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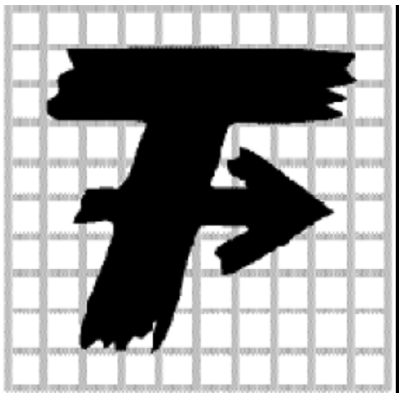

Disertačni Práce
Ph.D. Dissertation

Dye Extraction from Eucalyptus Leaves and Application for Silk and Wool Fabrics Dyeing

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ABSTRACT (ENGLISH)

This research was concerned with analysis the colour components of dye extraction from the leaves of eucalyptus (*camaldulensis*) and application for silk and wool fabrics dyeing by the use of two padding techniques, namely the pad-batch and pad-dry techniques under different conditions.

The major colouring component found in eucalyptus leaves are tannin (ellagic acid and gallic acid) and flavonoids (quercetin and rutin) as minor components. Silk and wool fabrics dyed in a solution composed of eucalyptus extract from leaves showed a shade of pale yellow to brown. The exception was when the fabric was dyed with ferrous mordant, resulting in a shade of dark grayish-brown.

Wool and silk fabrics were dyed using the water extract obtained from eucalyptus leaves; essentially higher utilization of dyestuffs and shortening of the dyeing procedure was achieved as a result of the padding dyeing principle followed prior to drying. The dye exploitation of wool is higher than that of silk, and in both cases common “exhaustion” methods are better than “long baths.” The ecological and economical considerations of dyeing by natural dyestuffs are discussed.

It was observed that with an increase in the dye concentration, the ultraviolet (UV) protection factor (UPF) values ranged between good and excellent for the silk fabric. In addition, a darker colour, such as that provided by a $FeSO_4$ mordant, gave better protection because of higher UV absorption. The results confirmed that natural dyes from eucalyptus leaf extract with metal mordants have potential applications in fabric dyeing and in producing UV protective silk fabrics.

The colour fastness to washing, water, perspiration and rubbing of the silk and wool fabrics treated with the mordant after dyeing was investigated and the results showed good to excellent fastness, whereas colour fastness to light was at a fair to good level.

ABSTRACT (CZECH)

Tato práce se zabývá analýzou barvicí složky extraktu z listů eukalyptu (camaldulensis) a její aplikací na hedvábnou a vlněnou tkaninu pomocí dvou postupů klocování. Jmenovitě jde o techniky pad-batch a pad-dry za různých podmínek.

Hlavní barevnou složkou nalezenou v extraktu z eukalyptu je tanin (kyselina ellagová a kyselina gallová) a minoritními složkami jsou flavonoidy (quercetin a rutin).

Odstíny světle žlutého až hnědého vybarvení hedvábné a vlněné tkaniny byly dosaženy lázňovým barvením v extraktu z listů eukalyptu. Tmavého šedavě-hnědého odstínu bylo dosaženo v případě barvení tkaniny s mořidlem na bázi solí železa.

Podstatně vyšší výtěžnosti barviva a zkrácení doby barvicího postupu bylo dosaženo pomocí klocovacího postupu barvení pad-dry (klocování-sušení). Výtěžnost barviva na vlně je vyšší než na hedvábí a v obou případech je dosaženo vyššího využití barviva než v „dlouhých“ lázních typických pro vytahovacím barvení. V práci jsou diskutovány ekologické a ekonomické aspekty barvení přírodními barvivy.

Bylo zjištěno, že s rostoucí koncentrací barviva u hedvábných tkanin vzrůstají hodnoty ultrafialového ochranného faktoru (UPF) až do hodnot poskytujících výbornou ochranu proti ultrafialovému (UV) záření. Při použití mořidla na bázi $FeSO_4$ lze získat tmavší odstíny, které jsou schopné intenzivně absorbovat UV záření a poskytují vynikající ochranu proti UV záření. Výsledky potvrdily, že přírodní barviva z listů eukalyptu aplikovaná s modřidly na bázi kovů mají velké potenciální využití při barvení textilií a ve výrobě tkanin chránících před UV zářením.

Byly stanoveny stálosti vybarvení v praní, vodě, potu a otěru u hedvábných a vlněných tkanin upravených po barvení mořidly. Výsledky většiny stálostních zkoušek odpovídají dobrým až výborným stálostem vybarvení. Pouze u stálostí vybarvení na světle relativně nižší.

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Mr. Rattanaphol Mongkholrattanasit

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CHAPTER I
INTRODUCION

1.1 Introduction

Natural dyes are known for their use in colouring of food substrate, leather, wood as well as natural fibers like wool, silk, cotton and flax as major areas of application since ancient times. Natural dyes may have a wide range of shades, and can be obtained from various parts of plants including roots, bark, leaves, flowers, and fruit [1]. 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].

For successful commercial use of natural dyes, the appropriate and standardized dyeing techniques need to be adopted without scarifying required quality of dyed textiles materials. Therefore, to obtain newer shades with acceptable colour fastness behaviour and reproducible colour yield, appropriate scientific techniques or producers need to be derived from scientific studies on dyeing methods, dyeing process variable, dyeing kinetics and compatibility of selective natural dyes. A need has also been felt to reinvestigate and rebuild the traditional processes of natural dyeing to control each treatment and pre-dyeing process (preparation, mordanting) and dyeing process variables for producing uncommon shades with balanced colour fastness and eco-performing textiles.

In spite of the better performance of synthetic dyes, recently the use of natural dyes on textile materials has been attracting more and more scientists for study on this due to the following reason [2]:

- Wide viability of natural dyes and their huge potential.
- Available of experimental evidence for allergic and toxic effects of some synthetic dyes, and non-toxic, non-allergic effects of natural dyes.

- To protect the ancient and traditional dyeing technology generating livelihood of poor artisan or dyers, with potential employment generation facility.
- To generate sustainable employment and income for the weaker section of population in rural and sub-urban areas both for dyeing as well as for non-food crop farming to produce plants for such natural dyes.
- To study the ancient dyeing methods, coloured museum textiles and other textiles recovered by archaeology for conservation and restoration of heritage of old textiles.
- Specialty colours and effects of natural dyes produced by craftsman and artisans for their exclusive technique and specialty work.
- Availability of scientific information on chemical characterizations of different natural colourants, including their purification and extraction.
- Availability of knowledge base and database on application of natural dyes on different textiles.

Production of synthetic dyes is dependent on petrochemical source, and some of synthetic dyes contain toxic or carcinogenic amines which are not ecofriendly [7]. Moreover, the global consumption of textiles is estimated at around 30 million tonnes, which is expected to grow at the rate of 3% per annum. The colouration of this huge quantity of textiles needs around 700,000 tonnes of dyes which causes release of a vast amount of unused and unfixed synthetic colourants into the environment [2]. This practice cannot be stopped, because consumers always demand coloured textiles for eye-appeal, decoration and even for aesthetic purposes. Moreover, such a huge amount of required textiles materials cannot be dyed with natural dyes alone. Hence, the use of eco-safe synthetic dyes is also essential. But a certain portion of coloured textiles can always be supplemented and managed by eco-safe natural dyes [2, 4]. However, all natural dyes are not ecofriendly. There may be presence of heavy metals or some other form of toxicity in natural dye. So, the natural dyes also need to be tested for toxicity before their use [4].

One of the plants use for dyeing is eucalyptus leaves which are the waste material and remaining from the pulp industry. Eucalyptus is one of the most important sources of natural dye that gives yellowish-brown colourants [4, 8]. Although, eucalyptus leaves have been used in textiles dyeing for several years but the dyeing techniques and colour components have not yet been reported in the literature. The aims of this research were thus

to analyze colour component in eucalyptus leaves and also extract the eucalyptus leaves as well as applying the compounds obtained on silk and wool fabrics.

1.2 Research objective

- To analyze the colour components from eucalyptus leaf extract.
- To study the interaction of tannins with ferrous ion.
- To apply eucalyptus leaf extract on silk and wool fabric using pad dyeing techniques.
- To study adsorption isotherm of eucalyptus leaf extract onto silk and wool fabrics.
- To investigate the effect of UV-Protection properties of wool and silk fabrics dyed with eucalyptus leaf extract.

CHAPTER II
THEORY

2.1 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 [9, 10]. Non-toxic dyes of plant and insect origin are also used in food and cosmetic industries [11]. 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 2.1 [9].

Table 2.1 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

2.1.1 Organic non-nitrogenous molecules

Organic non-nitrogenous molecules can be divided into 3 groups; a) flavonoids, b) quinonoids and c) polyenes/carotenoids.

a) Flavonoids

Flavonoids are polyphenolic pigments widely present in plants. The term flavonoid has been derived from the Latin word *flavus* meaning yellow, as a large number of the flavonoids are yellow in colour. They also exhibit a range of biological activities in mammals, the most important one being antioxidant activity. The colours and application of flavonoid and related molecules are shown in Table 2.2 [9].

Table 2.2 Colours and application of flavonoid and related molecules

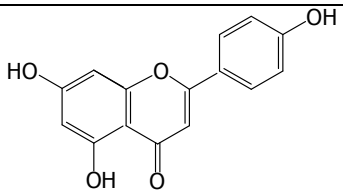
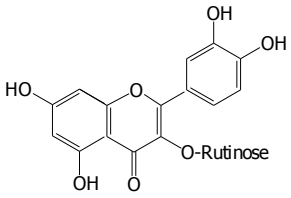
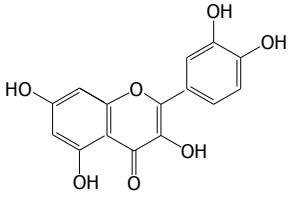
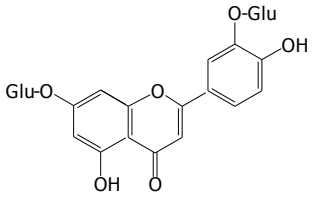
Natural Dyes **Compound/Class** **Colour**	**Structure**	**Source part/ Application**
Apigenin Flavone Yellow		*Matricaria Chamomilla L* Flower head Dyeing silk, wool and textiles
Rutin Flavonol Yellow		*Sophora japonica* Flower buds Dyeing silk, threads embroidery
Quercetin Flavonol Yellow		The flower of *Cedrela Toona* Dyeing silk and wool
Butrin Flavonone Yellow-orange		*Butea monospherma* Flowers Dyeing silk and cotton

Table 2.2 Colours and application of flavonoid and related molecules (continued)

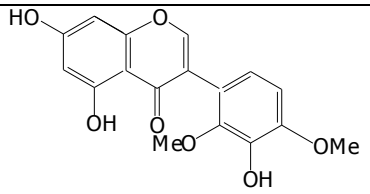
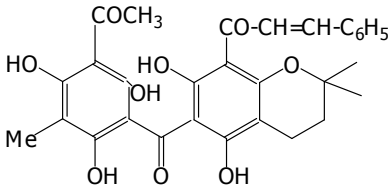
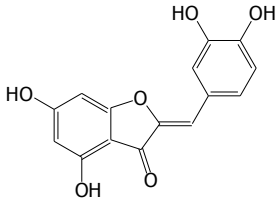
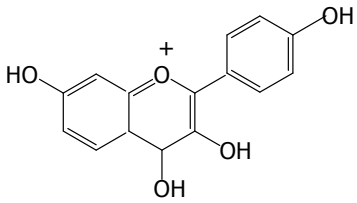
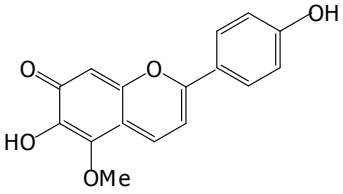
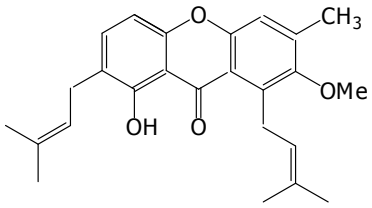
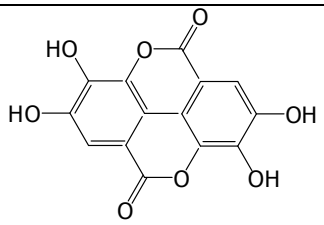
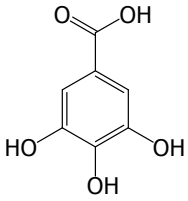
Natural Dyes **Compound/Class** **Colour**	**Structure**	**Source part/ Application**
Santal Isoflavone Red		*Pterocarpus santalinus* Wood Dyeing cotton, wool, leather, wood
Rottlerin Chalcone Salmon		*Mallotas phillippinensis* Seeds and flowers Dyeing textiles
Aureusidin Aurone Yellow		Flower of snapdragon and cosmos Dyeing textiles
Pelargonidin Anthocyanins Orange		Geranium, pomegranate Dye-sensitized solar cell Dyeing textiles
Carajurin Anhydro base Red		*Bignonia chika* Dyeing textiles
Mangostin Xanthone Yellow		*Garcinia magostana* Dyeing textiles

Table 2.2 Colours and application of flavonoid and related molecules (continued)

Natural Dyes **Compound/Class** **Colour**	**Structure**	**Source part/ Application**
Ellagic acid Tannins Light yellow		Walnuts, pomegranate Dyeing cotton, wool, silk leather,
Gallic acid Tannins Yellowish to light brown		Gallnuts, tea leaves Dyeing cotton, wool, silk leather,

b) Quinonoids

Quinonoids contain a quinone moiety which contributes to the yellow-red range of colours. Four types of quinonoid dyes such as benzoquinones, naphthoquinones, anthraquinones and extended quinones are known. Table 2.3 shows some natural quinones and anthraquinones dyes and their application.

Table 2.3 Natural quinones and anthraquinones dyes

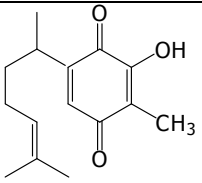
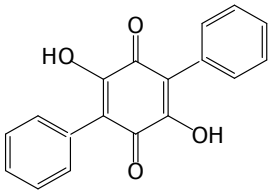
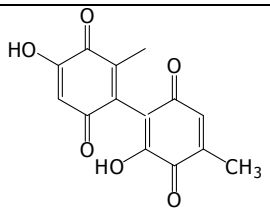
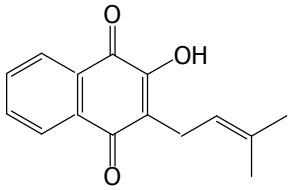
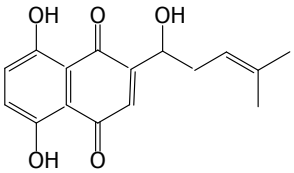
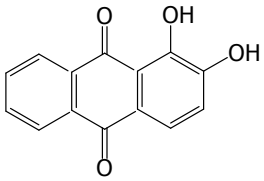
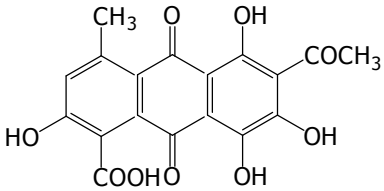
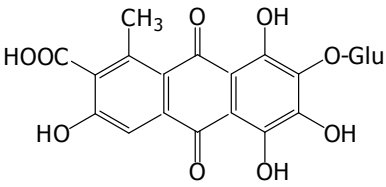
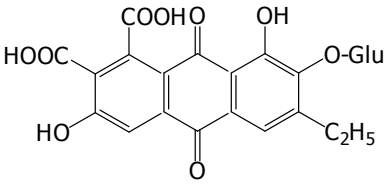
Name	**Structure**	**Source/ Application**
Perezone Benzoquinone Orange		*Trixis pipitzahue* Root Dyeing textiles
Polyporic acid Benzoquinone Bronze		*Polyporus fries* Fungus

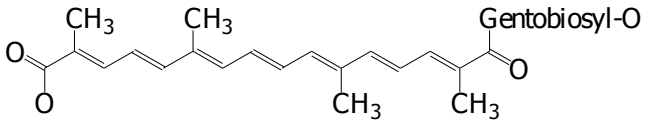
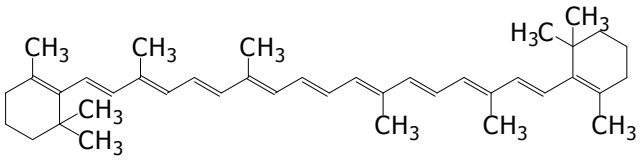
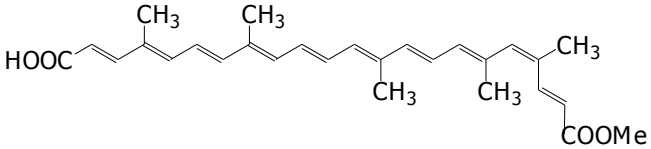
Table 2.3 Natural quinones and anthraquinones dyes (continued)

Name	Structure	Source/ Application
Phoenicin Di-benzoquinone Yellow		Trixis pipitzahue Root Dyeing textiles
Lapachol Naphthoquinone Yellow		*Tecoma leucoxylon*
Alkannin Naphthoquinone Red		*Anchusa tinctori* Root Red dye, cosmetic and food
Alizarin Anthraquinone Red		*Rubia cordifolia* Dyeing cloth
Kermesic acid Anthraquinone Red		*Coccus ilici* (Insect) Dyeing cloth
Carminic acid Anthraquinone Red		*Coccus Spp* (Insect) Dyeing cloth
Laccaic acid Anthraquinone Red		*Coccus laccae* (Insect) Dyeing wood

c) Polyenes/carotenoids

Polyene dyes contain a series of conjugated double bonds, usually terminating in aliphatic or alicyclic groups. The best-known group of polyene dyes is the carotenoids, which are widely encountered natural colourants. Some examples and their application are given in Table 2.4.

Table 2.4 Some examples of polyenes and their application

Plant origin **Compound class/ Colour**	**Structure**	**Source/ Part/ Application**
Crocin Apocarotinoid Golden yellow		*Crocus sativus* Pistil Food
β-Carotene Carotenoid Orange red		*Daucas carota* Tuber Food
Bixin Apocarotenoid Golden yellow		*Bixus Orellena* Seedcoat Food

2.1.2 Organic-nitrogenous molecules

Organic-nitrogenous natural pigments are a chemically heterogeneous group of basic nitrogen containing substances. They can be divided into 3 groups; a) pyrrole, b) pyrimidine and c) alkaloids.

a) Pyrrole

Pyrrole is a heterocyclic aromatic organic compound with a five membered nitrogen-containing ring. Pyrroles are components of larger aromatic rings, including the porphyrins of heme, the chlorins and bacteriochlorins of chlorophyll, and the corrin ring of vitamin

B12. There are 3 major groups of pyrrole dyes namely porphyrinoids, porphyrins, and chlorophyll/hemoglobin.

Porphyrinoids, tetrapyrrole macrocycles are natural pigments displaying beautiful range of colours, which occur in many living organisms such as plants, animals, marine organism, birds, bacteria, fungi, etc. They have important roles to play in nature, which include electron transfer, oxygen transfer and photosynthesis.

Porphyrins are the substituted porphins, which are macrocyclic compounds formed by joining four pyrrole rings with four methine bridges (Figure 2.1).

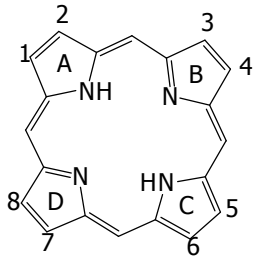
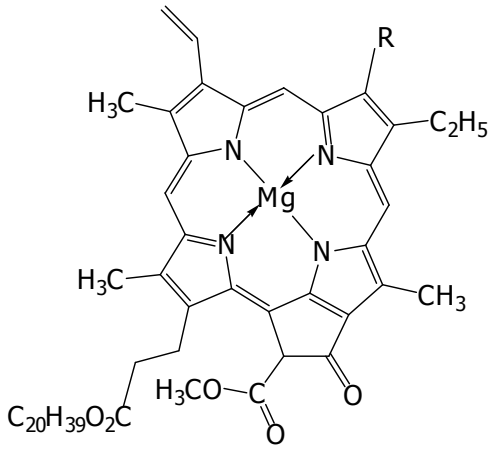


Figure 2.1 A fundamental skeleton of porphyrins

Chlorophyll and hemoglobin (Figure 2.2) form two important porphyrins containing magnesium and iron metal-complexes respectively. Chlorophyll is the green pigment occurring in the leaves and green stems of various plants. It acts as catalyst for absorption of the light energy from the sun to convert carbon dioxide and water into carbohydrates in plants and this process is known as photosynthesis.

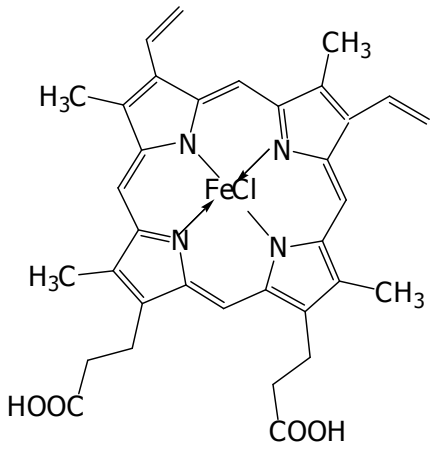
b) Pyrimidine

Pyrimidine is a heterocyclic aromatic organic compound similar to benzene and pyridine, containing two nitrogen atoms at positions 1 and 3 of the six membered ring. Pteridines are pyrimidine-based natural pigments that are widely distributed in butterflies (e.g. *Gonopterix rhamni*) and insects (Figure 2.3) [9]. Most of them are derived from xanthopterin, which contains a pyrimidine ring fused to a piperazine moiety.



Chlorophyll a: R = CH_3

Chlorophyll b: R = CHO



Heamin

Figure 2.2 Chemical structures of chlorophyll and heamin

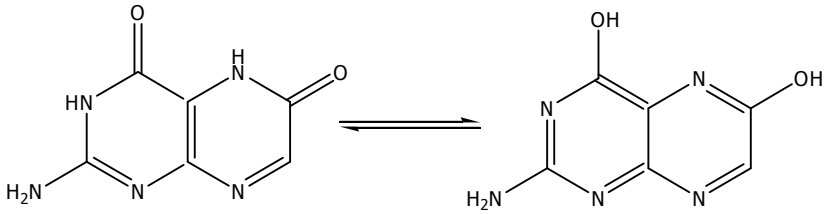
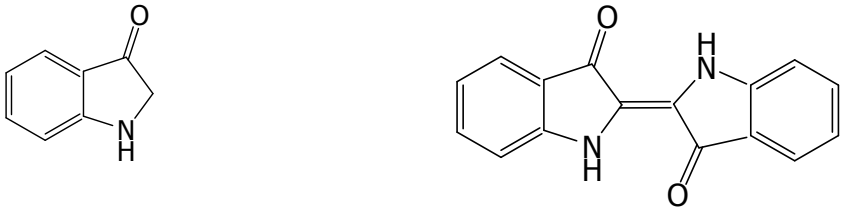


Figure 2.3 Xanthopterin from the butterfly *Gonopterix rhamni*

c) Alkaloid

Alkaloids are naturally-occurring amines (and derivatives) produced mainly by plants, but also by animals and fungi. Many alkaloids have pharmacological effects on humans and animals. The name derives from the word alkaline; originally, the term was used to describe any nitrogen-containing base.

The famous blue dye, indigo, used to dye burial clothes during ancient times and denims in recent times, is an alkaloid occurring in the form of its glucoside, indicant, in the leaves of *Indigofera tinctoria* and *Isatis tinctoria*. The leaves, on maceration with water, release an enzyme which hydrolyses the glucoside to give indoxyl and glucose. Air oxidation of two molecules of indoxyl forms indigo (indigotin), which is insoluble in water (Figure 2.4).



Indoxyl Indigo (Indigotin)

Figure 2.4 Structure of indoxyl and indigo (indigotin)

2.2 Synthetic dyes

Synthetic dyes for textile fibers may be classified according to chemical structure features or according to the method of application [12]. The classification of synthetic dyes according to chemical structure can be grouped into thirteen dye classes as shown in Table 2.5. Examples of the structures of azo dye, carbonyl dye, nitro dye, methane dye and arycarbonium ion dye are illustrated in Figure 2.5 [12].

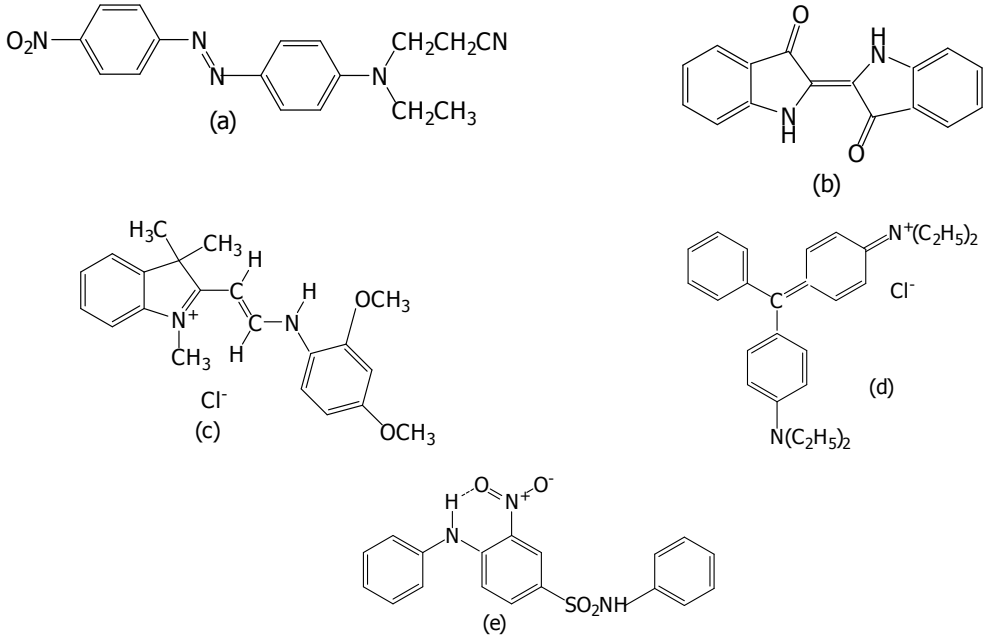


Figure 2.5 Examples of the structures of an azo dye, carbonyl dye, nitro dye and arycarbonium ion dye (a) C.I. Disperse Orange 25, monoazo dye; (b) C.I. Vat Blue 1, indigo; (c) C.I. Basic Yellow 11, methane dye; (d) C.I. Basic Green 4, triphenylmethane dye and (e) C.I. Disperse Yellow 42, nitro dye

Table 2.5 A summary of the characteristics of the main chemical classes of dyes and pigments

Chemical class	Distinctive structural feature	General characteristics	Main application class(es)
Azo	-N=N-	All hues, but yellow to red most important	Dominate most, but not vat dyes
Carbonyl	C=O	All hues, but blue most important	Important in most Applications
Phthalocyanine	16-membered heterocyclic ring, metal complex	Blue and green only	Most important in pigments
Triarycarbonium ion	Positively-charged carbon atom	All hues, but reds and blues most important	Cationic dyes and pigments
Sulfur dyes	Complex polymeric S-containing species	Mostly dull colours, such as blacks and browns	Often considered as an application class itself
Methine dyes	-C=	All hues, but yellows most important	Disperse, cationic
Nitro	$-NO_2$	Mainly yellows	Disperse, hair dyes
Inorganic colourants	Range of inorganic types	All hues, white and Metals	Exclusive pigments

2.3 Textile fibers

Textile fibers have been, and continue to be, derived from an enormous range of materials [13]. The classification of textile fibers is based on the principal origin of the fiber (natural or man-made), chemical type (cellulosic, man-made cellulosic), generic term (seed,

hair, rayon) and common names and trade names of the fibers (cotton, viscose, rayon) [14]. For the application of dyes, a simpler classification into three broad categories is often used [12]:

- Protein fibers e.g. silk and wool;
- Cellulosic fibers e.g. cotton, viscose rayon, and flax (linen);
- Synthetic and cellulose acetate fibers e.g. polyester, polyamide, acrylic and cellulose acetate.

2.3.1 Natural protein fibers

Natural protein fibers are generally obtained from animal hair and animal secretions. They have poor resistance to alkalies but have good resiliency and elastic recovery [15]. The most prominent protein fibers are wool and silk. Protein molecules are polypeptides, derived from different naturally occurring α-amino acids, most of which can be represented by the general formula (Figure 2.6).

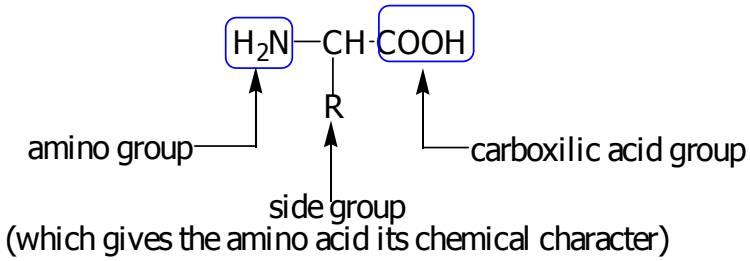


Figure 2.6 General amino acid formula

2.3.1.1 Wool fiber

Wool is a protein, and all protein material is composed of polymer chains containing many different amino acids as monomer units [16]. The differences between the various proteins lie in the proportions of each acid they contain, and the sequence in which they appear along the length of the polymer chain. All amino acids contain carbon, hydrogen, nitrogen and oxygen, and some contain sulphur too. Some proteins have globular molecules, and these are soluble in water. Others, the fibrous proteins that form the structural material of animal life, are insoluble. Wool is one of the keratin groups of fibrous proteins, which includes other animal hairs, horn and nails.

Each amino acid contains a carboxylic acid group (-COOH) and a basic amino group ($-NH_2$). This pattern is common to all the amino acids, the simplest of which is glycine (R=H); structure (Figure 2.6) shows the generalized formula. The middle carbon atom in glycine is linked to a carboxylic acid group, an amino group and two hydrogen atoms. One of the hydrogen atoms can be replaced by another group to form a different amino acid and thus a whole series of such acids can be obtained, each containing a different side-group (R). The side-group (R) of amino acid of wool fiber is shown in Table 2.6 together with the formula for each of the amino acids [17].

Table 2.6 Structure and amount of major amino acid in wool

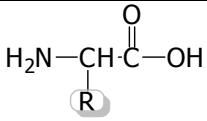
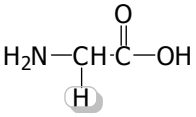
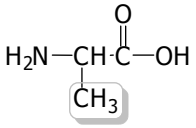
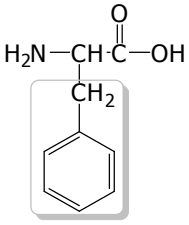
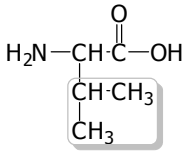
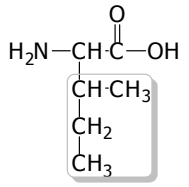
Name of amino acid	**Structure**	**Mol % (from two sources)**		**Nature of side chain**
In general formula (R = Side chain)		-		-
Glycine		8.6	8.2	Hydrocarbon
Alanine		5.3	5.4	Hydrocarbon (Non polar)
Phenylalanine		2.9	2.8	Hydrocarbon (Non polar)
Valine		5.5	5.7	Hydrocarbon (Non polar)
Isoleucine		3.1	3.1	Hydrocarbon (Non polar)

Table 2.6 Structure and amount of major amino acid in wool (continued)

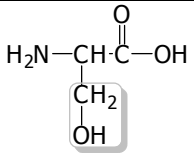
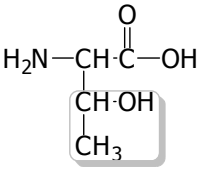
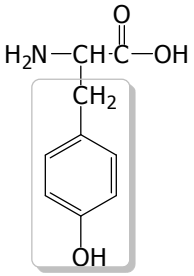
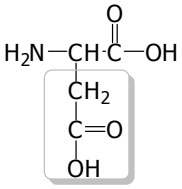
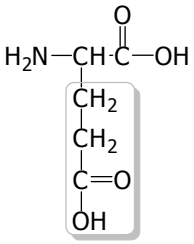
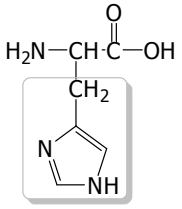
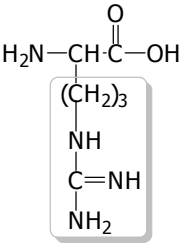
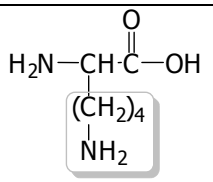
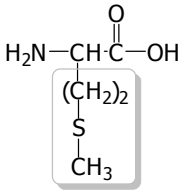
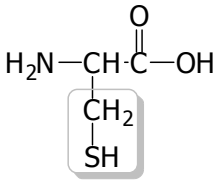
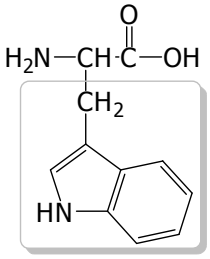
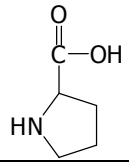
Name of amino acid	Structure	Mol % (from two sources)		Nature of side chain
Serine		10.3	10.5	Polar
Threonine		6.5	6.3	Polar
Tyosine		4.0	4.7	Polar
Aspartic acid		6.4	6.6	Acidic
Glutamic acid		11.9	11.9	Acidic
Histidine		0.9	0.8	Basic
Arginine		6.8	6.9	Basic

Table 2.6 Structure and amount of major amino acid in wool (continued)

Name of amino acid	Structure	Mol % (from two sources)		Nature of side chain
Lysine		3.1	2.8	Basic
Methionine		0.5	0.4	Sulphur containing
Cystine		10.5	10.0	Sulphur containing
Tryptophan			-	Heterocyclic
Proline		5.9	7.2	Heterocyclic

Growth of a protein chain requires the amino group of one acid to react with the carboxylic acid group of the next. In the reaction one molecule of water is lost and an amide linkage is formed (Figure 2.7 (a)). This process is repeated at each end of the new molecule, and thus the molecule steadily grows in length (Figure 2.7 (b)).

One particular amino acid has a significant influence on wool during wet processing. This is cystine, which has two atoms of sulphur in its molecule. The two sulphur atoms bridge the two halves of the molecule, each of which contains one acid group and one amino group. Because of its structure cystine can become incorporated into more than one wool molecule, forming a disulphide bridge between them. The formula of cystine and a diagrammatic representation of the way in which it bridges (crosslinks) two wool molecules

are shown in (Figure 2.8). The disulphide bridge is susceptible to hot wet conditions and alkaline solutions, both of which split the crosslink; other reagents can have the same effect. If the reactions are not controlled the properties of the fiber are harmed.

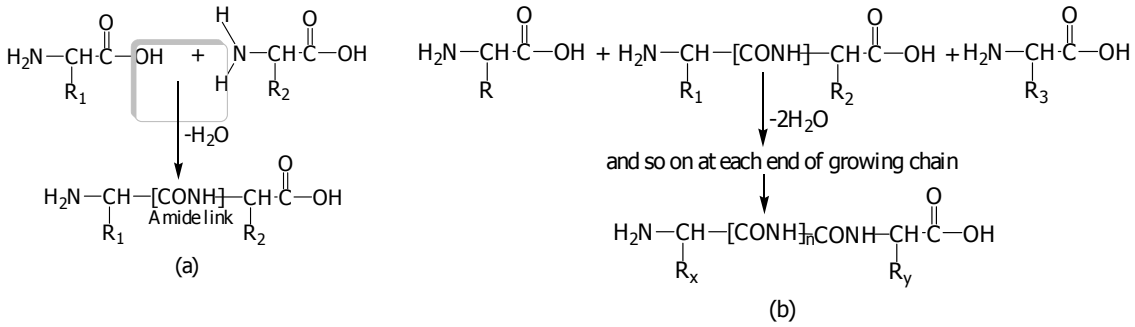


Figure 2.7 Schematic representations of the amino acids to condense into a long molecular chain

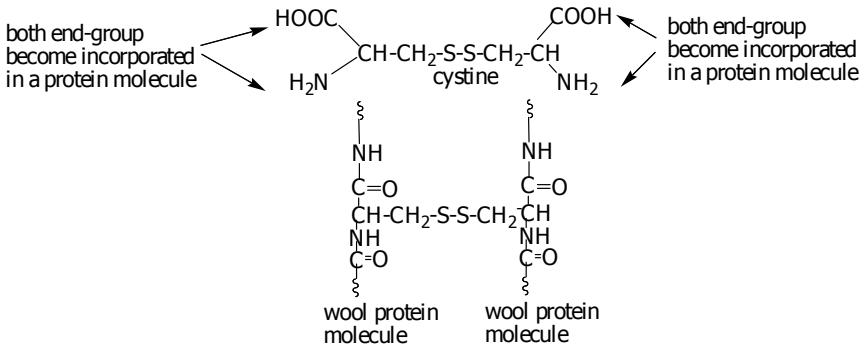


Figure 2.8 The origin of disulphide crosslinks in wool molecule

All the side-groups of the constituent amino acids are found along the length of the wool protein molecule. Since these include both acidic and basic groups, wool is able to absorb and combine with acids through the basic groups and alkalis through the acid groups. Molecules with this ability are termed amphoteric. The acid and basic groups of adjacent chains also react with each other to form salt linkages, and their role in the dyeing of wool with acid dyes. At high pH values (alkaline solutions) the acidic groups ionise to form negative ions, leaving the wool with a net negative charge (Figure 2.9 (a)). At low pH values (acidic solutions) the situation is reversed, the basic groups reacting with hydrogen ions in the solution to form positive ions and the wool is left with a net positive charge Figure 2.9

(b). It follows that there must be a pH at which the numbers of negative and positive charges are equal. This pH is called the isoelectric point of the protein Figure 2.9 (c).

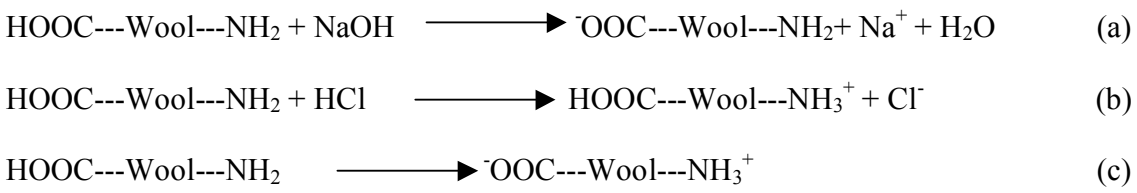


Figure 2.9 Isoelectric state of wool fiber (a) upper isoelectric point; pH>9 (b) below isoelectric point; pH<5 and (c) isoelectric point; pH ≈5.5

2.3.1.2 Silk fiber

Silk is a natural protein fiber excreted by the moth larva *Bombyx mori* [18-19]. The silk fiber is almost a pure protein fiber composed of two types of proteins, namely, fibroin and sericin. It also contains small quantities of carbohydrate, wax and inorganic components which also play a significant role as structural elements during the formation of silk fibers.

Silk is one of the strongest fibers, only slightly less strong than steel wires, but at the same time also one of the lightest (2000 m of silk thread unwound from a cocoon weigh about 0.250 g) [20]. Silk is a tough fiber with tenacity in the range of 3.0 to 4.5 grams per denier. At the same time it is very elastic fiber with an elongation value of 18-22%. It is very hygroscopic and absorbs about 11% moisture under standard atmospheric conditions of 65% RH and 27°C. As well as this, its unique thermal properties make silk a fabric suitable for wear in all seasons. It is used for making winter jackets, comforters and sleeping bags because it wraps the body in a layer of warm air that acts as an insulator against radiation of heat from the body to the cold surroundings. During summer, its hygroscopic nature makes it a cool body cover [20].

The actual fiber protein in silk is called fibroin and the protein sericin is the gummy substance that holds the filament together. Raw silk has an average composition of 70-75% fibroin ($C_{15}H_{23}N_5O_8$), 20-25% sericin, 2-3% waxy material and 1-1.7% mineral matter [14]. Sericin is amorphous and can be selectively removed by dissolution in hot soap solution. Both fibroin and sericin are protein substances built up from 16-18 amino acids out of which

glycine, alanine, serine and tyrosine make up the largest part of the silk fiber, and the remaining amino acids containing bulky side groups are not significant [14]. The composition of fibroin and sericin with respect to the four main amino acids is shown in Table 2.7; the side groups R refer to the general structure in Figure 2.6.

Table 2.7 Amino acid composition of sericin and fibroin

Amino acids	Side groups R	Sericin (% mol)	Fibroin (% mol)
Glycine	H −	14.75	45.21
Alanine	CH_3 −	4.72	29.16
Serine	$HOCH_2$ −	34.71	11.26
Tyrosine	*p*-$OHPhCH_2$ −	3.35	5.14

The structures of *Bombyx mori* silk fibroin has been studied by using solid state ^{13}C- and ^{15}N-NMR spectroscopies [14, 21]. This work indicated that the main amino acid sequence of silk fibroin is Gly−Ala−Gly−Ala−Gly−Ser where Gly, Ala and Ser denote glycine, alanine and serine respectively [21]. In addition, the X-ray crystal structure of silk fibroin has been reexamined by using newly collected intensity data. It was found that the crystalline region of silk is composed of rather irregular stacks of the antipolar-antiparallel beta sheets with varying orientations. The crystal structure of the polypeptide chains in silk fibroin is shown in Figure 2.10.

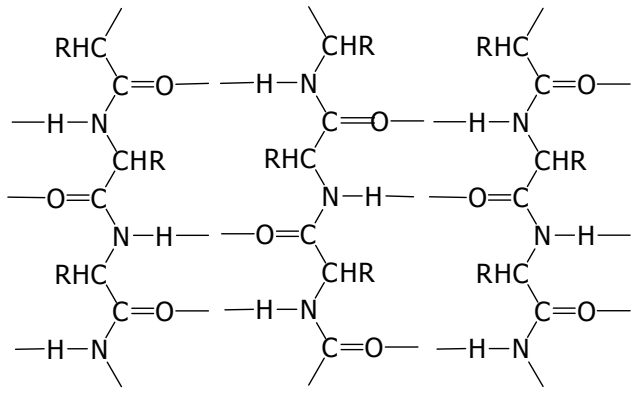


Figure 2.10 Crystalline structure of polypeptide chains in fibroin

2.3.2 Cellulosic fibers

Cellulose fibers are natural fibers derived from plant sources. The most important cellulosic fibers are cotton, viscose, linen, jute, hemp and flax. Cotton accounts for half of the world's consumption of fibers [22]. The principal component of cotton fibers is cellulose (88-96%), a high molar mass, linear polymeric sugar or polysaccharide. The polymer is formed [12] from molecules of the monosaccharide, β-D-glucose, linked through carbon atoms in the 1- and 4-positions. Cotton may be described chemically as poly (1,4-β-D-anhydroglucopyranose) [14] (Figure 2.11). Large dye molecules can penetrated easily into the fiber because cellulose has a fairly open structure [23]. There are three hydroxy groups in each glucose unit of the cellulose structure, two of which are secondary and one primary, and these give the cellulose molecule a considerable degree of polar character [23].

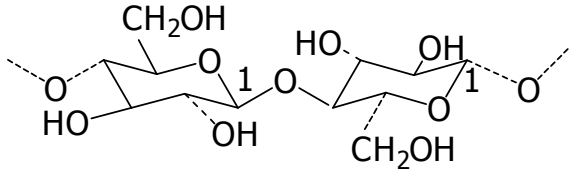


Figure 2.11 Molecular structure and configuration of cellulose

2.4 Natural dyes for fibers

Natural dyes were the main source of textile colourants until the mid- to late-19th century. From the application point of view these dyes are classified as: (i) direct dyes, (ii) vat dyes, or (iii) mordant dyes [9].

2.4.1 Direct dyes

For direct dyes no pretreatment is required either to the dyestuff or to the fabric. These dyes form hydrogen bonds with the hydroxyl groups of appropriate fibers, and an example of such a dye is curcumin (from tumeric) which is a yellow dyestuff.

2.4.2 Vat dyes

Vat dyes are used mainly on cellulosic fibers, but some can be applied to protein fibers [24]. They are usually classified into three groups such as indigoid, anthraquinone, and fused ring polycyclic dyes.

2.4.3 Mordant dyes

The word mordant is from the Latin word *mordere*, which means to "bite" or "fasten". The main reason for using a mordant in dyeing is to make the dyestuff stick to the fiber, which it does through various mechanisms. The most commonly used mordant dyes have hydroxyl and carboxyl groups and are negatively charged, i.e. anionic. A mordant dye forms a lake with a metal; there is a strong colour change. The incorporation of metals which have low energy atoms into the delocalized electron system of the dye causes a bathochromic shift in the absorption. Since different metal atoms have differing energy levels, the colour of the lakes may also differ.

A second reason for using a mordant is that the mordant can affect the colour of the dyestuff that is used. It can deepen and intensify the colour, or it can lighten it, or it can completely change the colour. Thirdly, use of a mordant can positively influence the fastness of the dye [3, 8]. The basic principle of mordanting (with metal ions) is the formation of metal ion bonds with the electron donating chromophores of dyes. For this bond formation a range of ligand groups are important, including ortho dihydroxy, 3-hydroxy-4-keto-,4-keto-5-hydroxy-, carboxyl group or sulfonyl groups.

Mordants are of two types: (i) Natural or organic and (ii) Inorganic [9].

(i) Natural mordants consist of tannic acid, ellagic acid, tannins and sulfated and sulfonated oil obtained from vegetable oil.

(ii) Inorganic mordants include alum or potash alum $Al_2K_2(SO_4)_4$, ammonia alum $(Al_2NH_4)_2(SO_4)_4 \cdot 24H_2O$, soda alum $Al_2(Na_2((SO_4)_4 \cdot 24H_2O)$, chrome alum $Cr_2(SO_4)_4 \cdot 24H_2O$, ferric alum $Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$, potassium dichromate $K_2Cr_2O_7$, ferrous sulfate $FeSO_4 \cdot 7H_2O$, Cupric sulfate $CuSO_4 \cdot 5H_2O$, stannous chloride and stannic chloride.

2.5 Synthetic dyes for protein fibers

Classification of dyes by application method is most useful to the technologist concerned with colouration of textile products. There are eight major classes according to the method of application. Protein fibers may be dyed using a number of application classes of dyes, the most important of which are acid, mordant, premetallised and reactive dyes.

2.5.1 Acid dyes

Acid dyes contain acidic groups in their structure; these are usually sulfonate ($-SO_3$) groups, either as $-SO_3Na$ or $-SO_3H$ groups, although -COOH groups can sometimes be incorporated [17]. The most common structural types of acid dyes are monoazo and anthraquinone dyes. They have been used to dye protein fibers such as wool and silk. Wool, silk and other protein-based natural fibers have basic amino groups that can interact with acid dyes. The protein molecules carry a positive charge which attracts the acid dye anion by ionic forces. Van der Waal's forces, dipolar forces and hydrogen bonding between appropriate functional groups of the dye and fiber molecules may also play a part in the acid-dyeing of protein fibers [12, 24].

The most common structural types of acid dyes are anthraquinone and monazo dyes as shown in Figures 2.12 (a) and (b), respectively [24].

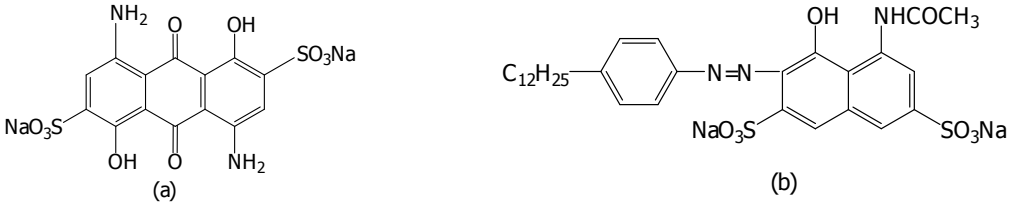


Figure 2.12 Examples of acid dyes; (a) C.I. Acid Blue 45 and (b) C.I. Acid Red 138

2.5.2 Mordant dyes

Mordant dyes generally have the characteristics of acid dyes but with the additional ability to form stable complexes with chromium (III) ions. Most commonly, this takes the form of two hydroxyl (-OH) groups on either side of (*ortho* to) the azo group of a monoazo dye as shown in Figure 2.13. The dye is generally applied to the fiber as an acid dye and then treated with a source of chromium. As a result, a chromium complex of the dye is

formed within the fiber as shown in Figure 2.14. The chromium atom in complexes of this type always bonds to six atoms and the complexes show octahedral geometry. It is not established with certainty how the remaining three valencies of chromium are satisfied in the mordant dyeing of protein fibers, although the possibilities include bonding with water molecules, or coordinating groups on the fiber or with a second dye molecule.

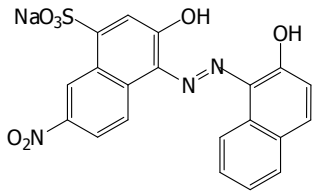


Figure 2.13 Mordant dye (C.I. Mordant Black 1)

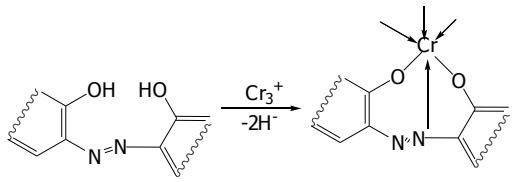


Figure 2.14 The chrome mordanting process

2.5.3 Premetallised dyes

Premetallised dyes are pre-formed metal complex dyes. They are usually six coordinate complexes of chromium with octahedral geometry as exhibited in Figure 2.15. They are applied to protein fibers as acid dyes and, because of the special stability of chromium complexes, provide dyeing with excellent light fastness.

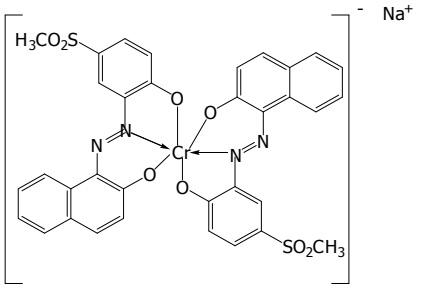


Figure 2.15 Premetallised dye (C.I. Acid Violet 78).

2.6 Natural organic dyes from eucalyptus

Eucalyptus is members of evergreen hardwood genus endemic in an Australasian region. There are approximately nine hundred species and sub-species. Eucalyptus has been successfully grown in many parts of the world including southern Europe, Asia and the west coast of the United States [25].

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% [26]. 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 [27]. 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 [28-30]. (The structures of the colouring components found in eucalyptus leaves are given in Figure 2.16. 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 yellowish-brown colour. An exception is that when the fabric is dyed with ferrous mordant, the fabric shade becomes which 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 [31-32].

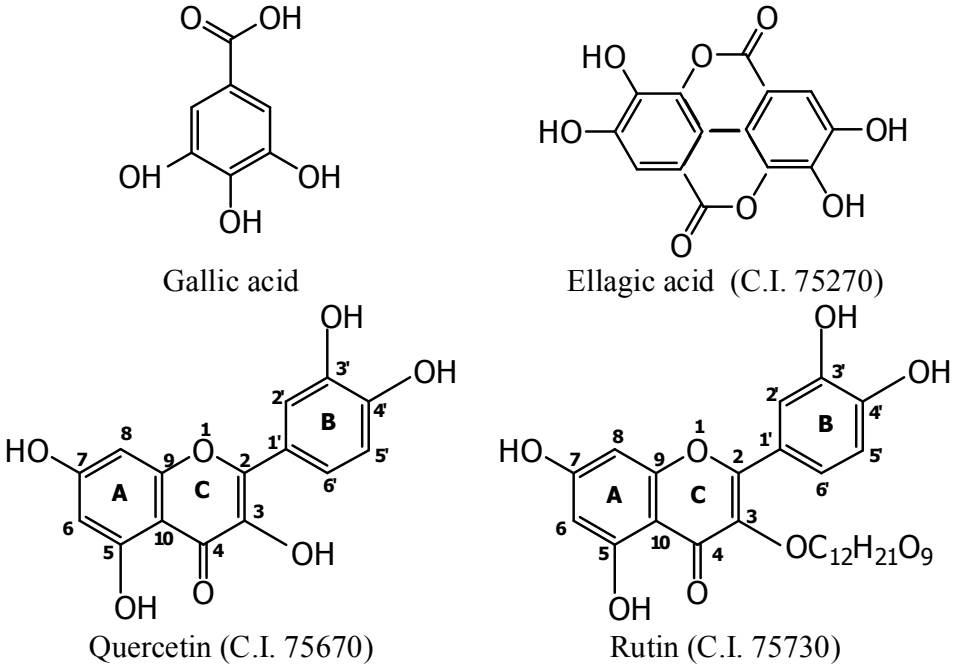


Figure 2.16 Colour composition of eucalyptus leaf extract dye

2.7 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:

2.7.1 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.

2.7.2 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, 33-34].

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 [34].

2.7.3 Mordanting

In the actual dyeing process, there are four ways of using mordant [3, 8] 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.

2.8 Theoretical presuppositions of natural dyes to dyeing

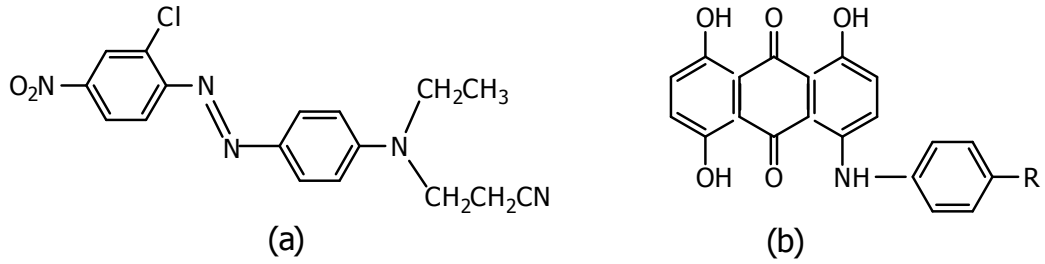
Achieving a good, or at least a relatively good, water solubility using natural dyes is rather exceptional. No chemical group is capable of electrolytic dissociation or ionization in a molecule; an interesting and important exception is the *anthocyanins*, for example, pelargonidine, cyanidine, and betanidine 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 2.16) is compared with the typical azo and anthraquinone disperse dye (Figure 2.17).



C.I. Disperse Red 50

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

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

Figure 2.17 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.

2.9 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) [35].

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.

CHAPTER III
LITERATURE REVIEW

3.1 Application of natural dyes on textiles

3.1.1 Characterization and chemical/ biochemical analysis of natural dyes

3.1.1.1 Macro- and micro- chemical analysis

Gilbert and Cooke [36], NIIR Board Consultants & Engineering [37] and Vankar [4, 10] have reviewed the chemistry, chemical composition and chemical based classification of natural dyes having indigoids (indigo and tyrian purple), anthraquinone (madder), alpha hydroxyl naphthoquinone (*Lawsonia inermis;* henna or lawsone), flavonids (*Reseda luteola*; weld), anthocyanins (*Bigonia china*; carajurin), carotenoids (annatto, saffron), etc. which give a basic understanding of chemical nature of such colourants. Indigoid dyes are perhaps the oldest natural dyes used by man. It is product from indole glucoside precursors. The indigo precursor, indoxyl, mainly in the form of the glucoside, indicant (indoxyl-β-D-glucoside), is found in the plant *Indigofera tinctoria*. The main dyeing component of this plant is indigo. Madder dyes are hydroxyl-anthraquinone which are extracted from the root bark of various *Rubiaceae*, e.g. from madder root (*Rubia tinctorum*). The root contains approximately 1.9% of dye, present in the free form or bound as the glucoside. Anatto pulp is rich tannin but contains mixture of eight colourants carotenoid group such as nor-bixin and bixin. Tyrian purple is derived from the Mediterranean shell fish of the general Purpura and Murex. Henna contains high proportion of coloured species other than Lawsone, as is evident from HPLC analysis of its aqueous extract, i.e. 0.57% Lawsone. It is non-ionic moiety and is expected to bind with polyester through interaction, such as hydrogen bonding in addition to van der Waals forces or even dipole-dipole interactions of the Lawsone molecule with polyester fiber molecules [2]. The flavonoids from the large group of aromatic chemicals, although not all of them are useful of dyes. The principle flavonoids colouring matter is luteolin. This produces the most vibrant and light fast dye. However, several other flavonoids from different plant sources were in common use, e.g., epigenin, quercetin, emodin, berberine, rutin and tannin.

3.1.1.2 UV-visible spectroscopic study

UV-visible of any dye shows its peaks at predominating wavelength, indicating main hue. For natural dyes, the spectra specially indicate different peaks for mixed colourants available in their extract in both UV and visible region. UV-visible spectroscopic studies of different natural dyes were carried out by Vankar [4] using different for extraction. The UV-visible spectrum of morin in aqueous solution without pH control is characterized by two major absorption bands with maxima at 378 nm and 261 nm [38]. *Eclipta alb*a shows two absorption maxima at 402 and 665 nm [39] while *Melastoma malabathricum colourant* shows three absorption bands at 235, 275 and 550 nm [33]. UV-visible spectrum of onion skin extract (*Allim cepa*) shows peak at 430 nm and 662 nm [40]. The methanolic extract from *Allium cepa* shows the following peaks: IR: 3412, 2922, 2852, 1721, 1613, 1503, 1446, 1326, 1209, 1093, 1042, 919, 758, and 574 cm^{-1}. *Scfe shikonin* shows absorption bands at λ_{max} 207, 216, 274, 521 and 559 nm [41]. The peak at 274 nm is due to the quinonoid absorption. The UV-visible spectrum of beetroot dye extract shows two absorption peaks corresponding to betaxanthin (480 nm) and betanin (530 nm) [42]. The spectra of apigenin in water/ methanol (2/1 v/v) at neutral form show maximum absorption at 265 and 337 nm, but under acid condition there is shift towards 372 nm [43]. However, under alkaline is observed at 392 nm. *Mahonia naupalensis* shows a characteristic visible spectrum from which a λ_{max} of 410 nm [44]. UV-vis spectrum of *Symplocos spicata* shows five coloured fractions [45]. Each of colour fraction was isolated from leaves of *Symplocos spicata* which showed characteristic visible spectrum. Extraction, spectroscopic and colouring potential studies of the dye in ginger rhizome (*Zingiber officinale*) were studied and reported by Popoola et al. [46]. This dye is soluble in hydroxyl based organic solvents and gives one homogenous component of 0.86 R_f value on chromatographic separation, having wavelength of maximum absorption at 420 nm.

3.1.1.3 Chromatographic analysis

Thin layer chromatography (TLC) was used by many works to identify different colour components in natural dyes to be applied on textiles [47]. Dyes detected were insect dyes and vegetable dyes, viz. yellow, red and blue colours. TLC has also been employed for the analysis of flavonoids in various plant extracts. Flavones, flavone glycosides and biflavones were extracte from *Phillyred latifolia* L. leaves and separated on

silica, octadecylsilica (C_{18}) and cellulose layers, using various mobile phases [48]. Koren also analyzed the natural scale insect, madder and indigoid dyes by high performance liquid chromatography (HPLC) [49]. Guinot et al. [50] used the TLC preliminary evaluation of plants containing flavonoids (flavonols, flavones, flavanones, chalcones, aurones, anthocyanins, hydroxycinnamic acids, tannins and anthraquinones) colour compounds found in the plants. HPLC has also been used to evaluate the purity of commercially available colourants deriving from natural plant pigments [51].

Identification of dyes used in historic textiles through chromatographic and spectrophotometric methods as well as by sensitive colour reaction has been reported by Blanc et al. [52]. Szostek et al. [53] studied the retention of carminic acid, indigotin, corcetin, gambogic acid, alizarin, flavonoids, anthraquinone and purpurin. A non-destructive method was reported for identifying faded dyes on fabrics through examination of their emission and absorption spectra. Balakina et al. [54] analyzed quantitatively and qualitatively the red dyes, such as alizarin, purpurin, carminic acid, etc. by HPLC. Study of historical Scottish textiles excavated from peat bogs was reported by high performance liquid chromatography with photodiode array detection (PDA HPLC) [55]. Dye components of historical Scottish textiles were identified in 36 of the 81 samples analyzed. Cristea et al. [56] reported the quantitative analysis of weld (*Reseda luteola* L.) by HPLC and found that after 15 min extraction in a methanol/water mixture, 0.448% luteolin, 0.357 % luteolin-7-glucoside and 0.233% luteolin-3', 7-diglucoside were obtained. This technique has been used by several workers to identify different components of synthetic as well as natural dyes.

Lee et al. [57] analyzed the various dye components, textiles dyed with plant extracts, and ancient Korean textile samples by the static time-of-flight secondary ion mass spectrometry (TOF-SIMS). The plant dyes investigated belong to a variety of chemical groups, which include curcumin, crocin, carthamin, purpurin, alizarin, brazilin, shikonin, and indigo. TOF-SIMS spectra for the dyed textiles show element ions from metallic mordants, specific fragment ions, and molecular ions from organic dyes. The ancient Korean textile sample shows the present of indigo. Puchalska et al. [58] carried out the separation and identification of anthraquinone colouring matter in natural red dyes from cochineal, lac-dye and madder by electrospray mass spectrometry coupled to capillary electrophoresis. The

method developed made it possible to identify unequivocally carminic acid and laccaic acids A, B and E as colouring matters in the cochineal and lac-dye, respectively. In madder, alizarin and purpurin were found.

In general, it has been observed from the literature that identification of natural dyes in textiles involves selective extraction of dyes and comparison of each dye by various characterization techniques, viz. UV-visible and IR spectroscopy, TLC and HPLC including methods of identification of vegetable dyes on cellulose fibers, animal fibers and man-made fibers.

The above reports are however exclusive but not exhaustive and many further analyses of colour components of natural dyes are possible by other modern techniques, like Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), Atomic Absorption Spectrometry (AAS), Differential scanning calorimetry (DSC), Thermogravimetric Analysis (TGA) and elemental analysis of natural dyes/ colourants to study the chemical functional nature, presence of different elements for understanding the chemistry of natural dye component well [2].

Recently, Nadiger et al. [59] have studied UV-vis apectra, FTIR and AAS of six selective natural dyes (Anar extract, Thar, Catechu extract, Kango, Basant and Amber) and found that the natural dyes show absorption bands 200-300 nm region. The FTIR study shows the types of chemical functionality and bonds present in the main colour components of each of the individual purified dyes. AAS analysis shows the quantitative of heavy metal in natural dyes and found that the amount of heavy metals content of dyes (Cu, Zn, Cd, Ni, Co, and As) have exceeded standard.

3.1.2 Extraction and purification of colourants from natural dyes

The extraction efficiency of colourant components present in natural plant, animal and mineral sources depends on the media type (aqueous, organic solvent, acid and alkaline), pH of the media and conditions of extraction, such as temperature, time, material-to-liquor ratio and particle size of the substrate [2].

Ali et al. [26] extracted colourant from the dead eucalyptus bark by using aqueous medium under varying condition. The colour strength obtained at room temperature was minimum, slightly getting better at 60 °C and maximum when the extractions were carried

out at boiling temperature. Sarkar and Seal [60] obtained the dye extraction from cochineal, red sandalwood, osage orange and madder root by using deionized water at the medium. Chan et al. [61] studied the optimum extraction condition for Lung Ching tea dye. The results show that water was a good solvent to extract tea dye and the optimum extraction condition was 100°C at 90 min. Dyeing of wool fabric with tea dye can be carried out at room temperature but the affinity on fabric was relative low. Umbreen et al. [62] also studied the extraction of turmeric rhizomes under 25 extraction conditions and applied for cotton fabric dyeing. The colour strength of dye extracts obtained at boiling temperature. Samanta et al. [63] dyed the bleached jute fabric with single and binary mixtures of aqueous extracts of red sandalwood with aqueous extract of other natural dyes like manjistha, jackfruit wood, marigold, sappan wood and babool. Vankar et al. [64] extracted colour component from *Acer pectinatum* Wallich under various extraction conditions and applied for cotton fabric dyeing by sonicator technique. Aqueous extract prepared from dried *Acer* petioles was used for the optimization.

Bairagi and Gulrajani [65] utilized the supercritical carbon dioxide to extract shikonin (di-hydroxy 1,4-napthaquinone) from ratanjot (*Onosma echioides*) and used to study the kinetics of dyeing on polyester fabric. The extraction of natural dye from beetroot using ultrasound has been studied and compared with static/magnetic stirring as control process at 45°C, as reported by Sivakumar et al. [42]. It has been found that a mixture of 1:1 ethanol-water with 80 W ultrasonic power for 3 hours contact time provide better yield and extraction efficiency. The use of ultrasound is found to have significant improvement in the extraction efficiency of colourant obtained from beetroot. Xinsheng et al. [66] studied ultrasonic extraction of colouring matter from *Sargentodoxa cuneata* and applied of colouring matter on wool fabric dyeing. Kamel et al. [67] studied extraction lac by ultrasonic technique in 100 ml distilled water using varying amounts of the dye material (2-12%) at different temperatures (50-80°C) using different sonic powers (100-500 W) and for different time intervals (20-120 min, followed filtration and application on wool fabric dyeing . Fruit pulp of *Melastoma malabathricum* was extracted in sonicator and applied on cotton fabric dyeing, as studied and reported by Vankar and Tiwari [40].

Paniwnyk et al. [68] extracted rutin from *Sophora japonica* under methanol by using ultrasound with 20 kHz ultrasonic probe at 23°C for varying time lengths of time. The

application of ultrasound to the methanolic extraction of rutin from *Sophora japonica* gave a significant increase in maximum extraction yield. Sumanta and Agarwal [69] studied the extraction of the dye from jackfruit wood under various pH condition and reported that the optimum conditions for extraction of colour component from jackfruit is achieved at pH 11, given absorbance of colour component at 2.77, λ_{268} nm. Ali al et. [70] extracted henna leaves under alkaline pH using sodium hydroxide. It was observed that the alkaline conditions for extraction of natural dye from henna leaves were optimized and the resulting extract was used to further optimize its dyeing condition on cotton by exhaustion method.

3.1.3 Different mordants and mordanting methods

Mordanting is the treatment of textile fabric with metallic salts or other complex forming agents which bind the natural mordantable dyes onto the textile fibers. Mordanting can be achieved by either pre-mordanting, simultaneously mordanting or post-mordanting [2]. Different types and selective mordants or their combination can be applied on the textile fabrics to obtain varying colour or shade, to increase the dye uptake and improve the colour fastness behaviour of any natural dye [2]. Extensive work has been reported [71-84] in this area study.

Ali et al. [70] studies the effect of pre-mordanting and post-mordanting with aluminium sulfate, ferrous sulfate under different and reported that pre-mordanting and post-mordanting with ferrous sulfate, there was huge change in hue and a great deal of decrease in the chroma or purity of colour. Also, alum and iron did not result in any appreciable increase in fastness properties [70]. Wool and silk fabrics have been dyed with colourant extracted from *Rheum emodi* in the absence and presence of magnesium sulfate, aluminium sulfate and ferrous sulfate mordants for producing shades of different colours, ranging from yellow to olive green as reported by Bhattacharya et al. [85]. Bhattacharya et al. [86] reported the methods of dyeing silk with some natural colourants derived from arjun bark (*Terminilia-Arjuna*), babul bark (*Acacia arabica*) and pomegranate rind (*Punica granatum*) and also mordanted with various mordants viz. tannic acid, copper sulfate, stannous chloride, ferrous sulfate and aluminium sulfate by using different mordanting techniques (pre, post and meta mordanting). It was found that dyed samples were compared to the un-mordanted dyed samples which indicate that mordanting improves colour strength,

brightness as well as fastness properties of the dyed silk fabric. Shin and Cho [87-88] studied the wool and cotton fabrics treated with different mordant types and also various mordanting techniques were used to dye with American fleabane colourant. It was found that the dye affinity of cotton fiber lower than wool and the *K/S* value of pre-mordanting was higher than simultaneous mordanting or post-mordanting. Ameican fleabane produced mainly yellowish colour on mordants and mordanting method. Pruthi et al. [89] optimized the dyeing of silk with barberry bark dye (*Berberis aristata* Dc.) using mordant combination and found that the dyed samples possess very good to excellent fastness. Chairat et al. [90] extracted colour dye component from the dried fruit hulls of mangosteen (*Garcinia mangostana* Linn) was used for dyeing of cotton and silk yarn. The results showed that the dyeing of cotton using the post-mordanting method with ferrous sulfate and calcium hydroxide not only provided better depth of shade but also provided better wash fastness and light fastness than with mordants (alum; zinc tetrafluoroborate) or without a mordant. Deo and Desai [91] reported the dyeing of cotton and jute with an aqueous extract of tea and shows that dyeing was carried out with and without metal salts as mordants, using three different dyeing methods: pre-mordanting, meta-mordanting and post-mordanting. The resulting wash and light fastness of the dyed fabrics were good to excellent. The exhaust dyeing process of wool yarn, cotton fabric and polyamide 6, 6 with immediate use of the ash-tree bark (*Fraxinus excelsior* L.) extract as a dyebath and direct addition of $FeSO_4.7H_2O$ stock solution as a meta-mordant process showed good shade reproducibility and satisfying levelness of the dyed material as reported by Bechtold et al. [92]. Vankar and Shanker [93] studied dyeing of silk fabric with flower of *Delonix regia* extract and using a biomordant and enzyme. A bright reddish brown hue colour was observed when 30% owf *Delonix* extract was used on the pretreated silk material and also found that dyed fabric showed resistance to fading when mordanting with an enzyme or biomordant. Osman et al. [94] evaluated the effect of levelness by using different variables, including: three different natural fabrics; namely, wool, silk and cotton dyed with yellow natural dye from onion skins under the effect of different mordants, and also three different natural dyes; namely, onion skins, turmeric and madder applied on wool fabric samples under the effect of different mordants. The results show that dyed samples with the highest colour strength (*K/S*) have the highest unlevelness and the lowest colour difference values (i.e. the highest light

fastness). Hou et al. [95] studied dyeing and mordanting methods properties to wool fabrics of catechu dye purified by micro-filtration membrane. The results show that the liquor of catechu dye is stable at pH values of 3-7 and its colour changes to a deeper brown-red when its pH value is above 8. The dyed wool fabric has good colour fastness to washing, alkaline perspiration and dry rubbing. Shanker and Vankar [96] reported the use of aqueous extract of Gulzuba flower (*Hibiscus mutabilis*) with metallic salts yield shades with good fastness properties for cotton, wool and silk dyed fabric. Cotton and silk fabrics were dyed with *Cassia tora L.* extract at 90°C for 60 min with pre-mordant of various metal salts as mordants as studied by Lee and Kim [97]. It was found that the *K/S* of cotton fabrics increased in the order of the dyeing using $FeSO_4 > CuSO_4 > ZnSO_4 > MnSO_4 \approx Al_2(SO_4)_3 > NiSO_4 >$ none, however, the *K/S* of silk fabrics increased in the order of the dyeing using $FeSO_4 > CuSO_4 > ZnSO_4 \approx Al_2(SO_4)_3 > MnSO_4 \approx NiSO_4 >$ none. Mordants $FeSO_4$ and $CuSO_4$ for cotton fabric, $FeSO_4$ and $CuSO_4$ and $Al_2(SO_4)_3$ for silk fabric were found to give good light fastness. El-Shishtawy et al. [98] studied dyeing of modified acrylic fibers with curcumin and madder natural dyes by using absence and presence alum and ferrous sulfate as mordant. It can be seen that acrylic samples dyed with madder in the absence and presence mordant show the beige to brownish shade. However, lemon yellow to brownish-yellow was found in acrylic dyed with curcumin. Cotton and silk fabrics dyed with African marigold flower (*Tagetes Ereecta* L.) extract by using iron and copper sulfate as a mordant have a good light fastness and also good to excellent wash fastness as studied by Jothi [99]. Lokhande and Dorugade [100] also studied and reported the effect of nylon fabric was dyed with three natural dyes derived from onion (*Allium cepa*), lac (*Laccifer Lacca*) and turmeric (*Curcuma longa*) using various mordants by two different techniques. (viz. open bath and high temperature high pressure (HTHP) dyeing methods). HTHP dyeing has been found to give better results as compared to the open bath dyeing. Good wash fastness was obtained with all three natural dyes.

3.1.4 Ultrasonic method of natural dyeing

Customer's demand for ecofriendly textile and ecofriendly dyes led to the revival of natural dyes for textiles, with the newer energy efficient dyeing process and more reproducible shade developing process [2]. Vankar et al. [101] studied and reported

ecofriendly sonicator dyeing of cotton with *Rubia cordifolia* Linn. using biomordant. Use of biomordant replaces metal mordants, thus making natural dyeing more ecofriendly. Vankar et al. [39] also studied conventional and ultrasonic methods of dyeing cotton fabric with aqueous extract of *Eclip alba*. The effects of dyeing show higher colour strength values obtained by the latter. Kamel et al. [67, 102] dyed wool and cationised cotton with lac as a natural dye using both conventional and ultrasonic techniques. Ultrasonic provide effectiveness in dye-uptake of cationised cotton and wool fabrics with lac dye, and enhanced effect after was about 66.5% for cationised cotton and 41-47% for wool. Ecofriendly ultrasonic textile dyeing with natural dyes such as *Acacia catechu* and *Tectona grandis* show better and faster dye uptake after enzyme pretreatment on cotton fabric, and results of dyeing are better than metal mordanted fabric, as reported by Vankar and Shanker [103]. Vankar and Tiwari [33] studied the sonicator and conventional dyeing of cotton fabric from *Melastoma malabathricum* and found that the percentage dye uptake of sonicator dyeing technique shows higher than the conventional dyeing. Vankar et al. [44, 45] also studied sonicator dyeing of cotton, wool and silk with *Mahonia napaulensis DC* and *Symplocos spicata*. Vankar et al. [64] reported the sonicator dyeing of cotton with the leaves extract *Acer pectinatum* Wallich and the results show that the net enhancement of dye uptake due to metal mordanting and sonication has been found to range from 25% to 60% in the case of cotton compared to the controlled samples at 19-55%. Sivakumar et al. [42] also reported ultrasound energy dyeing of leather with beetroot for industrial and also found to be beneficial in natural dyeing of leather with improved rate of exhaustion. The ultrasonic technique has been used to dyeing on wool fabric with *Sargentodoxa cuneata* as natural dye, as studied by Xinsheng et al. [66].

3.1.5 Physico-chemical studies on dyeing process variables and dyeing kinetics

It is felt essential to develop a knowledge base on dye chemistry and effects of dyeing process variables as well as rate of dyeing and chemical kinetics of dyeing for different natural dyes and fibers combinations to manipulate the processes of natural dyeing efficiently in order to get maximum colour yield in economical way [2].

Das et al. [104] studied the diffusion coefficient, rate of dyeing and effect of variation in salt and pH of wool and silk with annato (*Bixa orellana*). Wool dyed at 90°C

appears to have more time of half dyeing (t ½) than silk dyed at the same temperature, thereby indicating that the wool has lower rate of dyeing as compared to silk. The diffusion coefficient of annato on silk higher than on wool. The exhaustion of annato to wool and silk is found to be maximum at dye bath pH ~ 4.5. The exhaustion of the dye increases with the increase in dye bath pH. For pre- and post- salt application, the ability of the salt to incorporate colouring component present in annato in the structure of wool and silk fiber follow a common trend: ferrous sulfate > aluminium sulfate > magnesium sulfate, as dividend from the *K/S* values of the respective dyes substrate. Samanta et al. [105] has studied the dyeing adsorption isotherm, heat of dyeing, free energy and entropy of dyeing for jackfruit wood. Study with jackfruit wood revealed that this dyeing process follows a Nernst adsorption isotherm, except jute-$FeSO_4$-jackfruit combination of natural dyeing, where it follows Langmuir adsorption isotherm. Farizadeh et al. [106] reported the extraction, identification and sorption of dyes from madder on wool fabric. The results show that adsorption dependent on the pH and temperature, and the adsorption isotherm of madder on wool is a Langmuir type. The adsorption of madder on wool is an exothermic process. Gupta and Gulrajani [107] studied and reported the kinetics and thermodynamics of dyeing with lawsone (2-hydroxy-1, 4-naphthoquinone) on wool, hair, silk, tussah, nylon and polyester fibers. Diffusion coefficient of silk and nylon showed the highest rate of dyeing followed by wool, tussah and hair fibers. Polyester dyed at 130°C had the slowest rate of dye uptake. The linear isotherm of dyeing for all fibers conformed to the partition mechanism of dyeing corresponding to the solid-solution model observed in dyeing hydrophobic fibers with disperse dyes. The standard affinity for all fibers increased with increase in temperature. Kongkachuichay et al. [108] studied thermodynamics of adsorption of laccaic acid on silk. The adsorption isotherm obtained was identified to be Langmuir type. When the temperature increased, the partition ratio and standard affinity decreased drastically. The values of heat of dyeing and entropy of dyeing were -13 kcal/mol and -0.03 kcal/mol/K, respectively. Chairat et al. [109] also studied an adsorption and kinetic of lac dyeing on silk and found that the experimental data fitted well to the Langmuir and Freundrich isotherms with a high correlation coefficient (R^2). The pseudo second-order kinetic model was indicated with the activation energy of 47.5 kJ/mol. The values of the enthalpy (ΔH) and entropy of activation (ΔS) were 44.7 kJ/mol and -175.7 J/mol K,

respectively. The free energy of activation (ΔG) at 30°C was 97.9 kJ/mol. Chairat et al. [110] reported adsorption and kinetic of lac dyeing on cotton under dyeing conditions of pH 3.0, liquor ration 1:100 and an initial dye concentration 480 ± 10 mg/L. It was found that the adsorption kinetics of lac dyeing on cotton with pH control was found to follow the pseudo second-order kinetic model with an activation energy of 42.4 kJ/mol. Dyeing properties of silk fabric with berberine in terms of the thermodynamic and kinetic factors, including standard affinity, enthalpy change, entropy change, dyeing rate, diffusion coefficient and activation energy of diffusion, as reported by Ke et al. [111]. The results show that the adsorption isotherm of berberine on silk fabric belongs to Langmuir type. The analysis of dyeing thermodynamics shows that the adsorption of berberine on silk fabric is an exothermic process. When the fabric is dyed at higher temperature, the lower affinity and less dye uptake are obtained; however, the higher temperature increases the initial dyeing rate and diffusion coefficient. Vinod et. al. [112] studied and reported the kinetic and adsorption of dyeing with natural colourant from the bark of *Macaranga peltala* for silk yarn. The adsorption studies of *Macaranga peltala* for silk yarn revealed that the process fits well with the Langmuir isotherm model. The experiment results found that the adsorption was exothermic and spontaneous in nature, and exhibited first-order kinetics. The rate of adsorption increases as the disrupting effect of the added electrolyte cation increases and follows the order: $Al^{3+} > Ca^{2+} > Na^{+}$. Aydin et al. [113] investigated of the adsorption isotherm used for wool dyeing by aqueous extraction of Cehri fruit (*Fructus Rhamni Petiolari*) and reported that the adsorption isotherm can identified to be Nernst type. Septhum et al. [114] studied an adsorption of alum-morin dyeing onto silk yarn and revealed that the pseudo second-order kinetic model was indicated for alum-morin dyeing (simultaneous mordanting) of silk at pH 4.0 with ac activation energy (E_a) of 45.26 kJ/mol. The value of the enthalpy of activation (ΔH) for alum-morin dyeing on silk at pH 4.0 was 31.29 kJ/mol. Also the free energy ($\Delta G°$) and entropy changes ($\Delta S°$) for alum-morin on silk were -17.73 kJ/mol and -45.7 kJ/mol K, respectively consistent with a spontaneous and exothermic adsorption process.

3.1.6 Ultra-violet (UV) protection property of natural dyes

From extensive literature surveying, it can be observed that there are some recent reports for application of natural dyes on UV protective textile materials. Sarkar [115] evaluated of UV protection for different structures of cotton fabrics (plain, twill and sateen weave) dyed with madder, cochineal and indigo at different conditions and reported that dyeing of cotton fabrics with natural colourants increases the ultraviolet protective abilities of the fabrics and can be considered as an effective protection against ultraviolet rays. The Ultraviolet Protection Factor (UPF) is further enhanced with colourant of dark hues and with high concentration of the colourant in the fabric. Kim [116] studied the dyeing characteristics and UV protection property of green tea dyed on cotton fabric by using chitosan mordanting condition. The results show that chitosan mordanting can effectively increase the UV protection property of both UV-A and UV-B of green tea dyed cotton fabrics. Chitosan mordanted undyed cotton and chitosan unmordanted dyed cotton did not show an increase in UV protection property. Feng et al. [117] reported the ultraviolet protective properties of the cotton and silk fabrics dyed by *Rheum and Lithospermum erythrorhizon*. Experiment results revealed that the fabrics dyed with natural dyes had good ultraviolet protective properties. They could absorb about 80% of the ultraviolet rays. Wang et al. [118] researched the dyeing and ultraviolet protection of silk fabric using vegetable dyes extracted from Flos Sophorae. It was found that the aqueous solution of this vegetable dye has excellent thermal stability in acid conditions. The optimum extraction conditions were obtained for Flos Sophorae: extraction temperature of 100°C, extraction time of 60 min, and material, and material to liquor ratio of 1:10. The UPF and T $(UVA)_{AV}$ values for the silk fabric dyed by the optimum dye solution were found to meet the Chinese Standard (UPF = 69 > 30, T $(UVA)_{AV}$ = 1.07% < 5%). According to the standard, the silk fabric can claim to be a “UV-Productive product”. Grifoni et al. [119] studied the UV protection properties of flax and hemp fabrics dyed with weld, dyer’s woad, logwood lipstick tree, madder, brasil wood, and cochineal as natural dyes. Experiment results revealed that natural dyes could confer good UV protection. Weld-dyed fabric gave the highest protection level.

3.1.7 Antibacterial and deodorizing properties of natural dyes

The use of natural products and natural dyes for antimicrobial finishing of textile materials has been widely reported. Han and Yang [120] studied the antimicrobial activity of wool fabric dyed with curcumin and found that the antimicrobial ability of curcumin finished wool is semidurable, more durable to home laundering than to light exposure. The inhibition rates against *Staphylococus aureus* (*S. aureus*) and *Escherichia coli (E. coli)* were 45% and 30% respectively, after 30 cycles of home laundering. The inhibition rate against *S. aureus* was almost 80% after 5-AFU (AATCC Fading Unit) light exposure but started to decrease substantially after 10-AFU. The *E. coli* inhibition against light was poor. After 5-AFU exposure, the fabric retained only 30% of its original antimicrobial ability. Dahl et al. [121] also studied photokilling of bacteria by the natural dye curcumin and revealed that Gram-negative bacteria displayed greater resistance to curcumin phototoxicity relative to Gram-positive bacteria. Oxygen was required for curcumin phototoxicity. The crude methanolic extracts of stem root, leaves, fruit, seeds of *Artocarpus heterophyllus* [122] and their subsequent partitioning with petrol, dichloromethane, ethyl acetone and butanol fractions exhibited a broad spectrum of antibacterial activity. The butanol fractions of the root bark and fruit were found to be the most active. None of the fraction was active against the fungi test. Mariegold [123] showed negative test against microbiological control for *E. coli* and *Salimonella*. Singh et al. [124] tested *acacia catechu*, *kerria lacca*, *quercus infectoria*, *rubia cordifora*, and *rumex maritimus* against pathogens like *E. coli*, *Bacillus subtilis*, *Klebsiella pneumoniae*, *Proteus vulgaris*, and *Pseudomonas aeruginosa*. Minimum inhibitory concentration was found to vary from 5 μg to 40 μg. Gupta et al. [125] studied antimicrobial property of eleven natural dyes (acacia, indigo, lac, kamala, pomegranate, gall nuts, cutch, myrobolan, himalayan rhubarb, Indian madder and golden dock) against three types of Gram-negative bacteria (*E. coli*, *Klebsiella pneumoniae* and *Proteus vulgaris*. Seven out of the eleven natural dyes (lac, kamala, pomegranate, gall nuts, cutch, myrobolan and himalayan rhubarb) showed activity against one or more of the three bacteria studied. Kamala, pomegranate and gall nuts were found to be efficient biocides after dyeing on cotton, particularly gall nuts. The latter was highly effective against *E. coli* and *Proteus vulgaris*, reducing the number of colonies by 99%. The dyes examined exhibited good wash fastness. Ke et al. [126] reported the colour evaluation and antibacterial property of wool

fabric dyed with root of *Rhizoma coptidis* (berberine). Results indicated that wool fabrics dyed with mordant, or at higher temperature, or in alkaline solution processed deeper shades and darker colour. And the wool fabric showed good antibacterial property after dyeing with *R. coptidis* extracts. Chen and Chang [127] studied the antimicrobial activity of cotton fabric pretreated microwave plasma and dyed with onion skin and onion pulp extraction. The best inhibition zone of anti *S. aureus* is found to be 1.1-0.8 cm by 10 min plasma-treated grafting time of onion skin extraction and 0.7-0.5 cm by 30 min plasma-treated grafting time of onion pulp extraction. The samples with 10 and 30 min plasma-treated grafting of both onion skin and onion pulp show anti *S. aureus* ability even after 5 times test washing, but both the samples lost their anti *S. aureus* property with 60 min grafting. The FTIR-ATR spectrum of dyed cotton fabric shows flavonoids function peak at 1624 cm^{-1} of onion skin that provide cotton fabric brown colour with wash fastness rating 4. Perumal et al. [128] reported the antibacterial activity of pigment from *Sclerotinia sp*. and its use in dyeing cotton. Dev et al. [129] studied the dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. The microbial reduction percentage values for chitosan treated samples against both *E. coli* and *S. aureus* show that the microbial reduction is better against both bacteria. The fabrics dyed with henna alone without chitosan application do exhibit significant antimicrobial activity. The combined antimicrobial effect of chitosan and natural dyes is very good and can be used to develop clothes for protecting against common infection. Joshi et al. [130] also studied a comprehensive review on natural product based bioactive agents such as chitosan, natural dyes, neem extract and other herbal products for antimicrobial finishing of textile substrate.

There are only few reports [6, 131, 132] on the dyeing of natural fibers for the improvement of deodorizing property with natural dyes. Hwang et al. [6] reported deodorizing property of cotton, silk, and wool fabrics dyed with gardenia, coffee sludge, *Casia tora*. L., and pomegranate extracts. The deodorizing performance of fabrics dyed with various natural colourants extracts was in the range of 50-99%. The deodorizing performance increased in the order of gardenia < *Casia tora*. L. < coffee sludge < pomegranate. Especially the deodorizing performance of all fabrics dyed with pomegranate was found to be highest 99%. Lee [131] studied deodorizing property of cotton, silk, and wool fabrics dyed with coffee sludge (*Coffee Arabica* L.) extract. It was found that fabrics

dyed with the *Coffee Arabica* L. extract showed good deodorization performance. Lee et al. [132] also studied deodorizing and dyeing properties of cotton, silk, and wool fabrics dyed with Amur Corktree, *Dryopteris crassirhizoma*, *Chrysanthemum boreale*, *Artemisia* extracts. The results revealed that deodorizing performance of fabrics dyed with various natural colourant extracts between 34% and 99%. It is worth nothing that the use of natural colourant notably enhanced the deodorizing performance. Wool fabrics showed the highest performance increase at 98-99%, followed by silk and cotton.

3.1.8 Application of natural dyes for textile printing

There are four reports [133-136] on the printing of textile materials with different natural dyes. Rekaby et al. [133] studied the printing of natural fabrics (wool, silk, cotton and flax) with natural dyes from alkanet and rhubarb by using pigment-printing technique. Results show that the highest *K/S* value was obtained by using Meypro gum as a thickener. The *K/S* increases rapidly as the concentration of the natural dye powder in the printing paste increases from 10 to 40 g/kg printing paste. Moreover, results show that the printed goods, which were fixed via steaming, have relatively higher colour strength than their corresponding samples fixed via thermodynamics. The best results were obtained by using metal mordants at a concentration of 20 g/kg printing paste. The colour fastness results were ranging between very good and excellent. Karolia and Buch [134] studied the resist printed natural dyed textile of *Ajarkh*. Hebeish et al. [135] evaluated the reactive cyclodextrin in cotton printing with *Lawsonia Intermis Linn lythracease* (henna) as natural dye. Hakeim et al. [136] studied the pretreated cotton fabric by chitosan was printed with natural colouring matter, curcumin. The colour yield of the prints increased by increasing the molecular weight of chitosan. The stiffness results of the printed cotton fabric pretreated with low molecular weight chitosan showed better performance. The rubbing fastness of the prints was good.

3.2 Natural dyes as photosensitizers for dye-sensitized solar cell

It has been emphasized by many researches to obtain useful dyes as photosensitizer for dye-sensitized solar cell (DSC) from natural products; some natural dyes as sensitizer of DSC have been reported [137-145]. Hao et al. [138] studied the DSC by using natural dyes

extracted from black rice, capsicum, erythrina variegate flower, rosa xanthina and kelp as sensitizer. The results show that the short-circuit current (I_{sc}) from 1.142 mAcm^{-2} to 0.225 mAcm^{-2}, the open-circuit voltage (V_{oc}) from 0.551 V to 0.412 V, the fill factor (*ff*) from 0.52 to 0.63, and the maximum output power (P_{max}) 58 μWcm^{-2} to 327 μWcm^{-2} were obtained from the DSC sensitized with natural dyes extracts. In the extracts of natural fruit, leaves, and flower chosen, the black rice extract performed the best photosensitized effect. Sirimanne et al. [139] applied the natural pigment extracted from pomegranate fruit as sensitizer in solid-state solar cells and found that pomegranate pigments sensitized TiO_2/dye/CuI cells exhibited a higher incident photon to photocurrent conversion efficiency than this type of cells with other pigments. Polo et al. [140] reported the application blue-violet anthocyanins from Jaboticaba (*Myrtus cauliflora* Mart) and Calafate (Berberies *buxifolia* Lam) as TiO_2 dye-sensitizer. The results revealed that solar cells sensitized by Jaboticaba extracts achieved up to I_{sc} = 9.0 mAcm^{-2}, V_{oc} = 0.59 V, P_{max} = 1.9 mWcm^{-2} and *ff* =0.54, while for Calafate sensitized cells the values determined were up to I_{sc} = 6.2 mAcm^{-2}, V_{oc} = 0.47 V, P_{max} = 1.1 mWcm^{-2} and *ff* = 0.36. The results obtained with extracts Jaboticaba and Calafate show a successful conversion of visible light into electricity by using natural dyes as wide band-gap semiconductor sensitizer in DSC. A DSC made by coating pigments in an extract from shiso leaves on a nanocrystalline film of TiO_2 and subsequent deposition of p-CuI, as studied by Kumara et al. [141]. It is found that solar cells sensitized by shiso leaves with chlorophyll extracts shows I_{sc} = 4.80 mAcm^{-2}, V_{oc} = 534 mV, and *ff* = 0.51, while for pure shino leaves sensitized cells the values determined were up to I_{sc} = 3.56 mAcm^{-2}, V_{oc} = 550 mV, and *ff* = 0.51. The energy conversion efficiency is about 1.3%. Wongcharee et al. [142] studied the DSC by using natural dyes extracted from rosella and blue pea flower. The cell sensitized by the rosella extract alone showed the best sensitization. The dyes were extracted at 100°C, using water as extracting solvent, an energy conversion efficiency of the cell consisting of rosella extract alone, blue pea extract alone, and mixed extract was 0.37%, 0.05% and 0.15%, respectively. Roy et al. [143] reported the dye-sensitized solar cell based on Rose Bengal dye and nanocrystalline TiO_2. The cell shows photo response in term of I_{sc} 3.22 mAcm^{-2}; V_{oc} 890 mV; *ff* 0.53, and an energy conversion efficiency 2.09%. The incident photon to current conversion efficiency (IPCE) was found to be 20.3% at 550 nm contributed by electron injection into the conduction band of TiO2 and

17.24% at 400 nm which is assigned to direct excitation of TiO_2 band gap. Calogero and Marco [144] also reported dye-sensitized solar cell by using Red Sicilian orange (*Citrus Sinensis*) and purple eggplant (*Solanum melongena*, L.) fruits as natural sensitizer of TiO_2 films. The best solar energy conversion efficiency (0.66%) was obtained by red orange juice dye that, under air mass (AM) 1.5 illuminations, achieved up to I_{sc}= 3.84 $mAcm^{-2}$; V_{oc} = 0.340 V, and fill factor = 0.50. In the case of the extract of eggplant peels, the values determined were up to I_{sc}= 3.40 $mAcm^{-2}$; V_{oc} = 0.350 V, and fill factor = 0.40. Gómez-Ortíz et al. [145] prepared the DSC using the carotenoids bixin and norbixin, which were obtained from the extract of achiote seeds (*Bixa orellana* L.). The best results were obtained with bixin-sensitized TiO_2 solar cells with efficiencies of up to 0.53%. The results for norbixin-sensitized ZnO cells were slightly better than for bixin-sensitized cells, but the efficiencies were much lower than for the TiO_2-based cells.

CHAPTER IV
EXPERIMENTAL

4.1 Materials and chemicals

(a) Eucalyptus leaves (*Eucalyptus camaldulensis*), Thailand

(b) Wool fabric (thickness 0.71 mm, weight 298 g/m^2, fabric count per inch 93 x 58, twill weave)

(c) Silk fabric (thickness 0.15 mm, weight 67 g/m^2, fabric count per inch 96 x 80, plain weave), Chul Thai Silk Co. (Thailand)

(d) Aluminium potassium sulfate ($AlK(SO_4)_2.12H_2O$), commercial grade

(e) Ferrous sulfate ($FeSO_4.7H_2O$), commercial grade, Lachner

(f) Copper sulfate ($CuSO_4.5H_2O$), commercial grade, Lachner

(g) Stannous chloride ($SnCl_2.5H_2O$), commercial grade, Lachner

(h) Syntapon ABA (anion active wetting agent), Chemotex Děčin, Czech Republic

(i) Altaran S8 (soaping agent), Chemotex Děčin, Czech Republic

(j) Quercetin dehydrate, 98% purity ($C_{15}H_{10}O_7.2H_2O$, FW 338.80), Sigma

(k) Rutin hydrate, 95% purity ($C_{27}H_{30}O_{16}.xH_2O$, FW 610.52), Fluka

(l) Tannin Ph. Eur. 5 ($C_{76}H_{52}O_{46}$, FW 1701.20), Lachner

(m) Ellagic acid, 95% purity from tree bark ($C_{14}H_6O_8$, FW 302.19), Sigma

(n) Gallic acid, 98% purity ($(HO)_3C_6H_2CO_2H \cdot H_2O$, FW 188.13), Fluka

(o) Apigenin, 95% purity ($C_{15}H_{10}O_5$, FW 270.24), Sigma

(p) Hyperin, 97% purity ($C_{21}H_{20}O_{12}$, FW 646.38), Sigma

(q) Vanillin, 97% purity (4-$(HO)C_6H_3$-3-(OCH_3)CHO), FW 152.15), Aldrich

(r) Luteolin, 99% purity ($C_{15}H_{10}O_6$, FW 286.24), Fluka

(s) Kaempferol, 96% purity ($C_{15}H_{10}O_6$, FW 286.24), Sigma

4.2 Experiment process

4.2.1 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 grams of crumbled eucalyptus leaves was mixed in a litter 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) [29-30].

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 [28-30]. 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.

4.2.2 Characterization of tannin-ferrous sulfate [Tannin/ Fe (II)] complexes

4.2.2.1 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).

4.2.2.2 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 micro molar 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.

4.2.3 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 grams of crumbled eucalyptus leaves was mixed with 1 litter of distilled water and subjected to stirring at room temperature for 3 hours.

- 70 grams of crumbled eucalyptus leaves was mixed with 1 litter of distilled water and refluxed for 1 hour.
- 70 grams 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.

4.2.4 An adsorption study of dyeing on silk fabric with aqueous extract of eucalyptus leaves

4.2.4.1 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 grams of crumbled eucalyptus leaves was mixed with 1 litter of distilled water and refluxed for 1 hour. 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 [146]. 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.

4.2.4.2 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 [147].

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

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

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.

4.2.5 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. All measured samples showed the λ_{max} value at 400 nm.

4.2.6 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 [31,148]. The fabric was then

immersed in the dye solution at room temperature and padded on a two-bowl padding mangle at 80% pick up. After padding for 2 seconds, the samples were dried at 90°C for 5 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 24 hours.

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°C, 60°C and 90°C) for different duration 1-10 minute 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 reflectance of the soaped samples was measured on a spectrophotometer (Datacolor 3890). Relative colour strength (*K/S* values) were determined using the the Kubelka-Munk equation, $K/S = (1-R)^2/2R$, where R is reflectance. All measured samples showed the λ_{max} value at 400 nm.

4.2.7 The percentage yield (exploitation) of silk and wool fabrics dyed with eucalyptus leaf 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)

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

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.

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

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

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

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

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

The crude eucalyptus leaf extract dye, quercetin, rutin, and tannin were characterized by UV-visible spectroscopy. The crude extraction solution (50 mg/l) and tannin (20 mg/l) were prepared by dissolution in distilled water. 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.

4.2.8.2 Mordanting and pad-dyeing

The simultaneous padding and mordanting was used. To study the effect of dye concentration, 2 and 5 g/l concentration of dye (eucalyptus leaf extract, quercetin rutin, and tannin) were chosen. Ferrous sulfate was varied at 2, 5 and 10 g/l for each concentration of dye, and an anion wetting agent, Altaran S8 (1 g/l), was added to the solution. The wool 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 90ºC for 5 minutes. The samples were then washed in 1 g/l solution of the soaping agent, Syntapon ABA, at 80°C for 5 minutes and then air-dried at room temperature.

4.2.8.3 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 measured samples showed the λ_{max} value at 400 nm. The colour fastness to washing, light, and rubbing of dyed samples was determined according to ISO 105-C06 A1S: 1994; ISO 105-B02: 1994; and ISO 105-X12: 2001, respectively.

4.2.9 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 [31,148]. The fabric was then immersed in the dye solution at room temperature and padded on a two-bowl padding

mangle at 80% pick up. After padding for 2 seconds, the samples were dried at 90°C for 5 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 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 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 [149]:

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

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" [115]. There is no rating assigned if the UPF value is greater than 50.

4.2.10 The fastness properties of silk and wool fabrics dyed with eucalyptus leaf 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. 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.

CHAPTER V
RESULTS AND DISCUSSION

5.1 Components determination of water extract of eucalyptus leaves

Table 5.1 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 5.1).

Table 5.1 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% (+ + + + +)

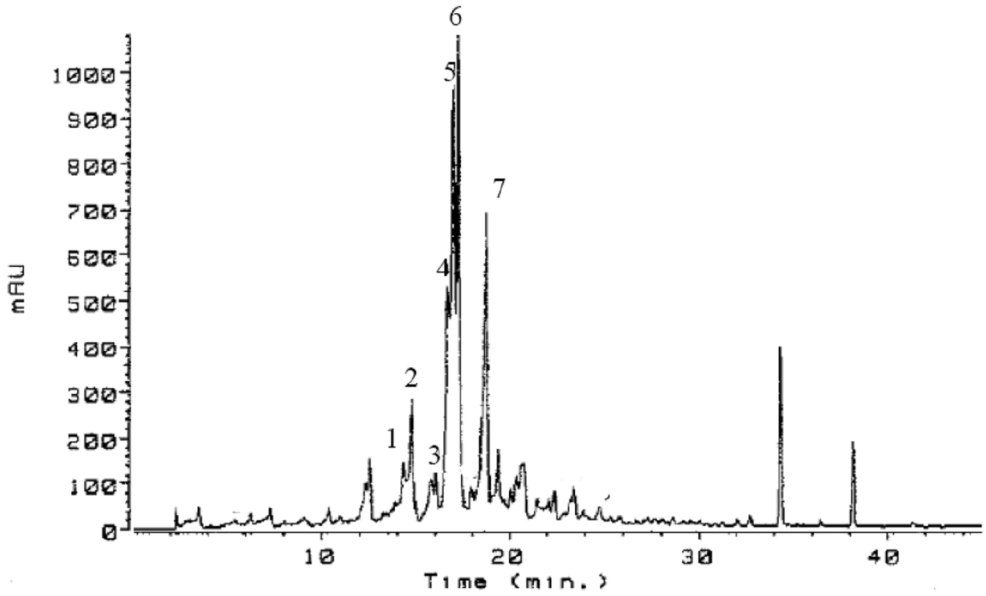


Figure 5.1 HPLC chromatogram of an ether extract of leaves of eucalyptus. Key to peak identity: 1-hyperin; 2- apigenin; 3- kaempferol; 4- rutin; 5- gallic acid; 6- ellagic acid; 7-quercetrin

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 5.2.

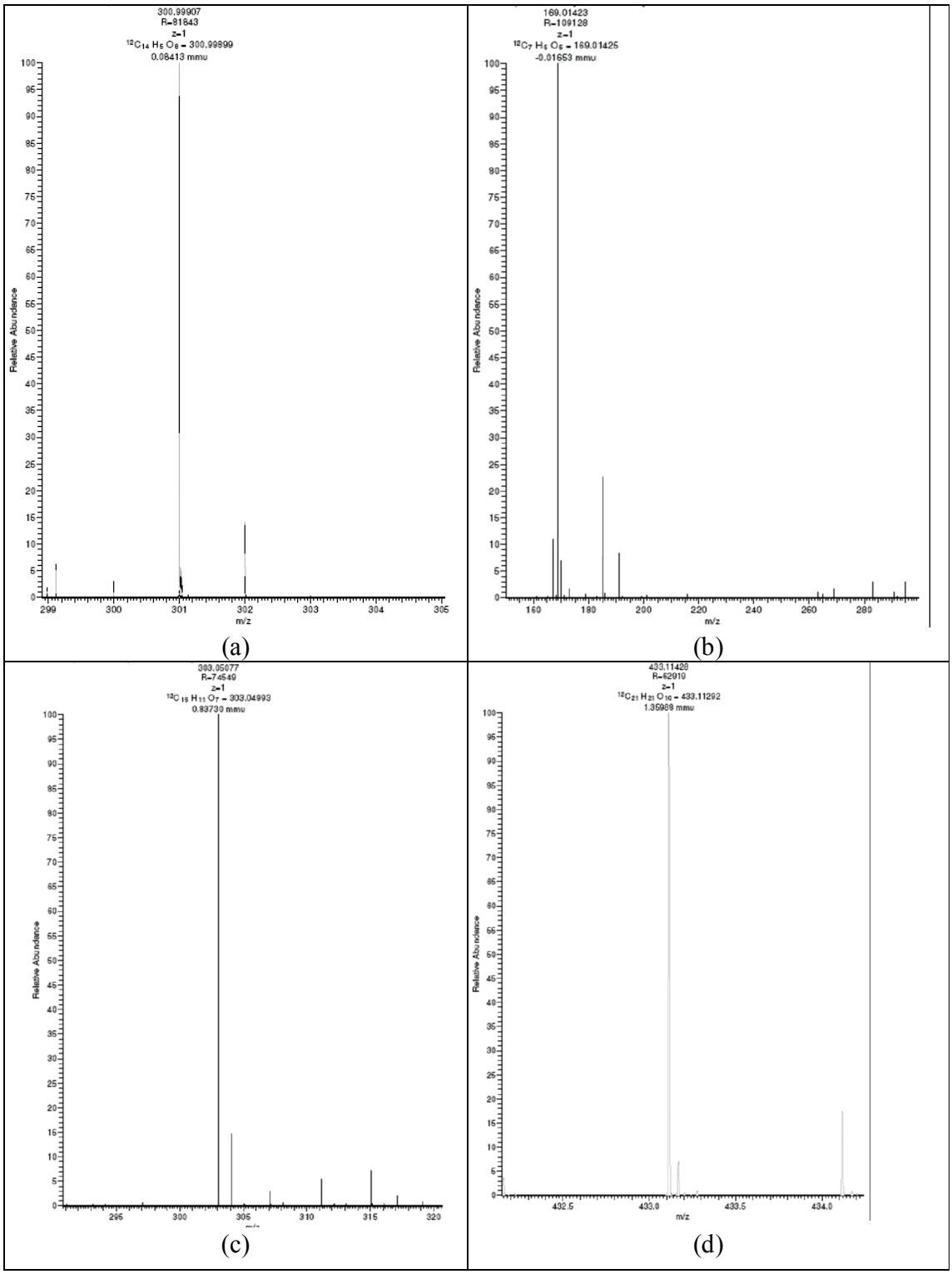


Figure 5.2 Full scan mass spectrum of some flavonoids in eucalyptus leaves (a) ellagic acid, (b) gallic acid, (c) quercetin and (d) apigenin

5.2 Characterization of tannin-ferrous sulfate [Fe (II)] complexes

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

The UV-vis spectrum of tannin in aqueous solution without pH control (Figure 5.3) 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.

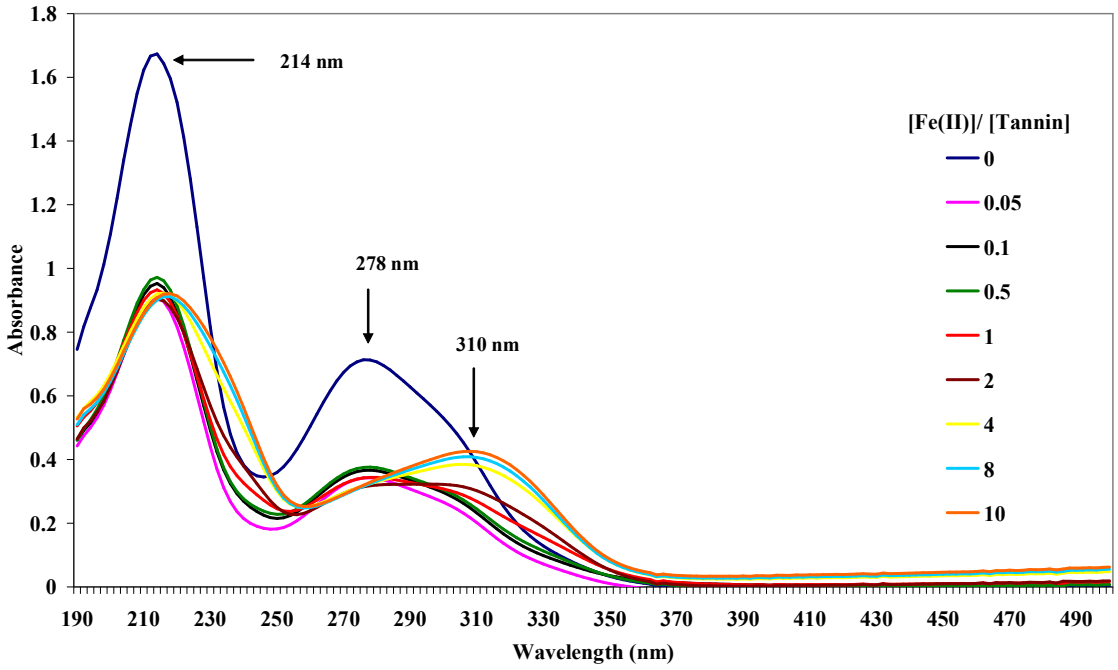


Figure 5.3 Absorption spectra of tannin (1×10^{-5} Molar) in aqueous solution in the absence and in the presence of Fe (II) (0-100 micro molar)

The result of the study of the effect of Fe (II) on the visible spectra (λ_{max}) of tannin is presented in Figure 5.3 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 5.4).

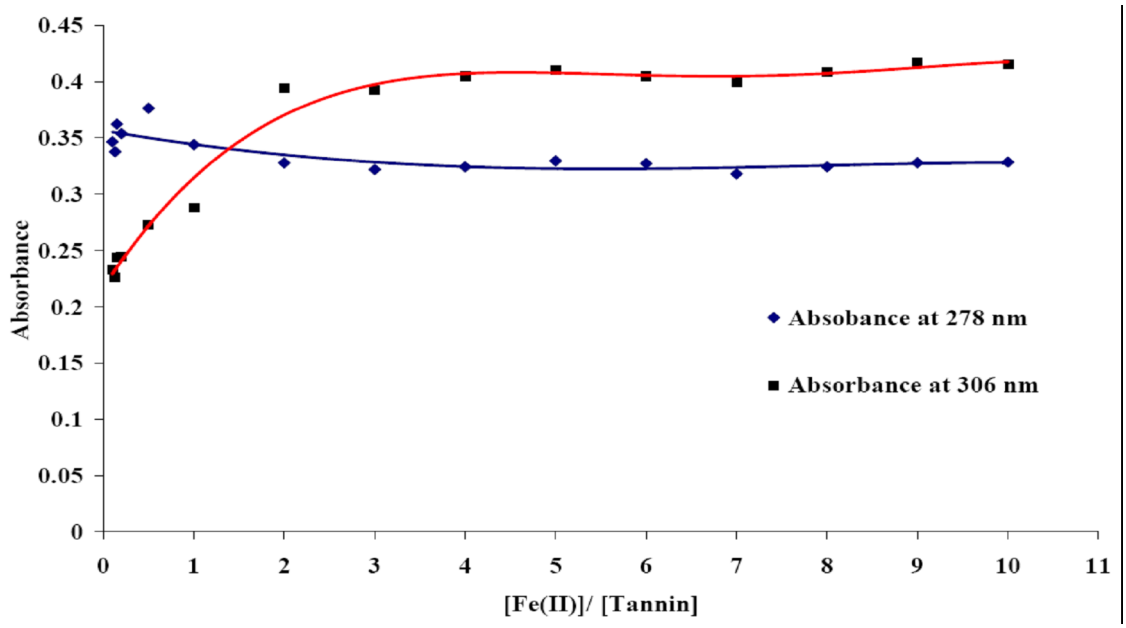


Figure 5.4 Absorbance versus [Fe (II)]/ [Tannin] molar ratios

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

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 5.5) and start to be constant at [Fe(II)]/[tannin] 2:1 stoichiometry in 1.0-5.0 x 10^{-5} Molar tannin concentrations (solid line in Figure 5.5).

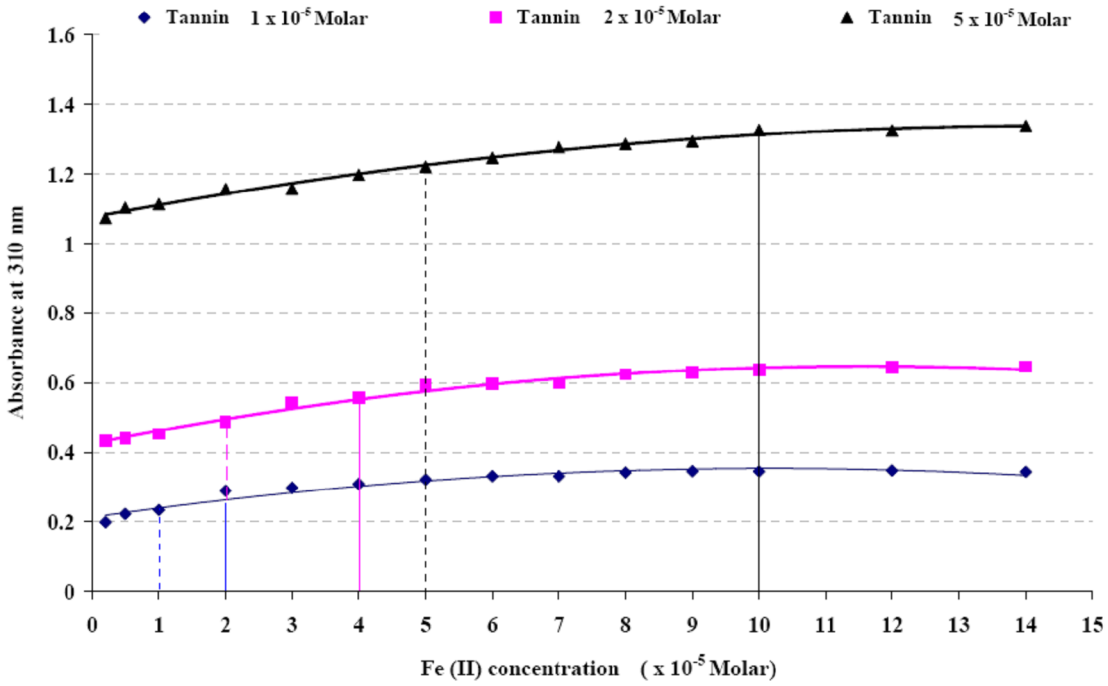


Figure 5.5 The effect of Fe (II) concentration on tannin in aqueous solution. Dash line is the [Fe(II)] / [tannin], 1:1. Solid line is the [Fe(II)] /[tannin], 2:1.

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 5.6) 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.

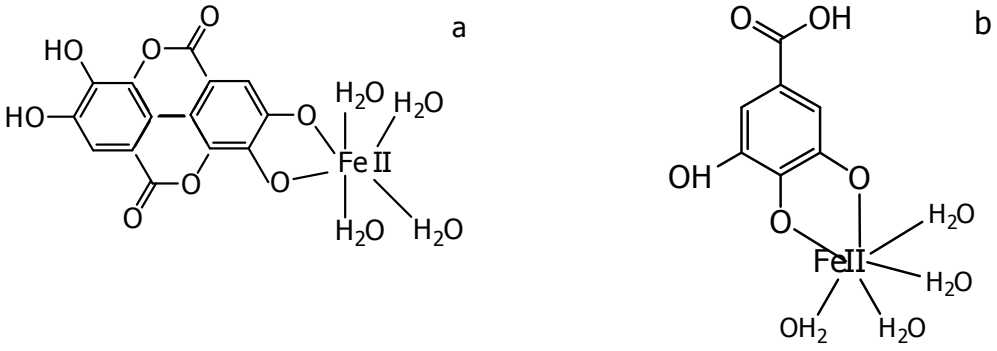


Figure 5.6 Proposed the structure of ferrous-tannins complex (a) 1:1 [Fe(II):ellagic acid], and (b) 1:1 [Fe(II): gallic acid

5.3 Optimization of extraction conditions and identification of crude eucalyptus leaf extract dye

5.3.1 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 5.2. As can be seen from the Table 5.2, *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 5.2. 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 5.2 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

5.3.2 UV–visible spectrum

The UV-vis spectrum of the crude eucalyptus leaf extract dye in an aqueous solution is presented in Figure 5.7. 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) [150]. Absorption in the 250–270 nm regions may be attributed to the electronic transitions of benzene and its

derivatives, which may include various aromatic compounds such as phenolics [150]. It can be observed from Figure 5.7 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) [117].

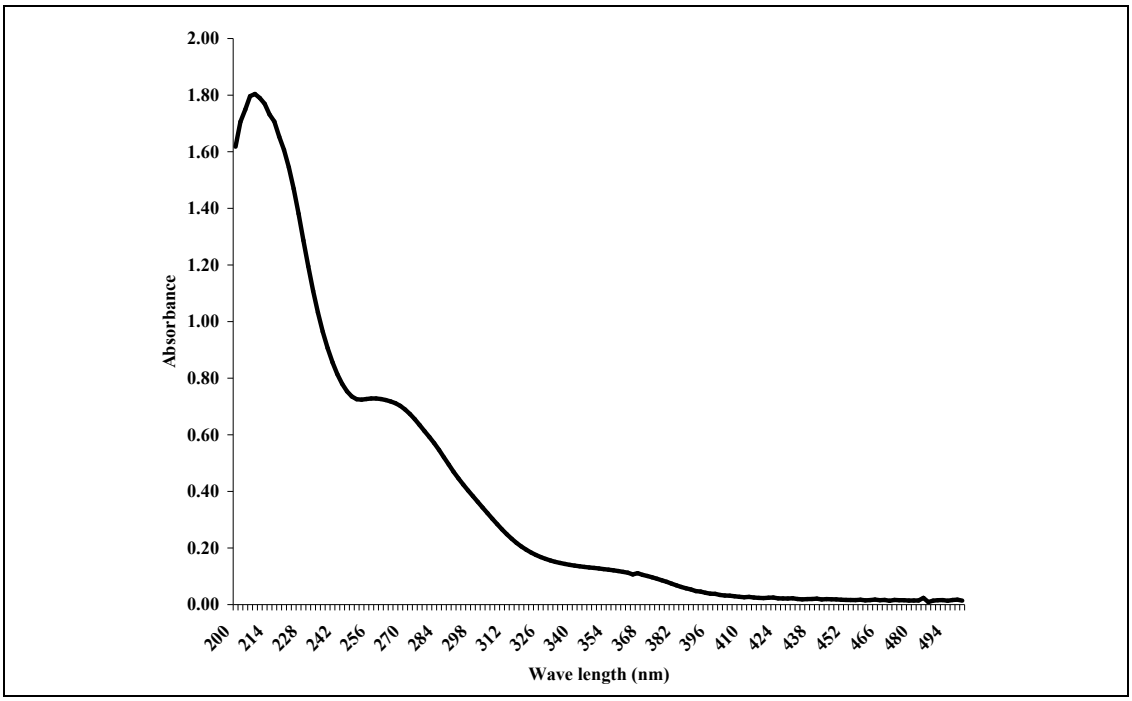


Figure 5.7 UV-VIS spectra of 50 mg/l crude eucalyptus leaf extracted dye in distilled water.

5.4 An adsorption study of dyeing on silk fabric with aqueous extract of eucalyptus leaves

The dye concentration in residual bath [C_L] and dye on silk [C_S] at 30°C, 60°C and 90°C are shown in Table 5.3.

The typical results (on unmordanted silk) at 30°C, 60°C, 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 5.8 (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 [107].

Table 5.3 Initial dye concentrations [C_0], dye concentration in residual bath [C_L] and dye on silk [C_S]

Temperature 30°C		**Temperature 60°C**		**Temperature 90°C**	
[C_L] mg/ml	**[C_S] mg/g**	**[C_L] mg/ml**	**[C_S] mg/g**	**[C_L] mg/ml**	**[C_S] mg/g**
0.56	0.18	0.58	0.37	0.50	0.68
8.95	40.30	8.69	75.60	5.90	90.40
13.87	65.90	13.01	105.30	8.60	158.10
17.62	66.07	17.40	109.40	11.40	198.40
23.02	66.50	22.50	109.21	16.20	200.50
26.92	65.20	26.50	110.13	24.10	199.20

The results of exhaustion (%), partition ratio (K), and saturation values are reported in Table 5.4. It can seen that the temperature was increased, the partition ratio, saturation values, and exhaustion percentages increased.

Table 5.4 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)	7.48	11.67	36.32
Partition ratio (K)	3.80	6.67	17.80
Saturation (mg/g)	65.92	109.55	200.10

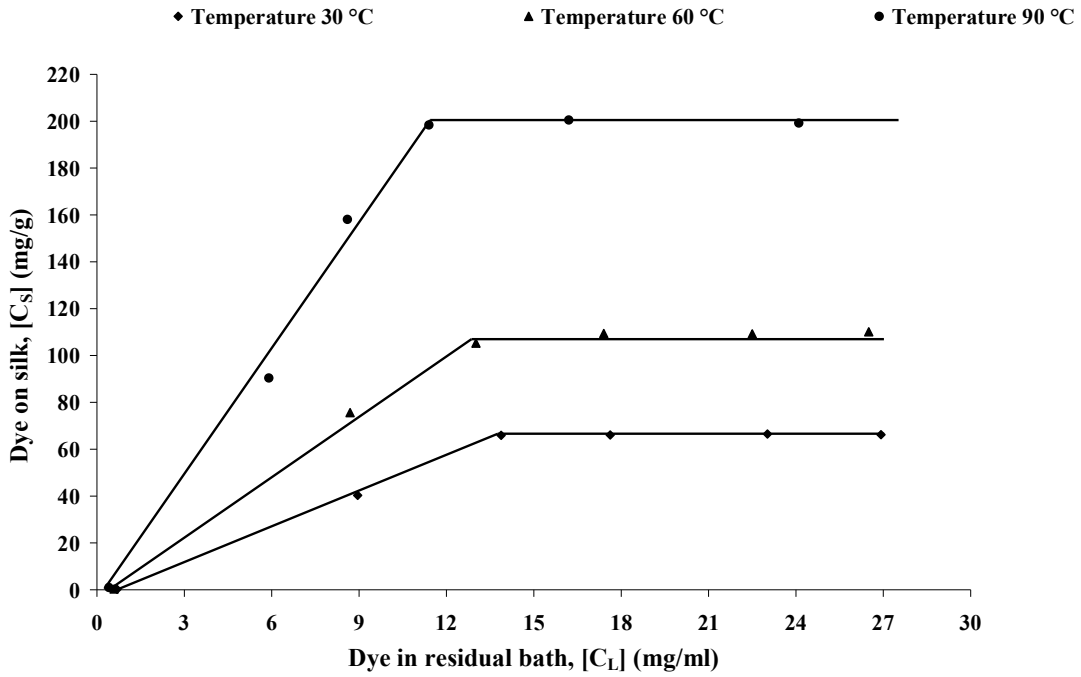


Figure 5.8 Quasi-sorption isotherm after 120 min dyeing of silk fabric (unmordanted) with eucalyptus leaves extract at 30°C, 60°C, and 90°C

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

The effect of mordanting methods and padding techniques on dyeing of silk and wool fabrics with different mordants are shown in Table 5.5 to Table 5.10. The *K/S* values were measured for silk and wool fabrics as shown in Figure 5.9 to Figure 5.14. All measured sample showed the greatest λ_{max} value at 400 nm.

Table 5.5 to Table 5.10 show CIELAB *L**, *a**, *b** values for the silk and wool fabrics dyed with different mordants by three mordanting methods (pre-mordanting, simultaneous mordanting and post-mordanting) and using two padding techniques, namely the pad-batch and pad-dry techniques. *L**, *a**, *b** refer to the three axes of the CIELAB system. The *L** value indicates perceived lightness in CIELAB colour space. The *L** scale run from 0 (black) to 100 (white); the higher the *L** reading the lighter colour. The *a** value indicates

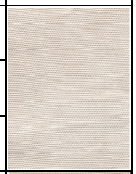
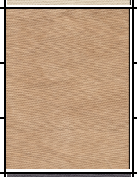
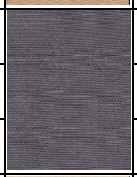
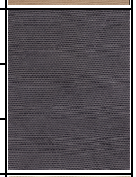
red (+a^*) and green (-a^*) while the b^* value indicates yellow (+b^*) and blue (-b^*) [60, 151, 152].

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 [29-30], which are phenolic compounds that can form hydrogen bonds with carboxyl groups in the protein fibers [35].

Table 5.5 Colour value of silk fabric dyed with eucalyptus leaf extract by pre-mordanting and padding techniques and using 10 g/l of metal mordants at different concentration of the dye

Type of mordant	**Dye Conc. (g/l)**	**Pad-batch on silk fabric**					**Pad-dry on silk fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	5	0.60	86.4	2.9	3.7		0.50	88.5	3.0	0.9	
	10	0.66	86.4	2.8	4.2		0.63	88.0	2.7	1.6	
	20	0.75	84.5	2.8	8.3		0.75	84.5	2.8	8.3	
$AlK(SO_4)_2$ (Al)	5	0.78	87.4	0.8	8.6		0.80	87.1	0.8	9.9	
	10	0.87	85.8	0.9	10.6		0.90	86.2	0.8	10.8	
	20	1.07	84.3	1.2	11.7		1.01	85.5	1.0	10.5	
$CuSO_4$ (Cu)	5	2.10	71.8	3.9	17.8		2.31	71.2	3.7	18.5	
	10	2.70	67.3	4.9	20.3		2.64	68.1	4.8	19.2	
	20	3.20	65.2	5.5	20.9		3.12	66.2	4.9	17.8	
$FeSO_4$ (Fe)	5	2.80	50.4	2.6	0.1		2.82	50.0	2.5	0.1	
	10	2.90	45.7	2.8	-3.4		3.09	47.4	2.8	-1.1	
	20	3.80	39.8	3.4	-4.3		3.52	41.9	3.2	-4.0	
$SnCl_2$ (Sn)	5	1.02	88.8	0.9	9.8		1.04	89.0	0.4	9.3	
	10	1.10	88.4	0.9	11.0		1.08	88.1	0.6	10.4	
	20	1.53	86.5	1.0	16.0		1.28	87.2	0.4	11.9	

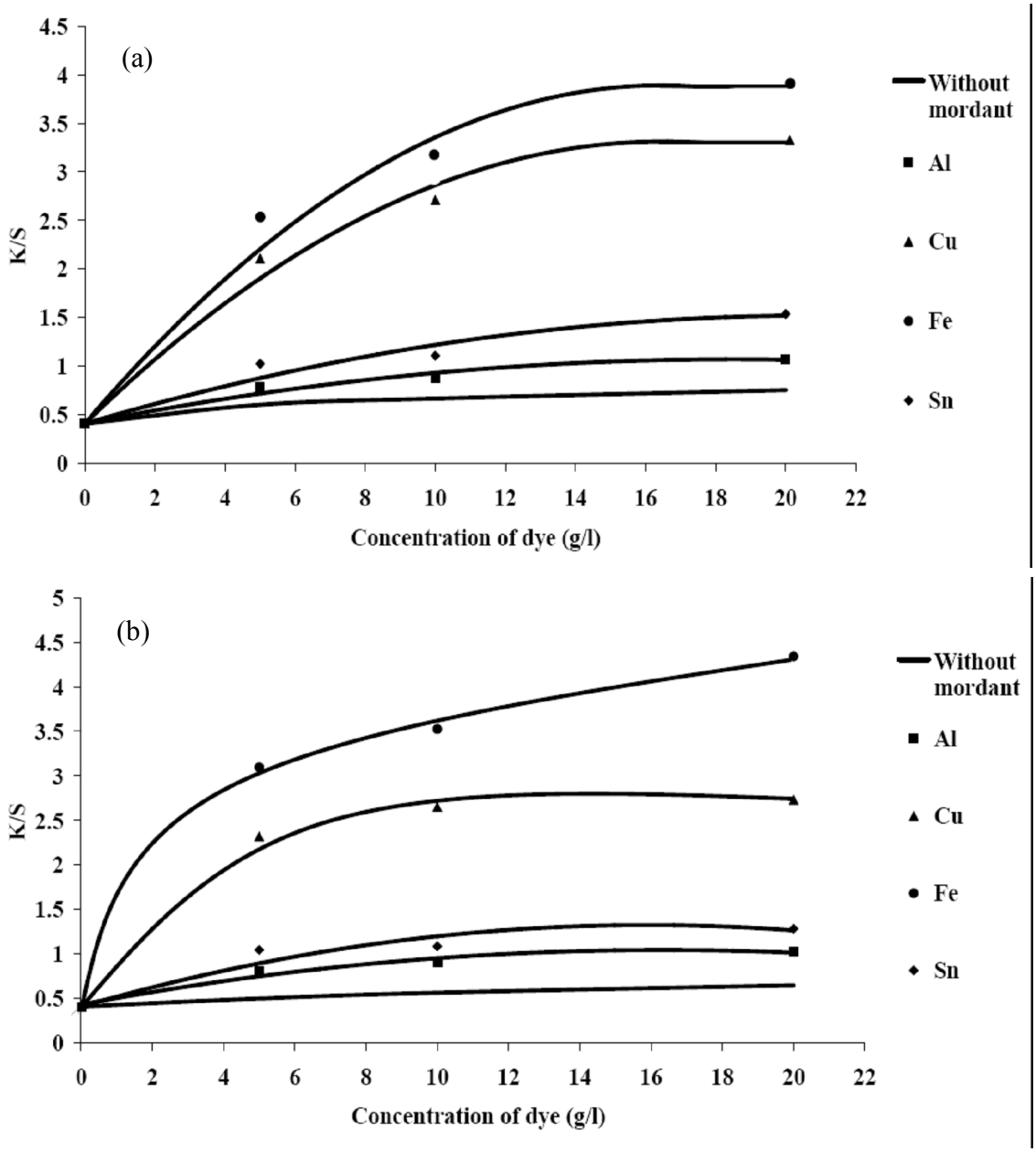


Figure 5.9 Effect of dye concentrations on *K/S* values of silk fabric dyed with 10 g/l mordants by pre-mordanting and using (a) pad-batch technique (b) pad-dry technique

Table 5.6 Colour value of silk fabric dyed with eucalyptus leaf extract by simultaneous mordanting and padding techniques and using 10 g/l of metal mordants at different concentration of the dye

Type of mordant	**Dye Conc. (g/l)**	**Pad-batch on silk fabric**					**Pad-dry on silk fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	5	0.60	86.4	2.9	3.7		0.50	88.5	3.0	0.9	
	10	0.66	86.4	2.8	4.2		0.63	88.0	2.7	1.6	
	20	0.75	84.5	2.8	8.3		0.75	84.5	2.8	8.3	
$AlK(SO_4)_2$ (Al)	5	0.92	85.6	0.5	14.0		1.19	86.3	0.4	17.0	
	10	1.16	84.5	0.8	14.9		1.51	83.7	0.5	19.7	
	20	1.35	82.1	1.1	16.9		1.60	82.0	1.1	18.1	
$CuSO_4$ (Cu)	5	2.22	69.2	4.6	17.3		2.47	68.7	3.8	18.7	
	10	2.52	67.5	5.0	18.5		2.72	66.6	5.2	18.8	
	20	3.02	64.5	5.7	18.6		3.09	63.8	6.0	18.6	
$FeSO_4$ (Fe)	5	3.37	46.2	2.6	-1.1		3.63	43.7	2.6	-2.3	
	10	3.69	42.6	2.7	-2.8		3.99	40.0	2.7	-4.4	
	20	4.04	39.3	2.8	-4.4		4.05	38.7	2.8	-5.1	
$SnCl_2$ (Sn)	5	0.91	89.4	1.2	7.6		1.02	88.5	0.1	12.9	
	10	1.08	88.9	1.4	7.3		1.20	88.0	1.1	7.1	
	20	1.33	87.0	1.0	9.5		1.48	86.2	0.9	14.4	

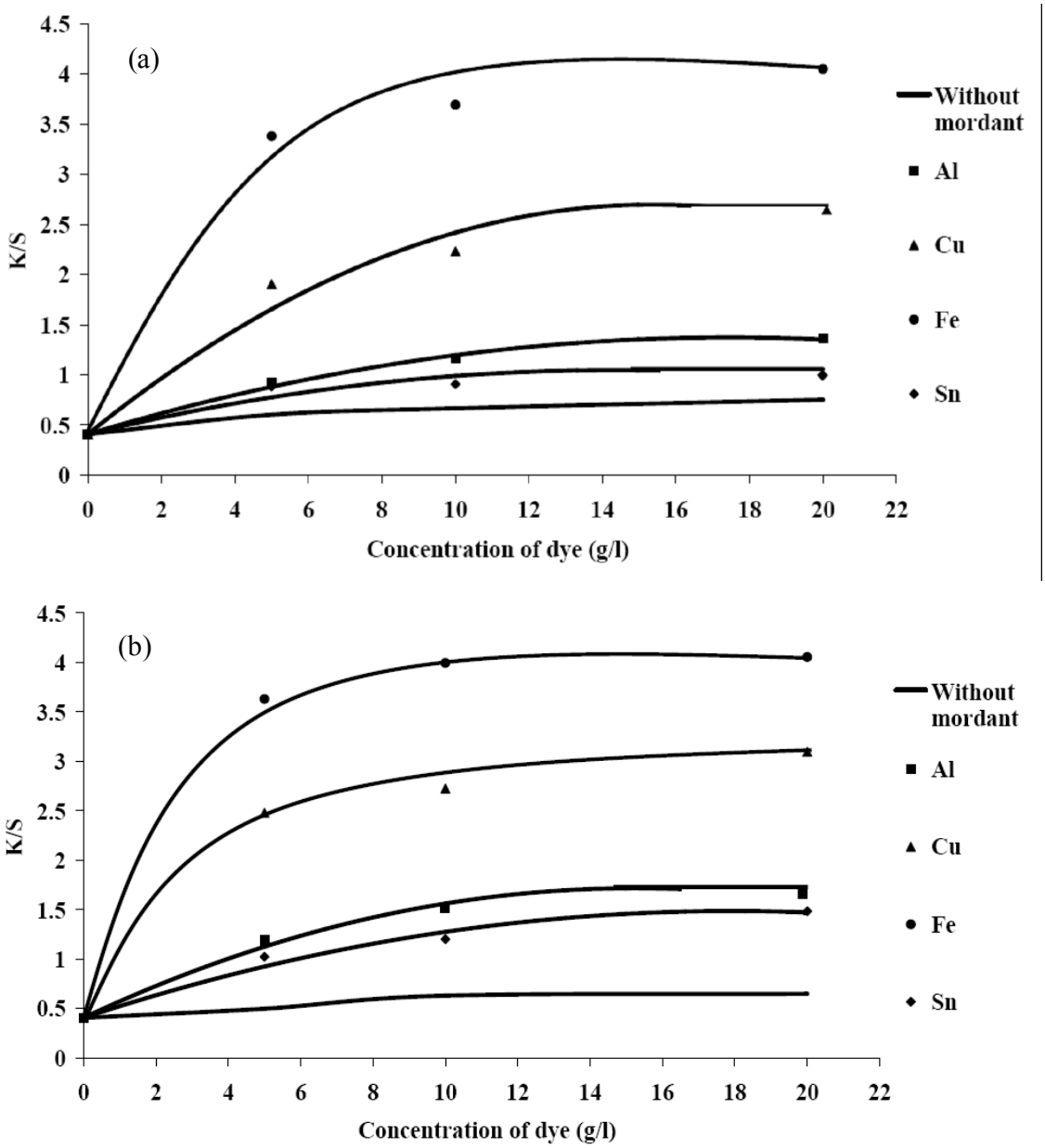
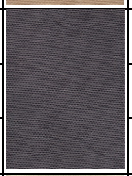
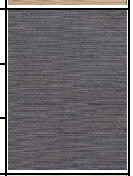


Figure 5.10 Effect of dye concentrations on *K/S* values of silk fabric dyed with 10 g/l mordants by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

Table 5.7 Colour value of silk fabric dyed with eucalyptus leaf extract by post-mordanting and padding techniques and using 10 g/l of metal mordants at different concentration of the dye

Type of mordant	**Dye Conc. (g/l)**	**Pad-batch on silk fabric**					**Pad-dry on silk fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	5	0.60	86.4	2.9	3.7		0.50	88.5	3.0	0.9	
	10	0.66	86.4	2.8	4.2		0.63	88.0	2.7	1.6	
	20	0.75	84.5	2.8	8.3		0.75	84.5	2.8	8.3	
$AlK(SO_4)_2$ (Al)	5	0.78	87.1	0.1	10.2		0.78	87.1	0.1	10.3	
	10	0.81	86.7	0.2	11.1		0.81	86.7	0.1	11.1	
	20	0.94	85.6	0.4	11.5		0.94	85.6	0.4	11.5	
$CuSO_4$ (Cu)	5	1.65	73.2	2.6	15.2		1.70	73.6	0.8	13.8	
	10	1.80	72.4	3.0	15.6		1.81	72.4	1.8	15.0	
	20	2.07	69.6	3.9	19.7		2.36	67.8	3.8	16.9	
$FeSO_4$ (Fe)	5	3.33	50.9	2.1	-0.2		2.53	51.9	2.4	-1.0	
	10	3.46	46.2	2.5	-0.5		3.30	45.8	2.5	-2.0	
	20	3.55	42.3	2.7	-3.5		3.40	43.5	2.5	-3.7	
$SnCl_2$ (Sn)	5	1.05	89.1	0.1	14.0		0.84	91.0	-0.2	8.3	
	10	1.12	88.6	0.5	11.9		0.93	90.0	-0.1	10.7	
	20	1.35	87.4	0.2	16.5		1.21	88.4	-0.2	13.8	

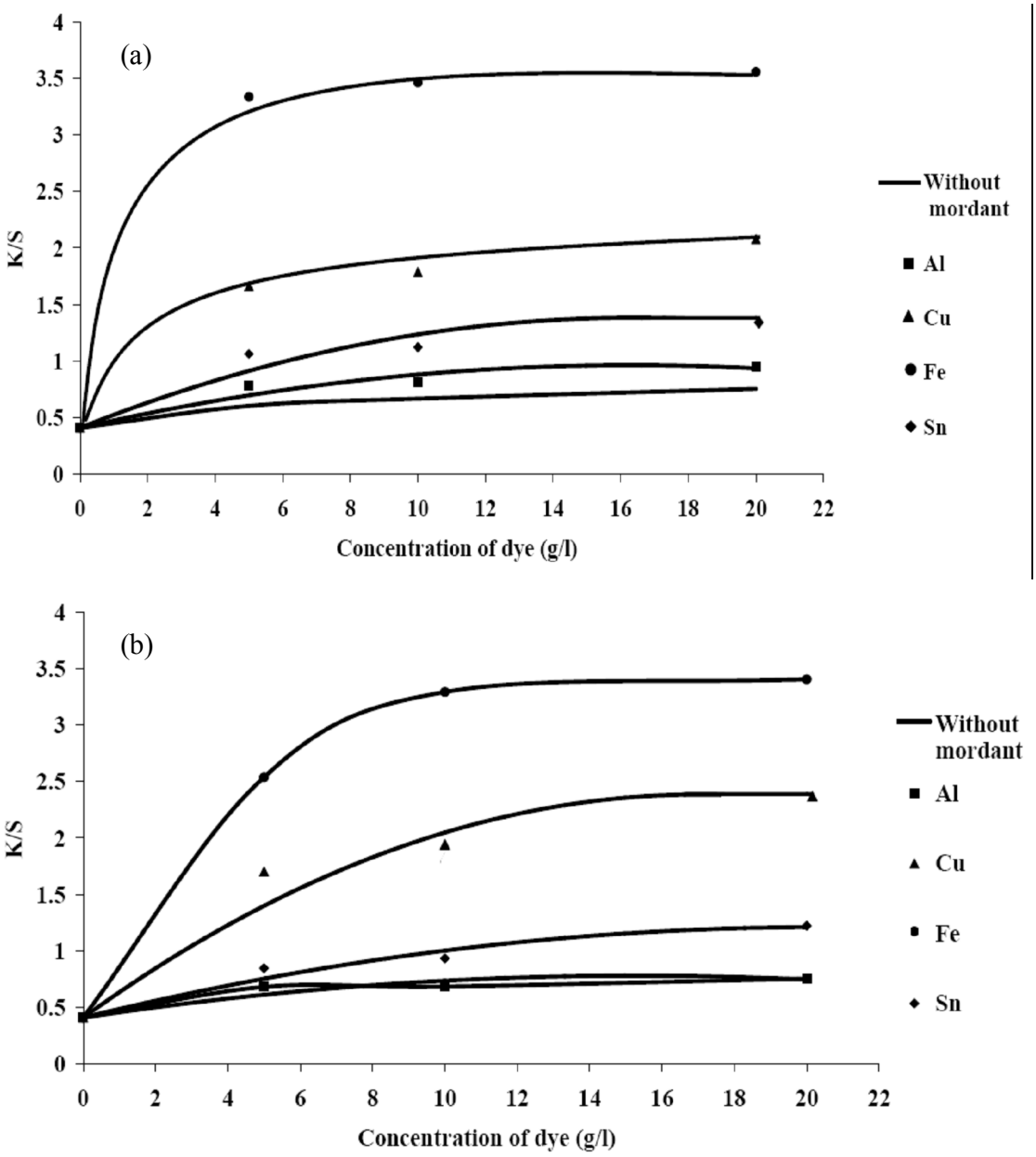
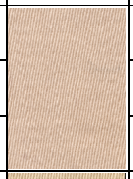
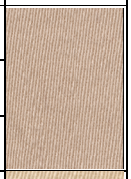
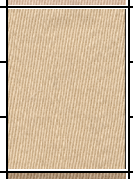
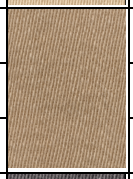
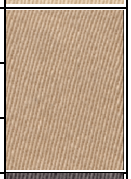
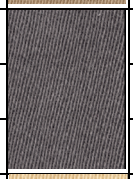
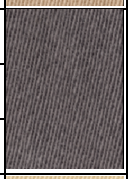
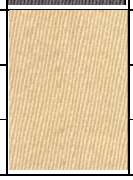
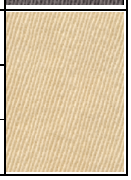


Figure 5.11 Effect of dye concentrations on *K/S* values of silk fabric dyed with 10 g/l mordants by post-mordanting and using (a) pad-batch technique (b) pad-dry technique

Table 5.8 Colour value of wool fabric dyed with eucalyptus leaf extract by pre-mordanting and padding techniques and using 10 g/l of metal mordants at different concentration of the dye

Type of mordant	**Dye Conc. (g/l)**	**Pad-batch on wool fabric**					**Pad-dry on wool fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	5	1.50	76.1	3.5	14.2		1.13	77.7	3.5	12.0	
	10	1.60	76.0	3.5	15.0		1.54	76.3	3.6	14.1	
	20	1.86	75.4	3.5	15.8		1.86	75.9	3.4	15.8	
$AlK(SO_4)_2$ (Al)	5	1.44	79.0	0.4	19.1		1.36	79.6	0.1	20.3	
	10	1.70	77.6	0.1	19.3		1.45	78.8	0.2	19.7	
	20	1.75	75.2	0.8	20.4		1.70	76.5	0.8	19.0	
$CuSO_4$ (Cu)	5	2.58	67.2	2.2	20.6		2.02	70.8	2.8	20.0	
	10	3.36	63.7	2.9	21.3		2.20	69.3	3.1	19.4	
	20	3.42	63.0	3.3	21.8		2.70	67.1	3.4	20.1	
$FeSO_4$ (Fe)	5	2.16	50.9	1.5	0.1		2.66	46.8	2.3	0.4	
	10	2.94	45.2	1.8	-0.6		3.52	43.1	3.1	0.6	
	20	4.22	40.0	2.2	-0.6		4.34	38.6	3.4	0.7	
$SnCl_2$ (Sn)	5	1.86	84.5	-0.4	26.2		2.14	83.0	-0.3	26.9	
	10	2.28	83.7	-0.3	28.4		2.25	83.0	-0.4	26.9	
	20	2.98	81.5	0.5	30.8		2.37	81.6	0.1	26.7	

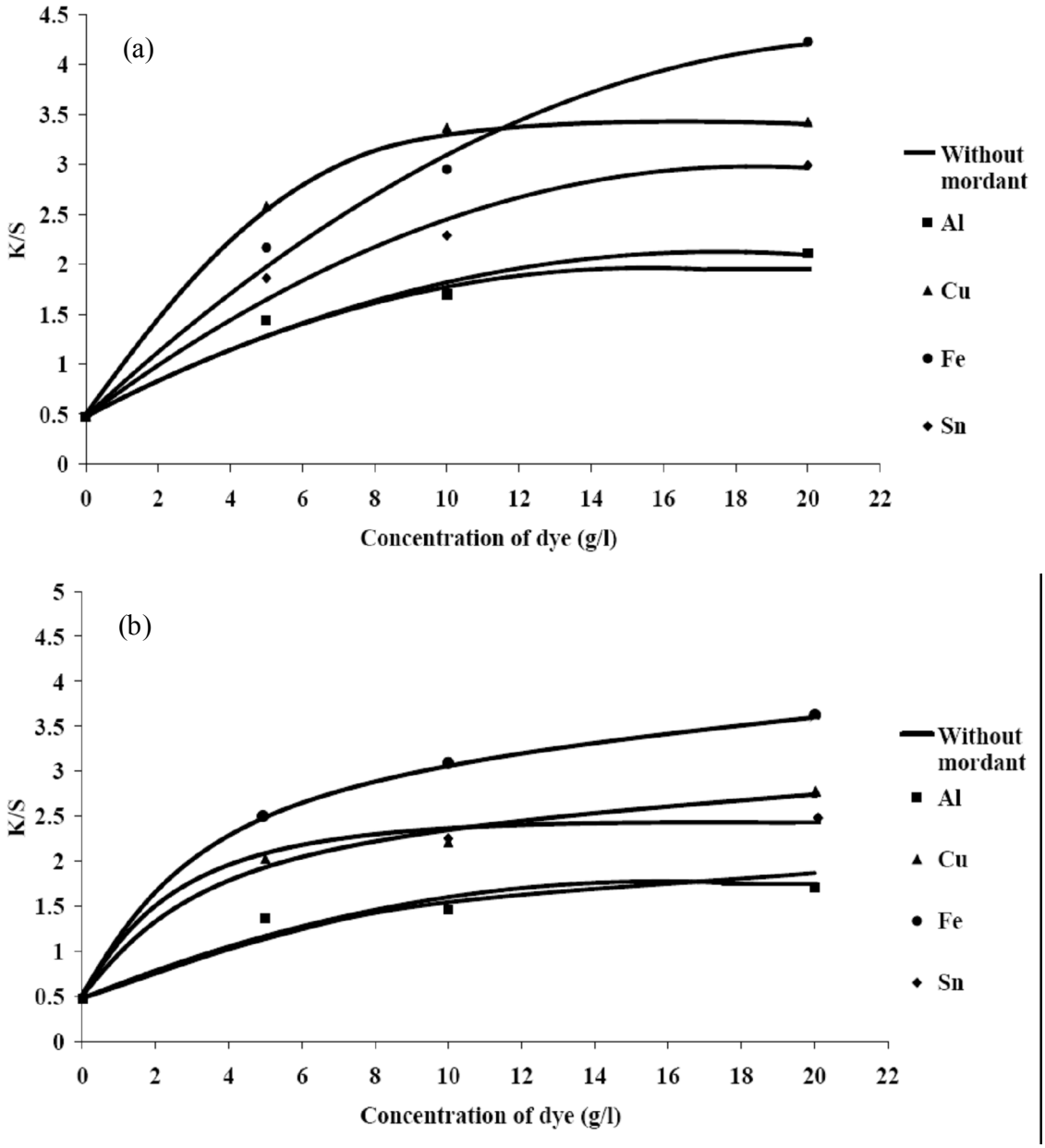


Figure 5.12 Effect of dye concentrations on *K/S* values of wool fabric dyed with 10 g/l mordants by pre-mordanting and using (a) pad-batch technique (b) pad-dry technique

Table 5.9 Colour value of wool fabric dyed with eucalyptus leaf extract by simultaneous mordanting and padding techniques and using 10 g/l of metal mordants at different concentration of the dye

Type of mordant	**Dye Conc. (g/l)**	**Pad-batch on wool fabric**					**Pad-dry on wool fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	5	1.50	76.1	3.5	14.2		1.13	77.7	3.5	12.0	
	10	1.60	76.0	3.5	15.0		1.54	76.3	3.6	14.1	
	20	1.86	75.4	3.5	15.8		1.86	75.9	3.4	15.8	
$AlK(SO_4)_2$ (Al)	5	1.65	78.2	0.4	23.6		1.65	79.4	0.1	27.2	
	10	1.91	76.8	0.1	24.0		1.81	78.0	0.1	27.6	
	20	2.55	74.9	0.7	22.9		2.60	74.5	1.0	27.2	
$CuSO_4$ (Cu)	5	3.27	63.8	0.04	21.1		2.32	65.5	2.0	19.6	
	10	3.44	62.6	1.0	21.2		2.62	64.0	2.8	19.5	
	20	4.12	59.6	2.2	21.1		2.80	62.5	3.3	19.0	
$FeSO_4$ (Fe)	5	3.93	40.1	1.3	-1.3		4.54	40.6	1.3	-1.0	
	10	4.23	40.0	1.1	-0.9		4.81	37.1	1.3	-1.0	
	20	4.62	38.5	1.2	-1.1		5.14	37.2	1.0	-0.9	
$SnCl_2$ (Sn)	5	2.15	83.8	-0.2	28.5		1.58	84.7	-0.9	22.5	
	10	2.38	84.1	-0.7	28.3		2.01	83.5	-0.4	27.4	
	20	2.67	83.4	-0.8	30.4		2.92	81.5	0.4	30.4	

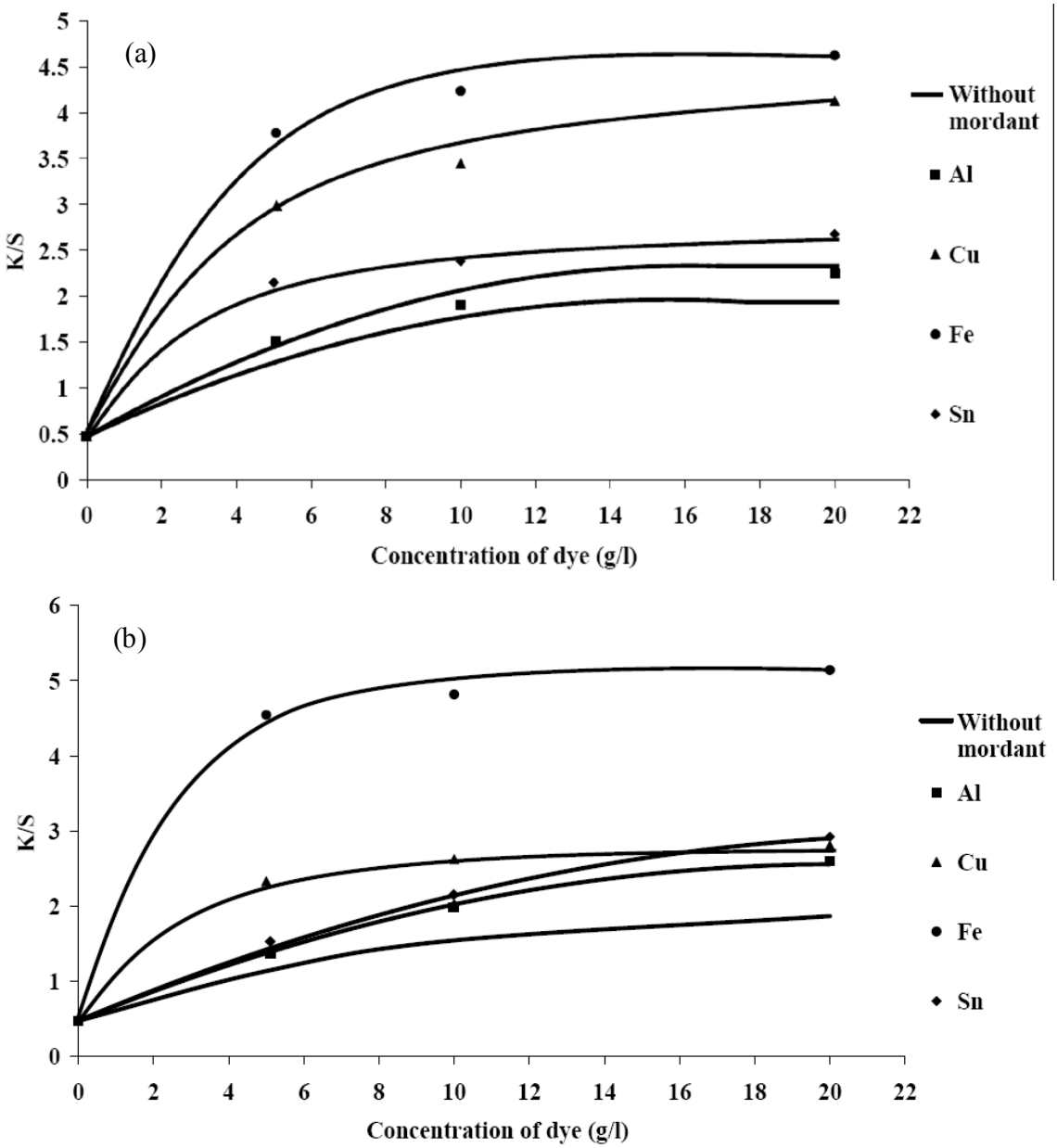
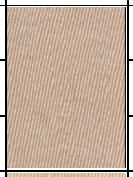
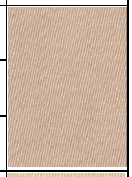
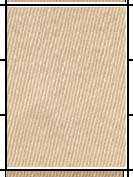
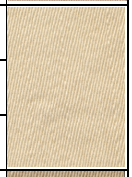
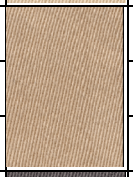
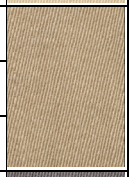
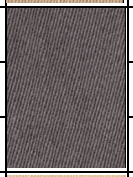
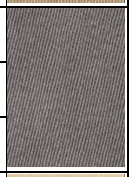
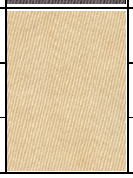
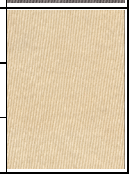


Figure 5.13 Effect of dye concentrations on *K/S* values of wool fabric dyed with 10 g/l mordants by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

Table 5.10 Colour value of wool fabric dyed with eucalyptus leaf extract by post-mordanting and padding techniques and using 10 g/l of metal mordants at different concentration of the dye

Type of mordant	**Dye Conc. (g/l)**	**Pad-batch on wool fabric**					**Pad-dry on wool fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	5	1.50	76.1	3.5	13.7		1.13	77.7	3.5	12.0	
	10	1.60	76.0	3.5	15.1		1.54	76.3	3.6	14.1	
	20	1.86	75.4	3.5	15.7		1.86	75.9	3.4	15.8	
$AlK(SO_4)_2$ (Al)	5	1.11	81.3	-1.2	19.2		0.93	82.1	0.6	16.9	
	10	1.23	80.2	-1.0	20.1		1.10	80.8	0.4	18.5	
	20	1.39	79.3	-0.8	21.4		1.28	79.7	0.2	19.9	
$CuSO_4$ (Cu)	5	2.50	66.8	-1.1	19.5		1.84	68.5	0.4	17.3	
	10	2.81	65.4	-0.1	20.3		2.12	66.8	0.6	18.7	
	20	3.06	63.7	0.2	20.2		2.87	63.1	1.7	20.2	
$FeSO_4$ (Fe)	5	3.18	53.0	1.8	8.4		2.28	55.8	1.5	6.1	
	10	3.35	50.2	2.0	8.5		2.71	51.1	1.5	3.9	
	20	3.86	46.7	1.5	2.7		3.13	45.7	1.6	1.0	
$SnCl_2$ (Sn)	5	1.54	85.4	-0.3	25.6		1.52	86.6	-0.3	24.8	
	10	1.90	85.0	-0.2	27.8		1.88	85.1	-0.2	25.7	
	20	2.05	84.0	-0.1	28.1		2.01	84.1	-0.2	26.6	

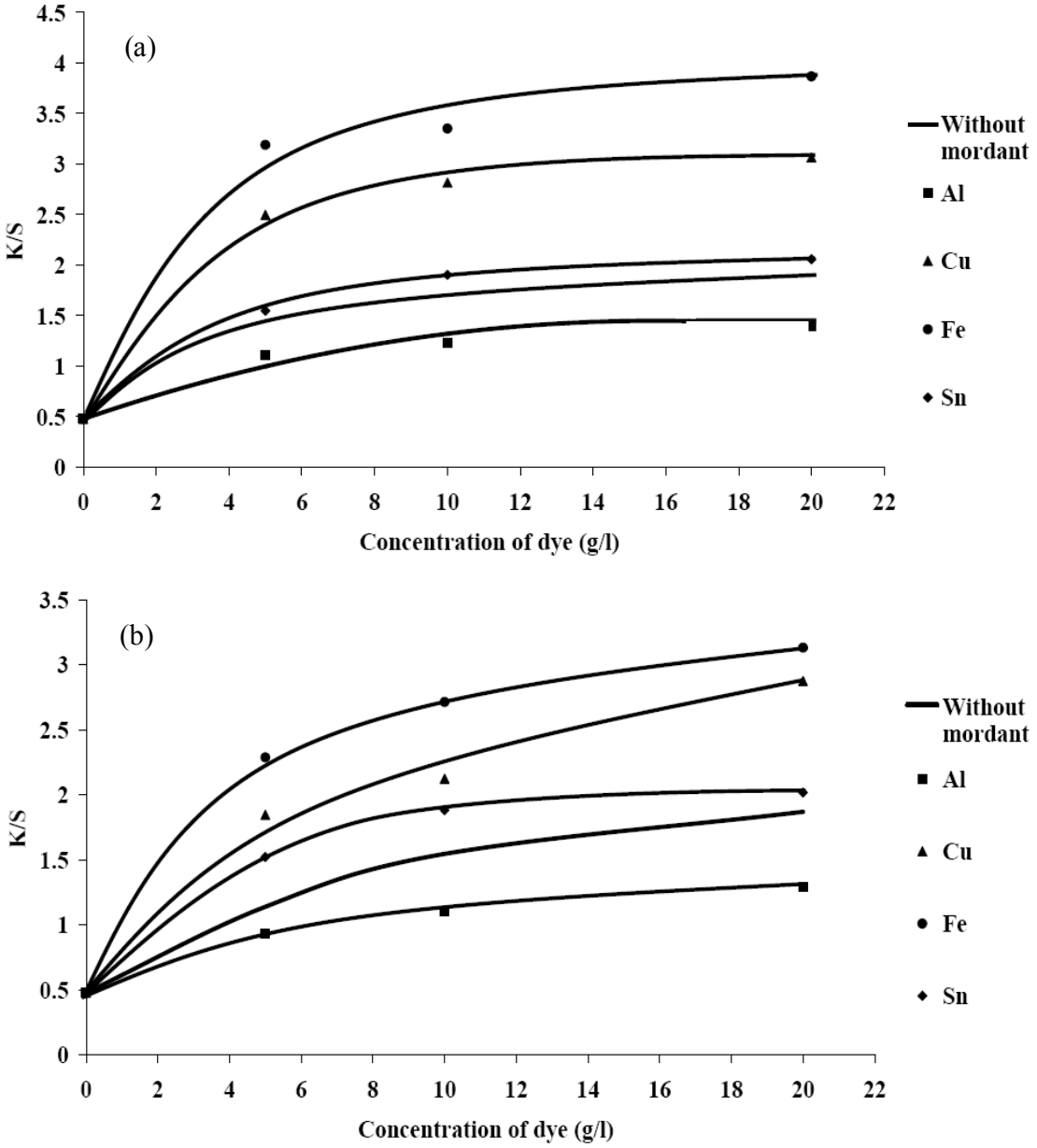


Figure 5.14 Effect of dye concentrations on *K/S* values of wool fabric dyed with 10 g/l mordants by post-mordanting and using (a) pad-batch technique (b) pad-dry technique

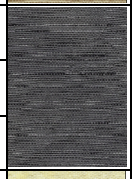
5.6 Dyeing property of silk and wool fabrics dyed with eucalyptus leaf extract using padding techniques. Effect of quantity of mordant concentrations, time/ temperature on pad-dry and batching time on pad-batch

Tables 5.11 and 5.12 show the colour values of silk and wool fabrics dyed with eucalyptus leaf extract by varying quantity of mordant concentrations. All measured sample showed the greatest λ_{max} value at 400 nm. It can be seen that the *K/S* values in Figure 5.15 and Figure 5.16 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, the absorption of colour by wool and silk fabrics were enhanced by using metal mordants.

Table 5.11 Colour value of silk fabric dyed with eucalyptus leaf extract by simultaneous mordanting and padding techniques and using 20 g/l of dye concentration at different concentration of the mordant

Type of mordant	**Conc. (g/l)**	**Pad-batch on silk fabric**					**Pad-dry on silk fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	-	0.75	84.5	2.8	8.3		0.75	84.5	2.8	8.3	
$AlK(SO_4)_2$ (Al)	5	0.91	87.2	-0.1	11.1		0.99	86.1	-0.3	13.9	
	10	1.35	82.1	-0.2	16.9		1.60	82.0	-0.5	18.1	
	20	2.22	79.0	-0.4	23.3		2.53	77.1	-0.8	24.3	
$CuSO_4$ (Cu)	5	1.73	70.6	4.4	13.2		1.70	71.3	4.4	14.8	
	10	3.02	64.5	5.7	18.6		3.09	63.8	6.0	18.6	
	20	3.76	63.0	6.0	23.8		3.79	62.4	6.3	22.4	
$FeSO_4$ (Fe)	5	3.64	40.0	3.3	-5.2		3.78	39.0	3.1	-6.1	
	10	4.04	39.3	2.8	-4.4		4.05	38.7	2.8	-5.1	
	20	5.48	35.0	1.7	-3.9		5.56	34.8	2.1	-4.2	
$SnCl_2$ (Sn)	5	0.78	89.3	0.2	6.8		0.79	89.9	0.2	6.8	
	10	1.33	87.0	1.0	12.5		1.48	86.2	0.9	14.4	
	20	1.85	84.6	0.6	18.4		1.90	83.2	0.7	22.1	

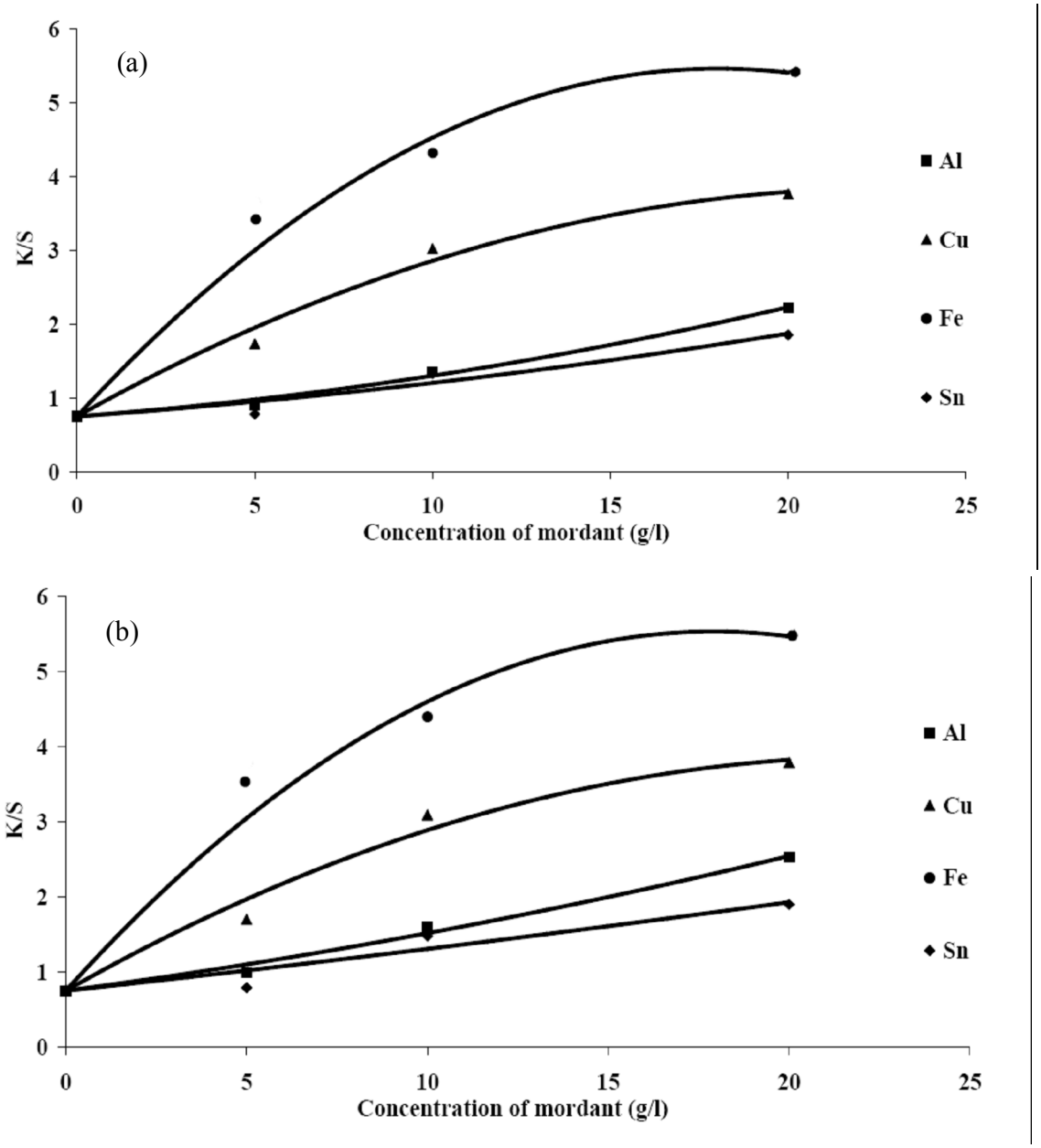


Figure 5.15 Effect of mordant concentrations on *K/S* values of silk fabric dyed with 20 g/l eucalyptus leaf extract by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

Table 5.12 Colour value of wool fabric dyed with eucalyptus leaf extract by simultaneous mordanting and padding techniques and using 20 g/l of dye concentration at different concentration of the mordant

Type of mordant	**Conc. (g/l)**	**Pad-batch on wool fabric**					**Pad-dry on wool fabric**				
		K/S	***L****	***a****	***b****	**Dyed sample**	***K/S***	***L****	***a****	***b****	**Dyed sample**
Without mordant	-	1.86	75.4	3.5	15.8		1.86	75.9	3.4	15.8	
$AlK(SO_4)_2$ (Al)	5	2.18	76.2	0.5	28.2		2.09	77.8	0.8	28.0	
	10	2.55	74.9	0.7	29.9		2.60	74.5	1.0	29.1	
	20	3.91	72.8	1.0	32.1		3.97	72.0	1.2	31.6	
$CuSO_4$ (Cu)	5	3.84	61.3	2.4	20.9		3.80	62.4	2.3	20.2	
	10	4.12	59.6	2.7	21.1		4.08	60.0	3.3	19.0	
	20	5.00	54.4	2.8	23.1		4.87	55.7	3.2	20.1	
$FeSO_4$ (Fe)	5	4.81	40.0	1.0	-0.9		4.95	39.1	1.1	-0.6	
	10	4.98	38.5	1.2	-1.1		5.14	37.0	1.0	-0.9	
	20	7.28	36.9	0.7	-1.4		7.60	36.0	0.9	-0.7	
$SnCl_2$ (Sn)	5	2.64	83.3	-1.6	32.2		2.66	83.1	-2.3	31.8	
	10	2.67	83.4	-1.2	30.4		2.71	82.5	-2.4	30.4	
	20	3.11	81.8	-2.1	35.3		3.13	81.4	-2.7	34.6	

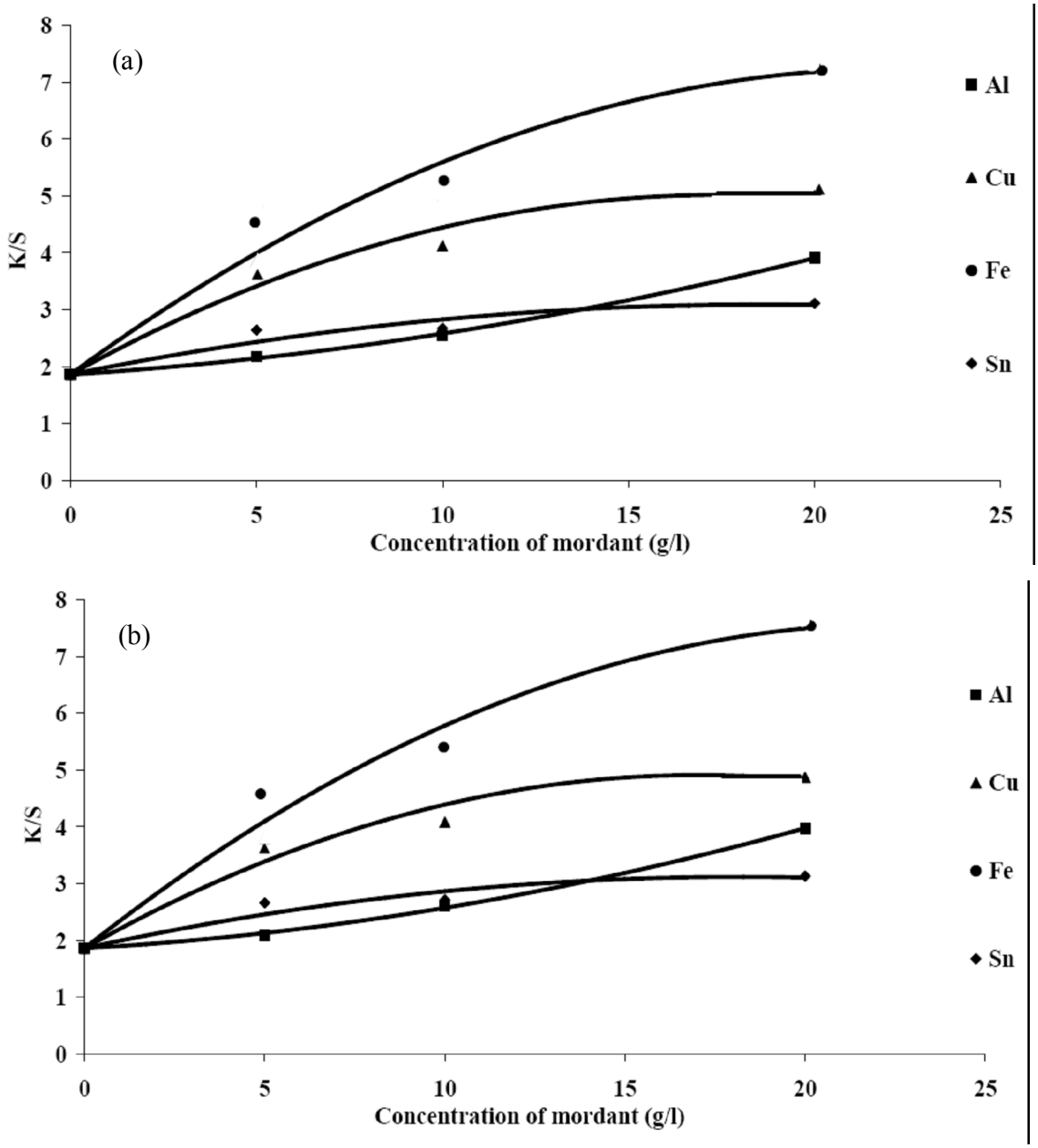


Figure 5.16 Effect of mordant concentrations on *K/S* values of wool fabric dyed with 20 g/l eucalyptus leaf extract by simultaneous mordanting and using (a) pad-batch technique (b) pad-dry technique

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 [153]. 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 [153].

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°C, 60°C and 90°C for 1, 3, 5 and 10 minutes; The *K/S* values obtained are shown in Figure 5.17. 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.

A study of Figure 5.17 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 5.18 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.

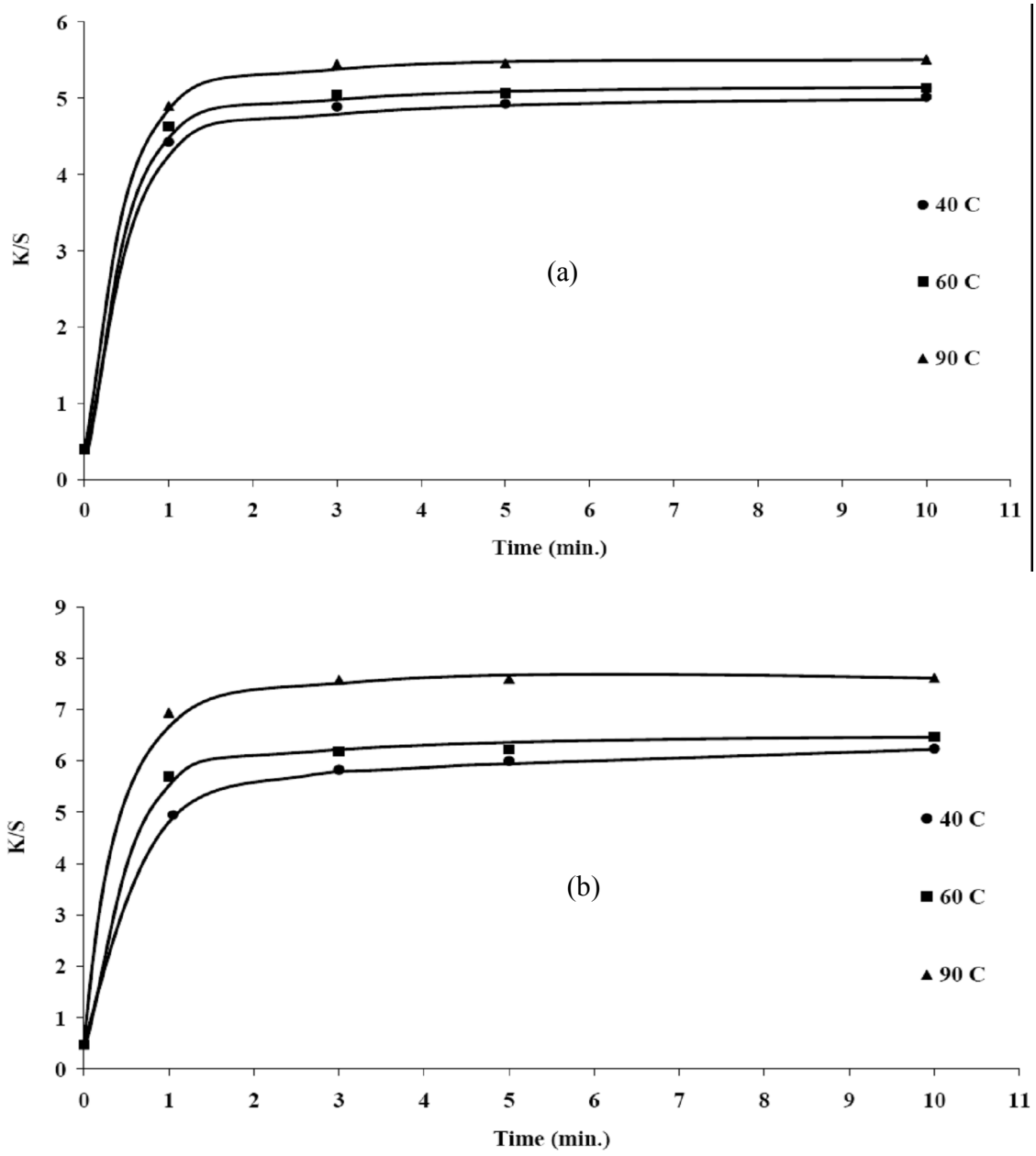


Figure 5.17 Effect of drying time and temperature of pad-dry technique on the colour strength (*K/S* values) of (a) silk fabric and (b) wool fabric dyed with 20 g/l eucalyptus leaf extract and using 20 g/l ferrous sulfate by using simultaneous mordanting

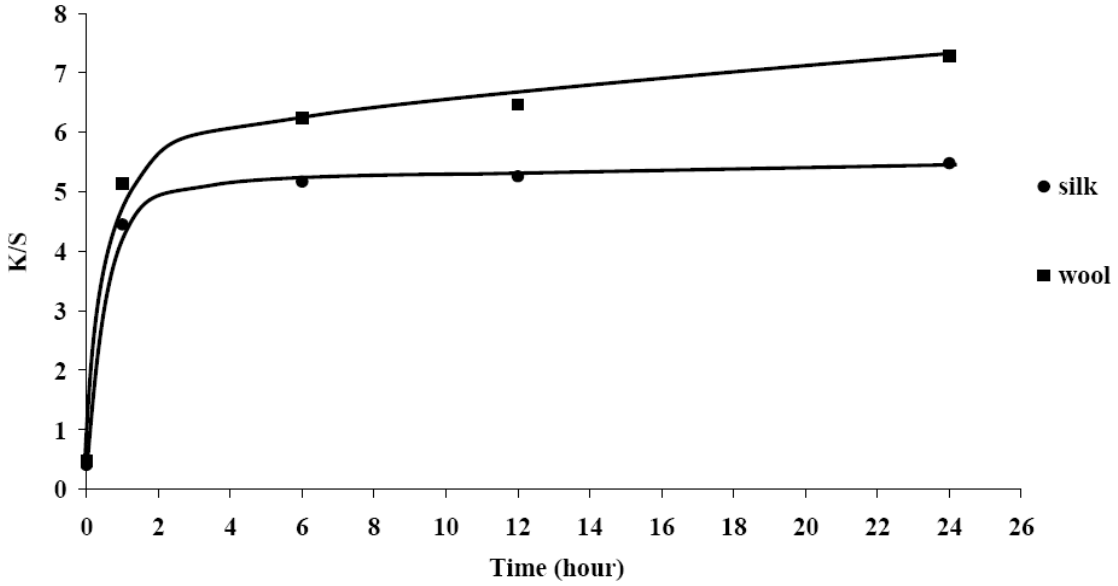


Figure 5.18 Effect of batching time of pad-batch technique on the colour strength (*K/S* values) of silk and wool fabric dyed with 20 g/l eucalyptus leaf extract and using 20 g/l ferrous sulfate by using simultaneous mordanting

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

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 5.13 and 5.14, 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).

Table 5.13 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 5.14 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

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 [35] 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 [154], 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 [35], would seem to be less probable.

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

5.8.1 The UV-visible spectra

The UV spectra of the crude eucalyptus leaf extract dye and the tannin (in an aqueous solution) are presented in Figure 5.19. 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 [150]. Absorption in the 250 nm to 285 nm regions is attributed to electronic transition of benzene [150].

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 5.20). Absorption band II is considered to originating from the $\pi \rightarrow \pi^*$ transitions for the benzene system in the A ring in Figure 2.16, whereas absorption band I is attributed to transitions in the B ring for the cinnamoyl system [155, 156, 157].

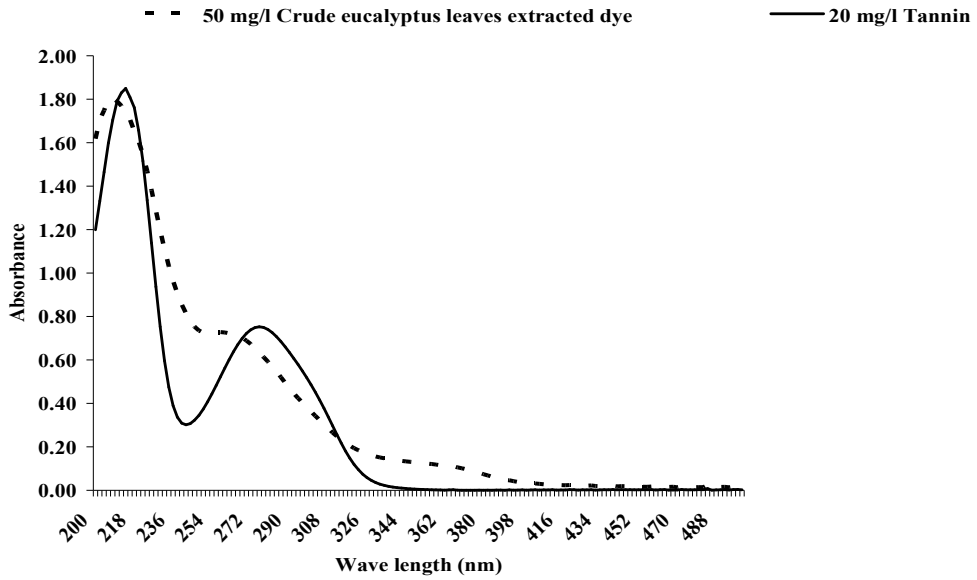


Figure 5.19 UV-VIS spectra of 50 mg/l crude eucalyptus leaf extract dye and 20 mg/l tannin in distilled water.

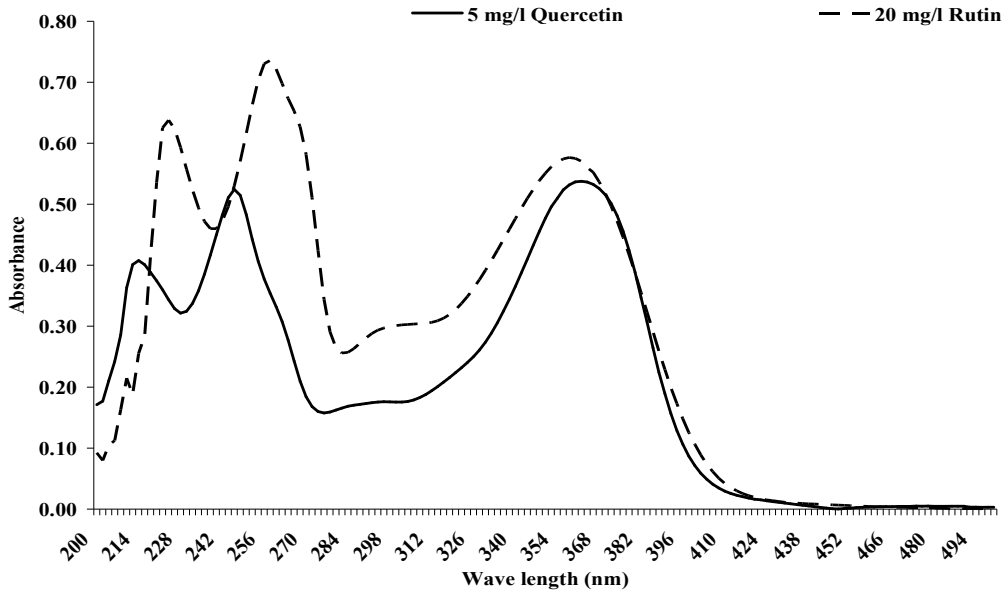


Figure 5.20 UV-VIS spectra of 5 mg/l quercetin and 20 mg/l rutin in methanol.

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

The colour value results are presented in Table 5.15. 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 Table 5.15, 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 5.21 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 5.22 [158-161].

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 [153]. 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.

Table 5.15 Colour value of wool fabric dyed with eucalyptus leaf extract, quercetin, rutin and

tannin dye by using simultaneous-mordanting and pad-dry technique

Type of dye	$FeSO_4$ conc. (g/l)	Dye concentration (2 g/l)					Dye concentration (5 g/l)				
		K/S[1]	*L**	*a**	*b**	Dyed sample	*K/S*[1]	*L**	*a**	*b**	Dyed sample
Euca-lyptus	without	0.94	75.6	2.5	11.8		1.07	75.6	2.5	11.8	
	2	2.00	59.0	1.3	7.9		2.82	47.2	1.1	0.9	
	5	2.20	57.6	1.9	10.0		3.32	45.7	1.2	1.9	
	10	2.60	55.1	1.4	8.8		3.53	44.6	1.2	1.7	
Querce-tin	without	3.80	74.2	-2.1	28.1		4.43	73.6	-2.1	30.1	
	2	4.62	48.6	3.0	16.9		5.40	45.4	3.1	16.3	
	5	5.47	45.4	2.9	16.8		6.67	40.7	2.4	15.6	
	10	5.73	45.0	2.9	16.8		6.98	39.2	2.5	14.8	
Rutin	without	0.98	78.0	-1.8	15.4		1.03	78.4	-1.6	16.1	
	2	4.44	52.5	2.3	16.9		5.22	49.8	2.1	16.5	
	5	5.28	51.1	3.0	19.1		5.65	48.4	2.3	16.8	
	10	5.44	50.7	2.6	17.7		5.70	47.7	2.2	15.9	
Tannin	without	0.76	77.1	1.9	9.5		0.82	77.1	1.7	9.9	
	2	2.57	45.9	1.7	-1.2		2.87	43.1	2.1	-2.0	
	5	2.89	43.8	1.4	-1.7		3.34	39.6	1.9	-2.9	
	10	3.04	42.8	1.6	-1.8		3.95	37.1	1.8	-3.0	

Note: [1] All measured sample showed the greatest λ_{max} value at 400 nm.

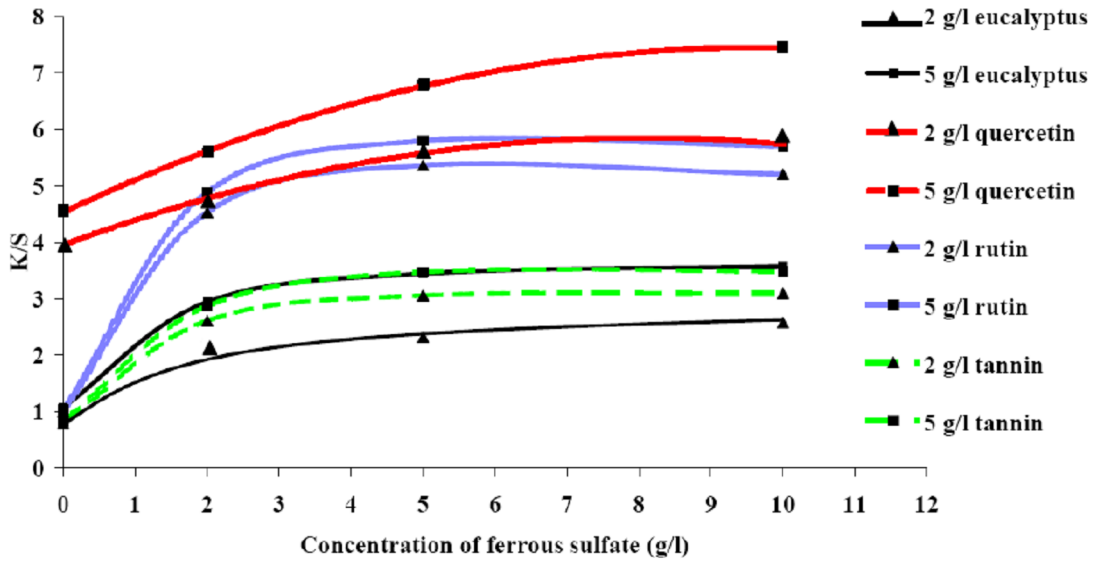


Figure 5.21 The *K/S* values of dyed wool fabric with eucalyptus leaf extract, quercetin, rutin and tannin dye by varying concentration of dyes and ferrous sulfate

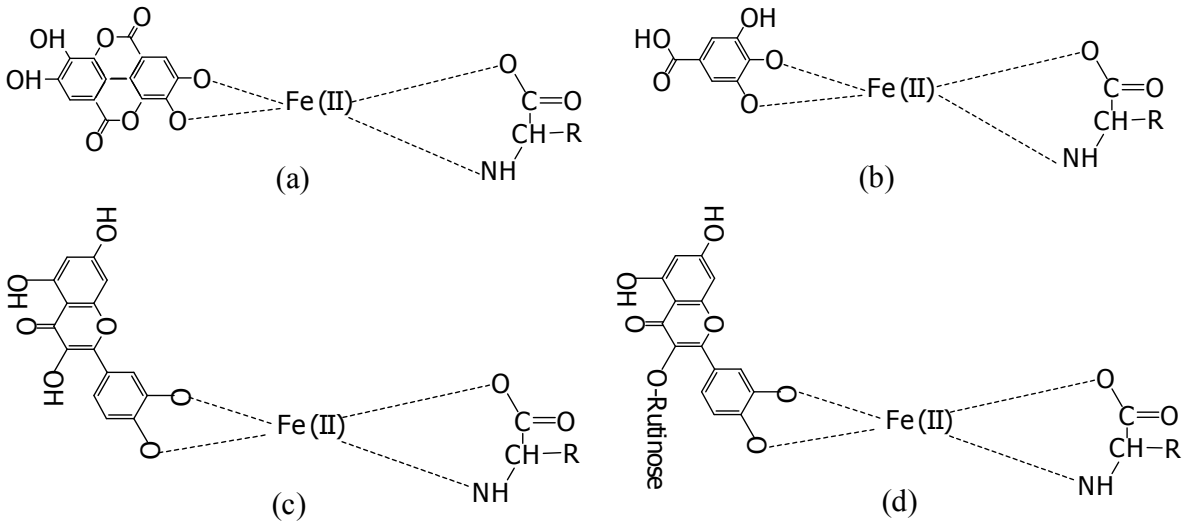


Figure 5.22 The proposed structure of Fe (II)/ dyestuff/ wool complexation (a) ellagic acid (b) gallic acid, (c) quercetin and (d) rutin

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 fabric but also because

of the *K/S* similarities and absorption spectra similarities of eucalyptus leaves extracts and tannin solutions.

5.8.3 The colour fastness properties

The fastness ratings of wool fabric dyed with and without mordants at a dye concentration of 5 g/l and ferrous sulfate (10 g/l) are presented in Tables 5.16 to 5.19. Table 5.16 indicates that 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.

As seen in Table 5.17, 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 [9]. 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 [9].

From Table 5.18, 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 [162-164].

Table 5.16 Colour fastness to washing at 40°C (ISO 105-C06 A1S: 1994)

Dyeing and	Colour	Colour staining of adjacent fibers

		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
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

Note: Fe = $FeSO_4$

Table 5.17 Colour fastness to light (ISO 105-B02: 1994)

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

Table 5.18 Colour fastness to rubbing (ISO105- X12: 2001)

	Warp direction	Weft direction
	Colour staining	Colour staining

conditions	Colour staining		Colour staining	
	Dry	Wet	Dry	Wet
Eucalyptus	4-5	4-5	4-5	4-5
Eucalyptus + Fe	4	3-4	4	3-4
Quercetin	4-5	4-5	4-5	4-5
Quercetin + Fe	3-4	3	3-4	3
Rutin	4-5	4-5	4-5	4-5
Rutin + Fe	4	3-4	4	3-4
Tannin	4-5	4-5	4-5	4-5
Tannin + Fe	3	2	3	2

Note: Fe = $FeSO_4$

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

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 5.23 and Figure 5.24. 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 [117]. Additionally, the colour and colour depth of the fabric can be related to UV transmittance, with light colours transmitting more UV than dark colours [165].

Table 5.19 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.

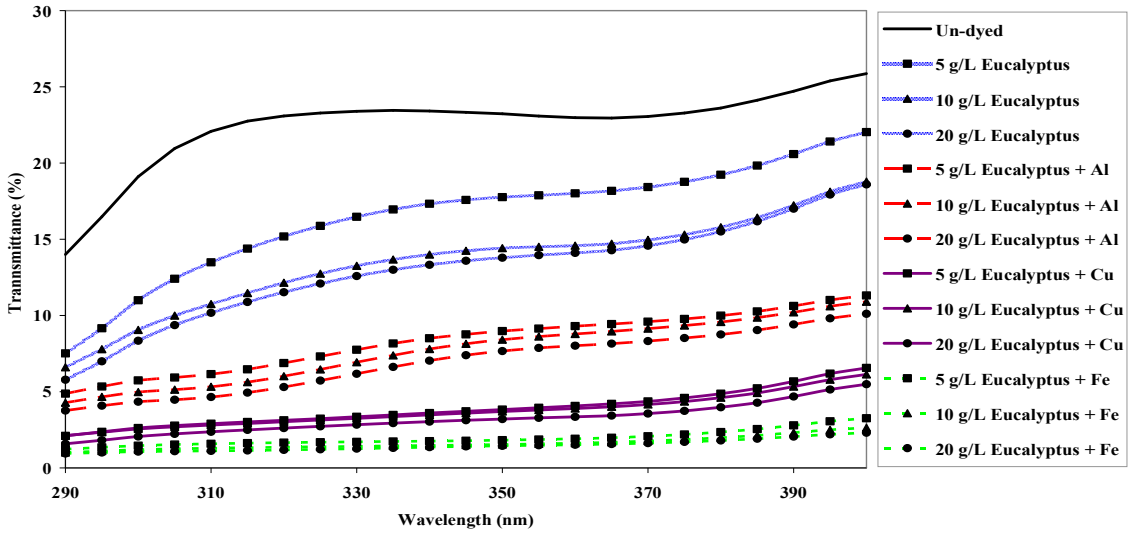


Figure 5.23 UV transmission of silk fabrics dyed with eucalyptus leaf extract in the absence and in the presence of metal mordants by the pad-dry technique Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$

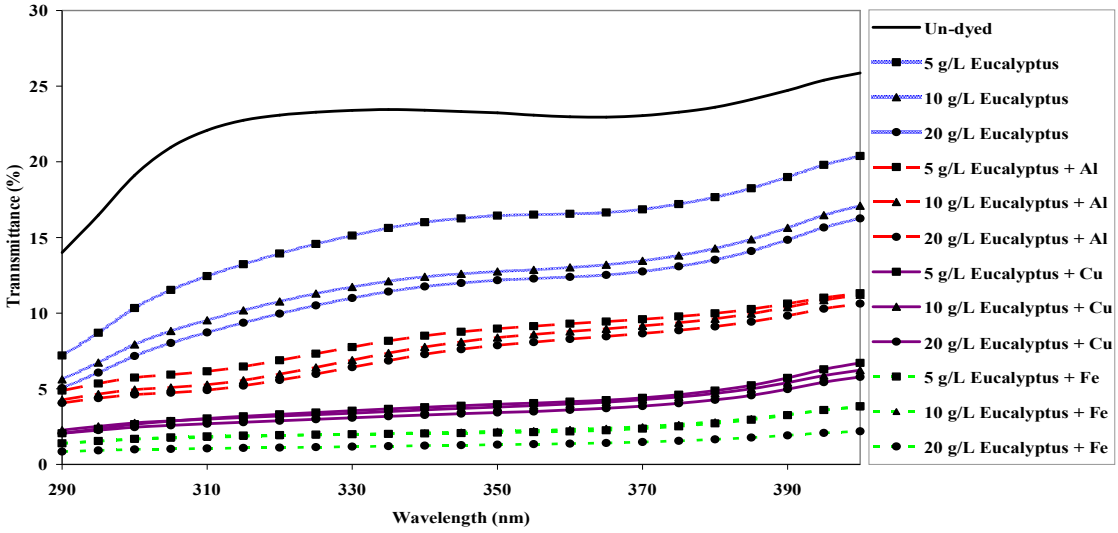


Figure 5.24 UV transmission of silk fabrics dyed with eucalyptus leaf extract in the absence and in the presence of metal mordants by the pad-batch technique
Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$

Table 5.19 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 [115], 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. [149] and Wilson et al. [165], who indicated that dyeing fabrics in deeper shades and darker colours improves their UV protection properties. Thus, although the studies by Gies et al. [149] and Wilson et al. [165] were done with synthetic dyes, their conclusion seems to hold with natural colourants as well. We also accept the results of Feng et al. [117], 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.

5.10 The fastness properties of silk and wool fabrics dyed with eucalyptus leaf extract

The fastness rating of silk and wool fabrics dyed with or without mordants are presented in Tables 5.20 to Table 5.25. 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. Table 5.20 indicates that 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), as shown in Table 5.21. 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, as shown in Table 5.22. 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), as shown in Table 5.23. 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 as seen in Tables 5.24 and 5.25.

Table 5.20 Colour fastness to washing at 40ºC (ISO 105-C06 A1S: 1994)

Fabric/ Fastness	**Pad-batch**					**Pad-dry**				
	With-out	**Al**	**Cu**	**Fe**	**Sn**	**With-out**	**Al**	**Cu**	**Fe**	**Sn**
Standard depths	1/25	1/25	1/12	1/12	1/25	1/25	1/25	1/12	1/12	1/25
Silk and wool fabrics										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Nylon	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Polyester	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$, Sn = $SnCl_2$

Table 5.21 Colour fastness to light (ISO 105-B02: 1994)

Fabric	**Pad-batch (Colour change)**					**Pad-dry (Colour change)**				
	Without	**Al**	**Cu**	**Fe**	**Sn**	**Without**	**Al**	**Cu**	**Fe**	**Sn**
Silk	3	3	4	3-4	3	3	3	3-4	4	3
Wool	3	3	3-4	4	3	3	3	3-4	3-4	3

Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$, Sn = $SnCl_2$

Table 5.22 Colour fastness to rubbing (ISO 105-X12: 2001)

Fabric/ mordant	Colour staining							
	Pad-batch				Pad-dry			
	Warp direction		Weft direction		Warp direction		Weft direction	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Silk								
without	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Al	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Cu	4-5	4-5	4	4-5	4-5	4	4-5	4
Fe	4	4	4	3	4	3	4	3
Sn	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Wool								
without	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Al	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5
Cu	4-5	4-5	4	4-5	4-5	4	4-5	4
Fe	4	4	4	3-4	4	3-4	4	3-4
Sn	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$, Sn = $SnCl_2$

Table 5.23 Colour fastness to water (ISO 105-E01: 1994)

Fabric/ Fastness	Pad-batch					Pad-dry				
	Without	**Al**	**Cu**	**Fe**	**Sn**	**Without**	**Al**	**Cu**	**Fe**	**Sn**
Silk fabric										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4	4	4	4-5	4	4	4	4	4-5	4
-Nylon	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5	4-5
-Polyester	4-5	4-5	4	4	4	4-5	4-5	4	4	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4
Wool fabric										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4	4	4	4	4	4	4	4	4	4
-Nylon	4-5	4-5	4	4	4-5	4-5	4-5	4	4	4-5
-Polyester	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4

Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$, Sn = $SnCl_2$

Table 5.24 Colour fastness to perspiration: acid (ISO 105-E04: 1994)

Fabric/ Fastness	Pad-batch					Pad-dry				
	Without	**Al**	**Cu**	**Fe**	**Sn**	**Without**	**Al**	**Cu**	**Fe**	**Sn**
Silk fabric										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4	4-5	4	4	4-5	4-5	4-5	4	4	4-5
-Nylon	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5
-Polyester	4-5	4-5	4	4	4-5	4-5	4-5	4	4-5	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4	4	4-5	4-5	4-5	4	4	4-5
Wool fabric										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4	4-5	4	4	4-5	4	4-5	4	4	4-5
-Nylon	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5
-Polyester	4-5	4-5	4	4	4-5	4-5	4-5	4	4	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5

Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$, Sn = $SnCl_2$

Table 5.25 Colour fastness to perspiration: alkaline (ISO 105-E04: 1994)

Fabric/ Fastness	Pad-batch					Pad-dry				
	Without	**Al**	**Cu**	**Fe**	**Sn**	**Without**	**Al**	**Cu**	**Fe**	**Sn**
Silk fabric										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4	4-5	4	4	4-5	4	4-5	4	4	4-5
-Nylon	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5
-Polyester	4-5	4-5	4	4	4-5	4-5	4-5	4	4-5	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4	4	4-5	4-5	4-5	4	4	4-5
Wool fabric										
Colour change	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
Colour staining										
-Acetate	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Cotton	4	4-5	4	4	4-5	4	4-5	4	4	4-5
-Nylon	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5
-Polyester	4-5	4-5	4	4	4-5	4-5	4-5	4-5	4-5	4-5
-Acrylic	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
-Wool	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	4	4-5

Note: Al = $AlK(SO_4)_2$, Cu = $CuSO_4$, Fe = $FeSO_4$, Sn = $SnCl_2$

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 [35].

5.11 Potential of eucalyptus leaves dye

5.11.1 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 [91]. 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.

5.11.2 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 [91]. 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* [90] and harda (*Chebulic myrabolan*) [91]. The avoidance of metal-based mordants, or their replacement by natural mordants, may assist in the preservation of the environment.

CHAPTER VI
CONCLUSION

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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LIST OF RELATED PUBLICATION

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[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. 285-286, 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, 26 th -28 th November 2007. pp. 211-215, ISBN: 978-80-7372-271-5.

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[5] Mongkholrattanasit, R., Kryštůfek, J., Wiener, J., and Viková, M. Dyeing, fastness, and UV protection properties of silk and wool fabrics dyed with eucalyptus leaf extract by exhaustion process. **FIBRES and TEXTILES in Eastern Europe**. 19 (3) (2011). ISSN: 1230-3666.

[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)