus leaf extract

Fresh eucalyptus leaves were dried in sunlight for 1 month and crumbled using a blender and then were used as the raw material for extraction, which was achieved by the soaking technique; 70 g of crumbled eucalyptus leaves was mixed in a liter of water: methanol (20:80 v:v) and shaken for 24 hours. The solution was then filtered to separate out the residue and methanol was removed by vacuum distillation. The aqueous solution was filtered and extracted with diethyl ether. The dried ethereal solution was redissolved in methanol and analyzed by high performance liquid chromatography (HPLC) and thin layer chromatography (TLC) [13-14].

Identifications of polyphenols were carried out by comparing the ultra-violet (UV) spectra and the chromatographic behaviour (HPLC, TLC) of the unknown compounds with those of the standards and with literature data [12-14]. Some components were recognized as flavonols and flavonones according to their UV spectra but their full identification has not yet been possible. Semiquantitative determinations were carried out considering the areas of each chromatographic peak.

HPLC analyses were carried out using a chromatograph equipped with diode array detector. The HPLC column was a BEHC 18 (150 x 2.1 mm i.d.). Two solvents were employed for elution namely **A**: methanol:phosphoric acid (999:1) and **B**: water:phosphoric (999:1): the elution profile was from 20% **A** to 100% **A** (linear gradient ; 0-40 min) and then 100% **A** (isocratic: 40-45 min): the flow rate was 1 ml/min and the chromatographic oven was at 30 °C. Detection was carried out at 325 nm with a bandwidth of 150 nm.

Thin layer chromatography (TLC); Sigmacell (Sigma) microcrystalline cellulose plates were used. Two dimensional developments were carried out with *n*-butanol:acetic acid: water (4:1:5; upper phase) for the first dimension and 30% acetic for the second. For detection, plate were sprayed with a 0.6% solution of diphenylboric acid-*β*-aminoethylester in methanol, and a 2% solution of polyethylene glycol 1000 (PEG) in methanol.

The high performance liquid chromatography-electrospray ionization–mass spectrometry (HPLC-ESI-MS) with high resolution both positive and negative ESI mode were used for quantitative determination of colour component in eucalyptus leaf extract. HPLC-2D separation were carried out on a Rheos 2200 (Flux Instrument) employing an Ultra performance LC water, BEHC 18 column (150 x 2.1 mm i.d.). MS was carried out on a LCQ Fleet (Thermo Scientific) with an electrospray ion source.

Table 2 shows the HPLC semiquantitative determination of the components of the ether soluble fractions of eucalyptus leaves sample. Each component has an order number related to its position in the HPLC chromatogram (Figure 3).

Table 2 Semiquantitative HPLC determinations of the components of the ether extracts of leaves of *Eucalyptus Camaldulensis*

Peak	Component	Semiquantitative
-	Vanillin	-
1	Hyperin	+
2	Apigenin	+ +
3	Kaempferol	+
4	Rutin	+ + +
5	Gallic acid	+ + + +
6	Ellagic acid	+ + + + +
7	Quercetin	+ + + +
-	Luteolin	-

Note: The '+' means in terms of relative peak areas: 0.25-1.5% (+); 1.5-4% (+ +); 4-9% (+ + +); 9-20% (+ + + +); 20-35% (+ + + + +)

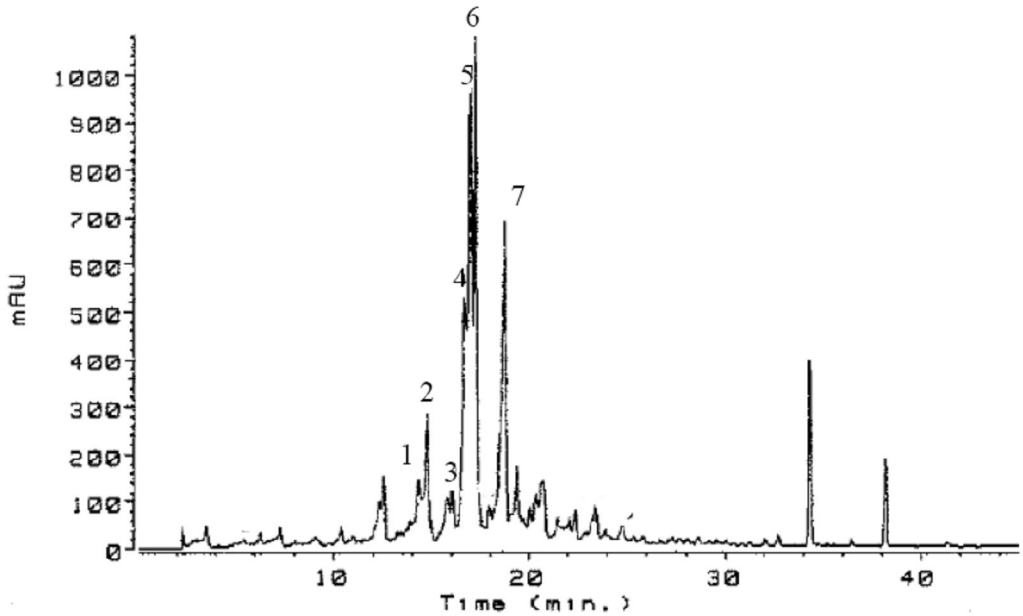


Figure 3 HPLC chromatogram of an ether extract of leaves of eucalyptus. Key to peak identity: 1-hyperin; 2- apigenin; 3- kaempferol; 4- rutin; 5- gallic acid; 6- ellagic acid; 7-quercetrin

The quantitative analytical results showed the main components of eucalyptus leaf extract by HPLC-ESI-MS analysis were as: 25.9% ellagic acid (2,3,7,8-tetrahydroxy (1) benzopyrano (5,4,3-cde) (1) benzo-pyran-5,10-dione), 16.4% gallic acid (3,4,5-trihydroxybenzoic acid), 10.8% quercetin (3,3‘,4‘,5,7-pentahydroxyflavone), 7.7% rutin (3,3‘,4‘,5,7-pentahydroxyflavone-3-ramno-glucoside), 2.1% apigenin (4',5,7-Trihydroxy-flavone) and 1.0% hyperin (Quercetin-3-galactoside). The full scan ESI mass spectrum of some flavonoids which are main components in eucalyptus leaves are shown in Figure 4.

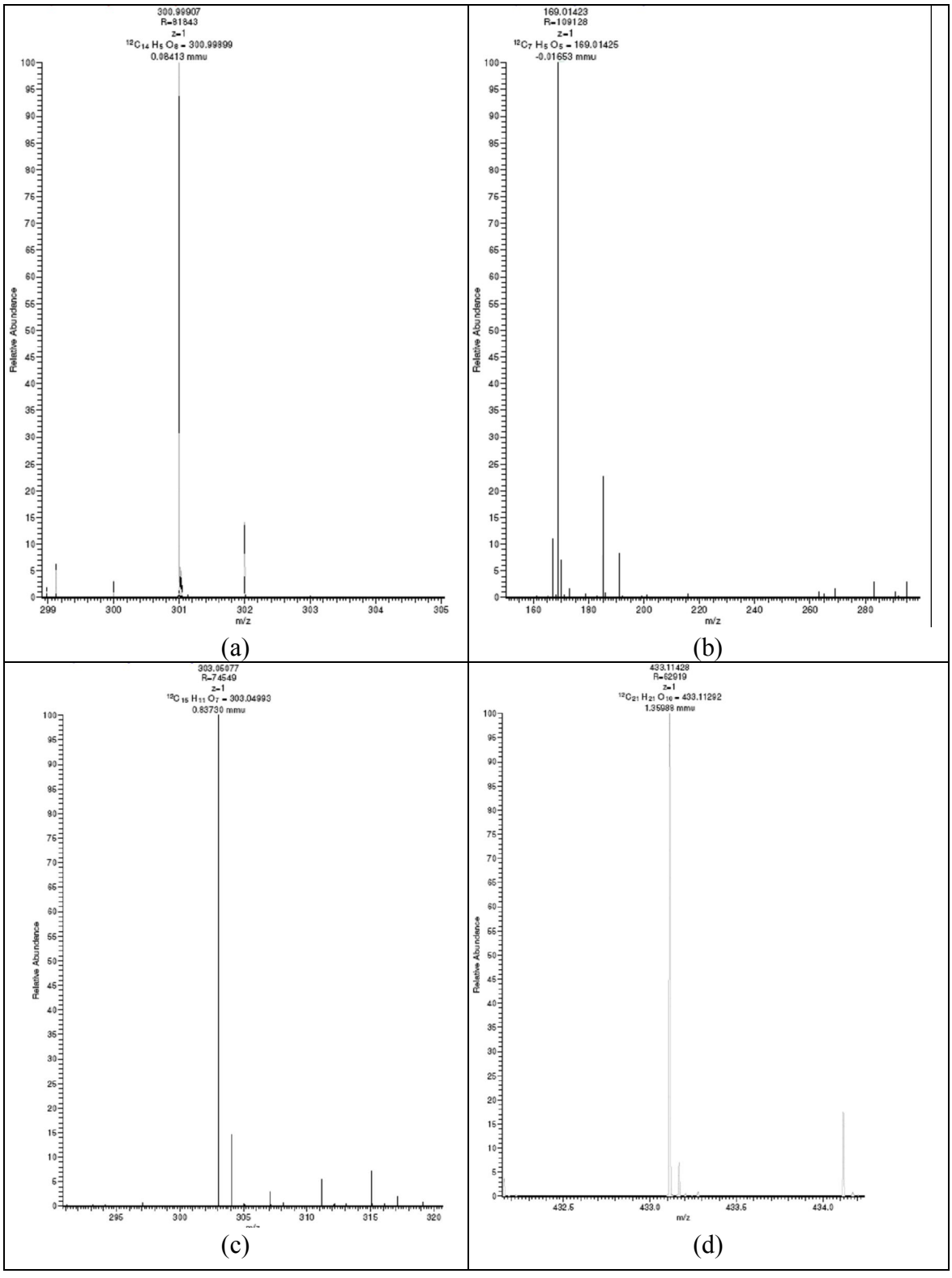


Figure 4 Full scan mass spectrum of some flavonoids in eucalyptus leaves (a) ellagic acid, (b) gallic acid, (c) quercetin and (d) apigenin

3.2 Characterization of tannin-ferrous sulfate complexes

3.2.1 Determination of the mole ratio for Fe(II) ion with tannin complexes

The molar ratio method has allowed us to determine the composition of the complex in solution from spectrophotometric spectra. For this method, the tannin stock solution (1.0×10^{-3} Molar) is prepared successively in distilled water. Fe(II) stock solution (0.1×10^{-3} Molar) is prepared in distilled water. A required concentration of 1×10^{-5} Molar of tannin in distilled water was diluted from stock solution and kept constant and then mixed well with Fe (II) at various concentration ranging from 0 to 100 micro molar (µM).

The UV-Vis spectrum of tannin in aqueous solution without pH control (Figure 5) is characterized by two major absorption bands with maxima at 214 nm and 278 nm. The absorbance of tannin decrease at 278 nm and a new band, which increases with the mount of added Fe (II), appear at 310 nm.

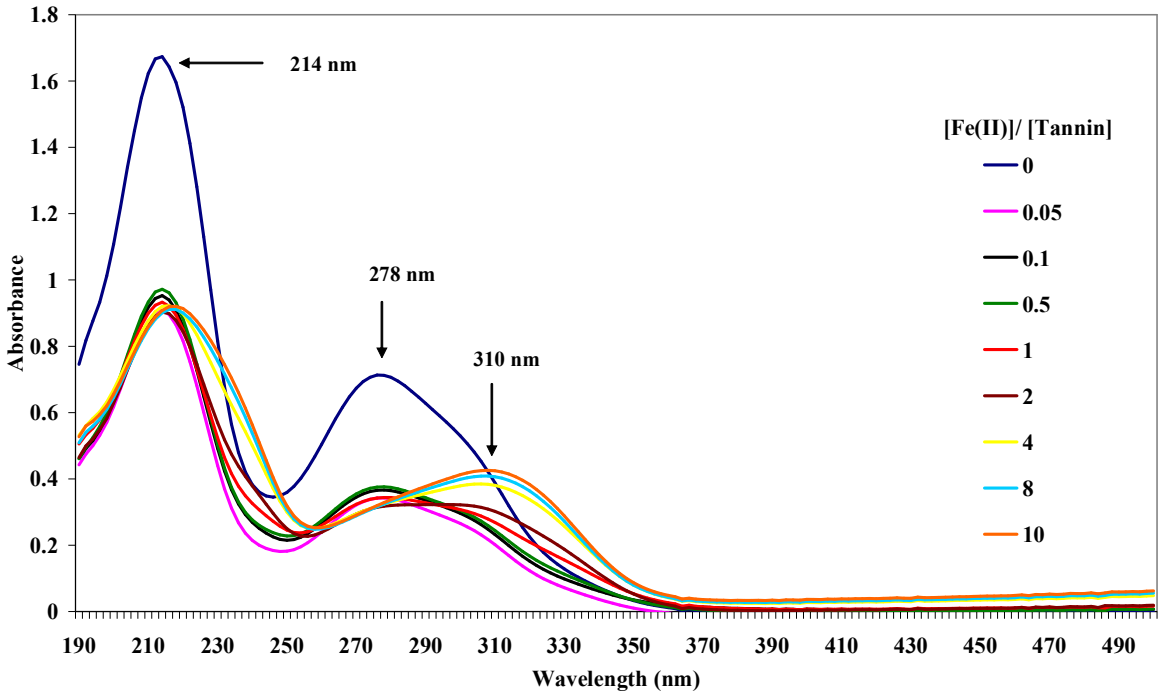


Figure 5 Absorption spectra of tannin (1×10^{-5} Molar) in aqueous solution in the absence and in the presence of Fe (II) (0-100 micro molar)

The result of the study of the effect of Fe (II) on the visible spectra (λ_{max}) of tannin is presented in Figure 5 which showed a large bathochromic shift of tannin as the Fe (II) concentration increases. The higher Fe (II) concentration result in higher amount of the tannin complex in solution and intensity of the absorption band at the longer wavelength is increased.

The stoichiometry of Fe (II) and tannin in aqueous solution without pH control was investigated. A molar ratio was found that the Fe (II): tannin ratio was 1:1 and 2:1 (Figure 6).

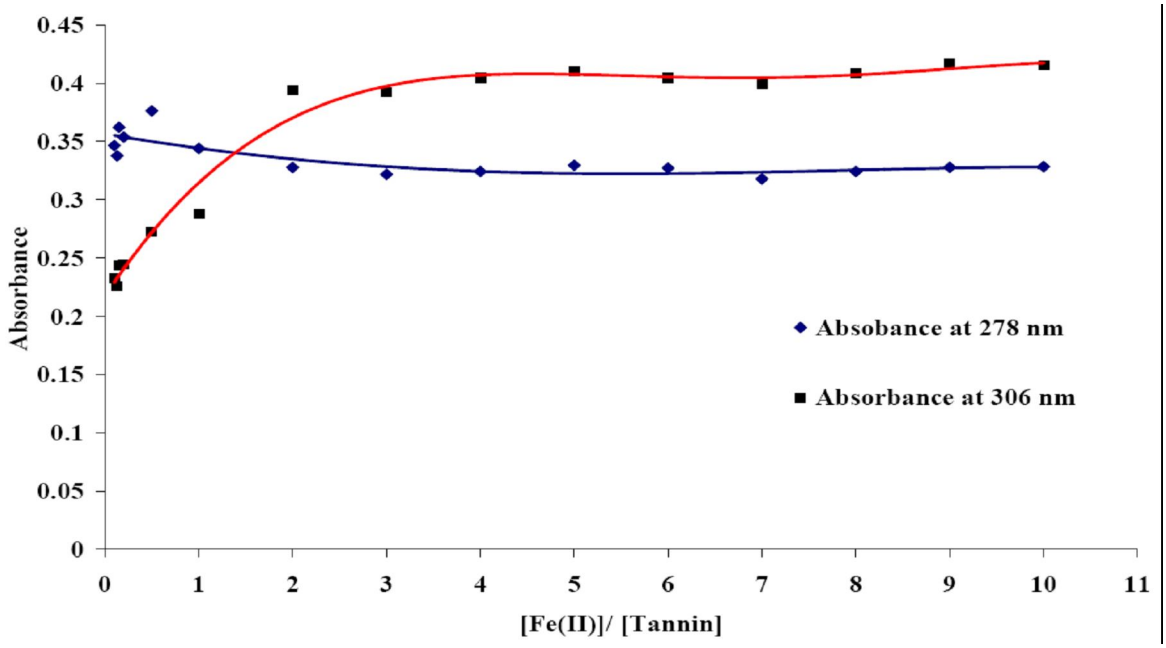


Figure 6 Absorbance versus [Fe (II)]/ [Tannin] molar ratios

3.2.2 Effect of Fe(II) concentration on tannin in aqueous solution

Tannin is a major component in eucalyptus leaves. In order to minimize the ratio of Fe (II)-tannin, optimization the amount of Fe(II) used for dyeing were investigated. A concentration of 1.0×10^{-5} Molar, 2.0×10^{-5} Molar, 5.0×10^{-5} Molar of tannin was diluted from stock solution and kept constant whereas Fe (II) was varied from 0 to 140 µM of each concentration of tannin. In order to reach the complexation equilibrium, the absorbance of each solution was recorded after standing for 30 minutes at 310 nm by using UV-Vis spectrophotometer.

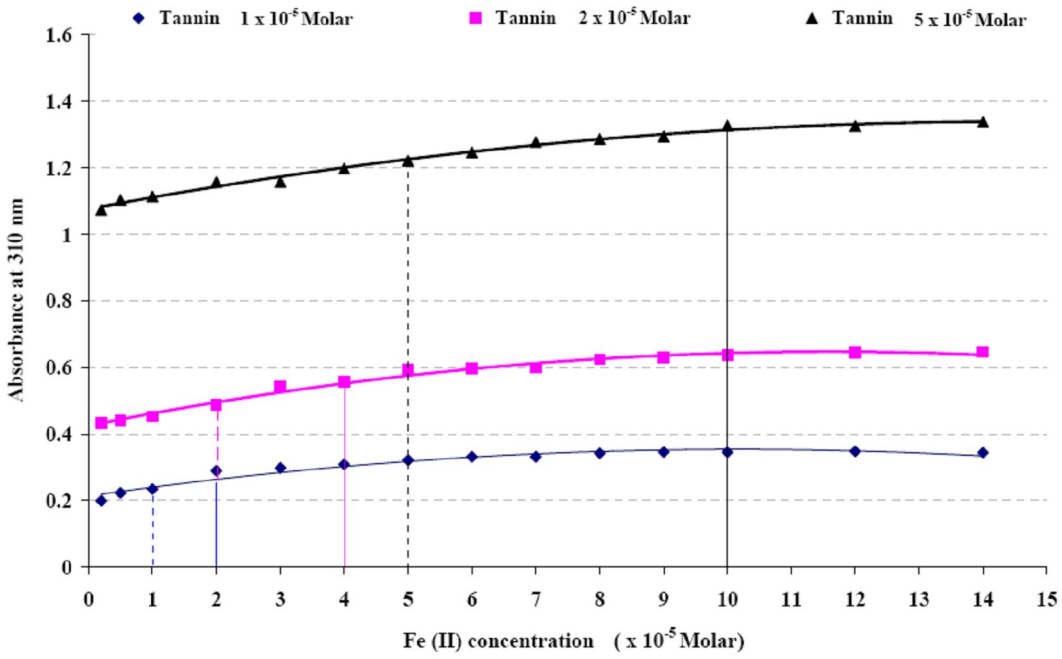


Figure 7 The effect of Fe (II) concentration on tannin in aqueous solution. Dash line is the [Fe(II)] / [tannin], 1:1. Solid line is the [Fe(II)] /[tannin], 2:1.

Fe (II) was mixed with tannin solution at different tannin concentration (1.0-5.0 x 10^{-5} Molar). It was found that the absorbance of Fe(II)-tannin at wavelength 310 nm still keep increasing with increased Fe(II) concentration at the ratio [Fe(II)]/[tannin], 1:1 (dash line in Figure 7) and start to be constant at [Fe(II)]/[tannin] 2:1 stoichiometry in 1.0-5.0 x 10^{-5} M tannin concentrations (solid line in Figure 7).

In the case of ferrous (II) -tannin complexes the phenolic groups (OH-groups) of the gallic and ellagic acids can form bidentate complexes with the ferrous iron of ferrous sulfate. This complex (Figure 8) is colourless while in slightly acid solution, but on aerial oxidation the iron moves from the ferrous to ferric state with a change in spectral absorption. As a result the ferric complex is blue-black in colour i.e. absorbs wavelengths in the red to green spectral range. The ferrous complex is colourless because it absorbs wavelength in the ultraviolet spectral range to which the eye is not sensitive.

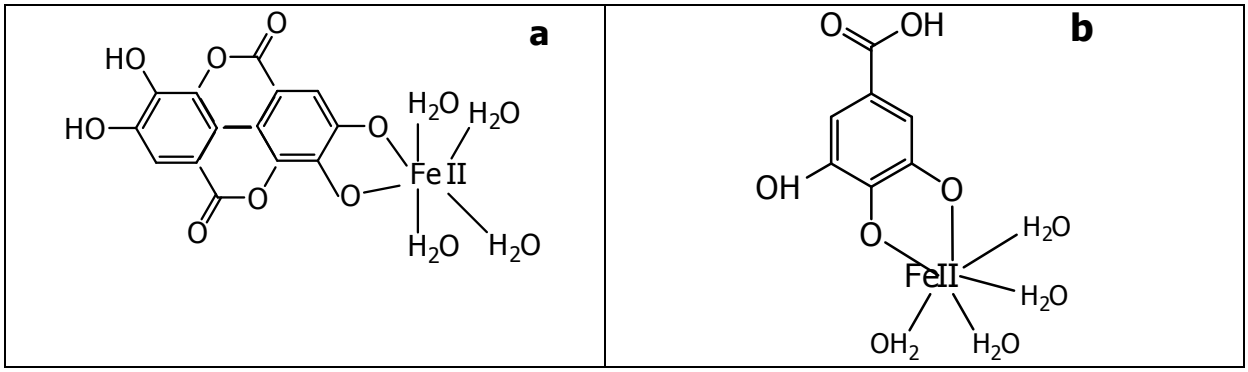


Figure 8 Proposed the structure of ferrous-tannins complex (a) 1:1 [Fe(II):ellagic acid], and (b) 1:1 [Fe(II): gallic acid

3.3 Optimisation of extraction conditions and identification of crude eucalyptus leaf extract dye

Fresh eucalyptus leaves were dried in sunlight for one month and crumbled using a blender and then were used as the raw material for dye extraction. In order to find out the optimum extraction conditions, a total number of three experiments were carried out at various conditions as given in the following:

- 70 g of crumbled eucalyptus leaves was mixed with 1 litter of distilled water and subjected to stirring at room temperature for 3 hours.
- 70 g of crumbled eucalyptus leaves was mixed with 1 litter of distilled water and refluxed for 1 hour.
- 70 g of crumbled eucalyptus leaves was mixed with 1 litter of distilled water and soaked for 24 hours.

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. The crude eucalyptus leaf extract dye was characterized by UV–visible spectroscopy. The crude extraction solution (50 mg/l) was prepared by dissolving in distilled water. The spectrophotometer was scanned from 190 nm to 820 nm to obtain the UV–visible spectra.

A simultaneous padding process was used in to dye. Silk and wool fabrics were 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 5 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.

The colour strength (*K/S*) and CIELAB of the dyed samples were evaluated using a spectrophotometer (Datacolor 3890). 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 representative of reflectance. The dye extract that gave the maximum *K/S* value of fabric was then selected for further experimentation in order to find out the optimum dyeing conditions.

3.3.1 Effect of extraction condition

The *L**, *a**, *b** and *K/S* values of silk and wool fabrics dyed with dye extracts obtained under different extraction condition is given in Table 3. As can be seen from the Table 3, *K/S* value of dyed sample dyed with dye extracts obtained by stirring at room temperature was minimum, slightly getting better by soaking for 24 hours and maximum when the extraction was carried out by reflux technique.

Wool fabric dyed with eucalyptus leaf extract shows higher *K/S* values than silk fabric. Only slight differences were observed between the two padding techniques (pad-batch and pad-dry) utilized for dyeing. The colour value results obtained is presented in Table 3. Wool and silk dyed with dye extract from eucalyptus leaves showed light brown and yellowish-brown, respectively. Then the next experiment will be extracted using a reflux technique which is the best optimization of extraction condition.

Table 3 Colour value of dyed silk and wool fabrics using padding techniques by varying the dye concentrations

Type of fabric	Extraction condition	Pad-batch				Pad-dry			
		L^*	a^*	b^*	*K/S* (400 nm)	L^*	a^*	b^*	*K/S* (400 nm)
Silk	Stirring at room temperature	87.10	0.48	1.87	0.42	85.50	0.70	3.41	0.45
	Reflux technique for 1 hour	87.15	2.12	3.95	0.64	86.40	2.12	-3.84	0.63
	Soaking for 24 hours	87.25	2.04	1.94	0.48	86.78	2.48	-5.48	0.51
Wool	Stirring at room temperature	74.23	2.45	13.51	1.24	75.96	3.85	11.50	1.23
	Reflux technique for 1 hour	75.44	3.64	15.13	1.68	75.31	1.35	15.57	1.74
	Soaking for 24 hours	73.66	1.86	15.51	1.61	75.60	3.60	14.60	1.62

3.3.2 UV–visible spectrum

The UV spectrum of the crude eucalyptus leaf extract dye in an aqueous solution is presented in Figure 9. The characteristic spectrum shows absorptions in the 205–210 nm and 250–270 nm regions. Absorption in the 205–210 nm region may be attributed to various

chromophores, including the C=C bond of various compounds, the C=O bond of carbonyl compounds, and the benzene ring (probably from aromatic compounds) [27]. Absorption in the 250–270 nm region may be attributed to the electronic transitions of benzene and its derivatives, which may include various aromatic compounds such as phenolics [27]. It can be observed from Figure 9 that the dye can absorb radiations in the UV-C region (200–290 nm), the UV-B region (290–320) and the UV-A region (320-400) [28].

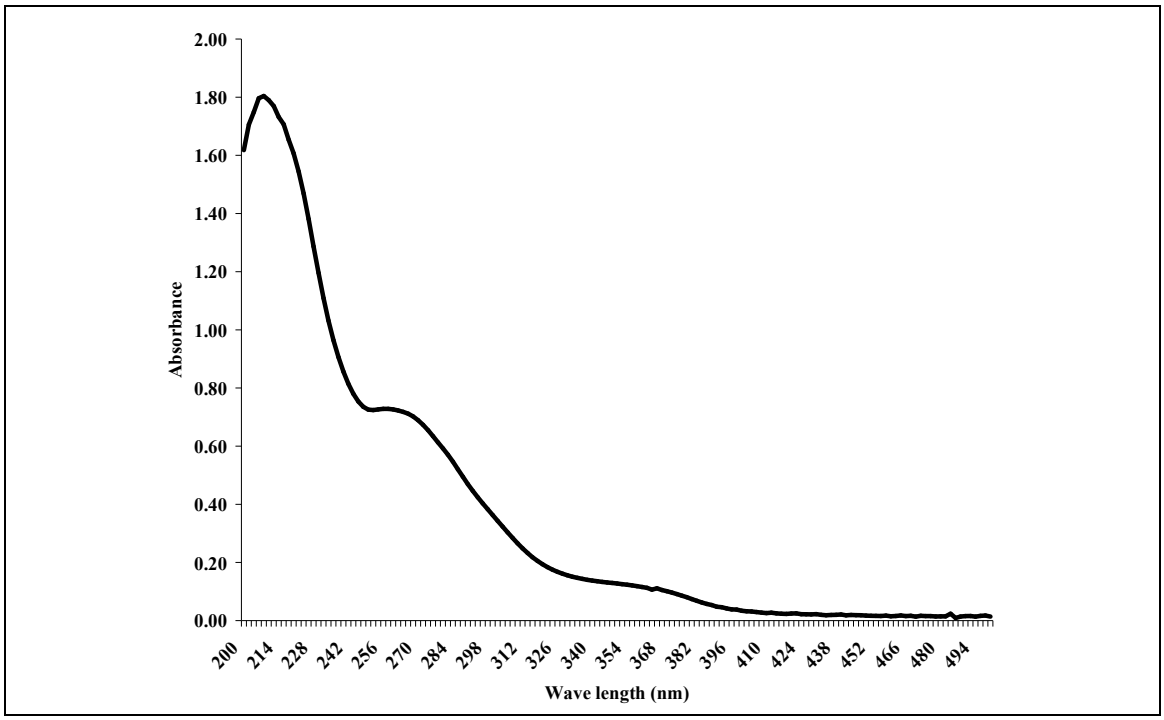


Figure 9 UV-VIS spectrum of 50 mg/l crude eucalyptus leaf extracted dye in distilled water.

3.4 An adsorption exact study of dyeing on silk fabric with aqueous extract of eucalyptus leaves.

3.4.1 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, absorption peak (λ_{max}) at 262 nm [29]. 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.

3.4.2 Dyeing procedure

Silk fabrics were dyed an aqueous extract of eucalyptus leaves at three different temperature ranges (30°C, 60°C, and 90°C) for 120 minutes and liquor ratio 1:50. The pH of

the dyeing solution (mixed with an acetic acid solution) was adjusted to 4. The amount of dye in the residual bath [C_L] was measured by using the UV-Vis spectrophotometer and the dye-uptake by silk fabric [C_S] was calculated. The equilibrium concentrations of dye in the residual bath and the dye uptake on fiber were calculated using the standard graph. Subsequently, an adsorption isotherm of eucalyptus leaves dye on silk, i.e. [C_S] *Vs* [C_L], was plotted and classified.

The value exhaustion and partition ratio were calculated at different temperatures by using the equation 1 and equation 2 [30].

$$E = [(C_0 - C_L) / C_0] \text{ x}100 \quad (1)$$

$$K = C_S / C_L \quad (2)$$

Where E is the dye exhaustion (%), C_0 and C_L are the initial and the final concentrations of dye in solution (mg/ml) respectively.

The typical results (on unmordanted silk) at 30, 60, and 90°C at 120 min and liquor ratio 1:50 show quasi-distribution sorption-isotherms, i.e., concentrations of dye in fiber [C_S] vs. concentrations in bath after dyeing [C_L] are plotted in Figure 10 (the ideal equilibrium of dyeing was not reached because the further dye distribution proceeds very slowly with time, namely the experiments at lower temperatures). The character of the adsorption isotherm obtained was nearest to the Nernst distribution law, which describes the behavior of disperse dyes in various kinds of fibers. After the first linear period of dependance [C_S] vs. [C_L], the "apparent saturation" was reached and further addition of dye into the bath showed only accumulation of dyestuffs in the bath (i.e., the approximately horizontal elongation of dependance). Then, the sorption of eucalyptus dyes into silk fiber seems to correspond with the "solid solution sorption model", observed during dyeing (staining) of wool with disperse dyes [31].

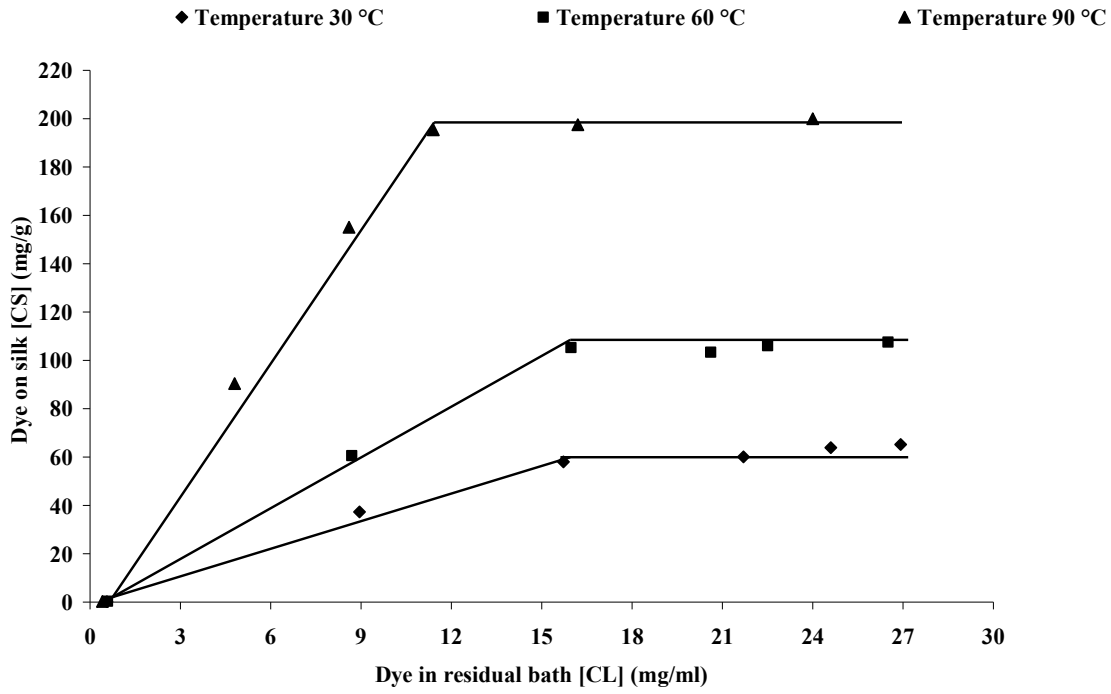


Figure 10 Quasi-sorption isotherm after 120 min dyeing of silk fabric (unmordanted) with eucalyptus leaves extract at 30°C, 60°C, and 90°C

The results of exhaustion (%), partition ratio (*K*), and saturation values are reported in Table 4. It can seen that the temperature was increased, the partition ratio and exhaustion percentages increased.

Table 4 Exhaustion (%), partition ratio (*K*), and saturation values of silk dyeing with eucalyptus leaf extract

Temperature / Parameter	30 °C	60 °C	90 °C
Exhaustion (%) (at equilibrium)	8.80	18.43	36.31
Partition ratio (*K*)	3.80	6.67	17.80
Saturation (mg/g)	65.92	109.55	200.10

3.5 Dyeing property of silk and wool fabrics dyed with eucalyptus leaf extract by using padding techniques by varying quantity of dye concentrations

Three different methods of dyeing employed were pre-mordanting, simultaneous mordanting (meta-mordanting) and post-mordanting. To study the effect of dye concentration, the eucalyptus dye concentrations were varied from 5, 10, and 20 g/l, four types of mordant (alum, copper sulfate, ferrous sulfate and stannous chloride) were used at 10 g/l for each concentration of dye, and an anionic wetting agent, Altaran S8 (1 g/l), was added to the liquor. The pH of the dyeing solution was adjusted to 4.0 with an acetic acid solution.

In the pre-mordanting methods, silk and wool fabrics were immersed in each mordant solution with anionic wetting agent and padded on a two-bowl padding mangle at 80 % pick up. Next, the mordanted sample was impregnated in each eucalyptus dye concentration. After padding for 2 seconds the samples were dried at 90 °C for 5 minutes for a 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. After the dyeing step, the samples were washed in 1 g/l of a soaping agent, Syntapon ABA, at 80 °C for 5 minutes, then air dried at room temperature.

For the simultaneous mordanting (meta-mordanting) method (i.e. dyeing in the presence of mordants), the fabrics were immersed in a bath containing a mordant and the dye extract at room temperature and padded on a two-bowl padding mangle at 80 % pick up. The processing of pad-dry, pad-batch and soaping were the same as above mention.

In the post-mordanting method, the fabrics were immersed in each eucalyptus dye concentration and without mordant, followed by padded on a two-bowl padding mangle at 80 % pick up. Then the padded samples were padded by mordanting. Further processing was the same as described in the pre-mordanting method. The colour strength (*K/S*) and CIELAB of the dyed samples were evaluated using a spectrophotometer.

The *K/S* values were measured for silk and wool fabrics as shown in Figure 11 to Figure 16. All measured sample showed the greatest λ_{max} value at 400 nm. It can be observed that the *K/S* values increase with an increase of dye concentration. Little difference between the two padding techniques utilized for the silk and wool fabrics dyes by three mordanting methods, except wool fabrics mordanted with copper sulfate whose gave a high *K/S* values on the pad-batch technique than pad-dry technique. In all cases ferrous sulfate mordant yielded the best dyeing results, and the next good result was obtained in the order of copper sulfate, stannous chloride and alum. However, alum mordant showed higher *K/S* values than stannous chloride mordant in silk dyeing using simultaneous mordanting method. As observed from the *K/S* values, in the case of wool fabrics dyed with alum by using post-mordanting method gave lower colour strength than without mordant.

Alum and ferrous sulfate were the best mordant during simultaneous mordanting method of dyeing. However, copper sulfate showed the best mordant during simultaneous mordanting and pre-mordanting method of dyeing. For the *K/S* value on dyed silk and wool fabrics were only little different using stannous chloride as mordant during three mordanting methods.

Wool fabric dyed with eucalyptus leaf extract showed a higher colour strength of the dyed samples than silk fabric. This is because there are more functional groups in wool than silk [6]. Wool and silk dyed without mordant showed light brown and yellowish-brown, respectively. The samples mordanted with copper sulfate, stannous chloride, and alum produced medium to dark grayish-brown, bright yellow and pale yellow shades, respectively. With ferrous sulfate, the colour was darker and duller. This may be associated with a change of ferrous sulfate into a ferric form by reacting with oxygen in the air. Ferrous and ferric forms coexisted on the fibers and their spectra overlapped, resulting in a shift of λ_{max} and consequent colour change to a darker shad [6]. Additional, the tannins combined with ferrous salts to form complexes, which also result in a darker shade of fabric [4]. From the results, it can be postulated that silk and wool fabrics can be successfully dyed with eucalyptus leaf extract. This may be attributed to the fact that eucalyptus leaves are rich tannin [13-14], which are phenolic compounds that can form hydrogen bonds with carboxyl groups in the protein fibers [20].

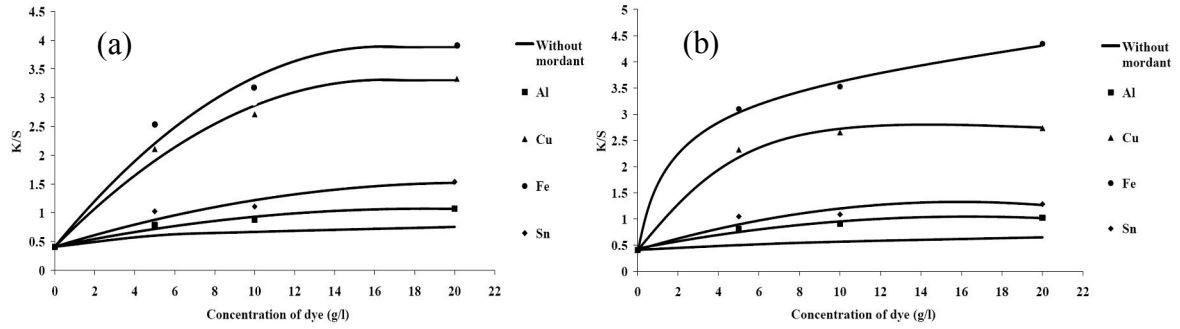


Figure 11 Effect of dye concentrations on *K/S* values of silk fabric dyed with 10 g/l mordants by pre-mordanting and using (a) pad-batch technique (b) pad-dry technique

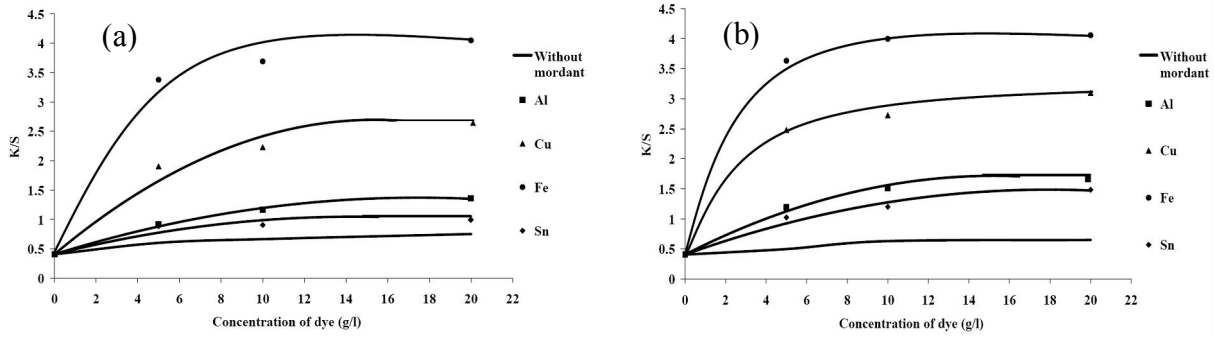


Figure 12 Effect of dye concentrations on *K/S* values of silk fabric dyed with 10 g/l mordants by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

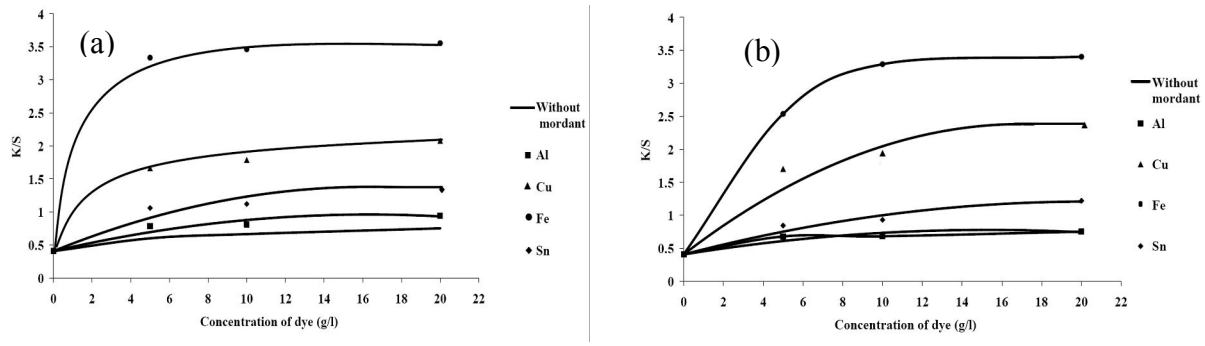


Figure 13 Effect of dye concentrations on *K/S* values of silk fabric dyed with 10 g/l mordants by post-mordanting and using (a) pad-batch technique (b) pad-dry technique

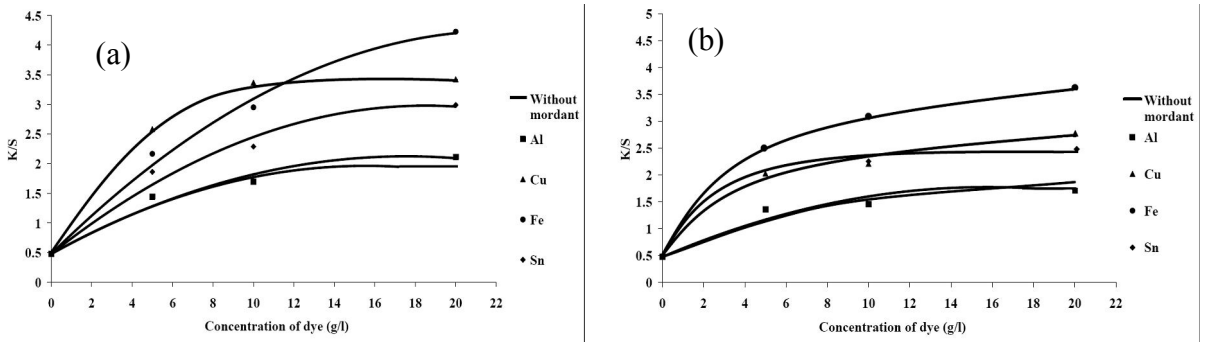


Figure 14 Effect of dye concentrations on *K/S* values of wool fabric dyed with 10 g/l mordants by pre-mordanting and using (a) pad-batch technique (b) pad-dry technique

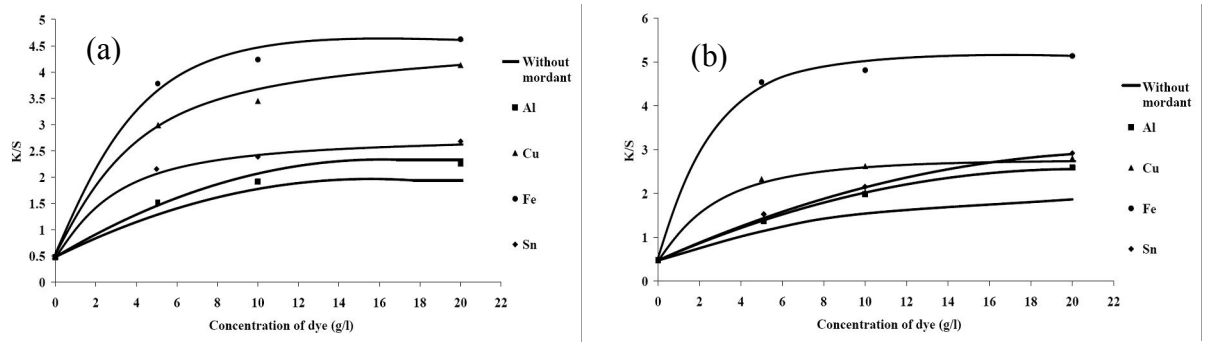


Figure 15 Effect of dye concentrations on *K/S* values of wool fabric dyed with 10 g/l mordants by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

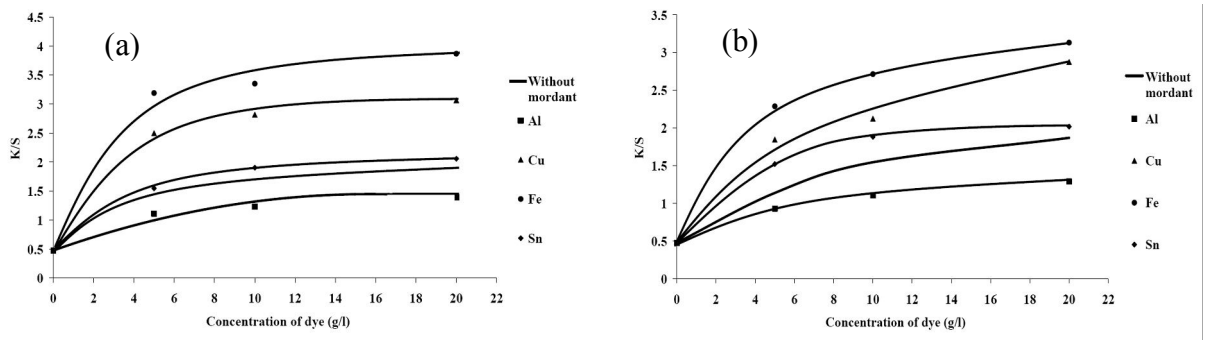


Figure 16 Effect of dye concentrations on *K/S* values of wool fabric dyed with 10 g/l mordants by post-mordanting and using (a) pad-batch technique (b) pad-dry technique

3.6 Dyeing property of silk and wool fabrics dyed with eucalyptus leaf extract using padding techniques. Effect of quantity of mordant concentrations, time/ temperature on pad-dry and batching time on pad-batch

A simultaneous padding process was used in this study. To study the effect of mordant concentration, three concentrations of four types of mordant were chosen: 5, 10, and 20 g/l. The eucalyptus dye concentration was used at 20 g/l for each mordant 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 optimized in the previous study [15,32]. Padding processes were carried out as described in the section 3.5

The ferrous sulfate ($FeSO_4 \cdot 7H_2O$), simultaneous padding and mordanting were used for the experiments of influence of batching time on pad-batch and drying time/temperature on pad-dry. In this technique, a concentration of 20 g/l of eucalyptus leaves dye was prepared; whereas ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was 20 g/l for concentration of dye. After padding for 2 seconds, the samples were dried at different temperature (40, 60 and 90 °C) for different duration 1-10 minutes 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 different duration 1-24 hours.

The samples were then washed in 1 g/l of the soaping agent, Syntapon ABA, at 80 °C for 5 minutes and air-dried at room temperature. The samples was measured on a spectrophotometer (Datacolor 3890).

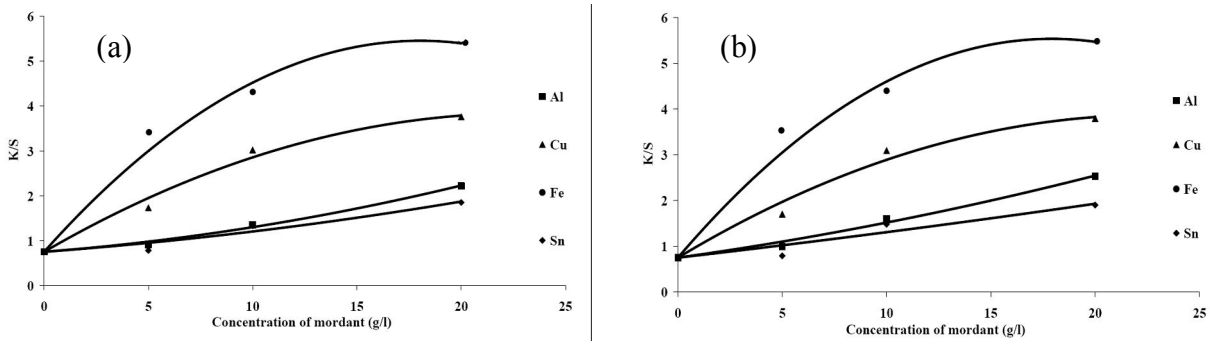


Figure 17 Effect of mordant concentrations on *K/S* values of silk fabric dyed with 20 g/l eucalyptus leaf extract by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

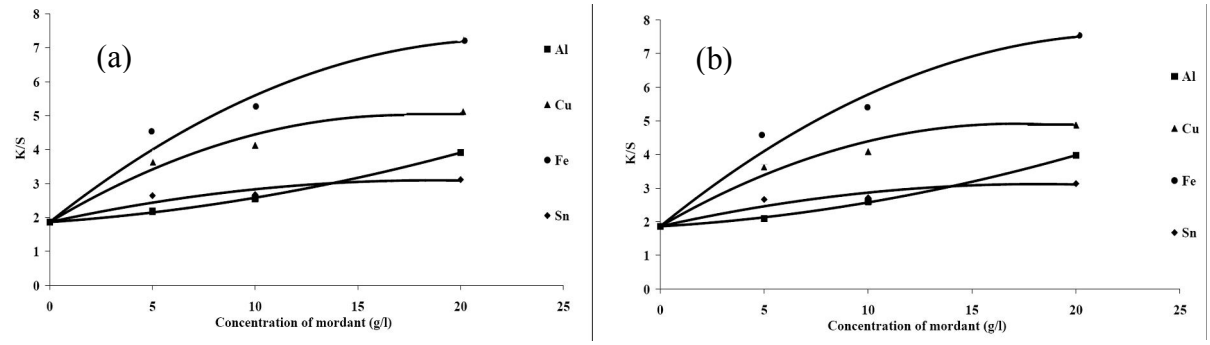


Figure 18 Effect of mordant concentrations on *K/S* values of wool fabric dyed with 20 g/l eucalyptus leaf extract by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

It can be seen that the *K/S* values in Figure 17 and Figure 18 increase with an increase of mordant concentration. The dyed uptake values were greater at the higher mordant concentration. This could be attributed to the darkening and dulling of shades due to mordant effect. Little different between the two padding techniques utilized for the study is observed.

Silk and wool fabrics dyed with eucalyptus leaf extract in the absence mordant showed light brown and yellowish brown shades, respectively. Comparison of four metal mordants showed that the ferrous sulfate metal mordant gave the highest depth of shade on wool and silk fabrics. Thus ferrous sulfate was the best mordant during mordanting method of dyeing. This could be attributed to difference in *CIELAB* values of the dyed samples.

The mordant activity of the five sequences was as follows: Fe > Cu > Al > Sn > without mordanted in silk and wool fabrics for eucalyptus leaf extract, the absorption of colour by wool and silk fabrics were enhanced by using metal mordants.

From the results, it is clear that ferrous sulfate and copper sulfate mordants are well known for their ability to form coordinate complexes and in this experiment both readily chelated with the dye. As the coordination numbers of ferrous sulfate and copper sulfate are 6 and 4 respectively, some co-ordination sites remained unoccupied when they interacted with the fiber. Functional groups such as amino and carboxylic acid groups on the fiber can occupy these sites. Thus this metal can form a ternary complex on one site with the fiber and on the other site with the dye [33]. Stannous chloride and alum metals formed weak coordination complexes with the dye, they tend to form quite strong bonds with the dye but not with the fiber, so they block the dye and reduce the dye interaction with the fiber [33].

The effect of time and temperature on colour strength (*K/S)* value was evaluated by padding a sample of silk and wool fabrics with eucalyptus leaf extract and ferrous sulfate as mordant. The samples were processed only by drying condition were 40, 60 and 90 °C for 1, 3, 5 and 10 minutes; The *K/S* values obtained are shown in Figure 19. It is clear that the colour strength (*K/S*) values increase with in crease in the drying time and temperature in both of silk and wool fabrics with pronounced increase in the wool case than the silk fabric.

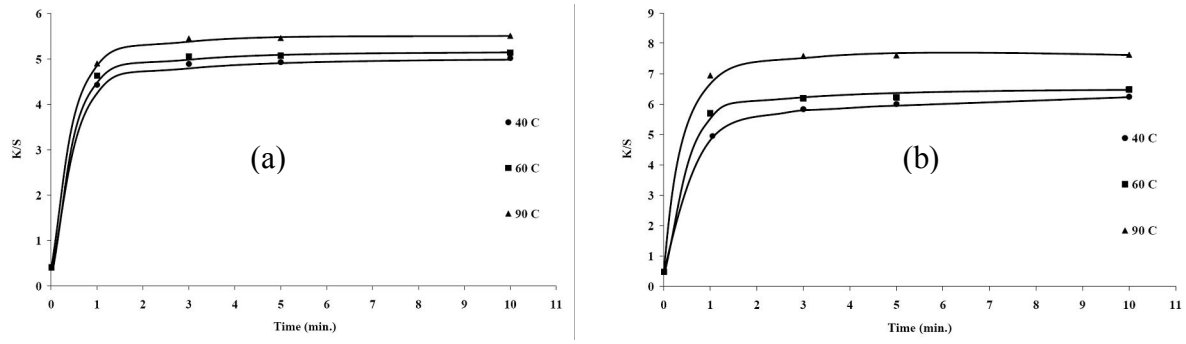


Figure 19 Effect of drying time and temperature of pad-dry technique on the colour strength (*K/S* values) of (a) silk fabric and (b) wool fabric dyed with 20 g/l eucalyptus leaf extract and using 20 g/l ferrous sulfate by using simultaneous mordanting

A study of this figure reveals that the high colour strength values (ca. 5.50) was achieved for the silk fabric on drying at 90 °C for 5 minutes, whereas the wool fabric shows very high colour strength values (ca. 7.60) on drying at 90 °C for 5 minutes.

The pad-batch dyeing process was carried out at room temperature with batching times of different lengths to assure an operation as economic as possible. Figure 20 shows that low colour strength required a period of 1 hour, medium colour strength of 6-12 hours and high colour strength a period of 24 hours. The colour strength obtained was increased as the batching time increased for both silk and wool fabrics, with a much higher colour strength value at all point in the wool case.

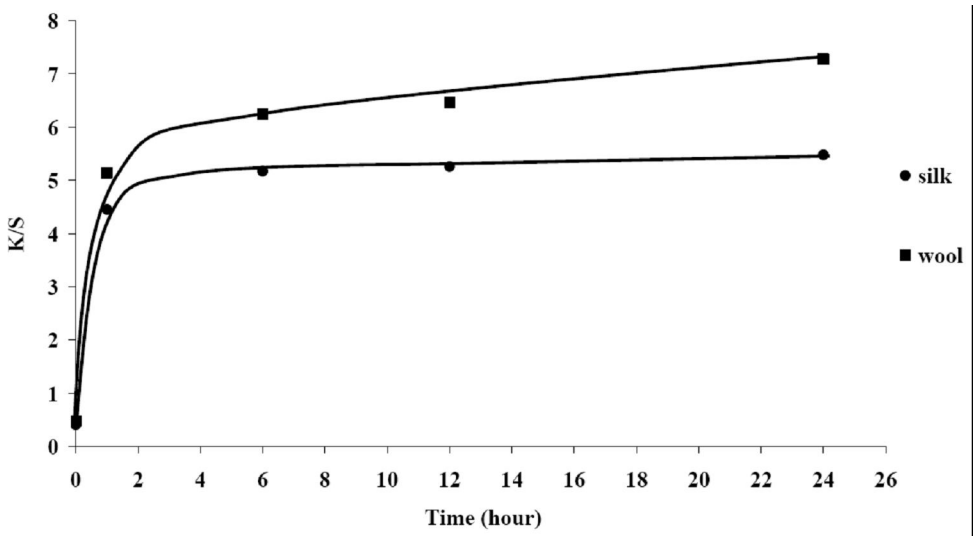


Figure 20 Effect of batching time of pad-batch technique on the colour strength (*K/S* values) of silk and wool fabric dyed with 20 g/l eucalyptus leaf extract and using 20 g/l ferrous sulfate by using simultaneous mordanting

3.7 The percentage yield (exploitation) of silk and wool fabrics dyed with eucalyptus leaves extract by simultaneous pad-dyeing

It was estimated that the best shades (deep and colour fastness) are obtained when mordanting with ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and, therefore, this mordant was used for the experiments. The following concentration range of eucalyptus leaf extract and mordant $FeSO_4 \cdot 7H_2O$ in the same concentration was used: 1, 5, 10, 20, 30, and 40 g/l, and in all cases anionic wetting agent in the concentration of 1 g/l was added to the padding bath. Glacial acetic acid was added to maintain the pH of the liquid at 4. The simultaneous padding was carried out at room temperature in a two-bowl padding mangle using 80% pick up. After padding (2 seconds), the samples were dried at 90ºC for 5 minutes and after 1 hour, all samples were repeatedly rinsed in warm water at 60ºC until the rinsing water remained colourless. The rinsed water was collected with the rest of dyeing bath in the volumetric flask and filled up to the defined volume for absorbance measurement by UV–vis spectrophotometer (at the wavelength of 270 nm at which the maximum absorbance was recorded). The concentration of eucalyptus leaf extract fixed in the fiber and percentage of its use (percentage of yield) from bath on fiber were calculated from the absorbance of the rinsing water by using the standard graph. Relationship Between bath concentration and padding condition were calculated from equation 3 to equation 8.

We assume when the initial dye concentration in the pad bath is C_0 (g/l). The quantity of dye transported by fabric is C_{pi} (mg/g)

$$C_{pi} = \frac{\%\ \text{pick up}}{100} \cdot C_0 \qquad 3$$

The concentration of dye in conjoined-water after rinsing can be expressed as:

$$C_r = \frac{\text{Absorbance}}{\varepsilon \cdot l} \qquad 4$$

where C_r = the concentration of dye in conjoined-water (mg/l), ε = absorption coefficient (l/mole.cm) and l = layer of solution (cm). Then the concentration of dye, which was stripped from material, is C_w (mg/g)

$$C_w = \frac{C_r \,.\, V}{1{,}000 \,.\, g} \qquad 5$$

where V = total volume after rinsing (ml) and g = weight of material (g). The concentration of dye absorbed on material, C_s (mg/g) was calculated as:

$$C_s = C_{pi} - C_w \qquad 6$$

The percentage of dye which stripped from the material can be shown as equation 7.

$$W = \frac{C_w \,.\, 100}{C_{pi}} \qquad 7$$

where W = the percentage of dye which stripped from the material (%). And the percentage of exploitation of dye (yield), E (%) can be calculated as:

$$E = 100 - W \qquad 8$$

Silk and wool fabrics dyed with the water extract of eucalyptus leaves in the presence of the $FeSO_4$ mordant in the same padding bath show a colour range of a brown grey shade to a dark grey shade. In Tables 5 and 6, the results are presented. The yield (exploitation) of the colouring component of eucalyptus leaf extract is surprisingly good in wool fabric (about 68%–52% from the lowest to the highest concentrations), and this corresponds to the medium deep brown-grey shades in the concentrations of more than 20 g/l eucalyptus leaf extract. In the silk fabric, the exploitation is less favorable and the decline with the changing to deeper shades is more distinct (about 22% to 15% exploitation).

The lower percentage of exploitation of eucalyptus leaf extract dye on silk compared with wool may be related to

(a) the greater crystallinity of silk when compared with the wool and

(b) the much lower content of groups that are able to form the hydrogen bonds with phenolic compounds as flavonoids dyes and parts of tannin (in the concrete):

-NH_2 groups	… on wool	10.8 Mol %	…	on silk 3.4 Mol %
-COOH groups	… on wool	18.5 Mol %	…	on silk 2.7 Mol %
-OH groups	… on wool	21.0 Mol %	…	on silk 17.0 Mol %

Because of linkages other than hydrogen bonds between tannins and wool, Agarwal and Patel [20] considered the ionic linkage of anionic groups of tannins with amino groups of wool. However, we considered that the dissociation constant of the phenolic OH groups in flavonoids and tannin is a very weak acid, with a *pKa* value of 10 [34], which cannot be in the subacid milieu markedly dissociated and setup the ionic bond with an ionized amino group of the fiber. The further possibility that the covalent bond between any quinone or semiquinone groups in the tannins and a reactive group on the wool, supposed by Agarwal and Patel [20], would seem to be less probable.

Table 5 Percentage yield and *K/S* values obtained by the simultaneous pad-dyeing/ mordant of wool fabric

C_0 (g/l)	Percentage of pick up	C_{pi} (mg/g)	C_s (mg/g)	Yield (%)	*K/S* value (400 nm)
1	80	0.8	0.5	68.0	1.8
5	80	4	2.5	62.8	2.8
10	80	8	4.2	53.2	3.7
20	80	16	8.3	52.0	3.9
30	80	24	12.6	52.6	4.0
40	80	32	16.0	52.2	4.5

Table 6 Percentage yield and *K/S* values obtained by the simultaneous pad-dyeing/ mordant of silk fabric

C_0 (g/l)	Percentage of pick up	C_{pi} (mg/g)	C_s (mg/g)	Yield (%)	*K/S* value (400 nm)
1	80	0.8	0.2	22.2	1.3
5	80	4	0.9	22.6	2.1
10	80	8	1.7	22.1	2.6
20	80	16	3.5	22.1	3.1
30	80	24	3.8	15.8	3.3
40	80	32	5.1	16.0	3.9

3.8 Properties of wool fabric dyed with eucalyptus, tannin, and flavonoids

The simultaneous padding and mordanting was used in this present work. In this technique, a concentration of 2 and 5 g/l of dye (eucalyptus leaf extract, quercetin rutin and tannin) was prepared; whereas ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was varied from 2, 5 and 10 g/l of each concentration of dye, the anion active wetting agent Altaran S8 (1 g/l) were added to the liquor. Then, the wool fabric was immersed in the above liquor at room temperature and padded on a two-bowl padding mangle (using 80 % expression). The padding, washing, soaping and *K/S* measuring processes were carried out as described in the previous part of this work.

Wool dyed with eucalyptus leaf extract and tannin dyed showed pale yellowish- gray shade, while that with ferrous sulfate showed a dark grayish-brown colour. Quercetin dyed on wool fabric without a mordant showed yellowish-green. Wool mordanted with ferrous sulfate produced dark yellowish-brown shade. Rutin dyed on wool substrates gave pale yellowish-green, while with ferrous sulfate, the colour was yellowish-brown.

From the results, it is clear that the colour shade of the fabric dyed by tannin (a major constituent of eucalyptus leaves) is colourimetrically and visually observed to be very similar to the eucalyptus leaf extract dye.

The colours obtained with 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 obtained.

Figure 21 shows the colour strength (*K/S*) values of wool fabric dyed with eucalyptus leaf extract, quercetin, rutin, and tannin, respectively. It can be observed that the *K/S* values increase with an increase of dye and ferrous sulfate concentrations.

The dyeing mechanisms of wool fabric with tannin (ellagic acid and gallic acid), quercetin and rutin by using ferrous sulfate as metal mordant can be considered as given in Figure 22 [35-37].

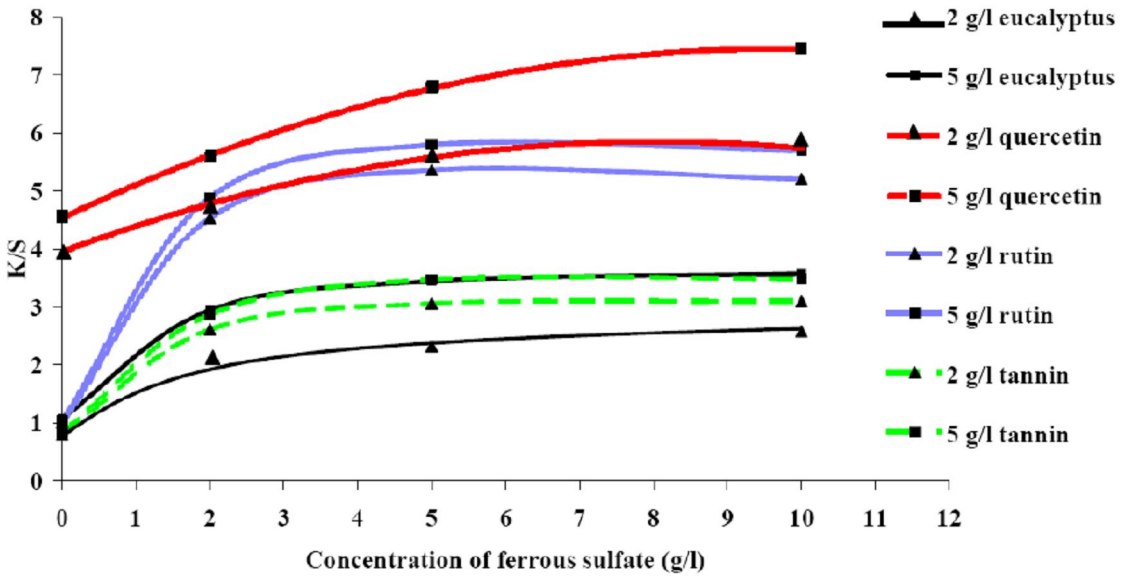


Figure 21 The *K/S* values of dyed wool fabric with eucalyptus leaf extract, quercetin, rutin and tannin dye by varying concentration of dyes and ferrous sulfate

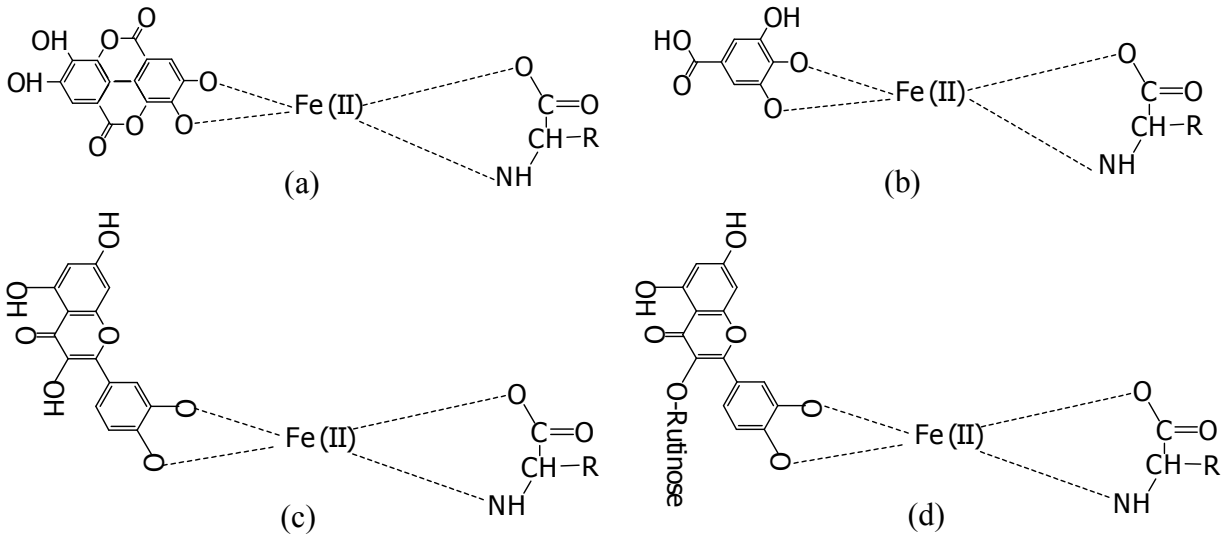


Figure 22 The proposed structure of Fe (II)/ dyestuff/ wool complexation (a) ellagic acid (b) gallic acid, (c) quercetin and (d) rutin

It can be concluded that wool fabric can be successfully dyed with the 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 numbers of ferrous sulfate is 6, some coordination sites remained unoccupied when they interacted 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 the other site with the dye [33]. Tannin has many carboxylic (-COOH) and hydroxyl (-OH) groups, which are able to bind with protein macromolecules in addition to having excellent opportunities for complexing with ferrous sulfate.

The washing fastness rating of wool fabric dyed with eucalyptus leaf extract, quercetin, rutin, and tannin are very good (4 to 4-5). The 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 and ultimately improve the washing fastness.

A light fastness in the range of 3-4 to 4-5 (fair to good) can be observed in the wool fabric, except for the wool fabric dyed with quercetin, whose rating was 2 (poor). This is attributed to the fact that the presence of 3-hydroxy groups in the quercetin reduces the light fastness due to lower photostability [7]. However, a rating of 4 to 5 (good) can be seen in the wool fabric mordanted with ferrous mordant. From these results, it can be concluded that the wool, bearing amino acids retards photo-oxidation by the reductive process [7].

From the results, very good (4-5) rubbing fastness can be observed in wool fabric dyed with eucalyptus leaf extract, quercetin, rutin, and tannin, except for fabrics mordanted with ferrous sulfate, whose ratings were 3 to 4 (fair to good). However, the fabric dyed with tannin and ferrous sulfate shows 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 deposited mostly at the periphery of the dyed fiber, resulting in a low rubbing fastness [38-40].

3.9 UV protection properties of silk fabric dyed with eucalyptus leaf extract

A simultaneous padding process was used in this study. To study the effect of dye concentration, three concentrations of the eucalyptus leaf extract dye were chosen: 5, 10, and 20 g/l. Three types of mordants were used at a concentration of 10 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 optimized in the previous study [15, 32]. The fabric was then immersed in the dye solution at room temperature and padded on a two-bowl padding mangle at 80% pick up. The padding, washing, soaping and *K/S* measuring processes were carried out as described in the previous part of this work.

The transmittance and UPF values of the original silk fabric and the silk fabrics dyed with the eucalyptus leaf extract were measured using a Shimadzu UV3101 PC (UV–VIS–NIR scanning spectrophotometer, 190–2100 nm range). The UPF value of the fabric is determined from the total spectral transmittance based on AS/NZ 4399:1996 as follows [41]:

$$\mathrm{UPF} = \frac{\sum_{290}^{400} E_\lambda S_\lambda \Delta_\lambda}{\sum_{290}^{400} E_\lambda S_\lambda T_\lambda \Delta_\lambda} \qquad 9$$

Where E_λ is the relative erythemal spectral effectiveness (unitless), S_λ is the solar UVR spectral irradiance in W/m^2/nm, T_λ is the measured spectral transmission of the fabric, Δ_λ is the bandwidth in millimetre, and λ is the wavelength in nanometre. Fabrics with a UPF value in the range of 15–24 are defined as providing “good UV protection”, 25–39 as “very good UV protection”, and 40 or greater as “excellent UV protection” [42]. There is no rating assigned if the UPF value is greater than 50.

Silk fabrics dyed with the eucalyptus leaf extract without a mordant showed a pale yellow shade. The samples mordanted with CuSO4 and $AlK(SO_4)_2$ produced medium-to-dark greyish-brown and pale yellow shades, respectively. With $FeSO_4$, the colour was darker and duller.

The percent UV transmittance data of silk fabrics dyed with and without a mordanting agent are shown in Figure 23 and Figure 24. It can be observed that since the relative erythemal spectral effectiveness is higher in the UV-B region (290–320 nm) than in the UV-A region (320–400 nm), the UPF values depend primarily on transmission in the UV-B region. As can be seen, there is a difference between the dyed fabrics and the undyed fabric for the UV transmittance spectra. The undyed fabric showed a high percent UV transmittance of about 14%. The percent UV transmittance of the dyed fabrics without a mordant was in the range of 5–7% in the UVB band. For the samples mordanted with $AlK(SO_4)_2$, $CuSO_4$, and $FeSO_4$, the percent UV transmittance was in the range of about 4–5%, 2–2.5%, and 0.5–1.5%, respectively. Among the dyed fabrics without a mordant, the value of the spectral transmittance could be decreased using mordants such as $AlK(SO_4)_2$, $CuSO_4$, and $FeSO_4$. It is clear that different mordants had different effects on the spectral transmittance of a fabric dyed with natural dyes [28]. Additionally, the colour and colour depth of the fabric can be related to UV transmittance, with light colours transmitting more UV than dark colours [43].

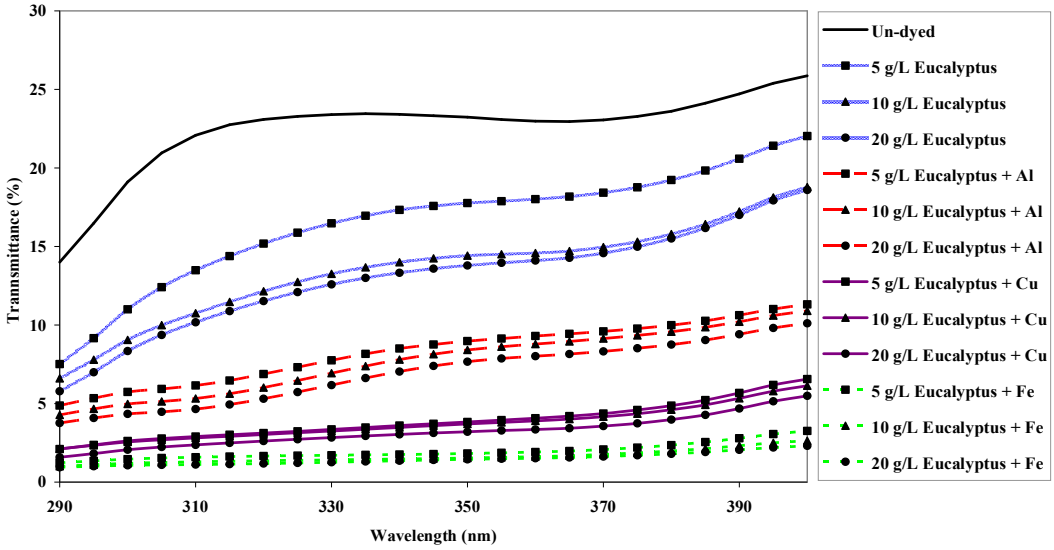


Figure 23 UV transmission of silk fabrics dyed with eucalyptus leaf extract in the absence and in the presence of metal mordants by the pad-dry technique
Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$

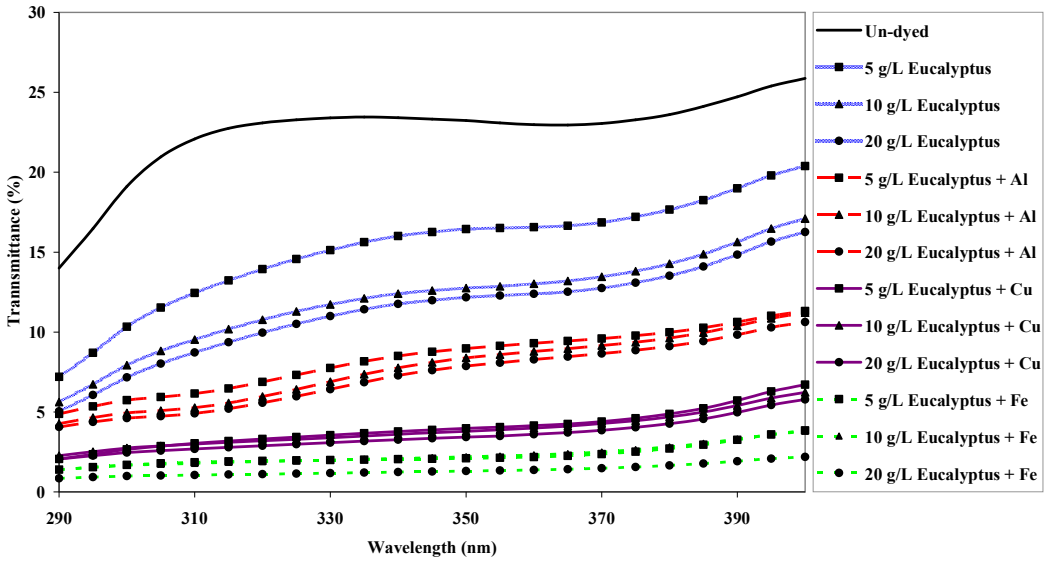


Figure 24 UV transmission of silk fabrics dyed with eucalyptus leaf extract in the absence and in the presence of metal mordants by the pad-batch technique
Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$

Table 7 shows the UPF values, protection class, and *K/S* values of silk fabrics dyed with the eucalyptus leaf extract with and without metal mordants by pad-batch and pad-dry dyeing techniques. It can be observed that the UPF values increase with an increase in the dye concentration. Little difference is observed between the two padding techniques utilized for this study.

The undyed fabric has a high transmittance value and a very low UPF value of 4.6. The dyed samples without a metal mordant at different concentrations of the dye using both dyeing techniques show UPF values between 7.92 and 11.33, which cannot be rated as offering any degree of protection because the UPF values were less than 15. This indicates that the resistance of both the undyed fabric and the dyed fabrics without a metal mordant to UV rays was very poor.

From the transmission data and the corresponding UPF values, it can be observed that all metal mordants used in this study caused a reduction in UVR transmission through the silk fabric. Silk fabrics dyed with the $AlK(SO_4)_2$ mordant at different concentrations of the dye using the pad-dry and the pad-batch dyeing techniques could be classified as offering "good UV protection" (UPF values between 15 and 24). The samples dyed with the $CuSO_4$ mordant were rated as "very good" (UPF values between 25 and 39). "Excellent UV protection" (UPF values equal to or greater than 40) was observed in silk fabrics dyed with the $FeSO_4$ mordant. The results also show that the samples dyed with higher concentrations of the eucalyptus leaf extract dye have higher UPF values. For example, the UPF value of the fabric dyed with the eucalyptus leaf extract and the $AlK(SO_4)_2$ mordant by the pad-dry technique at a dye concentration of 5 g/l was 15.60, which increased to more than 20.18 at a dye concentration of 20 g/l.

Table 7 UPF values, protection class, and *K/S* values of silk fabrics dyed with eucalyptus leaf extract by pad-dyeing techniques and using 10 g/l of metal mordants at different concentrations of the dye

Mordant	Dye Conc. (g/l)	Pad-batch			Pad-dry		
		UPF	UPF* Protection class	*K/S***	UPF	UPF* Protection class	*K/S***
-	Un-dyed	4.60	No Class	0.40	4.60	No Class	0.40
Without	5	8.01	No Class	0.60	7.92	No Class	0.50
	10	10.41	No Class	0.66	9.21	No Class	0.63
	20	11.33	No Class	0.75	10.76	No Class	0.71
$AlK(SO_4)_2$	5	15.57	Good	0.92	15.60	Good	1.19
	10	17.79	Good	1.16	17.95	Good	1.51
	20	19.55	Good	1.35	20.18	Good	1.60
$CuSO_4$	5	32.46	Very Good	2.22	33.70	Very Good	2.47
	10	33.77	Very Good	2.52	34.76	Very Good	2.72
	20	36.46	Very Good	3.02	37.45	Very Good	3.09
$FeSO_4$	5	53.70	Excellent	3.37	62.56	Excellent	3.63
	10	64.84	Excellent	3.69	76.33	Excellent	3.90
	20	86.76	Excellent	4.04	90.67	Excellent	4.05

Note: * UPF < 15 = No class UPF 15-24 = Good UPF 25-39 = Very Good
UPF > 40 = Excellent
** All measured sample showed the greatest λ_{max} value at 400 nm.

The *K/S* values of the dyed fabrics, which are a measure of colour strength, seem to confirm that higher colour strength increases the UPF values. For example, in the case of the silk fabric dyed with the eucalyptus leaf extract using the $CuSO_4$ mordant and the pad-batch technique, the *K/S* value increased from 2.22 to 3.02 and the UPF value rose from 32.46 to 36.46.

Therefore, it was proven that these results agree with previous data reported by Sarkar [40], who showed that a pale-coloured cotton fabric gives less protection against intense UV radiation. The results also show that the UPF values for colourants applied at higher concentrations are higher as compared with those for colourants applied at lower concentrations.

We agree with Gies et al. [41] and Wilson et al. [43], who indicated that dyeing fabrics in deeper shades and darker colours improves their UV protection properties. Thus, although the studies by Gies et al. [41] and Wilson et al. [43] were done with synthetic dyes, their conclusion seems to hold with natural colourants as well. We also accept the results of Feng et al. [28], who demonstrated that the UV protection properties of cotton and silk fabrics dyed with natural dyes using a metal mordant could effectively protect the skin from solar UVR.

3.10 The Fastness property of silk and wool fabrics dyed with eucalyptus leaves extract

With regard to the dyestuff properties of the dyeing agent, the ability of mordanting agent to fix on fiber is the important requirement. Obviously, this relates to the colour fastness properties. The colour fastness to washing, light, rubbing, water, and perspiration of the dyes samples was determined according to ISO 105-C06 A1S: 1994, ISO 105-B02: 1994, ISO 105-X12: 2001, ISO 105-E01: 1994, and ISO 105 E04: 1994, respectively.

A simultaneous padding process was used in this study. To study effect of dyeing technique on fastness properties, the eucalyptus dye concentration was 20 g/l, four types of mordant were used at 10 g/l for concentration of dye, and an anion wetting agent, Altaran S8 (1 g/l), was added to the liquor. The pH of the dyeing solution was adjusted to 4.0 with an acetic acid solution. The fabric was then immersed in the liquor solution at room temperature and padded on a two-bowl padding mangle at 80 % pick up. The padding, washing, soaping and *K/S* measuring processes were carried out as described in the previous part of this work.

When comparing the fastness rating of the samples dyed using the two padding techniques, it can be postulated that the pad-batch technique gives nearly the same fastness properties as the pad-dry technique.

The washing fastness ratings of silk and wool fabrics dyed with eucalyptus leaves were very good (4-5). However, light fastness was only fair to good (3-4). Colour fastness to rubbing is shown to be in the range of 4 to 4-5 (good to very good) except for silk and wool fabrics mordanted with ferrous sulfate, whose rating was only 3-4 (fair to good) when subjected to wet rubbing.

The rating obtained for colour fastness to water in term of the degree of colour change and colour staining were very good (4 to 4-5). The colour fastness to perspiration in acid and alkaline condition of fabrics dyed with and without metal mordants are shown in range of 4 to 4-5.

The good fastness properties of silk and wool fabrics dyed with eucalyptus leaf extract may be attributed to the fact that these dyes contain tannin, which may help covalent bond formation with the fiber, thereby resulting in good fixation on the fibrous material. Again, these tannins, having a phenolic structure, can form metal chelation with different mordants. Hence, after mordanting, these tannins are insoluble in water, ultimately improving the washing fastness [20].

4 Publications/Presentation

4.1 Conferences :

[1] Mongkholrattanasit, R. and Vitidsant, T. Dyeing and colour fastness properties of silk and cotton fabrics dyed with eucalyptus leaf extract, **6 th International Conference TEXSCI 2007 Textile Science 2007**, Technical University of Liberec, Textile Faculty, 5 th-7 th June 2007. pp. 83, ISBN: 978-80-7372-207-4.

[2] Mongkholrattanasit, R., Kryštůfek, J., and Wiener, J. An adsorption of dyeing on silk fabric with aqueous extract of eucalyptus leaves. **14 th International Conference STRUTEX 2007 Structure and Structural Mechanics of Textiles**, Technical University of Liberec, Textile Faculty, 26th-28 th November 2007. pp. 211-215, ISBN: 978-80-7372-271-5.

[3] Mongkholrattanasit, R., Kryštůfek, J., and Wiener, J. Dyeing and fastness properties silk and wool fabrics dyed with natural dye extracted from eucalyptus leaves using padding technique. **15 th International Conference STRUTEX 2008 Structure and Structural Mechanics of Textiles**, Technical University of Liberec, Textile Faculty, 1st-3rd December 2008. pp. 429-436, ISBN: 978-80-7372-418-4.

[4] Mongkholrattanasit, R., Kryštůfek, J., and Wiener, J. Dyeing, fastness and UV Protection properties of natural dye. **DHA 28th Meeting of Dyes in History and Archaeology**, Institute of Natural Fibres & Medicinal Plants, Poznan, Poland, 21st-24th October 2009. pp. 64.

[5] Mongkholrattanasit, R., Kryštůfek, J., and Wiener, J. UV Protection properties of natural dye from eucalyptus leaves. **16 th International Conference STRUTEX 2009 Structure and Structural Mechanics of Textiles**, Technical University of Liberec, Textile Faculty, 3rd-4th December 2009. pp. 155-157, ISBN: 978-80-7372-542-6.

4.2 Journals:

[1] Mongkholrattanasit, R., Wongphakdee, W., and Sirikasemlert, C. Dyeing and colour fastness properties of silk and cotton fabrics dyed with eucalyptus bark extract. **RMUTP Research Journal**. 1 (1) (2007): 41-49. ISSN 1906-0432.

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[6] Mongkholrattanasit, R., Kryštůfek, J., Wiener, J., and Viková, M. UV Protection property of silk fabric dyed with eucalyptus leaf extract. **Accepted** for publishing in **The Journal of The Textile Institute**. ISSN: 0040-5000 (paper), 1754-2340 (electronic)

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6 Summary

The Eucalyptus leaves contains tannin, gallic acid and ellagic acid which are major components and are associated flavonoids (quercetin and rutin apigenin and hyperin etc.), which are the minor substances.

Applying the molar ratio method, it was determined that stoichiometric composition of complex formed is Fe_2(tannin) and Fe(tannin) in aqueous solution. The bathochromic shifts observed are consistent with the lone pair electrons in the donor atoms (O in the dye) participating in metal ion coordination and stabilizing the excited state relative to the ground state.

Extraction and dyeing of natural dye from *Eucalyptus camaldulensis* were optimized. The adsorption isotherm obtained was nearest to the Nernst distribution law, which describes the behavior of disperse dyes in various kinds of fibers. Then, the sorption of eucalyptus dyes

into silk fiber seems to correspond with the “solid solution sorption model”, observed during dyeing (staining) of wool with disperse dyes.

Wool fabric dyed with eucalyptus leaf extract shows higher *K/S* values than silk fabric. Only slight differences were observed between the two padding techniques (pad-batch and pad-dry) utilized for dyeing. Ferrous sulfate mordant gave rise to the best dyeing, and exhibited a darker shade. Copper sulfate mordant gave a yellowish-brown shade. The use of mordants not only improves colour strength but also provides shade differences.

Silk fabrics dyed with a eucalyptus leaf extract with metal mordants ($AlK(SO_4)_2$, $CuSO_4$, and $FeSO_4$) have “good to excellent UV protection” properties. However, undyed and dyed silk fabrics without a mordant cannot be rated as offering any degree of protection. The degree of protection imparted after dyeing was a function of the concentration of the dye in the fabric. In addition, darker colours, such as those obtained using the $FeSO_4$ mordant, provided better protection on account of the higher degree of UV absorption. Therefore, it can be concluded that dyeing with a eucalyptus leaf extract can be useful in developing UV-protective silk fabrics and that the metal mordanting process using $AlK(SO_4)_2$, $CuSO_4$, and $FeSO_4$) would be necessary to enhance not only the dyeing efficiency but also the UV-protective properties of silk fabrics.

The ratings for washing, rubbing, water and perspiration fastness of the samples dyed by both padding techniques were good to very good (4–5), whereas that for light fastness was fair (3–4).

The application of eucalyptus leaves dye on silk and wool fabrics by pad-batch and pad-dry technique of dyeing can be considered as an affective eco-option because it gives extremely good results with substantial minimization of processing cost. In case of pad-dry technique, the average hot air consumption is considerably high whereas no hot air is being consumed in cold pad-batch process which leads to energy conservation. However, the time employed for the fixation of eucalyptus leaves dye is very long in cold pad-batch technique. So, these techniques can be considered as best suitable for small scale industries or cottage dyeing of eucalyptus leave.

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