Application of Natural Dyes by Padding Technique on Textiles

A thesis submitted in fulfilment of the requirements
for the degree of

Doctor of Philosophy

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March 2013

Declaration

I, Saminathan Ratnapandian, certify that:

a) Except where due acknowledgement has been made, the work is that of the author alone.

b) The work has not been submitted previously, in whole or in part, to qualify for any other academic award.

c) The content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program.

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Saminathan Ratnapandian

Date 4.09.2013

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Acknowledgements

I express my deepest gratitude to my supervisors Associate Professor Dr Lijing Wang and Mr Stanley M. Fergusson for their continuous guidance, support and encouragement during all phases of my doctoral research. Dr Wang focused me on defining and describing a structured path towards my ultimate goal. Mr Fergusson shared his invaluable knowledge of textile colouration.

I place on record my heartfelt thanks to Associate Professor Dr Rajiv Padhye, Director, Centre for Advanced Materials and Performance Textiles, for his technical, administrative and moral support. I appreciate the input of Adjunct Professor Dr Max White during the initial stages of the research. I am grateful to Mr Keith Cowlishaw, Head of School, who kindly provided a clear path regarding all administrative matters.

I express my gratitude to Ms Fiona Gavens, Administrative Officer, for assisting, guiding and when needed chasing me down in regards to all administration related matters. I thank Mr Martin Gregory and Ms Geraldine Van Lint for ensuring the availability of laboratory resources.

Ms Trudy Orchard and Ms Fiona Greygoose from Textile Testing Services, deserve special mention for sharing their technical knowledge and graciously permitting the use of their facilities. I thank Mr Clive Skelchy and Ms Michelle Matheson from RMIT library, for ensuring that all available resources were made accessible for my research. I thank all the academic and non-academic staff at the RMIT Brunswick campus that helped me during my research. I am grateful to Dr Muthu Pannirselvam and Ms Zahra Homan from RMIT city campus for their technical input and time while permitting use of their laboratory.

I thank Dr Maryam Naebe, Deakin University, for her help in plasma treatment experiments. I appreciate the efforts of Ms Mary-Jo O’Rourke, Accredited Editor, for editing and proof-reading this work.

I am grateful for the financial support provided by RMIT University through the RUIRS scholarship and DVC (R&I) postgraduate research student international conference grant.

I am fortunate to have had a supportive peer group that included Dr Saniyat Islam, Mr Amit Jadhav, Mr Javid Jalvandi, Dr Sinnappoo Kanesalingam, Mr Farzad Mohaddes and Dr Rajkishore Nayak. I thank them for their camaraderie, constructive criticism and enthusiastic encouragement.

Last but not least, my wife, S. P. Vijayaraanee, deserves a special note of thanks for her love, encouragement, understanding and support. I could not have carried out my research without the love and sacrifice of my parents-in-law and I am indebted to them. I am grateful for the fond memories of my daughters who found it funny that, just like them dad was also going to school.

Contents

List of figures

List of tables

Abstract

This thesis presents the findings from investigations into adapting the pad-dyeing process for dyeing cotton and wool using natural dyes. The aim was to apply traditional dyes employing current and emerging technologies of textile colouration. The scope of this research was to add to the knowledge regarding continuous dyeing methods for natural dyes with an ultimate goal of large-scale sustainable colouration.

The growing niche market for sustainable products is prompting the reintroduction of natural dyes on a commercial scale. However, the dominance of synthetic dyes for the past 150 years has stifled in-depth studies on industrial-scale use of natural dyes. Hobbyists and craftspeople, a minority, who continue to use natural dyes for textile colouration, adhere primarily to the conventional home-scale exhaust dyeing method. Such methods are not readily compatible with commercial application methods. Hence, this work was undertaken to explore the continuous dyeing method of padding for the application of natural dyes.

Two prominent classes of natural dyes namely mordant dyes (represented by dyes derived from Acacia *catechu* and Acacia *nilotica*) and vat dyes (Indigofera *tinctoria*) were evaluated.

The work on mordant dyes focused on determining optimal process parameters such as padding sequence, mordanting method and mordant concentration. Copper (II) sulfate and iron (II) sulfate, two widely used mordants, were employed in the research. Among the three possible mordanting methods, post-mordanting was found to yield the darkest shades for both mordants. A process sequence of *pad (dye) → dry → steam* followed by *pad (mordant) → steam → dry* resulted in the deepest shades when copper (II) sulfate was the mordant, while for iron (II) sulfate it was *pad (dye) → steam → dry* followed by *pad (mordant) → steam → dry*. A distinct shade of beige was obtained on mordanting with copper (II) sulfate while iron (II) sulfate yielded a yellow-grey shade. Ideal mordant concentration required for a 10 g/l dye concentration was either 15 g/l copper (II) sulfate or 5 g/l iron (II) sulfate. These concentrations were lower than those recommended for both exhaust dyeing (5% on the weight of material) and padding (60

g/l) as reported in the literature. The results reported above were similar for both mordant dyes (Acacia *catechu* and Acacia *nilotica*).

In order to gain a better understanding of the functioning of mordant in the dyeing process, the dyes, mordants and dyed fabrics were analysed using Atomic Absorption Spectroscopy (AAS) and Fourier Transform Infra-Red (FTIR) spectroscopy. AAS revealed the absorption of a significantly higher amount of metal by the dyed fabric as compared to a mordanted fabric. This confirmed the formation of a dye-metal-textile complex during dyeing. The FTIR spectra were distinctly different for the dyes derived from Acacia *catechu* and Acacia *nilotica*. However, when the dyed samples, coloured using the above dyes in combination with the same mordant, were analysed, the differences between the spectra diminished. This indicated that metal plays a major role in defining the bonds created during dye-metal-textile complex formation. This may be the reason for the similarity in shades observed for the dyes evaluated.

Improvement to the optimised padding process was achieved by employing atmospheric pressure plasma pretreatment of the textile, or including chitosan in the pad liquor. Pure helium and a 95/5 helium/nitrogen mixture were evaluated as the plasma gas. Irrespective of the gas used or the duration of treatment, exposure to plasma improved the wettability of wool fabric. Wool treated in pure helium plasma for 14 seconds exhibited an increase of 30% in the depth of shade as compared to an untreated fabric, both pad-dyed with 10 g/l dye solution. A tone-on-tone pattern was created in a single padding operation by selective pretreatment of the fabric. Incorporation of 0.05% chitosan in the pad liquor for cotton resulted in a 20% darker shade and imparted antimicrobial properties to the dyed fabric. However addition of an excess quantity of chitosan inhibited dye uptake by the fabric.

Indigo was applied, at a concentration of 16 g/l, on cotton by the vat dyeing process of *pad (dye) → dry → pad (reducing chemicals) → steam*. Sodium dithionite and sodium hydroxide, the common reducing agent and alkali employed in the exhaust dyeing of indigo, were replaced by thiourea dioxide (TUD) and sodium carbonate respectively. The advantage of TUD is its thermal stability in comparison to sodium dithionite. This made the dyeing process easy to control and avoided the effluent problems associated with sodium dithionite. Sodium carbonate, being a milder alkali than sodium hydroxide, poses reduced handling and disposal issues.

Experiments on colouration with indigo were conducted in two stages. First, the alternate reducing agent (TUD) was used in combination with sodium hydroxide to reduce the indigo. In the next stage, both reducing agent and alkali were replaced. The shade obtained in both cases was equivalent to that obtained by exhaust dyeing of a 1.5% shade of indigo. When TUD was used in the presence of sodium hydroxide, a steaming time of 90 seconds was sufficient to reduce the natural indigo and produce the darkest shade. However, when the alkali was also substituted, a prolonged steaming of up to 6 minutes was necessary. This increase may be due to the higher reaction energy requirements for sodium carbonate as compared to sodium hydroxide. A comparison between samples dyed using natural and synthetic indigo by the alternative chemicals indicated that the former produced a darker shade. This may be due to the higher reactivity of the less crystalline natural indigo.

Similar experiments were conducted on ‘table strike-off’ trials using a K-Bar hand coater that simulated screen printing. Cotton fabric printed with an indigo-containing paste was dried. The dried fabric was padded in a reducing bath containing either TUD and sodium hydroxide or TUD and sodium carbonate and then steamed for durations equal to that followed for dyeing. The results differed in that an equivalent shade was not obtained, neither between natural and synthetic indigo nor between the two alkalis. Overall, the darkest shade was produced by synthetic indigo reduced in the presence of sodium hydroxide. Natural indigo yielded a shade 20% lighter than synthetic indigo. The discrepancy in results between printing and dyeing may be attributed to the interference by the print paste thickener on the diffusion of the reduced indigo into the fabric.

The outcome of the research is a clear indication that natural dyes can be used in conjunction with current continuous dyeing practices. The reaction between natural dye, mordant and textile is unique and optimum combinations have to be determined in each case. The role of the mordant is critical in regards to the final shade and, as seen in this investigation; similar shades may be obtained from dyes derived from different plants. Judicial use of plasma treatment and chitosan can produce darker shades for a given amount of dye, leading to a cleaner production process. Any consequent benefit opens additional markets for the dyed materials. Colouration with indigo by the vat dyeing method and the use of alternate reduction chemicals increases process control while lowering the impact on the environment.

Research output from this thesis work

Publications

1. Ratnapandian, S., Islam, S., Fergusson, S. M., Wang, L. and Padhye. R., "Colouration of cotton by combining natural colorants and bio-polysaccharide," *The Journal of the Textile Institute*, DOI:10.1080/00405000.2013.797143, 2013.
2. Ratnapandian, S., Fergusson, S. M. and Wang, L., "Application of Acacia natural dyes on cotton by pad dyeing," *Fibers and Polymers*, vol. **13** (2), pp. 206–11, 2012.
3. Ratnapandian, S., Fergusson, S. M., Wang, L. and Naebe, M., "Effect of atmospheric plasma on pad-dyeing natural dyes on wool," *Journal of Fiber Bioengineering and Informatics*, vol. **4** (3), pp. 267–76, 2011.
4. Ratnapandian, S., Fergusson, S., Wang, L., and Padhye, R., Chapter 4 Indigo Colouration, in "Dyeing: Processes, Techniques and Applications", Nova Science Publishers, Inc. (in production),2013.

Conference papers

1. Ratnapandian, S., Fergusson, S. M., Wang, L. and Padhye, R., "An innovative approach to indigo dyeing," presented at TBIS conference, Shinshu University, Ueda, Japan, 2012.
2. Ratnapandian, S., Fergusson, S. M., Wang, L. and Padhye, R., "Sustainable developments in printing cotton fabric with indigo," presented at 88th Textile institute world conference, Shah Alam, Malaysia 2012.
3. Islam, S., Ratnapandian, S., Padhye, R., Wang, L., and Arnold, L., "Sustainable colouration of cotton fabrics utilizing chitosan and natural dyes," presented at APSCEET 2011 (8th Asia-Pacific conference on sustainable energy& environmental technologies), Adelaide, 2011.
4. Ratnapandian, S., Fergusson, S. M., Wang, L. and Naebe, M., "Effect of atmospheric plasma on pad-dyeing natural dyes on wool," presented at TBIS conference, Beijing, China 2011.

Chapter 1
Introduction

1.1 Introduction

Humanity has progressed from the stone age to the information age and is now making deep inroads into the environment age [1]. This is characterised by increasing awareness regarding the effect of human interaction, both short and long term, with the environment. The extrapolated detrimental effect has evoked the need to conserve and protect our fragile environment. The growing public awareness has been expressed through an expanding premium market for goods and services that carry ‘natural’ or ‘eco-safe’ or ‘green’ or similar labels [2, 3]. Extensive research and development in science and technology are underway in order to satisfy this need. This provides an excellent focus point for the textile industry.

The textile colouration sector uses dyes (colouring matter), chemicals (whose reaction ensures the colouring of textiles) and auxiliaries (chemicals that promote colouration) in addition to consuming large quantities of water. Unfixed dye, spent chemicals and auxiliaries and water not picked up by the fibre material are collectively discharged at the end of colouration as effluent. Marine life would be adversely affected if these effluents, usually coloured, were discharged without treatment into the water body [4]. Further, such effluents affect riverbeds, soil and crops [5, 6]. This intimate relationship with the environment offers textile colouration the maximum scope for capitalising on the eco-conservation trend [7, 8].

Several authors [9-12] summarize the efforts of the colouration industry in embracing eco-conservation as:

1) reducing the quantity of consumables by increasing process efficiency and reclaiming and reusing resources such as chemicals, water and energy
2) using materials and processes with a lower environmental impact; and
3) increasing the use of renewable resources such as natural fibres (silk, cotton and wool) and natural dyes.

This thesis contributes to the above effort by investigating the application of natural dyes employing the pad-dyeing process on cotton and wool. A comprehensive approach was adopted by evaluating either the use of plasma pre-treatment or the inclusion of chitosan for improving dye uptake during padding. On another front, the use of comparatively benign auxiliaries was studied. In order to understand the scope of this research, a brief introduction to textile colouration is given below.

1.2 Textile colouration

The primary objective of colour in textiles is enhancing aesthetic appeal. In addition, colour serves diverse purposes such as identification (uniforms), warning (safety and survival vests) and mark of status (religious robes). It even marks stages of life (white wedding gowns and bereavement black, in many Western cultures) [13]. Hence, textile colouration is of great importance and has developed into an art and science [11, 14, 15]. Most textile materials acquire the desired colour(s) by the application of appropriate dyes.

1.2.1 Dyes

Dyes are complex chemicals that are absorbed by and react with suitable substrates to yield a coloured product. There are two broad dye categories based on origin, namely natural dyes and synthetic dyes. Burdett [16] credits J. W. Slater with publishing the first book in 1870 that provided comprehensive data on dyes and pigments used in textile colouration. This collection of data has gone through various stages and finally emerged as the globally recognised Colour Index (CI) published jointly by the Society of Dyers and Colourists (SDC) and American Association of Textile Chemists and Colorists (AATCC). The index scientifically classifies the wide variety of dyes based on chemical structure, colour, application methods, fastness properties, manufacturer, synthesis route and date invented [12]. Fastness properties refer to the resistance to fading of a coloured textile on exposure to different environmental conditions during its normal usable life.

1.2.1.1 Synthetic dyes

Present day industrial dyes are termed *synthetic dyes* because they are synthesised or manufactured to specifications. Raw materials used are generally petroleum derivatives. A wide range of low-cost dyes, whose properties can be modified as needed, are produced by this US$16.2 billion global industry [17]. The standardized manufacturing processes make the application methods and dyeing results repeatable and consistent [14, 15]. Consequently, high performance standards and appropriate evaluation techniques have been developed for dyed products [18, 19]. The various synthetic dye classes shown in Figure 1.1 are briefly described below.

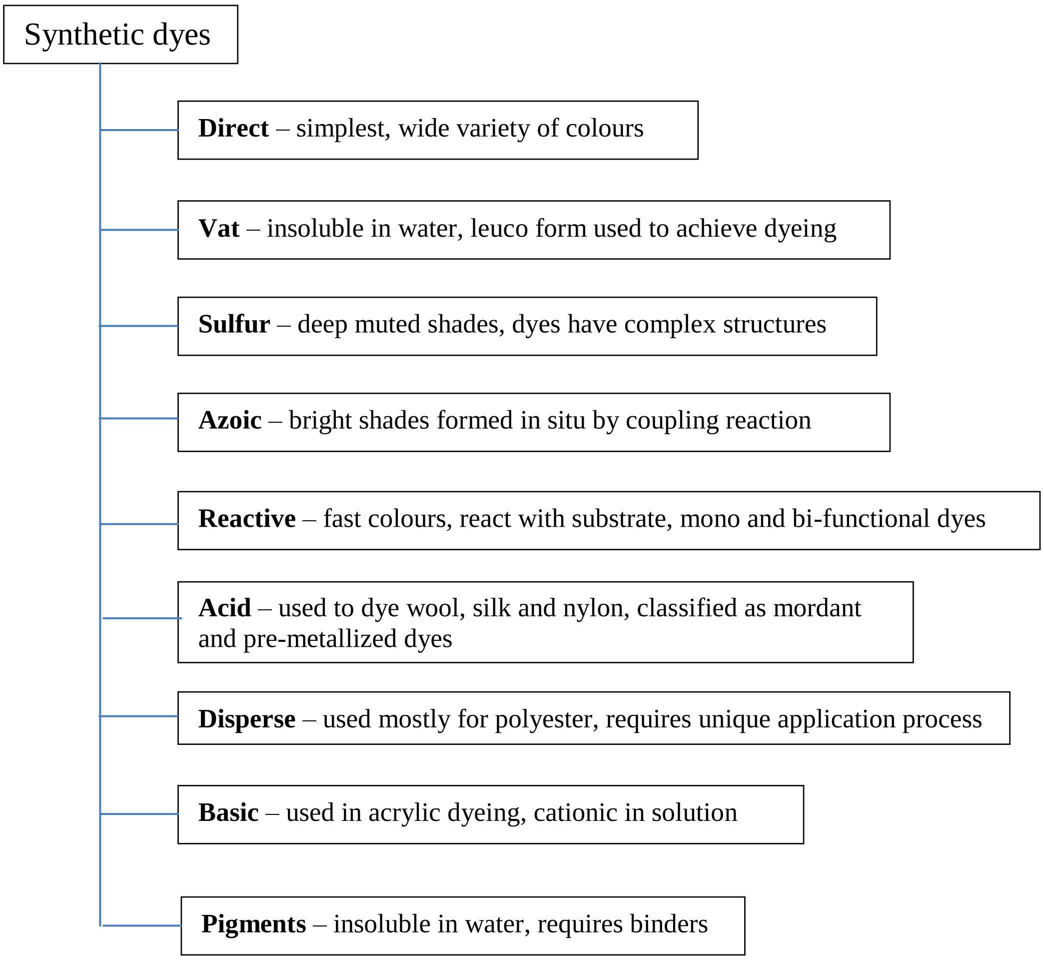


Figure 1.1 Classification of synthetic dyes

Direct dyes

These are relatively cheap and easy to apply. They provide a wide range of colours primarily for dyeing cotton. Starting from Congo Red (CI Direct Red 29), the first *direct* dye, these dyes can colour cotton directly from a dye-bath containing sodium chloride without the assistance of a mordant [20]. Mordant, a metallic salt, was considered essential for dyeing cotton using natural dyes [21]. This class of dye is sub-divided based on chromophore, fastness properties and application methods. The main drawback of these dyes is their moderate wet fastness.

Vat dyes

These dyes are usually insoluble in water. The typical presence of two carbonyl (C=O) groups permits the formation of a corresponding soluble leuco-compound by reduction under alkaline conditions. Cotton can be dyed under these conditions and in the subsequent oxidation step the dye is regenerated inside the fibre. This results in high light and wash fastness [11].

Sulfur dyes

These have complex structures obtained by the thionation of various aromatic intermediaries. Deep, muted shades with good wet fastness and moderate to good light fastness can be obtained using sulfur dyes. The Colour Index identifies different classes of sulfur dyes based on their solubility [11].

Azoic dyes

These are dyes formed in situ in the fibre by the interaction of a diazonium compound with a coupling compound. Bright shades especially in the orange-scarlet-red regions can be obtained by the use of these dyes [12].

Reactive dyes

These dyes are formed by either Michael's addition reaction involving vinyl sulfone groups or nucleophilic substitution reaction of halogen-o-heterocyclic groups [22]. If only one reactive group is present the dye is a *mono-functional* reactive dye, and if two groups are evident, then it becomes a *bi-functional* reactive dye. A bi-functional dye having two similar reactive groups is homo-bi-functional and if they are different then it is hetero-bi-functional. Dye hydrolysis, that is, the reduction in dye effectiveness by its reaction with water, a major drawback of reactive dyes, is minimized in the bi-functional class. These dyes react with the fibre, resulting in high substantivity [14].

Acid dyes

These are dyes primarily used to colour nylon, wool and silk under acidic conditions. The low number of reaction sites in nylon results in a poor colour yield. This is rectified by the formation of metal-complexes by mordanting, which is the application of metallic salts in a separate step or by using pre-metallized dyes. In the case of pre-metallized dyes, the metal is incorporated in the dye molecule during manufacture. Depending on the number of dye molecules attached to a metal atom, they are classed as 1:1 or 1:2 metal complex dyes. The dyes exhibit high saturation values, compatibility in mixed shades and good light and wet fastness properties [23].

Disperse dyes

These non-ionic, insoluble or sparingly soluble dyes are applied to hydrophobic fibres, generally from an aqueous dispersion. They are used primarily to dye polyester, although they have been used for other fibres as well [24]. Dyeing is usually followed by a reduction-clear to prevent staining from the unfixed dye. Some unique methods are used for the application of disperse dyes.

Basic dyes

These dyes are special in that they form coloured cations in solution. They are used particularly to dye acrylic and paper. Their variable migration properties necessitate the use of special auxiliaries during dyeing [11].

Pigments

These are colouring matter that is insoluble in water with minimal or zero affinity to textile materials. Special techniques are used to print pigments onto textiles [25].

1.2.1.2 Natural dyes

The name *natural dye* applies to all colouring matter derived from natural sources, such as plants, animals and minerals. The use of natural dyes has been recorded across the globe since ancient times [10, 26]. They were the only dyes available and used until 1856 when Sir W. H. Perkin discovered the first synthetic dye “mauviene”, a basic dye [27].

The extraction process for natural dyes, although time-consuming and laborious, is fairly straightforward and involves no applied chemistry. The dyes are mostly derived from flora and fauna. This organic origin makes them readily susceptible to climatic changes and other natural variations. The result is either a) the textile acquires a unique shade for every batch or b) consistent and repeatable shades can be produced with difficulty only by a skilled and knowledgeable dyer. Similar to the multitude of colours present in nature, a wide variety of colours can be obtained using these dyes. Dye classification, which began on simple alphabetical order, is now in line with the directives of the Colour Index and is based on the parameters of structure, origin, application method and colour [10, 21, 28].

Natural dyes are broadly classified as adjective and substantive dyes based on their inherent affinity for textiles. Substantive dyes possess a high affinity for textiles. They may be classified as belonging to vat, acid, direct and pigment classes [21, 29]. However, a large number of natural dyes have low affinity and require the use of a mordant to fix the dye to textiles and hence are known as mordant or adjective dyes [30]. The word ‘mordant’ is derived from Latin *mordere* meaning ‘to bite’ because mordants were believed to eat away the surface or open up the pores in a fibre and thus facilitate dye absorption [31]. Mordants are now identified as chemicals that react with fibre and/or dye and thereby are able to fix the dye [28, 31]. The three broad classes of mordants are single or bi-metallic salts, tannins and oil mordants [29].

Most natural dyes form metal complexes with mordants and, according to the metal involved, each complex has a distinct shade [32-34]. This gives the *monogenetic* and *polygenetic* classification of natural dyes. As the names suggest, the first type of dyes yields only one shade while the second yields different colours according to the mordant employed [21]. Naturally occurring aluminium, copper, potassium and iron salts were the traditionally used mordants and are employed even today. Their quality, in terms of purity, affects the richness and durability of the shades obtained [28]. Purer salts and other metals such as tin and chromium were introduced with advancements in chemistry [35]. Health and environmental hazards posed by incorrect handling of some of these salts, chromium salts in particular have been identified. Hence, at present the most widely used metal salt mordants are aluminium sulfate, potash-aluminium sulfate, stannous (tin) chloride, copper (II) sulfate and iron (II) sulfate. At times, tannin-metal complexes and oil-metal complexes serve as mordants for other natural dyes [36]. In general, the presence of metal increases the fastness property of the dyed material by mechanisms such as dye aggregation (lake formation) and absorption of free-radicals [37].

The process of applying mordants or mordanting is classified into the following three types [30, 31]:

a) **Pre-mordanting** is where the textile material is first treated with the mordant and then dyed. Intermediate drying allows storage of the mordanted material and helps in absorption of the dye liquor. Printing with different mordants and then dyeing with a polygenetic dye to obtain a multicoloured pattern is an application of this method. The disadvantage of pre-mordanting is that prolonged storage can damage the textile if the metal salt is corrosive. In addition, the mordant can leach into the dye bath resulting in colour variations.

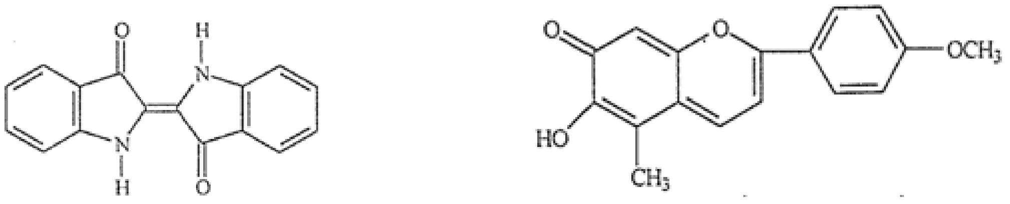
b) **Meta mordanting** involves a dye bath containing both dye and mordant. The fabric is dyed in one step. The major disadvantage is that the aggregation of dye-mordant complex in the dye bath interferes with the dyeing process. The large complex cannot be easily absorbed by the substrate resulting in uneven dyeing.
c) **Post mordanting** is a popular method for leather colouration. The mordant is applied after the dye has been applied. This method yields deeper penetration of the dye and a level shade. Prolonged storage of dyed fabric prior to mordanting has to be avoided in order to minimise loss of colour by fading or rubbing.

Although the function of a mordant is clear, the exact mechanism involved is difficult to identify [28]. The complexity of dye molecules hinders intimate understanding of the binding mechanism between dye and substrate or the precise role of the mordant in fixing the dye. Hence there is ongoing research in this area in terms of determining the optimum amount of mordant required and developing a theory that explains the precise role of the mordant.

Table 1.1 lists some typical colours obtained using natural colours and their plant sources. Plants yield the maximum variety of natural dyes. The dye can be derived from leaves, flowers, seeds, roots and bark. In certain instances, each of these parts of the same plant yield different colours [38, 39]. Other sources of natural dyes are naturally occurring metal salts termed mineral colours. Some examples are chrome-yellow, iron buff and mineral khaki. Tyrian purple is a well known colour obtained from shell-fish (Murex *brandaris*) while cochineal is obtained from insects (Dactylopius *coccus*). Lichen and fungi can also yield dyes but their slow rate of growth severely limits any commercial exploitation. Some of the important chemical groups present in natural dyes are given in Figure 1.2 [40].

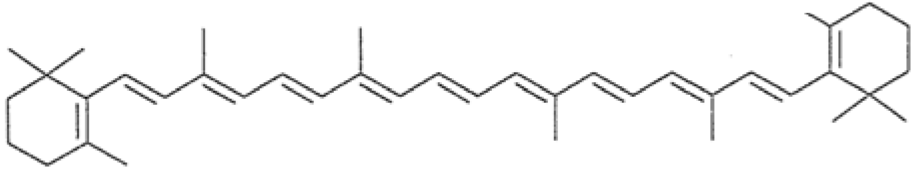
Table 1.1 Typical shades of natural dyes

Shade	**Source**	**Chemical group**
Blue	Indigofera *tinctoria*	indigo
Red	Caesalpinia *sappan*	anthocyanin
Yellow	Bougainvillea *glabra*	flavonoid
Green	Urtica *diacia*	chlorophyll
Black	Haematoxylum *campechianum*	tannins (Prorobinetidin & profisetininidin)
Brown	Acacia *catechu*	
Orange	Bixa *orellana*	carotenoid

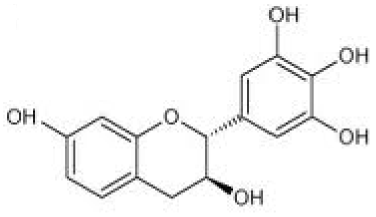


Indigo

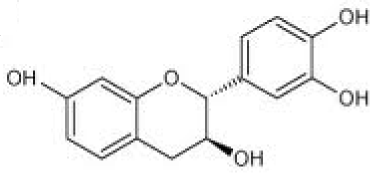
Anthocyanidin



Betacarotene



Prorobinetinidin



Profisetinidin

Figure 1.2 Typical chemical groups of natural dyes

Indigoid dyes

These are the blue dyes, especially indigo, derived primarily from the indigofera, isatis and polygonum species [13, 28]. Tyrian purple extracted from murex species of molluscs is another noted member of this group. These were the first vat dyes and are characterised by the two carbonyl (C=O) groups. The conversion to leuco-form was traditionally brought about by lengthy and inconsistent fermentation [10, 28, 29, 41-43].

Flavonoids

These are the largest group of natural dyes which are prominently yellow in colour. Luteolin is the primary colourant in these dyes. Weld, sawwort and fustic are some of the well known examples from this group. The fastness to light is typically poor as is evident from the fading of old tapestries [10].

Anthocyanins

These are water soluble flavonoids responsible for the red and blue colours of flowers and fruits. The colours are sensitive to pH and light. Their use as watercolours is well established [44]. In the case of anthocyanidins the glycosides of the anthocyanins are replaced by hydroxyl groups. Logwood is an excellent example of this class of dyes.

Carotenoids

These colourants are named carotenoids because they were initially isolated from carrots. Other common sources are tomatoes and sweet peppers while saffron and turmeric are exotic sources. A yellow to orange-red colour is obtained using these direct dyes [28].

Anthracenes

This class of dyes is extracted from plants (flowers, bark and roots), lichens and insects. The two main groups of this class are 1) anthraquinones with yellow, pink and red pigments [45]; and 2) napthoquinones with brown, pink or purple pigments [46]. Safflower, madder and cochineal are noted examples of this class of dyes.

Chlorophyll

This is the green pigment present in plants, algae and cyanobacteria that absorbs light energy during photosynthesis. Four types of chlorophyll have been identified although the commercial product is mainly made up of chlorophylls a and b. It is generally not used for textile colouration because of difficulties in application and browning on exposure to light, resulting in poor light fastness [29].

Tannins

This is the term introduced by Seguin in 1790 to describe plant extractions that can convert raw hide to leather [47]. In addition, they have the character of astringency (a term used in leather manufacturing to describe the reactivity of the tannin for the hide) to touch and taste and the propensity to give a greenish or bluish-black hue in the presence of iron salts. In spite of substitution by minerals and synthetics, annual global production of plant tannins was estimated to be 1,800,000 tonnes in 2007 [28, 47].

Tannins are identified chemically as polyphenols and are broadly classed as hydrolysable (gallo-tannins and ellagi-tannins) and condensed (proanthocyanidins) tannins. Their common characteristic reaction with iron salts is utilised for the manufacture of iron-gall inks. *Galling* or *sumaching* is a textile application of this reaction, wherein the tannin serves as a mordant. At times they serve the dual purpose of mordant and colourant due to their close association with some of the other colouring groups such as flavonoids and quinones [28, 47].

Limitations of natural dyes

Some typical limitations of natural dyes are inadequate availability and low colour yield and efficiency during both cultivation and dyeing [32, 39, 48]. Their unsuitability for colouring synthetic and synthetic-blended fabrics is another drawback. A widely accepted disadvantage is their poor performance as regards to desirable properties when compared to most synthetic dyes [30, 49]. The most significant shortcoming is their inherent variation, introduced by changes in growing and or harvesting conditions. Unlike synthetic dyes, most natural dyes are usually made up of more than one compound. The type of compounds present and their interaction (among themselves and the substrate) result in unique shades. A skilled dyer can utilise these same drawbacks to create specialty products for niche markets.

1.2.2 Fabric colouration

Colour can be introduced into textile materials at all stages such as fibre, yarn, fabric and garment. However, fabric colouration is the most popular and involves a wide variety of machines and methods. Dyeing and printing are the broad classifications of fabric colouration, as depicted in Figure 1.3. A simplistic description of dyeing is that the fabric acquires a single colour uniformly throughout. Similarly, printing may be defined as a process where one or more colours are applied in a desired pattern on the fabric [11, 12]. Dyeing and printing are described further in the following paragraphs.

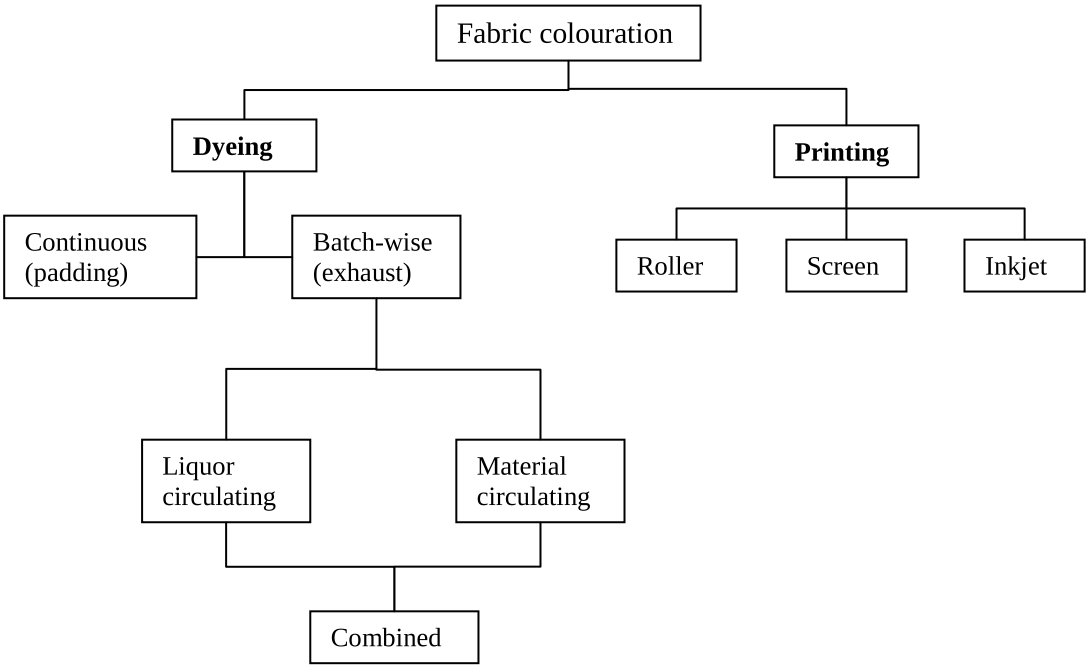


Figure 1.3 Fabric colouration methods [11, 12, 50]

1.2.2.1 Batch dyeing

This is an intermittent method used for dyeing short lengths of fabrics. It involves bringing together the fabric and dyes, which are partially or wholly dissolved in a transfer medium, usually water, so that the colour can be absorbed by the fabric. The dye is adsorbed on the fabric (fibre) surface and ideally diffuses (or is absorbed) into the gross structure. Depending on the dye and constituent material of the fabric, the interaction may be either chemical or physical. The process is generally called *exhaust dyeing* because it is usually conducted using dye liquor which is a dilute solution of dyes in water. The ratio of material to liquor can range from 1:4 to 1:30, normally termed *low-liquor* to *long-liquor* dyeing [11, 12]. In order to facilitate the initial dye adsorption and subsequent diffusion most exhaust dyeing processes follow a temperature gradient. Accordingly, dyeing commences at ambient temperature. The temperature is increased gradually to the required value depending on the dye used and held there for the required time period, as shown in Figure 1.4. Based on the dye-material combination, ionic or covalent fixation of dyes may be facilitated by altering the dye bath pH during diffusion [12, 14].

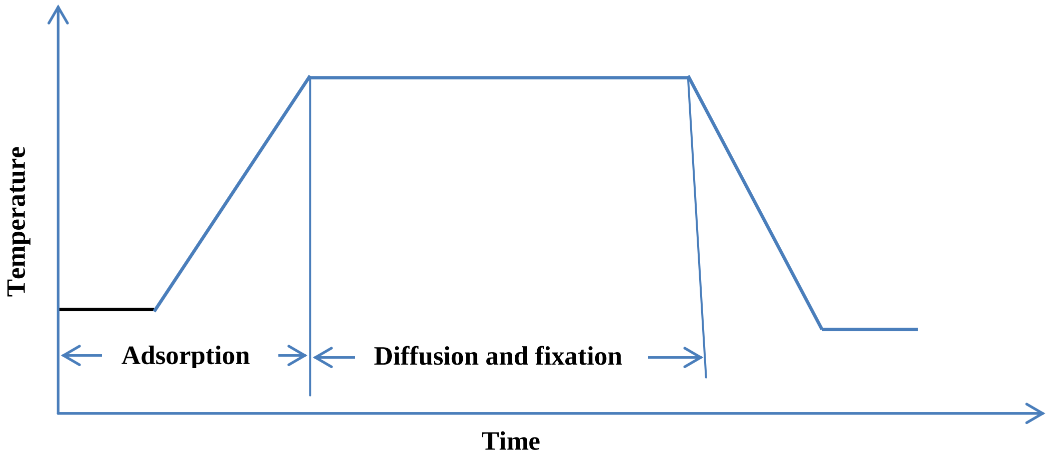


Figure 1.4 Exhaust dyeing line diagram

A traditional practice followed to this day is that exhaust dyeing recipes give the amount of auxiliaries and dyes as a percentage of the mass of the material being dyed. The auxiliaries are added first to the dye bath and allowed to mix thoroughly to obtain uniform concentration in the fibre. This is followed by addition of the dyes, which are allowed to mix completely before increasing the dye bath temperature [14]. These measures are necessary to achieve uniform and level dyeing. In addition to level dyeing, the other desirable aims of dyeing are short dyeing times, shade reproducibility and maximum exhaustion so that a minimum of dye is discharged in the effluent. Several authors [11, 12, 50] consider that the rate of dye uptake (exhaustion) or dyeing rate depends on:

a) the chemical reactivity of the dye for the fibre
b) physical properties of the dye
c) the type and construction of the fabric being dyed
d) dye concentration
e) liquor ratio
f) temperature

g) auxiliaries used; and
h) interchange of dye between liquor and fibre (fabric).

The process of dyeing is recognised as complete on reaching equilibrium, wherein there is no significant change in the final concentration of dye in the bath or on the fabric. Samples are now drawn for comparison against standards and corrections made as required.

In order to achieve short dyeing cycles and thereby higher production, most modern dyeing equipment is enclosed ensuring uniform dye bath temperature with minimum variations. Pressurisation of the equipment allows dyeing at elevated temperatures of up to 130°C. Circulating liquor and circulating goods (materials) are the two classes of exhaust dyeing machines [12].

Circulating liquor machines

The fabric is wound onto a perforated beam and placed in the dyeing vessel. Dyeing is brought about by pumping dye liquor from the inside of the beam to the outside through the multiple layers of fabric. This ensures uniform contact between fabric and dye liquor [51]. Bi-directional pumping, periodically reversing the flow direction of the dye liquor, is used for yarn dyeing. Consistent packing density ensures level dyeing [52].

Circulating goods machines

Jiggers and winches are the traditional dyeing machines of this class. In the former, fabric is mounted in open width on a roller and guided back and forth through the dye bath. On a winch, the fabric is traversed in rope form through the dye bath. The lower fabric tension of winch dyeing favours its use for knitted and other delicate fabrics, while woven fabrics are mostly processed on jiggers. Pressurised jet dyeing machines are often used for lightweight fabrics because of shorter dyeing times and uniform dyeing. The liquor is injected into the fabric as it passes through the jet. The combination of pressure and injection of liquor permits dyeing at a typical low liquor ratio of 1:8 and in some cases even 1:4 [52].

1.2.2.2 Continuous dyeing

This is a method for open-width dyeing of fabric lengths in excess of 10,000 metres in a single colour [11]. It generally involves the use of a *production line system* where machines of consecutive processes, which may include pre- and post-dyeing treatments, are arranged sequentially and operated in a synchronised manner. The process can also be utilized in a semi-continuous manner for shorter lengths. Fabric running speed controls the dwell time in each process although dwell may be modified by the use of 'festoon' type fabric transport [12, 52]. A material to liquor ratio of 1:1 or even 1:0.5 is an advantage of this method [53]. Some of the key features of batch and continuous dyeing are compared in Table 1.2 [52, 54].

Table 1.2 Continuous dyeing vs. batch dyeing [52]

Feature	**Continuous dyeing**	**Batch dyeing**
Shade uniformity	High and reproducible	Batch-to-batch variation possible
Quality of dyeing	Better	Good
Crease defects	Can be controlled	Difficult to control
Production	High due to short throughput time	Low due to long dyeing time
Labour requirements	Less	More
Process cost	Less	More

During continuous dyeing, the dye is applied by continuous immersion of fabric in a dye bath contained in a trough and removing excess liquor using squeeze rollers as shown in Figure 1.5 [11]. The position and number of squeeze rollers differ based on the model and manufacturer of the machine. The process in its entirety is termed *padding* and the padding process is repeated to ensure that the fabric is thoroughly wetted to obtain level dyeing. The amount of dye liquor retained by the fabric after squeezing is termed *wet pick-up* and is reported as a percentage of the dry weight of the fabric. Wet pick-up is primarily controlled by the pressure applied by the squeeze rollers. However, fabric construction and composition also influence wet pick-up. For example, the minimum wet pick-up of 60 – 70% for cotton cannot be reduced by increasing the pressure [11]. In general, lower pick-up minimises migration of dye liquor in the fabric and saves energy during drying. Alternate application methods of dye liquor are spraying and printing.

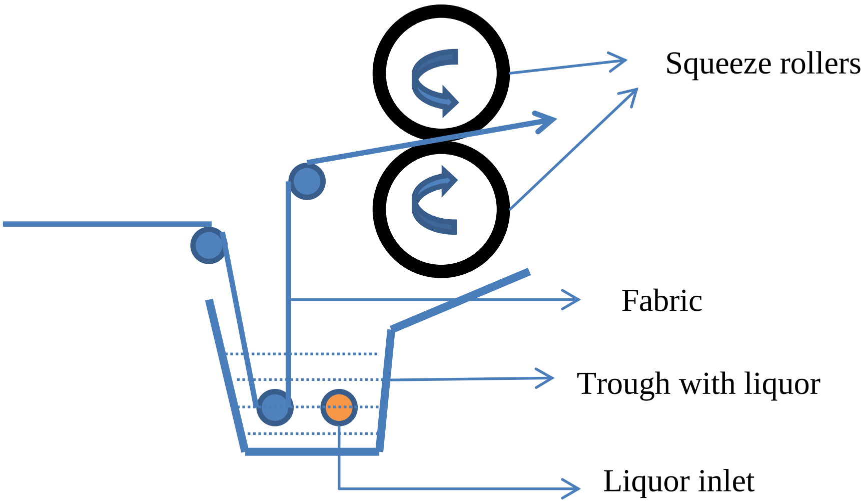


Figure 1.5 Schematic diagram of padding

With the exception of the pad-batch process, it is preferable to dry the fabric immediately after padding to obtain uniform dye fixation. Non-contact driers using a hot-air stream or infra-red radiation are employed to avoid soiling of equipment and marks on the fabric. At this stage the dye is present on the fibre surface and needs to be integrated into the material during fixation by chemical reaction, aggregation, ionic interaction or solid solution. A variety of methods and conditions are available for fixation depending on the dye and substrate. Saturated steam at 100°C is employed for a majority of the dyes [11]. Roller type steamers are usually used for this steam fixation process. They are designed to provide an air-free environment with a cold water exit seal (usually called *water-lock*). Each commercial range of dyes requires an appropriate duration of steaming. The major padding-fixing combinations are described below.

Pad – batch

This simple process involves padding the fabric with a dye solution containing a suitable dye and auxiliaries and then winding up the padded fabric onto a suitable roller. For dye fixation, the fabric wound on the roller is left undisturbed without steaming for 6–24 hours at ambient temperature. This process is therefore often called ‘cold’ pad-batch dyeing. During fixing, the fabric roll should preferably be rotated at low speed to avoid drainage of the internal liquid. In order to minimise evaporation from the exposed surfaces and edges of the roll, the fabric roll is wrapped with a plastic film. Finally, the fabric is thoroughly washed to remove unfixed dye and residual chemicals [11, 55]. The pad-batch dyeing process is the most economical of all pad dyeing processes for the reactive dyeing of cotton. It is claimed that this process is more economical than exhaust dyeing, mainly due to minimal energy requirements [56].

Pad – dry – cure

Curing in dry heat for 60–120 seconds may be used to fix the dyes after padding. A curing temperature of 160°C helps the formation of crosslinks in the finishing of cotton. Urea as humectant and dilute alginate solution as anti-migrant are special components of the padding liquor for cotton. Urea retains sufficient water to serve as a fluid medium for dye diffusion while alginate helps to avoid shade variation between the face and back of the fabric or the *two-sided effect* [11, 56, 57].

Pad (dye) – dry – pad (chemical) – steam

This two-step process sequence is widely employed for continuous dyeing of cotton fabrics using vat dyes. The fabric is first padded in a neutral dye solution that contains additional humectants and anti-migrants and dried in a hot flue drier. After drying, the fabric is padded with a solution of auxiliaries and other chemicals followed by steaming. The steam provides the necessary energy and additional moisture required to complete the dye-fibre reaction [11, 52]. Intermediate drying has been eliminated by employing super-heated steam and short steaming duration (flash-ageing), to make the process more efficient.

Drawbacks of continuous dyeing

Since the entire process is in open width, care has to be taken to avoid stretching of the fabric. Once processing has started, any machinery breakdown would cause significant fabric damage due to excessive dwell time [12]. Colour bleeding during chemical padding can cause shade variation. This is avoided by using a high concentration of electrolytes in the padding liquor. Urea removed during washing-off is a source of pollution because it can be a nutrient source for algae [11, 14].

1.2.2.3 Printing

A large number of methods exist for applying dyes by the printing technique of which *direct printing* is the most common. Direct printing involves applying the dye in the form of a print paste consisting of dyes, thickeners and auxiliaries. The print paste is applied by means of engraved rollers (roller printing) or flat/rotary screens (screen printing). After dye application, the printed fabrics are dried and steamed, similar to the processes used for padding depending on the dye-fabric combination. Each colour requires its own screen, thus making the printing range significantly long. Pigment printing uses binders to secure the pigment to the fabric surface. This is generally followed by a simple drying-curing step. Transfer printing involves sublimation of dye from a patterned paper onto the fabric [11, 12].

Inkjet printing produces patterns directly on the fabric by spraying the dye solution and is gaining popularity. Production speeds at 20–30 m/min are slow as compared to rotary screen printing but this is compensated for by the inherent flexibility and quick change characteristics. Soluble dyes are ideally suited for inkjet printing. Insoluble dyes especially disperse dyes have to be finely dispersed to avoid clogging of the inkjet nozzles [11].

1.2.2.4 Unconventional dyeing

Trials to replace water by super-critical carbon dioxide have been successful for different classes of dyes and substrates [58, 59]. Shishoo [60] has collated the output from investigations into the use of plasma technology in textiles aimed at application areas such as a) elimination of water and chemical based pre-treatments; b) enhancing dye uptake; and c) imparting functional finishes. Ultrasonics [61], microwave and sonicator [62, 63] have been used to assist in the dyeing process. Hot-air drying has been supplemented by the use of radio frequency (RF) [64] and infra-red (IR) [65] techniques.

1.2.2.5 Improving textile colouration

Considering the variety of dyes and dyeing methods available, there is ample scope for improving textile colouration to increase productivity, reduce waste, optimize process parameters, etc. This may include:

1) developing new dyes, dyeing machines and methods
2) reuse of resources such as water and energy
3) use of waste and by-products of textile and other industries; and
4) applying unconventional technologies as discussed above.

The above may be summed up as developing processes for producing darker shades with given amounts of dye [11, 12, 14, 15].

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1.2.3 Fastness testing

Coloured textiles are exposed to various influencing factors that may cause decomposition, sublimation, decolourisation or stripping (bleeding) of colour. Singly or in combination, these factors cause fading of the textile. Staining occurs when the colour is transferred to any adjacent textile during washing/rubbing. The most common degrading factors for coloured textiles are exposure to light, rubbing under dry and wet conditions and interaction with water as in perspiration, washing, chlorinated water and sea water during their useful life. Hence, in addition to producing level shades, colouration must also yield materials possessing sufficient resistance or fastness to the above factors during the intended end-use [66].

Test methods and standards have been developed to evaluate coloured textile materials for the above and other possible degrading factors. Each country has its own standards organization; for example, Standards Australia put forth standards equivalent to universal standards developed by organizations such as the International Organization for Standardization (ISO). Countrywise standards take into account local conditions. It should be noted that acceptable performance levels are usually agreed on by the concerned parties (supplier and customer) and do not form part of the test method especially in the case of textiles [19].

1.3 Present scenario

The textile industry in general and textile colouration in particular are embracing the global ‘go-green’ movement. Sustainability is being promoted in all aspects of colouration [2, 3, 7]. This is reflected as consistent efforts towards obtaining desired results in terms of shade and fastness with a reduction in the quantity of consumables by optimizing the process. Another pathway being explored is reclaiming and reusing consumables from effluent. Substitution with consumables possessing a lower environmental impact is an attractive development. In the above instances, consumables include dyes, chemicals, auxiliaries, water, energy (usually heat) and at times even the textile substrate. These efforts have led to constant reports on *zero-*

discharge processing [67, 68]. For example, Levi Strauss has gone further by encouraging recycling of denim and promoting efforts to reduce the amount of water required for washing during use [69].

In general, automation is gaining wide acceptance in the dye-house in order to minimise human error, especially in dyeing machine control and dye--dispensing operations. Integration of computer colour matching and recipe formulation has further reduced subjective errors and increased repeatability. Low-liquor and ultra-low-liquor machines are gaining popularity in batch-dyeing. These machines are pressurized to yield consistent results [52, 54]. Semi-continuous dyeing, that is continuous dyeing with intermediate storage, is gaining popularity for dyeing fabric lengths of 1000–5000 metres in view of the 1:1 liquor ratio possible [53].

The worldwide volume and variety of demand for colouring textiles is being met by a large range of synthetic dyes. With an annual growth of 3.9%, the market value for synthetic dyes is estimated to be US$16.2 billion distributed as shown in Figure 1.6 [17]. Synthetic dyes are manufactured using petroleum derivatives, for example benzene, as raw material. The dwindling estimate of long-term availability of petroleum resources, and thereby its derivatives, is encouraging the search for renewable alternatives [70]. With the advent of the environmental age, consumers have become aware of the environmental and health issues associated with some synthetic dyes [71]. Synthetic dyes identified as carcinogens have been banned or replaced. Effluents from dyeing process cause environmental hazards because some dyes and auxiliaries used are non-biodegradable, posing a great threat to marine life [4, 72]; hence they must be treated before discharge.

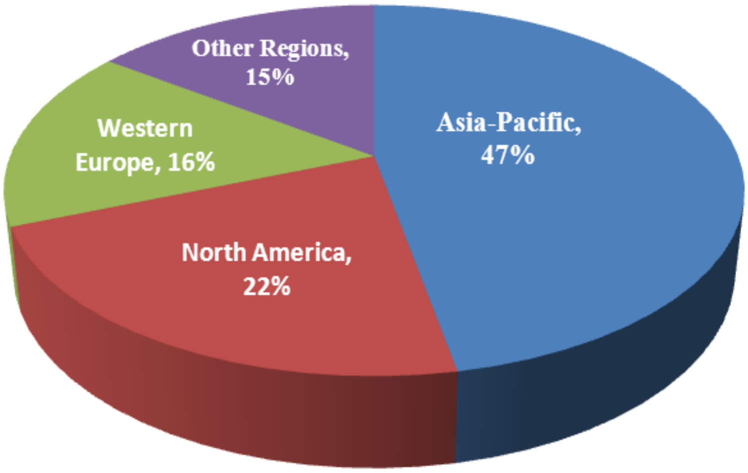


Figure 1.6 Distribution of global dye demand

Natural dyes are derived from renewable sources and hence it is commonly believed and claimed that they are biodegradable and non-polluting [73]. In some cases they also possess medicinal properties [74]. These features and a growing concern for the environment have created a niche market for the industrial scale use of natural dyes [40, 75].

1.3.1 Research on natural dyes

The growing interest in industrial use of natural dyes has exposed a knowledge gap on how to use natural dyes in modern dyeing facilities. In the past 150 years, these natural dyes have been used for textile colouration in limited quantities. Their reduced use over a long period has resulted in:

- loss of knowledge regarding extraction and application process due to absence of written records
- extinction of some dye sources and non-identification of new sources
- slowing down of scientific research on natural dyes, leading to stagnation in recipe development, modernisation and optimisation.

The new interest has brought about scientific investigations resulting in publications relating to dye sources, extraction and application methods, dye chemistry and performance of natural dyes [30, 40]. The following sub-sections discuss some of these findings.

1.3.1.1 Sources and extraction

Several authors have collated a wide variety of plant sources for natural dyes across the world [28, 38, 39, 48, 76]. Mohanty et al. [77] report that more than 300 indigenous plant species have been identified in India as traditional dye sources. The plants range from undesirable weeds to those that can be cultivated. They also include rare and exotic species. Different parts of the plants such as leaves, flowers, bark, seed pods and roots may contain maximum amounts of colourant and in some cases yield different colours from each part [38, 39]. Apart from these, the use of byproducts and waste products such as wood chips and sawdust (timber industry), grape pomace (wine making) and olive pomace (oil extraction) as cheap dye sources has been reported [78, 79]. Developments in genetic engineering have been applied to make micro-organisms produce dyes as well [80-83].

Steeping, boiling or fermentation in water of plant material forms the most common dye extraction technique. The extract is purified by simple filtration, settling and evaporation to obtain the final dye in paste, cake, granule or powder form. This process reduces transportation cost of raw materials and also helps to standardise the final product. Bechtold [10] has suggested moving the dye houses near the extraction facilities to eliminate the evaporation step. Spray drying and super-critical carbon dioxide extraction are the new developments in this sector. Commercial quantities of some natural dyes are now available [84, 85].

1.3.1.2 Application techniques

The industrial use of natural dyes declined at a time when long-liquor exhaust dyeing and hand or simple mechanical printing methods were the only colouration techniques available. Such methods were laborious, time consuming and sometimes convoluted compared to present day colouration techniques [11]. Some traditional recipes and techniques that were passed down by word-of-mouth only were lost [13, 28].

Enthusiasts like Dyer [39], Flint [86] and Adrosko and Furry [48] have collated recipes from across the world, simplified them based on their personal experiences and published books for use by other hobbyists. Interest groups conduct classes to disseminate their knowledge as well. Numerous national and international conventions, seminars and symposiums are being conducted to popularise the natural-dyeing concept. However, a common disclaimer among these protagonists is ‘These are my results. Your results will vary and you are welcome to try your own version.’

Researchers like Bechtold [10], Cardon [28], Chavan [87, 88] Gulrajani and Gupta [30] and Gulrajani [89] have approached these recipes in a scientific manner. Their efforts have been aimed at understanding the chemistry and then standardizing the dyes, assessing the relative merits of different dyes and evaluating the dyeing process. Variations in the exhaust dyeing method have been addressed [28, 30, 90]. The use of modern machinery for this process has been investigated [91]. Non-conventional methods such as ultrasound, microwave and radio frequency dyeing have been used with natural dyes [62, 92, 93]. Padding using natural dyeing has been reported by only a few researchers [94, 95]. However, the padding parameters mentioned are not in proportion, warranting further investigation. Application of chitosan to improve the uptake of some natural dyes during exhaust dyeing has been studied [96, 97]. However, the large number and variety of natural dyes offer opportunities for continued research [49].

1.3.1.3 Performance of natural dyes

Natural dyes have been used to produce a variety of shades [10, 28, 98]. However, with exceptions such as indigo, cochineal and madder, most natural dyes cannot perform to the fastness standards set for synthetic dyes. There is a constant scientific effort to improve this deficiency. The role of mordants for increasing fastness ratings has been studied [37, 99, 100]. Certain natural dyes have been shown to impart antimicrobial activity and UV protection [101, 102]. Thus research on natural dyes provides scope for innovative developments.

1.3.1.4 Objections to natural dyes

Common resistance to change has been seen with the idea of reintroducing natural dyes to industrial use. The question of whether natural dyes can provide the desired variety of shades has been answered positively by several researchers [10, 28, 32, 98]. The limitations indicated are quantity and quality. Glover [103] expresses doubts about the agricultural feasibility of replacing synthetic dyes with natural dyes. It should be noted that there is no move for complete replacement and natural dye consumption in Europe would probably constitute only 5% by volume of total dye consumed there. Research has revealed that this can be met by utilizing a small portion of non-agricultural semi-arable land in Europe [84, 104, 105]. Modern farming methods have made dye-crop cultivation a viable commercial proposition in some countries [84]. Queries regarding sustainability, safety and pollution with respect to natural dyes, for example the use and discharge of metal salts for mordanting, have to be considered [103]. The above arguments bring out the knowledge gap mentioned earlier and highlight the need for research.

1.4 Research conducted in this thesis

Exhaust dyeing of natural dyes is traditional and has been adopted widely by hobbyists and craftspeople. Consequently, previous researchers have concentrated most of their efforts on regularising and improving this method [40, 94, 95, 106]. The rising commercial interest in the use of natural dyes encourages research into the use of continuous colouration methods. Hence, this research investigated the padding of natural dyes. Commercially available natural dyes in powder form and laboratory grade chemicals were used to standardise and further simplify the process.

The study was conducted in progressive stages to obtain answers to:

a) How mordants are to be used with the selected natural dyes during padding?
b) What are the ideal padding parameters for a given dye concentration?
c) What means of improving the dye uptake may be employed?
d) Whether there is a potential for additional benefits from such improvement techniques? and,
e) What is the feasibility of a colouring process that uses chemicals with a lower environmental impact as compared to current practices?

At every stage of experimentation the depth of shade was measured and desirable fastness properties were evaluated. Keeping in line with the objective of utilising renewable resources, cotton and wool were selected for use as the textile substrates. In summation, sustainability in industrial-scale use of natural dyes as measured by the lowering of resultant environmental impact was the focus of this thesis.

1.4.1 Chapter outline

Chapter 2 lays out the research methodology of this study. It discusses the design of the experiments and gives details of the materials used.

Chapter 3 describes the padding process and optimisation steps involved. Specialised evaluation techniques used to gain an intimate understanding of dyeing mechanism are detailed. The results obtained are discussed.

Chapter 4 describes investigations regarding atmospheric pressure plasma pretreatment to improve natural dye uptake. Innovative applications of utilising this technology are explored.

Chapter 5 reveals the results of studies on whether including chitosan in the pad liquor of natural dyes produces darker shades. The resultant antimicrobial characteristics are also analysed.

Chapter 6 outlines the investigations into dyeing with indigo dye by the padding process. The effectiveness of using chemicals with a lower environmental impact is presented. The use of these chemicals in printing has also been evakuated. Finally, a comparison is drawn between using these chemicals in combination with natural and synthetic indigo.

Chapter 7 gives the overall conclusions drawn considering the results of the study. Future research directions are outlined.

1.4.2 Expected outcomes and potential benefits

It is expected that a better understanding of the pad-dyeing mechanism for natural dyes will be acquired. The insight into a) how mordants help to fix the selected dyes; and b) the unique relationship between individual dye and mordant will aid in optimising the process parameters for the selected natural dyes. The process will be improved by integrating atmospheric-pressure plasma technology or byproducts (chitosan) to obtain darker shades. Such improvement methods are also expected to result in additional benefits. Indigo colouration by using chemicals with lower environmental impact and the vat dyeing process will increase the scope of the use of this dye. The findings in this thesis are likely to encourage industrial trials in the padding of natural dyes. In summation, sustainability in the industrial-scale use of natural dyes is expected.

Chapter 2

Research methodology

2.1 Introduction

This chapter deals with the research methodology for investigating the pad-dyeing of natural dyes. It discusses the design of experiments based on which suitable materials and methods were selected. Evaluation techniques and procedures that were employed for determining either the effect of experimental variables or the desirable properties of dyed fabrics are described.

The research focused on two aspects of sustainability, namely 1) reducing the quantity of chemicals and dyes to obtain a desired shade; and 2) replacing harmful chemicals with relatively benign chemicals. A synergistic approach that benefits from the developments in technology as well as the renewable characteristic of natural dyes was adopted for the investigations.

2.2 Design of experiments

The feasibility of padding natural dyes in a sustainable manner was the prime objective of this study. Mordant and vat were the two classes of dyes selected for evaluation so as to obtain a broad perspective. The experimental design for the two classes is outlined in Figure 2.1. Exhaust dyeing recipes provided by the dye supplier were used to produce benchmark samples for the selected dyes. In the case of the vat dye, the performance of the natural dye was compared with its chemically equivalent synthetic counterpart.

Padding of natural dyes was approached in the following steps:

- determine optimum process sequence
- identify ideal padding recipe
- analyse the bonds formed during dyeing and develop a theory that explains the dyeing mechanism
- develop an improved padding process and identify additional benefits
- enhance current colouration methods by using chemicals with lower environmental impact.

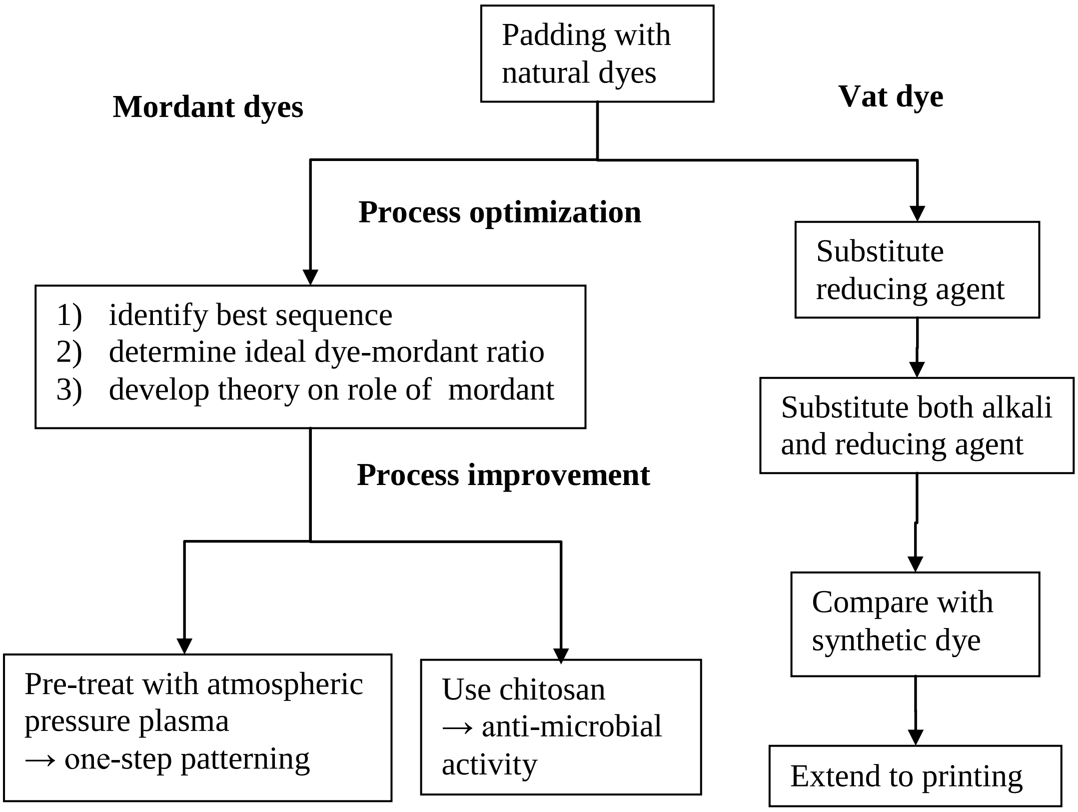


Figure 2.1 Design outline for padding natural dyes

Commercially available natural dyes were used to avoid the inconsistencies of collecting plant source, extracting and purifying the dye. It was also decided to use at least industrial grade chemicals for all recipes instead of any available traditional natural counterparts.

The final shade obtained was the deciding factor while optimising the dyeing process. All dyed materials were evaluated in accordance with relevant Australian or international testing standards.

2.2.1 Selection of materials

2.2.1.1 Fabrics

The use of fabrics produced from cotton or wool, natural fibres, enhances the sustainable aspect of the study. Further, they are the most compatible with natural dyes [28, 32, 48] and were chosen for this investigation. Mercerised and bleached cotton fabric was received from Bruck Textiles, Australia. Ready-for-dyeing 100% merino wool fabric was sourced from Macquarie Textiles, Australia. Both fabrics were used as received without any further chemical treatments. The fabric specifications are given in Table 2.1.

Table 2.1 Fabric specifications

Characteristic		**Cotton**	**Wool**
Weight (g / m^2)		297	230
Yarn count (Tex*)	Warp	42	36
	Weft	81	41
Ends/cm		32	36
Picks/cm		20	24
Weave		3/1 twill	2/1 twill

*Tex – weight in grams per 1000 m of yarn

2.2.1.2 Dyes

Two classes of natural dyes, namely mordant and vat, were selected. Representative dyes from each class were chosen based on widespread use and established large scale availability. Mordant dyes were obtained from Alps Industries Limited, Ghaziabad, India. Vat dyes were obtained from Kraftkolour, Melbourne, Australia.

Vat dye

Indigo (CI Natural blue 1), the blue dye used since ancient times, represents the vat dyes. The title ‘king of colours and colour of kings’ may be rightfully conferred on indigo because of its traditional use and cultural significance spread across the globe [13, 41, 42, 107-110]. Today, it retains its allure as the principal dye employed to colour the popular blue jeans [13, 43, 108].

Many plant species (sp.) belonging to Leguminosae, Polygonaceae, Apocynaceae and Acanthaceae families produce this dye. Some of the well known indigo sources are knotweed (Polygonum sp.), woad (Isatis sp.) and common indigo (Indigofera sp.) [13, 28]. Each species of indigo-producing plant may possess its own mix of precursors such as Indican (Indigofera sp.) or Isatan (Isatis sp.). The precursors are converted into pale-yellow (colourless) indoxyl by enzymatic reduction. This colourless secondary metabolite is extracted in water by crushing of the plants. During air-oxidation, two indoxyl groups combine to produce indigotin, the main colouring matter of indigo.

Indigo formation is shown in Figure 2.2 [111]. The combination of precursors and degree of interaction vary according to plant species and growing conditions ultimately determining the final yield and purity. This variation also results in isomers among which indirubin, the red shade of indigo, is well identified. The separation of these isomers (impurities) is not cost-effective.

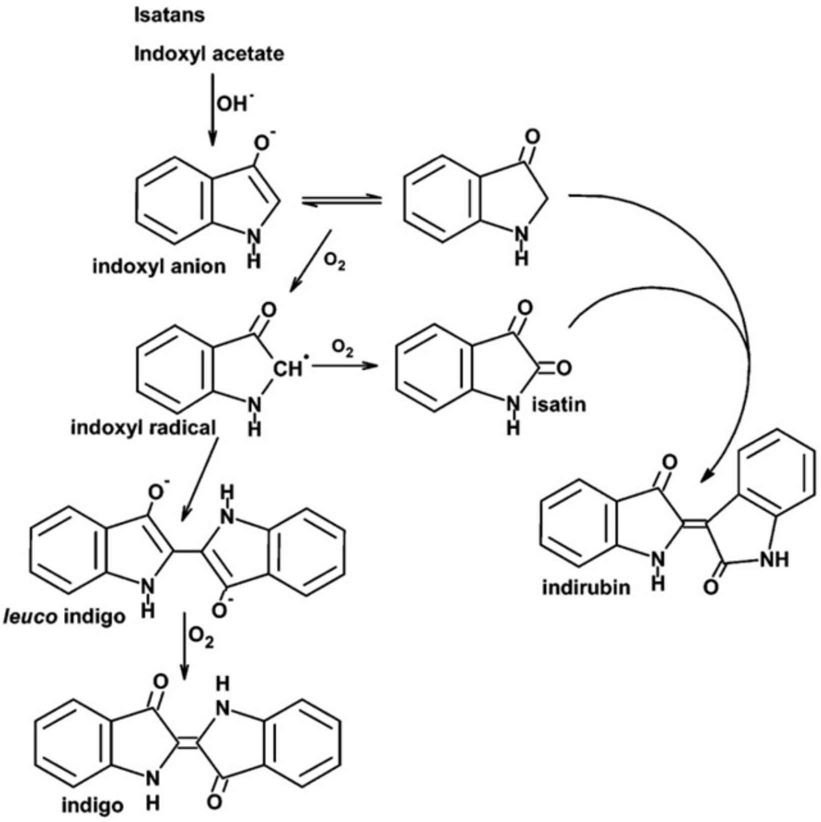


Figure 2.2 Indigo formation in plants

Chemically identical synthetic indigo, introduced by BASF in 1897, is a purer product with a higher degree of crystallinity [13, 112, 113]. Synthetic indigo has developed into a global multibillion dollar industry [112].

The commercially available natural indigo used in this study was extracted from Indigofera *tinctoria*.

Mordant dyes

Among mordant dyes, tannins are the most abundant chemical groups with an estimated global production of 1,800,000 tonnes annually [28, 47]. This yield is obtained from different plant species belonging to families such as Fagaceae, Pinaceae, Anacardiaceae, Combretaceae and Leguminosae. Plant tannins are extracted from leaves, nuts, bark, seed pods and heartwood. Tannins are classified as hydrolysable and condensed (non-hydrolysable) tannins based on how they are made up and their decomposition products. Hydrolysable tannins contain at least one carbohydrate molecule and yield gallic or ellagic acid on decomposition. Condensed tannins do not contain any carbohydrate and yield anthocyanidins on decomposition [114].

Two commercial dyes, Thar (CI Natural brown 3) and Caspian (CI Natural brown 3:3), both condensed tannins derived from Acacia *catechu* and Acacia *nilotica* respectively, were chosen to represent the mordant dyes. Both plants belong to the Leguminosae family. The dye is extracted from the heartwood of the first plant, while for the second it is from the bark [28]. The main components present in these dyes are prorobinetidine and profisenitidine shown in Figure 1.2. These multi-dentate polyphenols generally exist as dimers and trimers [28, 115]. As seen in Figure 2.3 and Figure 2.2, different stereo isomers of the dimers and at times even oligomers exist. The exact polymer formed and the final set of polyphenols present are subject to natural variation [115].

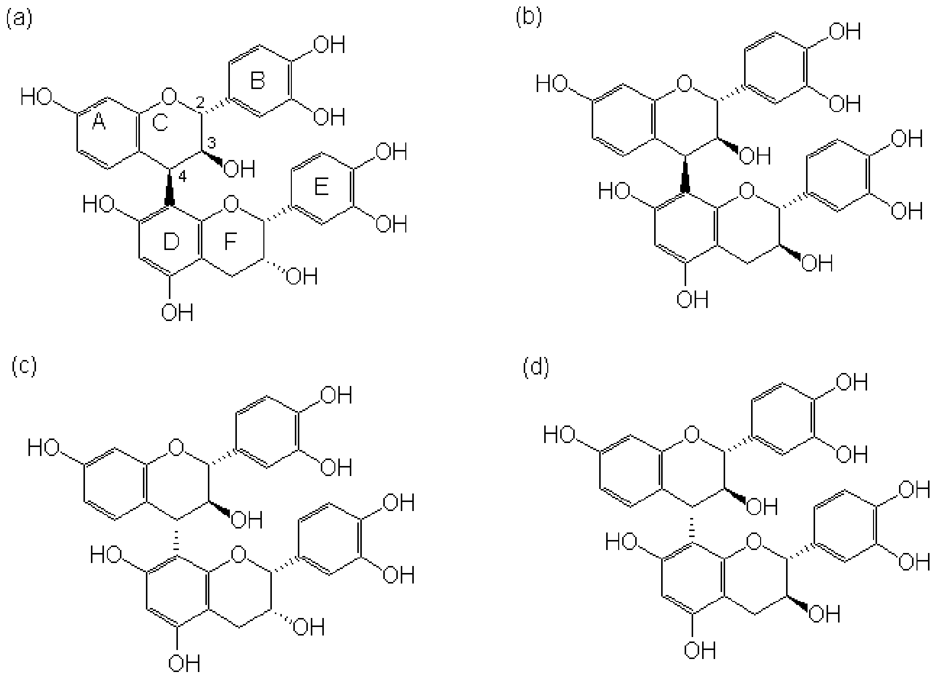
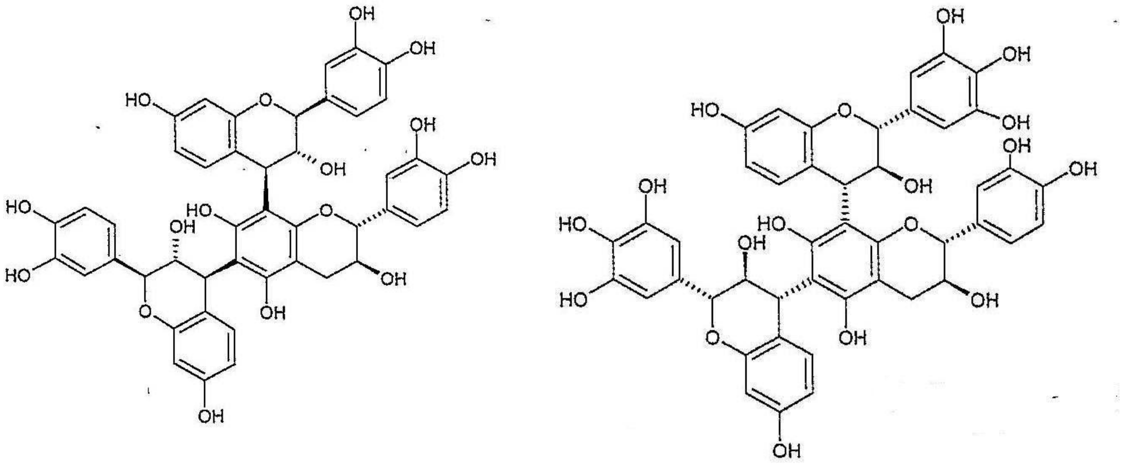


Figure 2.3 Four possible stereo-isomeric dimers of profisetinidine



Profisetinidin trimer Prorobinitidine oligomer

Figure 2.4 Polymers of condensed tannins

2.2.1.3 Chemicals

The sources of the various chemicals used are listed in Table 2.2. All the chemicals were of laboratory reagent grade except the industrial grade chemicals indicated.

Table 2.2 Chemicals used and their suppliers

Chemical	**Supplier**
Acetic acid (glacial)	Merck
Chitosan*	Sigma-Aldrich
Copper (II) sulfate ($CuSO_4.5H_2O$)	Merck
Delinol VB/LU	Impala Chemicals
Dextrose	Impala Chemicals
Iron (II) sulfate ($FeSO_4.7H_2O$)	Ajax Finechem
Nitric acid (70% w/w)	Sigma-Aldrich
Non-ionic detergent	SDC
Potassium sulfate (K_2SO_4)	Chem Supply
Prisulon 1550S	CHT
Sodium alginate NVS*	CHT

Sodium carbonate	Ajax Finechem
Sodium dithionite	Impala Chemicals
Sodium hydroxide	Chem Supply
Thiourea dioxide	Impala Chemicals
Tryptone soya agar	Oxoids, Australia
Tryptone soya broth	Oxoids, Australia

*Chemicals were of industry grade

2.2.2 Dyeing methods

Exhaust dyeing recipes provided by the dye supplier were followed to produce benchmark samples for the selected dyes. A two-step process is generally required for the application of both mordant and vat dyes. Hence from among the different padding techniques described in Chapter 1, the pad (dye) – dry –pad (chemicals) – steam method (Section 1.2.2.2) was adapted for use with the chosen natural dyes. This method was modified and used throughout the research. The modifications are discussed in relevant chapters. Steaming was carried out at 100°C using saturated steam for the required durations. All colouration trials were conducted in triplicate for each variable investigated. Consistency of shade obtained was the measure for process repeatability. Evaluation of other properties of the dyed fabric was limited to samples obtained from a single padding trial.

2.2.2.1 Mordant dyes

As mentioned in Section 1.2.1.2, copper (II) sulfate and iron (II) sulfate are widely used as mordants in natural dyeing. Hence, padding with the selected dyes was carried out in individual combinations with the above traditional mordants, either copper (II) sulfate or iron (II) sulfate. Initial dye-mordant ratio (1:6) and process sequence (simultaneous mordanting) were based on the information available from limited literature [94, 95]. In optimising the padding process, the first step was to identify the process sequence that would yield the darkest shade for a given concentration of dye. This ideal process sequence was used while determining the optimum dye-mordant ratio for a given dye concentration.

Two aspects of improvement to the padding process, from Section 1.2.2.5, were attempted using the optimised recipe and sequence. They were either a) application of the emerging technology of Atmospheric-Pressure Plasma (APP) pretreatment of fabric; or b) incorporating chitosan, derived from chitin, a byproduct of the seafood industry, in the pad liquor. The effects of varying the APP parameters or the amount of chitosan used were evaluated. Increased dye uptake leading to darker shades for a given amount of dye was the objective of these experiments. In addition, one step patterning was attempted using APP. Similarly, the consequential antimicrobial functionality brought about by the use of chitosan was evaluated.

2.2.2.2 Vat dyes

As a vat dye, indigo has to be reduced to its water-soluble colourless leuco form to be soluble for colouration. Oxidation of the leuco compound, after being absorbed, regenerates the dye inside the textile, imparting a fast blue colour. This reversible reaction is shown in Figure 2.5 [13].

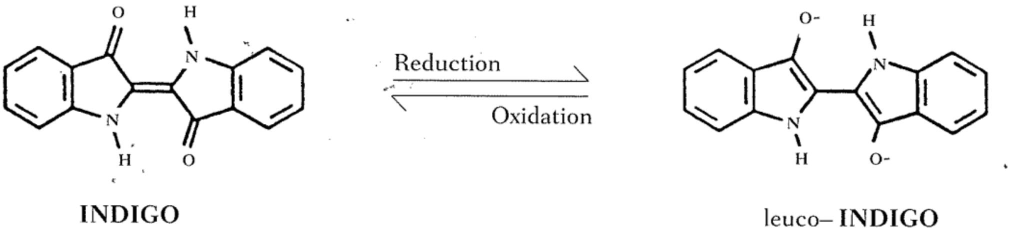


Figure 2.5 Solubilising reaction of indigo

Many authors [42, 110, 116, 117] list widely recorded traditional methods of indigo-reduction as:

i) the fermentation method
ii) the copperas vat method
iii) the zinc-lime vat method; and
iv) the bisulfite-zinc-lime vat method.

Each of the above methods has its own benefits and drawbacks. Inconsistent reduction of indigo and the time involved are the main drawbacks that have been identified.

Similarly, traditional indigo printing is equally varied and is summarised in Figure 2.6. Premature paste oxidation is the main concern in indigo printing [118-121].

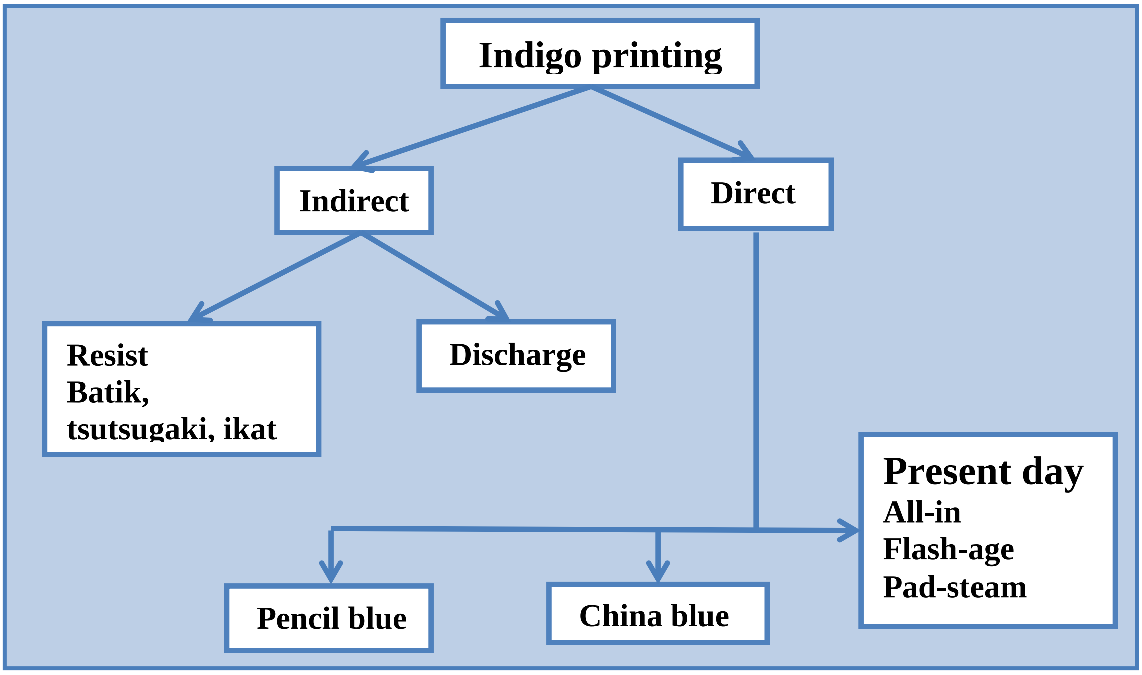


Figure 2.6 Various types of indigo printing

Commercial dyeing using indigo commonly employs sodium dithionite (sodium hydrosulfite or hydros) as reducing agent and sodium hydroxide (caustic soda) as alkali in the solubilising step [13, 109]. The ready decomposition of sodium dithionite in alkaline solutions is usually compensated by adding it to the dye bath in excess and at frequent intervals [122-124]. Further, the decomposition products, such as sulfur dioxide and thiosulfate, also pose effluent disposal problems [125]. Caustic soda, on the other hand is a strong alkali and needs careful handling and disposal [126]. In the case of indigo printing, sodium dithionite is too unstable for application by the all in method where dye, alkali, thickener and reducing agent are applied together. It is usual therefore to utilize a more stable reducing agent such as sodium formaldehyde sulfoxylate or the equivalent zinc salt of the same compound. These reducing agents pose their own usage and effluent issues [127]. Thus, the use of the above chemicals poses technical and environmental problems.

The search for alternate reduction methods for indigo has given rise to research literature on use of electro-chemical, biodegradable organic chemicals and enzymatic systems [25, 125, 128]. The use of pre-reduced indigo has also been encouraged [116]. The requirement of additional equipment and an increase in process time are some of the drawbacks of the above developments. Hence, in this research, substitution with chemicals that are stable and possess lower environmental impact for solubilising indigo was investigated. The chemicals used were thiourea dioxide (TUD) as reducing agent and sodium carbonate (soda ash) as alkali. TUD was selected because it has a reduction potential slightly higher than that of sodium dithionite [50, 129].

The padding parameters that produced the darkest shade for a given amount of indigo reduced by the action of the selected alternate chemicals were determined. Comparison dyeing was made between natural and synthetic indigo using the alternate chemicals. In addition, the effectiveness of the above process was evaluated in the area of indigo printing.

2.2.3 Evaluation

2.2.3.1 Colour measurement

Instrumental colour evaluation of the conditioned dyed samples was carried out using a Datacolour 600 spectrophotometer with 10° LAV (Large Area View) observer using D65 illuminant. An average of three measurements of colour strength (K/S) or reflectance was recorded.

Colour measurement is based on the ratio between total light absorbed K and scattered S by the substrate as defined by the Kubelka-Munk equation given in Equation 2.1 below.

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$ **Equation 2.1**

where R is the reflectance measured at a given wavelength.

The K/S value is commonly used as a basis for evaluating dye build-up or change in colour strength. Comparison of colour strength can be made based either on the K/S values at maximum absorption wavelength (λ_{max}) or on the sum of K/S values across the visible spectrum when no specific peaks are identifiable. Any particular colour may be represented by a graph of the K/S or reflectance values (across the visible spectrum) plotted against corresponding wavelength [130].

2.2.3.2 Fastness testing

Wash fastness was evaluated according to the AS 2001.4.15-2006 test method using an Atlas launder-o-meter. A composite sample (dyed fabric and standard multifibre fabric) was washed in a 5 g/l standard soap solution with 2 g/l soda ash at 60˚C for 30 minutes using a material-to-liquor ratio of 1:50. After washing, the sample was rinsed in hot followed by cold water and then dried at ambient temperature. The colour of the wash solution, staining of adjacent multifibre fabric and dyed fabric colour change were evaluated against AATCC grey scales for colour change and staining.

Light fastness was tested according to the AS 2001.4.21-2006 test method for a period of 48 hours. The amount of colour fading on exposure to an artificial light source (mercury vapour, tungsten filament, internally phosphor coated lamp) in comparison with simultaneously exposed blue wool standards was assessed.

Wet and dry rubbing fastness of samples was evaluated according to the AS 2001.4.3-1995 test method using a crock meter. Dyed samples were rubbed with a standard white cotton fabric, in a dry or wet state, under specified test conditions. The staining of the cotton fabric was evaluated using standard AATCC grey scales for staining.

2.2.3.3 Atomic Absorption Spectrometry (AAS)

AAS was used to determine the extent to which the cotton and wool fabrics retained metal ions from the mordant in the absence and presence of the dye respectively. An increase in metal retention in the presence of dye would confirm the formation of dye-metal-textile complex.

AAS is a precise technique for quantifying metals in the parts per million (PPM) range present in a sample. It works on the principle that metals in their elemental form absorb ultraviolet (UV) light when they are excited by heat. The results are very specific because each metal has a unique characteristic absorbance wavelength. This absorption follows Beer’s Law, which states that as concentration goes up, absorbance goes up. Hence a calibration curve for a metal may be constructed by recording the absorbance for a series of standards with known concentrations. The absorbance of an unknown sample can be measured and the quantity of metal estimated by comparing with the calibration curve.

Operating procedure

A fabric sample of known weight (approximately 0.2 g) is digested in concentrated acid to obtain a clear solution. This ensures that other than the metal all other organic matter has been completely destroyed. The volume of solution is brought down by boiling and then diluted with distilled water to produce a 2% w/w solution of the acid. The dilution is necessary to protect the instrument according to recommendations from the manufacturer. This dilute solution forms the sample solution.

The maximum quantity of metal that may be present in the sample solution prepared as above is calculated taking the following factors into consideration:

1) the wet pick-up during padding
2) concentration of metal salt in the padding liquor; and
3) the ratio of atomic mass of metal to the molecular weight of the metal salt.

Based on the above calculation, calibration solutions of required PPM range of concentrations are prepared by dissolving appropriate metallic salts in distilled water. As depicted in Figure 2.7, the AAS instrument aspirates the test solution, as an atomised spray, into a flame. A beam of UV light of appropriate wavelength is focused through the flame and into a detector. If the metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data acquisition system converts this change into an absorbance [131].

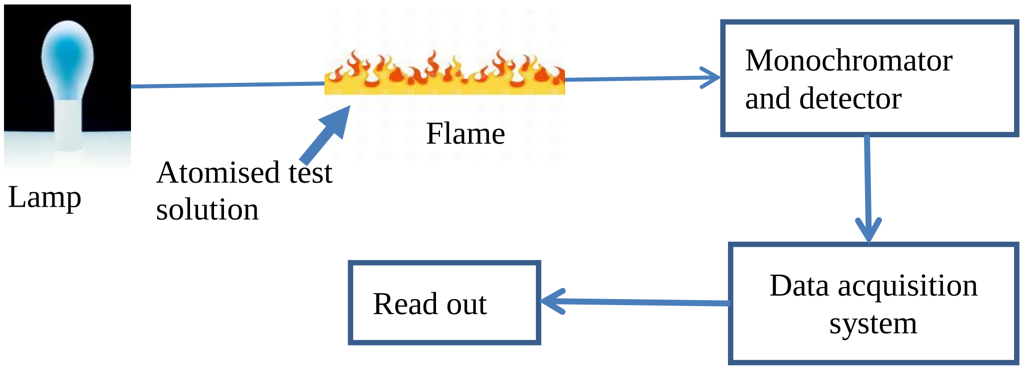


Figure 2.7 Schematic diagram of AAS

2.2.3.4 Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR)

This non-destructive testing method does not involve any special sample preparation. The spectrum is obtained by measuring changes in the total internal reflection of the incident light beam caused by the sample held in close contact with one face of the reflecting crystal [132, 133]. Figure 2.8 depicts the sample position in relation to the ATR crystal and the path of the infra-red light beam.

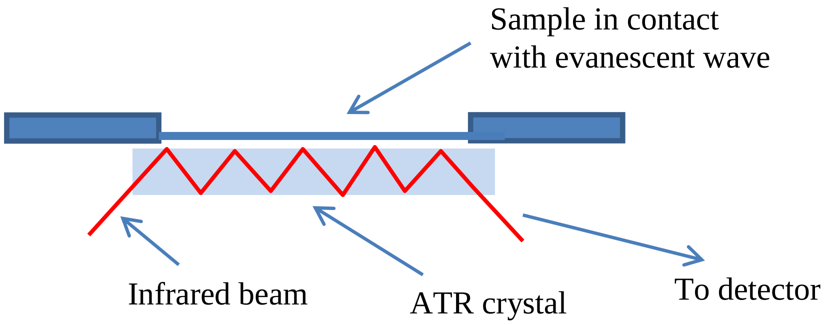


Figure 2.8 Schematic diagram of ATR – FTIR

The bonds in the individual dyes and the changes to these bonds during formation of the dye-mordant and dye-mordant-cotton complex were identified by analysing the ATR – FTIR spectrum. Dye-mordant complexes were prepared according to the following procedure. Individual 50 ml solutions, at the optimal ratio indicated by padding experiments, of all four combinations of dye and mordant were prepared. These solutions were heated at 80°C for 20 minutes to simulate exhaust dyeing and promote formation of a dye-mordant complex. The solutions were cooled and centrifuged for 10 minutes. The solids (dye-mordant complex) that settled at the bottom of the centrifuge tubes were collected and dried at ambient temperature.

The results of AAS and ATR-FTIR were used to develop a theory that explains the observations of the padding experiments.

2.2.3.5 Wettability testing

The wetting properties of fabric, especially after plasma treatment, were evaluated using the drop test and wicking test according to AATCC test method 79–2007 and BS 3424 part 18, method 21A, respectively. The time required for one drop of water to be absorbed by the treated fabric was compared to that taken by the untreated fabric. A similar comparison was done for the vertical wicking of coloured water. A 15 cm x 1.5 cm strip of fabric, marked at 1 cm intervals along the length, was clamped at the top and hung vertically. A small weight was attached to the bottom to keep the strip straight. The bottom two centimetres were immersed into distilled water coloured with blue dye. The height to which the water rose over a 15 minute period was recorded at 30 seconds, 1, 5 and 15 minutes.

2.2.3.6 Antimicrobial testing

This test was carried out to evaluate the effect of chitosan. A modified AATCC TM 100-2004 (clause 10.2) test method was followed to assess the antibacterial properties of dyed fabrics. Escherichia *coli* (E. *coli*) strain ATCC 11229, a gram-negative bacterium, was used as the test organism. Bacterial inoculums were prepared to obtain a suspension in an exponential growth of 10^8 colony forming units (CFU) mL^{-1} in 5 mL of modified tryptone soya nutrient broth. Fabrics dyed in the absence of chitosan were used as negative control samples.

Antibacterial tests were conducted on each sample individually as outlined by Zhang et al [134]. In brief, 1 ml of inoculum, prepared as described above, was added to a fabric swatch of 4 cm diameter in a conical flask. Immediately 100 ml of distilled water was added to the flask and this was shaken vigorously for 1 minute. From this solution, a series of dilutions were prepared as 10^0, 10^1, 10^2 and 10^3 times with sterile distilled water. The dilutions were then plated in triplicates and incubated for 18 hours at 37°C. After incubation, the control plates exhibiting 30--300 CFU were taken as reference. Test plates of a similar dilution were compared. The percentage reduction of bacteria was calculated with Equation 2.2:

$$\frac{(X-Y)}{X}\times 100\% \qquad \textbf{Equation 2.2}$$

where,

X= average number of bacterial colonies in the agar plate from control

Y = average number of bacterial colonies in the agar plates from fabric dyed in the presence of chitosan.

2.3 Summary

The above sections broadly outline the experiments carried out in this thesis. The specifications of the fabrics, dyes and chemicals used have been listed. A logically progressive framework of pad-dyeing experimental procedures has been laid out. Standard tests that were followed for evaluating the desirable fastness properties have been introduced. Procedures and equipment less widely employed were described in detail. Further details of the experiments will be discussed and the results analysed in the following chapters.

Chapter 3

Padding and its optimisation

3.1 Introduction

This chapter details the investigations into the padding of natural mordant dyes derived from Acacia *catechu* (Thar) and Acacia *nilotica* (Caspian). The optimisation and evaluation methods are described. FTIR investigations regarding the bonds originally present in the dyes, mordants and cotton and the changes they underwent on combining to form the final dyed fabric are discussed. AAS procedures used to determine the metal content in the dyed fabric are given. The results obtained are discussed.

3.2 Equipment

3.2.1 Padding mangle

Padding was carried out on a laboratory-scale two-bowl padding mangle, with horizontal squeeze-roller geometry, manufactured by Werner-Mathis. The nip between the rollers created the trough for pad liquor. Pressure, used to adjust the wet pick up, was controlled using compressed air. The fabric was guided vertically through the pad liquor and between the squeeze rollers, shown in Figure 3.1.

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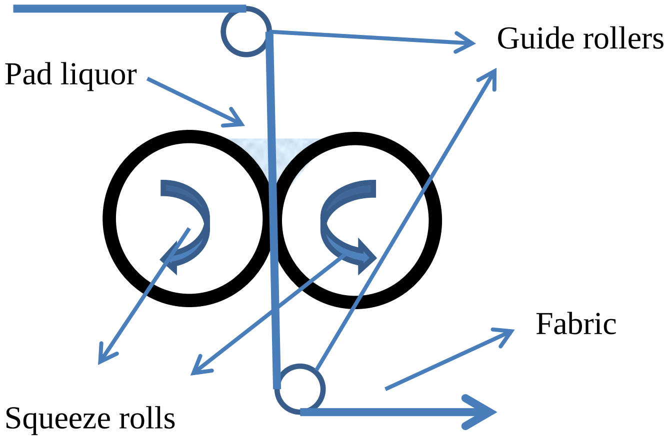


Figure 3.1 Padding mangle geometry

3.2.2 Steamer

A laboratory-scale steamer (Figure 3.2) manufactured by Werner Mathis was employed for the steaming of samples. The equipment featured a fully-contained steam atmosphere with temperature and humidity controls. The period of sample exposure was controlled using an integrated timer. In addition, this equipment could be used as a curing chamber by excluding steam. Samples were mounted on pins set in a frame and then introduced into the steaming chamber.

Figure 3.2 Laboratory scale steamer

3.2.3 Dryer

An Electrolux TS 560 forced-air-flow convection drying chamber was used to dry the samples. The samples were dried at either 40°C or 65°C in a tension-free state. Uniform airflow minimised shade differences between the face and back of the fabric.

3.2.4 Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR)

A Perkin Elmer Spectrum 400 with a universal single bounce diamond ATR attachment (Figure 3.3) and associated software (Spectrum version 6.3.5) was used to analyse dyes, mordants, dye-mordant complexes, undyed fabric and dyed fabrics. Other than the fabrics, all samples were examined as dry powders.

Figure 3.3 Perkin Elmer Spectrum 400 FTIR

3.2.5 Atomic Absorption Spectrometer (AAS)

A Varian-AA-280-FS AAS (Figure 3.4) was used to quantify the metal content in different fabric samples. An acetylene flame in air was employed to excite the metal atoms. Iron and copper were detected at wavelengths of 248.5 nm and 324.7 nm respectively.

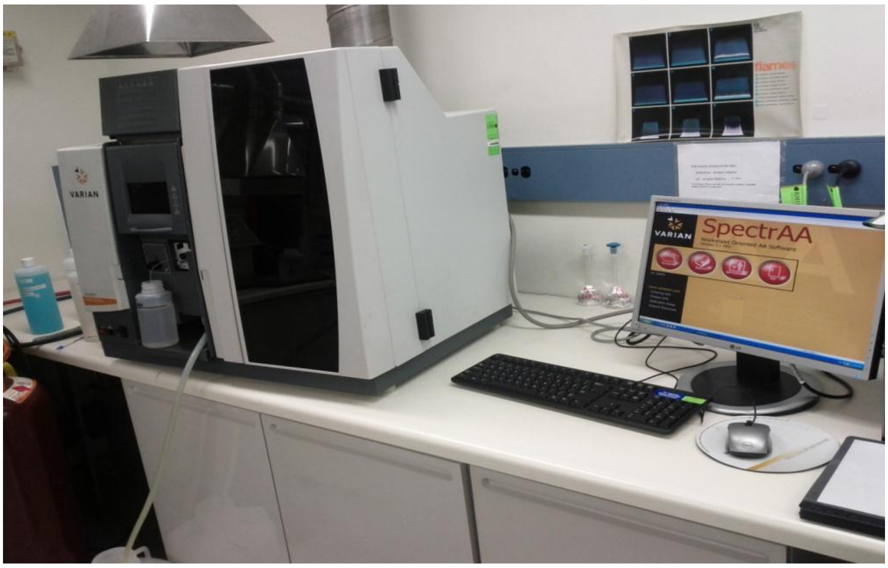


Figure 3.4 Varian AA 280 FS (AAS)

3.3 Materials

Cotton and wool fabric described under Section 2.2.1.1 and the mordant dyes mentioned in Section 2.2.1.2 were used in this investigation.

3.4 Methods

This section describes the exhaust dyeing process obtained from the supplier. The padding sequence and the variables were then investigated. Evaluation of desirable properties of the pad-dyed material is explained. The application of AAS and FTIR in understanding the dyeing mechanism is discussed.

3.4.1 Exhaust dyeing

Two commercially available mordant dyes derived from the Acacia family, Thar and Caspian, described in Section 2.2.1.2, were applied on cotton fabric by exhaust dyeing. A 1% shade on the weight of material (OWM) was used as the benchmark for both the dyes. The suggested material to liquor ratio of 1:30 was employed for dyeing, soaping off and rinsing steps.

In the case of Thar, a dye bath was prepared with the required amount of dye (1% OWM) and 5% OWM of mordant (either copper (II) sulfate or iron (II) sulfate) and stirred thoroughly. The fabric sample was introduced into the dye bath and the temperature raised to 80°C. Dyeing was continued for 45 minutes at this temperature. This was followed by soaping off with 0.5 grams per litre (g/l) solution of non-ionic detergent at 60°C for 20 minutes. Following soaping off, the dyed fabric was washed in hot water and then in cold water and finally dried.

Dyeing with Caspian required pretreatment of fabric with 3.5% OWM of Alpsfix, a cationic fixing agent, at 80°C for 30 minutes followed by drying. A dyebath containing the required amount of dye (1% OWM) and 5% OWM of either mordant was prepared and stirred thoroughly. The fabric sample was added to the dye bath and the temperature was raised to 80°C. Dyeing was continued for 45 minutes at this temperature. The sample was then soaped off with 0.5 g/l solution of non-ionic detergent at 80°C for 20 minutes. The dyed fabric was sequentially washed in hot water and cold water and then dried.

3.4.2 Padding

Thar and Caspian were padded individually on cotton fabric. The squeeze roll pressure was set to achieve 80% wet pick-up. In order to obtain a nominal 1% depth of shade, the dye liquor for padding was prepared according to the recipe shown in Table 3.1. Sodium alginate served as an anti-migrant to prevent the two-sided effect, while potassium sulfate acted as a cationising agent and promoted dye fixation. Freshly prepared liquor was allowed to stand for 2–3 hours for the sodium alginate to swell and become completely effective.

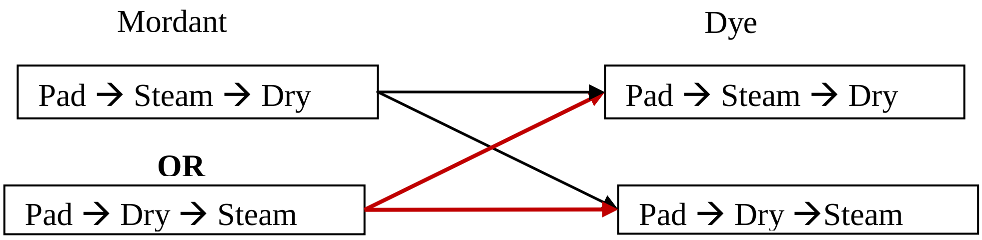
Table 3.1 Pad liquor (dye) recipe

Constituent	**Concentration (g/l)**
Caspian (A. *nilotica*) or Thar (A. *catechu*)	10
Sodium alginate	1
Potassium sulfate	1

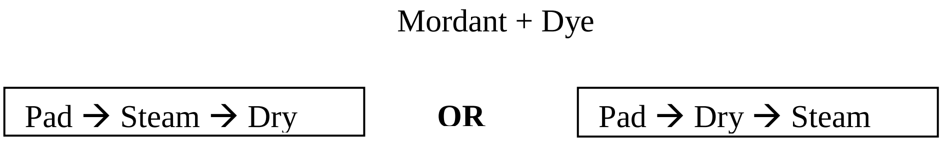
All three mordanting techniques, pre-mordanting, meta-mordanting and post-mordanting as described in Section 1.2.1.2, were evaluated individually for each of the selected mordants, copper (II) sulfate and iron (II) sulfate. A mordant concentration of 60 g/l was utilised based on the results published by Patel et al. [94]. Sodium alginate at 1 g/l was also incorporated into the mordant liquor. Similar to the dye liquor, the mordant liquor was prepared and left undisturbed for 2–3 hours.

3.4.2.1 Optimising process sequence

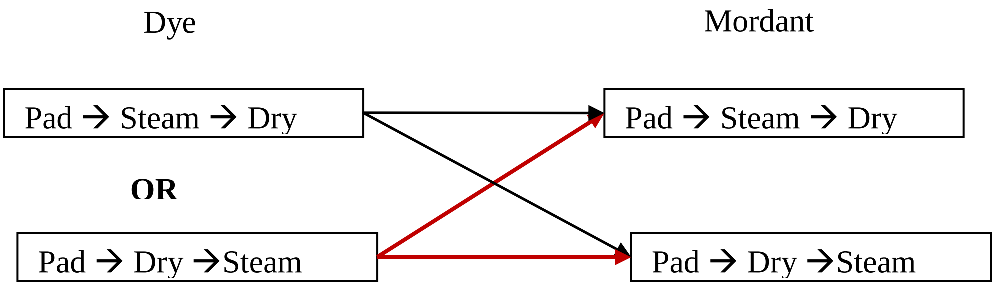
Padding can be differentiated into three distinct steps of pad (P), dry (D) and steam (S). The drying and steaming steps can be interchanged. Thus for every padding step two process sequences of PDS and PSD exist. Hence in the pad-dyeing of mordant dyes all possible process-sequence combinations need to be evaluated to identify the ideal sequence. This set of combinations is depicted in Figure 3.5. Each dye-mordant pair was individually pad-dyed in all the process-sequence combinations. After every PDS or PSD step, the samples were dried at 65°C to facilitate handling.



a) Pre-mordanting



b) Meta-mordanting



c) Post-mordanting

Figure 3.5 Mordanting and dyeing combinations

3.4.2.2 Optimising dye-mordant ratio

The next stage was to determine the optimum dye-mordant concentration. Mordanting liquors containing 5, 10, 15, 20 and 40 g/l of mordant were prepared. Cotton fabric samples padded with 10 g/l of dye were mordanted individually with each of these liquors. The evaluation was conducted for all four possible dye-mordant combinations namely: a) Thar-copper (II) sulfate; b) Thar-iron (II) sulfate; c) Caspian-copper (II) sulfate; and d) Caspian-iron (II) sulfate.

Wool fabric was padded with individual combinations of the two dyes and two mordants using the optimised process sequence and the ideal dye-mordant ratio determined from the above experiments.

3.4.3 Steaming and washing off

Steaming, in all scenarios, was conducted at 100˚C and 100% RH for 10 minutes, and followed by drying at 65˚C. The dried samples after padding and mordanting were washed off (soaped) with 1 g/l anionic detergent solution at the boil for 20 minutes to simulate extreme washing conditions. This was followed by consecutive rinses in hot and cold water respectively.

3.4.4 Dyeing evaluation

Dyed samples were conditioned for at least 24 hours under standard conditions of 65% RH and 20 ± 2°C and evaluated for colour strength and fastness properties as described in Section 2.2.3.

3.4.5 Atomic Absorption Spectrometry (AAS)

Sample solutions were prepared as detailed in Section 2.2.3.3 using concentrated nitric acid (70% w/w). Undyed and unmordanted pristine fabric was used as the reference (control). In order to establish the capacity of the fabric to retain metal ions by itself, AAS studies were conducted on cotton and wool fabrics mordanted by the PSD process and washed at the boil similar to final washing off (Section 3.3.1). Individual concentrations of 5, 10, 15 and 20 g/l of copper (II) sulfate and 3, 5, 10 and 15 g/l of iron (II) sulfate were evaluated. Fabrics dyed by post-mordanting with 5 g/l iron (II) sulfate or 15 g/l copper (II) sulfate were subjected to AAS to bring out the effect of dye in altering the ability of fabric to retain metal.

Table 3.2 and Table 3.3 present the calculations that were used to determine the maximum mass of metal that may be applied on a 0.2 gram fabric sample at the abovementioned mordant concentration, assuming a wet pick-up of 80%. This was the basis for preparing calibration solutions containing 0, 1, 2, 3, 4 and 5 PPM of metal ion (copper or iron). These solutions were analysed using AAS with the detector set at the wavelength specified for the metal under consideration as mentioned in Section 3.2.4. The average of three readings of absorbance was recorded for each of the samples. The data from the calibration samples was plotted as a scatter graph. A trend-line was fitted to this graph and its equation derived. This equation was used to calculate the amount of metal present in an unknown sample that is the sample solutions prepared by the digestion of fabric. The results were extrapolated to determine the mass of metal retained by a unit mass of fabric.

Table 3.2 Atomic mass of elements present in mordants

Element	Atomic mass
Cu (Copper)	63.55
Fe (Iron)	55.85
H (Hydrogen)	1.01
O (Oxygen)	15.99
S (Sulfur)	32.07

Table 3.3 Calculation to determine maximum mass of metal applied on 0.2 g of fabric

Mordant	Molecular weight	Metal content (%)	Concentration (g/l)	Mass of metal (mg)*
Copper (II) sulfate ($CuSO_4.5H_2O$)	249.63	25.46	20	0.81
Iron (II) sulfate ($FeSO_4.7H_2O$)	277.95	20.09	15	0.48

*Maximum mass of metal that may be present on 0.2 gram of fabric padded to 80% wet pick-up at given mordant concentration.

3.4.6 ATR–FTIR analysis

In order to understand the shades obtained, the dyes, dye-mordant complex and dye-mordant-fibre complex were subjected to ATR–FTIR analysis. The results were used to determine the original bonds present and identify the modifications caused by the complex formation.

3.5 Results and discussion

3.5.1 Shades obtained

Cotton fabrics were dyed with natural dyes derived from the Acacia family at a concentration of 10 g/l by padding to obtain a nominal 1% depth of shade. Shade variation between triplicate trials as indicated in Section 2.2.2 was less than 5%, confirming the repeatability of the process. It is evident from the reflectance curves shown in Figure 3.6 and Figure 3.7 that the shades were similar to the benchmark shades obtained by exhaust dyeing. The slightly lighter shade obtained from padding may be due to the fact that at 80% wet pick-up the quantity of dye applied would be equivalent to a 0.8% OWM shade of exhaust dyeing. The two mordants yielded different resultant shades for the same dye. Mordanting with copper (II) sulfate resulted in a copper-beige shade while iron (II) sulfate resulted in a yellowish-grey shade. The absence of a definite peak in both figures indicates the neutral nature of the colours obtained. When used as a mordant, copper is termed to bloom the final colour, while iron dulls it [28]. This effect is evident in the flatter and lower reflectance curve of grey, as compared to that of beige.

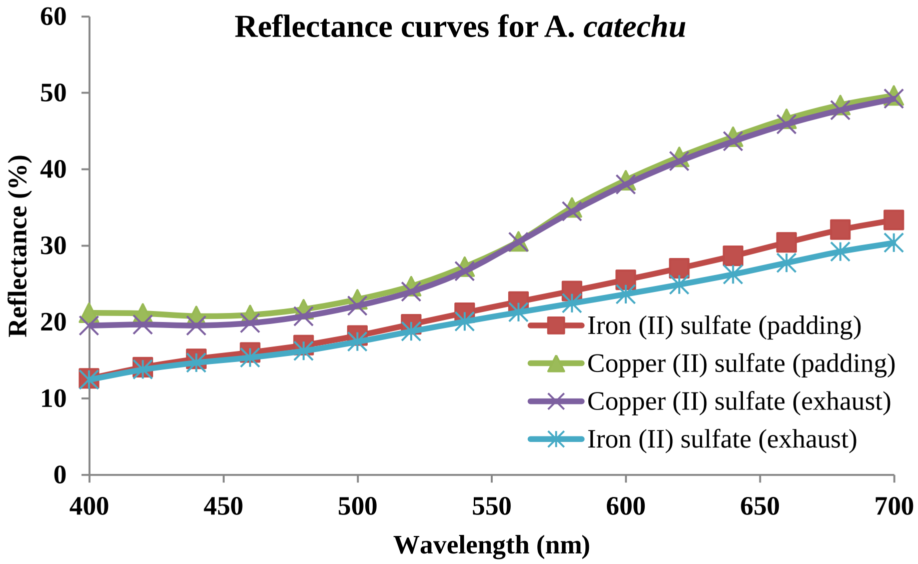


Figure 3.6 Reflectance curves of cotton fabrics dyed with A. *catechu*

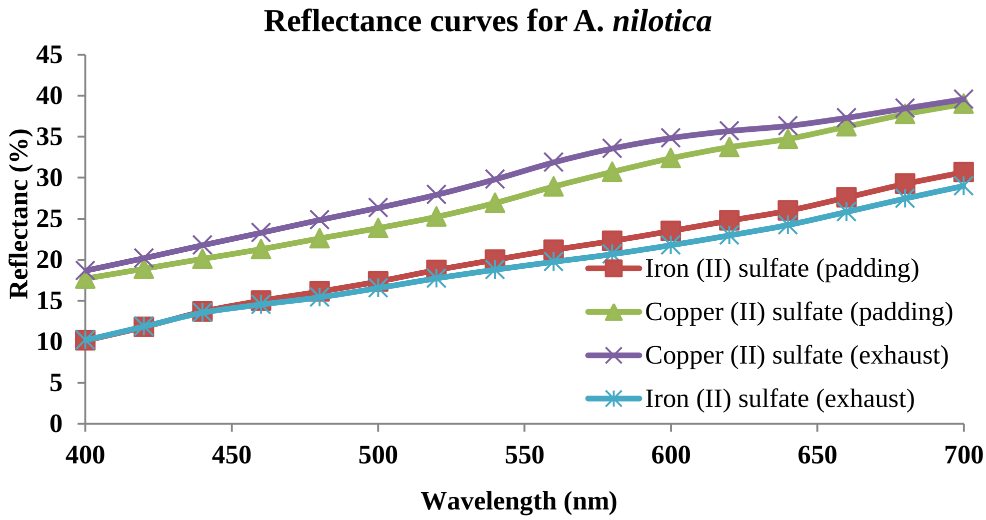


Figure 3.7 Reflectance curves of cotton fabrics dyed with A. *nilotica*

The change in colour according to mordant is consistent with the polygenetic behaviour of some natural dyes. Such dyes are claimed to yield up to 16 colours from a single natural dye depending on the mordant used [32]. This has been attributed to the formation of metal complexes (chelates) by the functional groups (tannins) present in the dyes derived from Acacia family [31, 94, 115, 135, 136]. Although a simple depiction of this interaction is shown in Figure 3.8, the polymeric characteristic of polyphenolic dyes precludes exact determination of the features of the metal complex [115].

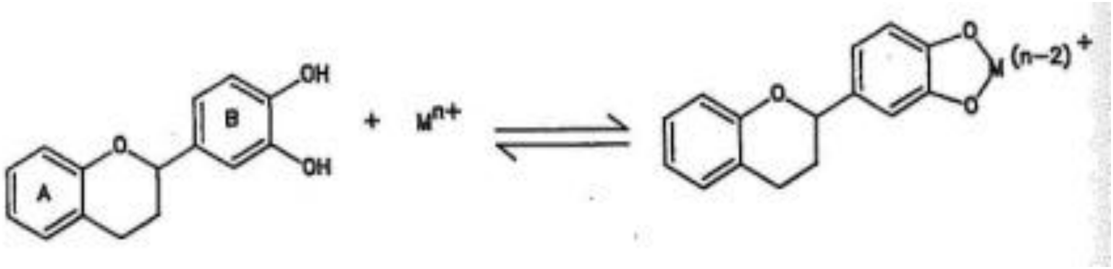


Figure 3.8 Schematic of metal complex formation [115]

Norkus et al. [137] outline the interaction between textiles and heavy metal ions to occur mainly by:

a) intercalation into the fibre matrix
b) adsorption onto the fibre
c) formation of chemical bonds with reactive groups of material; and
d) formation of complexes with dissolved hydrolysis products.

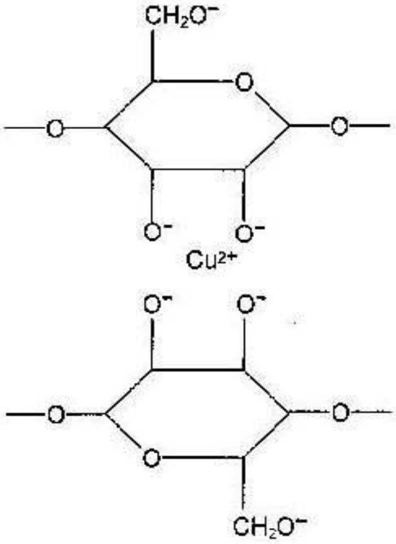


Figure 3.9 Equatorially coordinated copper with cellulose [138]

Figure 3.9 is a lattice structure with equatorially coordinated metal (copper) acting as a bridge between cellulose molecules, as proposed by Ajiboye and Brown [138]. Such a structure is possible when the cellulose molecules are loosely held in a gel. When cellulose exists in a relatively rigid state, as in cotton, only partial complexes can be formed. The inherent polymeric character of condensed tannins (Figures 2.3 and 2.4) favours the formation of multi-dentate three-dimensional isomeric structures. Consequently when cotton is dyed using a condensed tannin based dye in conjunction with metallic mordants, a highly complicated structure that incorporates metal, dye and fibre evolves. Under these conditions, although the presence of metal (M^{n+}) can be detected, definitive characterisation of the final resultant structure is inhibited. However, differences in structure become evident by changes in the shade obtained.

The role of the metal was highlighted when different dyes in combination with the same metal yielded near-equivalent shades. This can be readily identified by the almost parallel reflectance curves in Figures 3.6 and 3.7 for the two dyes in combination with iron (II) sulfate. On the other hand, the same dyes in combination with copper (II) sulfate yielded reflectance curves that are different due to dissimilar dye-fibre-mordant complex structures. This indicates that the metal is responsible for the ultimate structure of the dye-metal-fibre complex.

3.5.2 ATR–FTIR results

The FTIR spectra for the two dyes, Caspian and Thar, are given in Figure 3.10. Table 3.4 lists the peak assignments for the spectra. The combination of peaks around 767 and 1500 cm^{-1} can be attributed to aromatic ring breathing mode and CH out-of-plane deformation with two adjacent free hydrogen atoms respectively, indicating the prominent presence of procyanidin [139]. The other peaks are consistent with those reported for polyphenols [140]. A larger number of peaks are identified between the wavelengths of 1600 to 1280 in the spectrum for Thar enabling a distinction to be made between the two dyes.

Table 3.4 FTIR band assignment

Wavelength (cm^{-1})	**Bonds**	**Wavelength (cm^{-1})**	**Bonds**
3400–3100	vO-H glycosidic groups	1400–1050	Complex vC-O vibrations
1606	C=C aromatic ring	1280	-OH aromatic
1566	Aromatic ring stretch	1111	-C-OH alcohol
1516	C-H alkanes	1035	C-O alcohol
1445	C-O alcohol	767	C-H alkenes

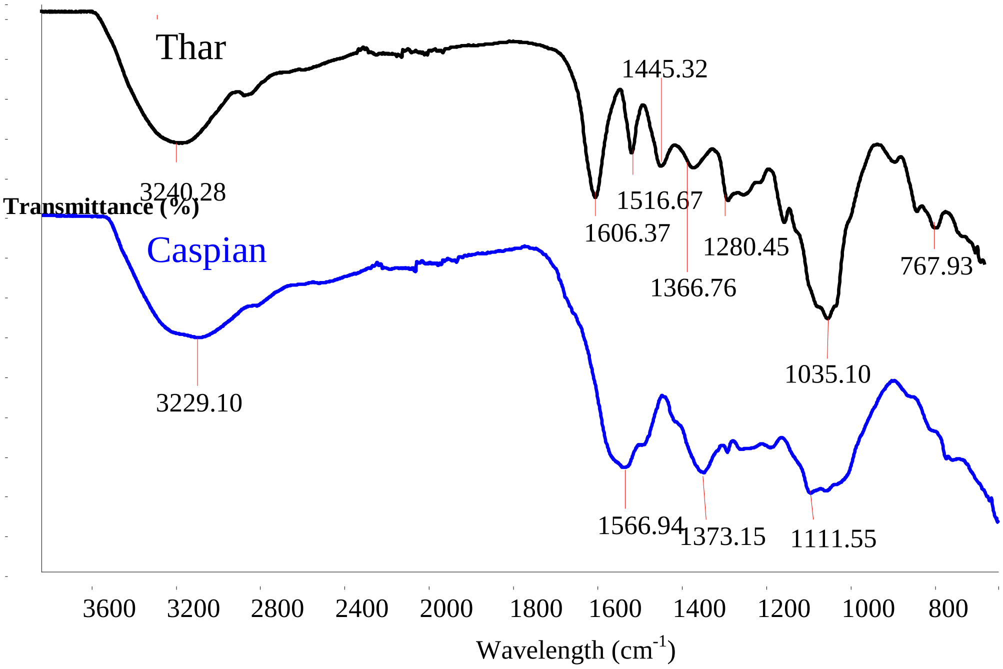


Figure 3.10 FTIR spectra of dyes

The two dyes under investigation were individually made to react with the chosen mordants (copper (II) sulfate and iron (II) sulfate). Figure 3.11 and Figure 3.12 show the spectra for the complexes formed from the above reaction. A lower difference is observed between the spectra for complexes resulting from the different dyes reacted with the same mordant. This may be due to a general suppression of aromatic ring stretch at a wavelength of 1566. However, the C-O vibrations identified in the wavelength range of 1050–1400 are not changed.

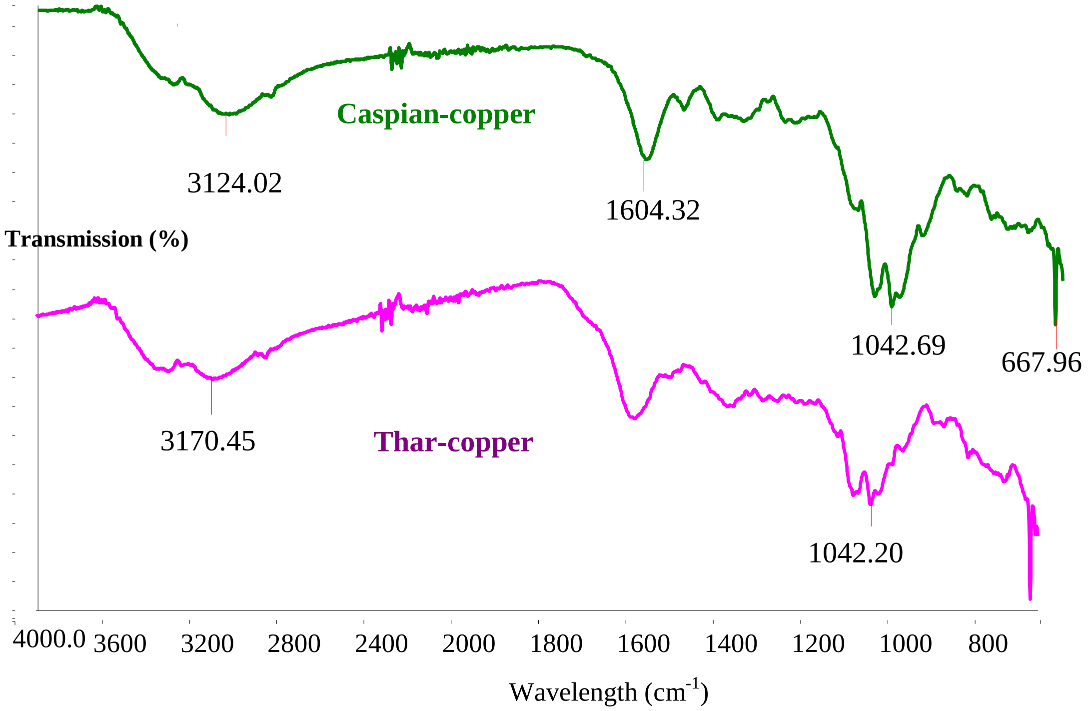


Figure 3.11 FTIR spectra of complexes formed by the two dyes in combination with copper

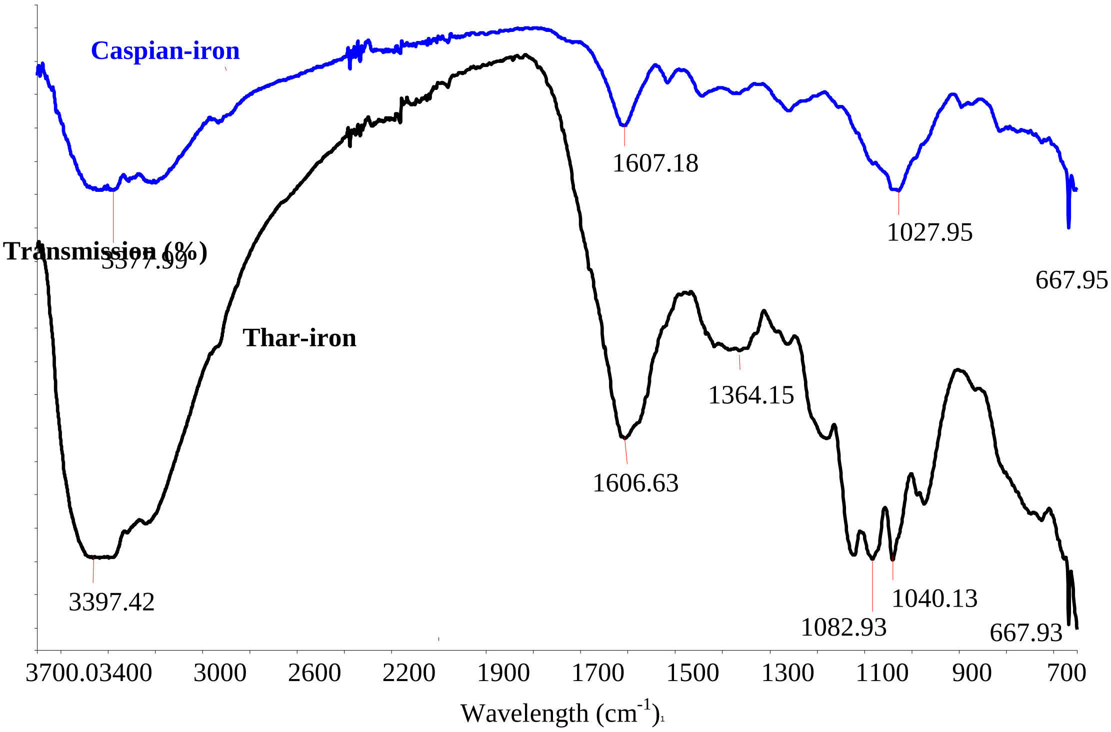


Figure 3.12 FTIR spectra of complexes formed by the two dyes in combination with iron

The spectra of the dyed fabric become near identical, as can be seen in Figure 3.13 and 3.14. Hence it may be inferred that in a textile matrix (cotton fabric), the bond-geometry becomes restricted as compared to the dye-mordant by itself. The mordant continues to govern the bonds present in the final complex formed for the dyes under consideration. As for iron, the bond angles and orientation are apparently identical for both dyes, resulting in the observed similarity in shade (reflectance curve). On the other hand, although copper forms the same bonds, there is a different orientation for each of the dyes, giving rise to the divergence in shade. The detection and confirmation of these subtle variations by 2D-IR spectroscopy, as suggested by Khalil et al. [141] and Noda [142], is beyond the scope of this thesis and hence recommended for future work.

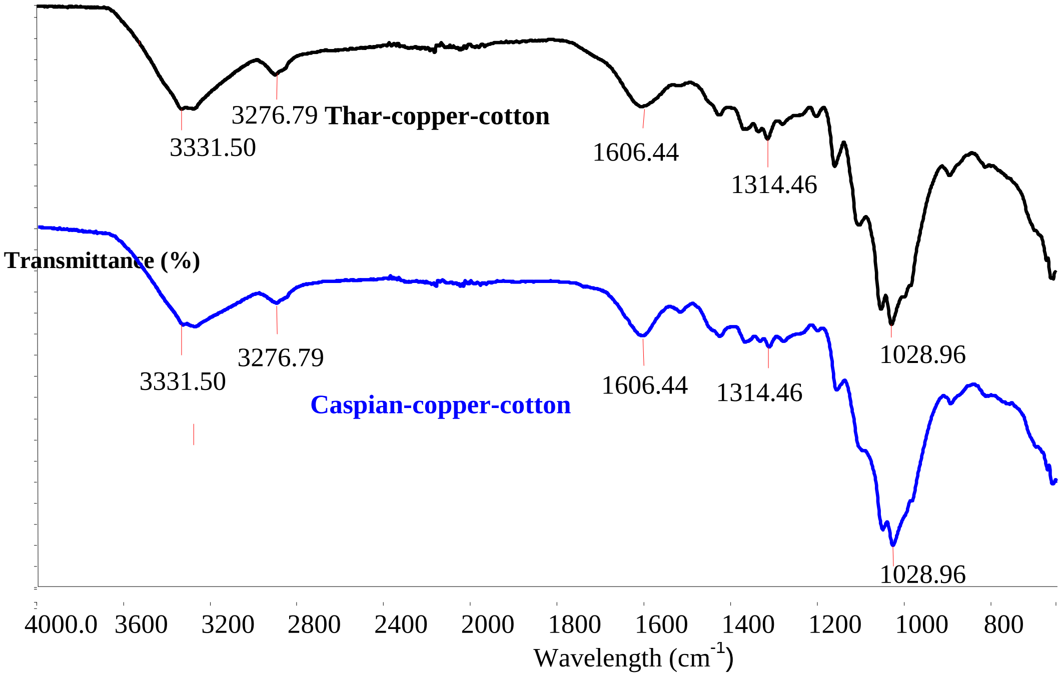


Figure 3.13 FTIR spectra of cotton fabric dyed in combination with copper as mordant

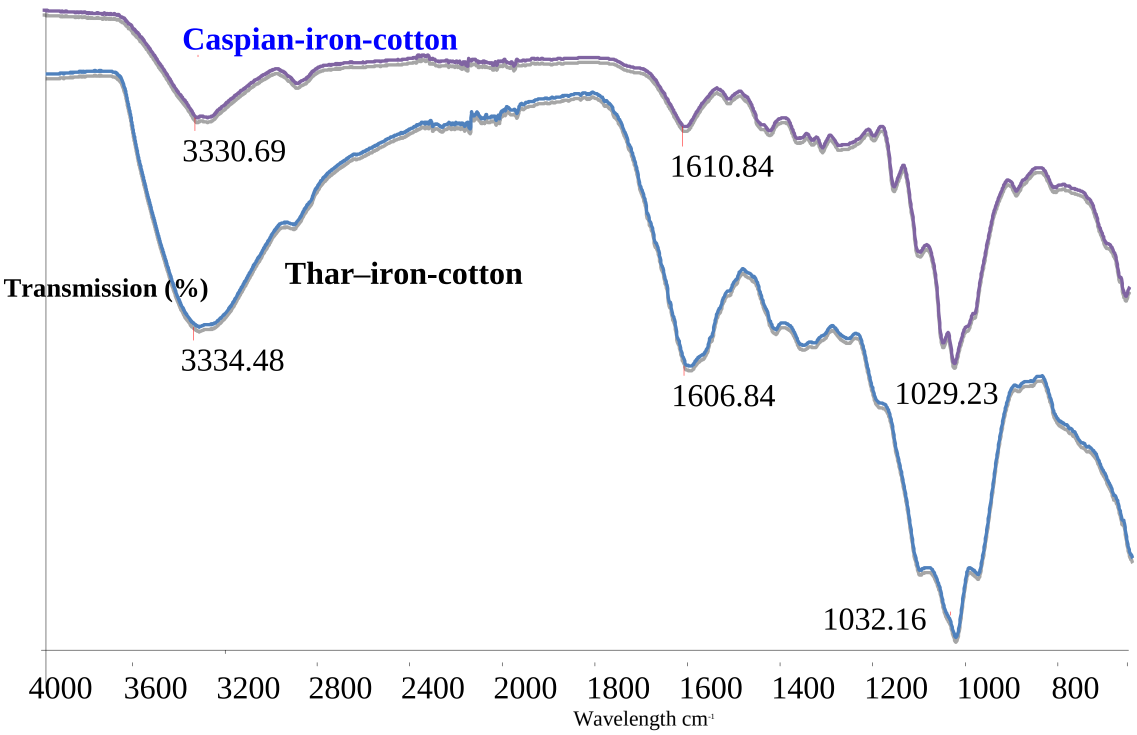


Figure 3.14 FTIR spectra of cotton fabric dyed in combination with iron as mordant

3.5.3 Optimal processing sequence

Mordant concentration of 60 g/l, suggested by Patel et al. [94], was used in this investigation. The reflectance results (K/S values) at a typical incident wavelength of 440 nm for all dyeing–mordanting combinations are shown in Table 3.5. It can be seen that post-mordanting and the PSD (dye) →PSD (mordant) sequence for iron (II) sulfate gave the highest K/S value of 2.77 for both dyes. In the case of copper (II) sulfate, however, similar conclusions cannot be drawn based on the K/S values. Pre-mordanting apparently gives the highest K/S of 2.97 for Thar whereas it was post-mordanting with a K/S of 2.48 for Caspian. Considering the fact that both grey and beige are neutral colours, additional factors have to be considered while selecting the optimum process sequence. These factors are 1) the overall shape of the reflectance curve; and 2) the visual evenness of shade under various standard illuminants. Post-mordanting and the PDS (dye) → PSD (mordant) sequence yielded a visually level shade and the smoothest curve for copper (II) sulfate as compared to the other sequences. Levelness of shade was confirmed by a less than 2% variation in the sum of K/S values measured across 10 places on the sample.

Table 3.5 Typical K/S values at 440 nm for dyed cotton fabric

Dye	**Mordant (60 g/l)**	**$CuSO_4.5H_2O$**				**$FeSO_4.7H_2O$**			
	Dye sequence	PDS		PSD		PDS		PSD	
	Mordant sequence	PDS	PSD	PDS	PSD	PDS	PSD	PDS	PSD
Thar	Pre-mordanting	1.85	1.65	**2.97**	1.68	1.89	2.56	2.58	2.31
	Post-mordanting	1.80	1.52	1.69	1.56	2.36	2.63	2.36	**2.77**
	Meta-mordanting	1.62		1.54		0.46		1.89	
Caspian	Pre-mordanting	1.43	0.64	1.38	0.71	1.18	1.47	1.23	2.65
	Post-mordanting	**2.48**	1.59	1.56	1.42	1.76	2.11	1.81	**2.77**
	Meta-mordanting	0.81		0.73		0.64		1.17	

In most cases, post-mordanting gave higher K/S values compared to the other methods. During pre-mordanting and meta-mordanting trials it was observed that dye-mordant complexes were formed in the padding liquor or on the fabric surface. As suggested by Ali [136], pre-mordanted samples were likely to have leached out the mordant during padding of dye, thereby facilitated complex formation in the dye bath. These complexes were unable to sufficiently penetrate and adhere to the substrate and hence were washed off during soaping and rinsing. Therefore, post-mordanting was selected as the optimum technique for padding with dyes derived from the Acacia family.

The current optimum mordanting technique contradicts an earlier study [94] that claim that meta-mordanting yields better results than pre-mordanting when padding cotton fabric with A. *arabica willd*. It is possible that the source and purity of dyes used, surface dyeing effect and final shade obtained, and reaction rate between mordant and dye could have contributed to the discrepancy. It should be noted that comparative literature that combines the padding of natural dyes and post-mordanting is not available.

3.5.4 Optimum mordant concentration

A single dye concentration of 10 g/l approximating a nominal 1% shade and the optimised technique and sequence determined above were used to identify the ideal mordant concentration. In accordance with the results discussed in Section 3.5.3, only post-mordanting trials were conducted. On the same basis, process sequence combinations of PSD (dye) → PSD (mordant) in case of iron (II) sulfate mordant and PDS (dye) → PSD (mordant) copper (II) sulfate mordant were followed.

No definitive assumptions can be made based on the K/S values at a single wavelength of 440 nm as listed in Table 3.6. As discussed earlier, additional factors had to be considered while evaluating neutral shades. Although the K/S values at 440 nm were not the highest at these mordant concentrations, 15 g/l for copper (II) sulfate and 5 g/l for iron (II) sulfate gave the most level visually observed shades for both dyes. Samples mordanted at these concentrations exhibited minimal or no colour bleeding during the soaping off process. Samples mordanted at higher than the above levels leached excess mordant into the soaping bath. The leached mordants tinged the bath a characteristic blue or grey. Further, the fabrics dyed using these mordant concentrations retained a supple handle. The other samples acquired a rough handle, probably due to incomplete removal (or redeposition) of excess mordant. In general, an unbalanced dye-mordant combination resulted in splotchy dyeing. These results lead to the inference that at the dye-mordant ratio of 10 g/l dye to either 15 g/l copper (II) sulfate or 5 g/l iron (II) sulfate, the dye-mordant-textile complex was completely balanced. Hence, these dye-mordant ratios are termed as the ideal dye-mordant concentrations in this thesis.

Table 3.6 K/S values at 440 nm for cotton fabric padded with different mordant concentrations

$CuSO_4.5H_20$ (g/l)	**Thar**	**Caspian**	**$FeSO_4.5H_20$ (g/l)**	**Thar**	**Caspian**
5	2.27	2.07	**5**	**2.48**	**2.57**
10	2.18	2.30	10	2.61	2.61
15	**2.38**	**2.64**	15	2.73	2.58
20	2.46	2.14	20	2.88	2.60
40	2.46	2.19	40	3.33	3.63
60	2.30	2.39	60	3.22	3.59

In the absence of a definite peak in the reflectance curves, the sum of the K/S values was chosen as the criterion on which to compare the depth of shade obtained by using different mordant concentrations. Based on the above observations, the sum of the K/S values at 15 g/l for copper (II) sulfate or 5 g/l for iron (II) sulfate was taken as the reference benchmark or 100% strength. Relative colour strength was calculated for the other mordant concentrations accordingly and the results are shown in Figure 3.15 and Figure 3.16. In the case of Thar (A. *catechu*), the use of 40 g/l iron (II) sulfate as mordant resulted in a 45% increase in the sum of the K/S values as compared to the benchmark. However, mordanting with different concentrations of copper (II) sulfate produced only marginal changes. The trend was reversed in the case of Caspian (A. *nilotica*), with copper (II) sulfate causing a similar 45% increase. These results reiterate the earlier observation that the final shade is dependent on the mordant employed.

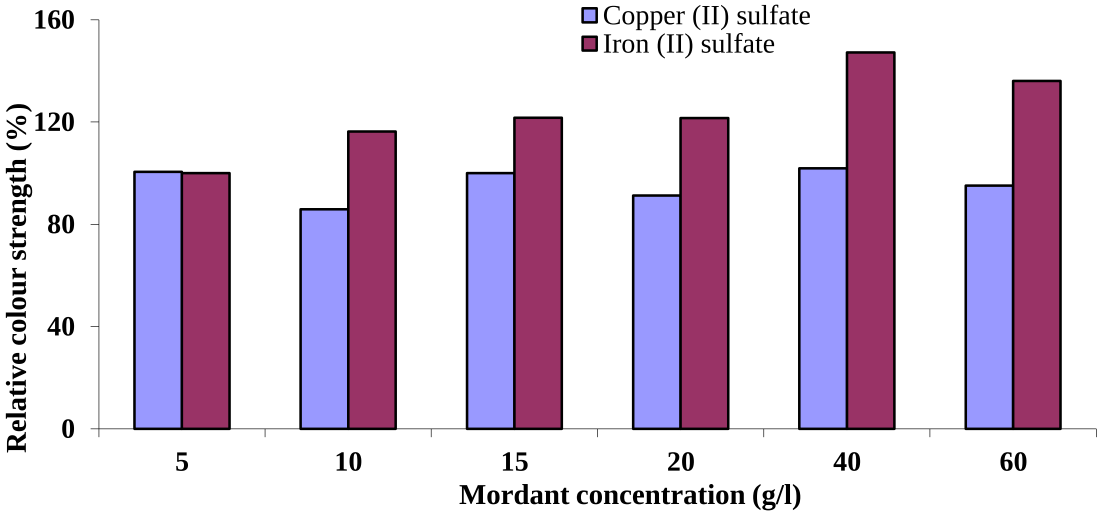


Figure 3.15 Comparison of colour strength (A. *catechu*) padded on cotton

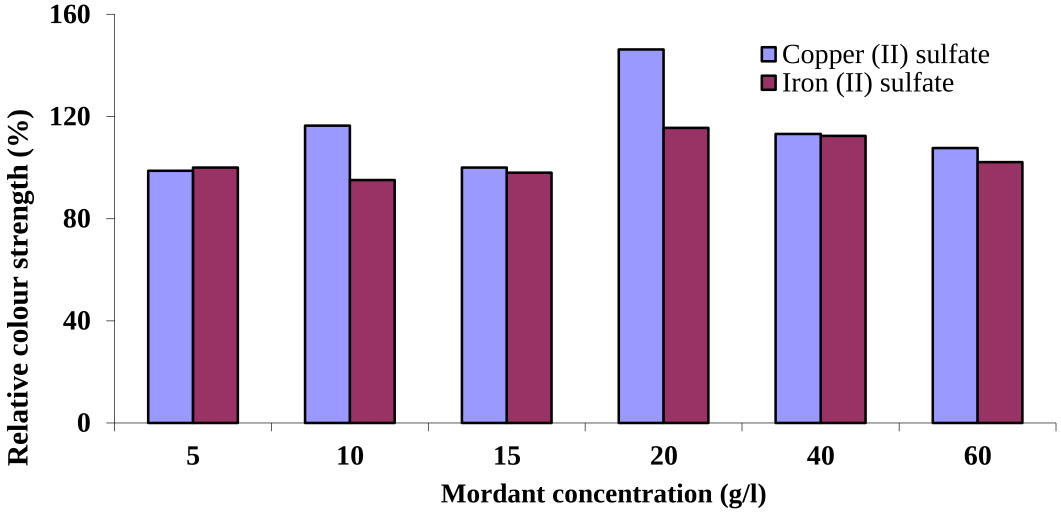


Figure 3.16 Comparison of colour strength (A. *nilotica*) padded on cotton

3.5.4.1 AAS results

The calibration graphs and trend-line equations for copper and iron are shown in Figure 3.17. The high degree of correlation for the trend-line is consistent with the working principles of AAS. The amount of metal in the fabric was calculated based on the trend-line equations.

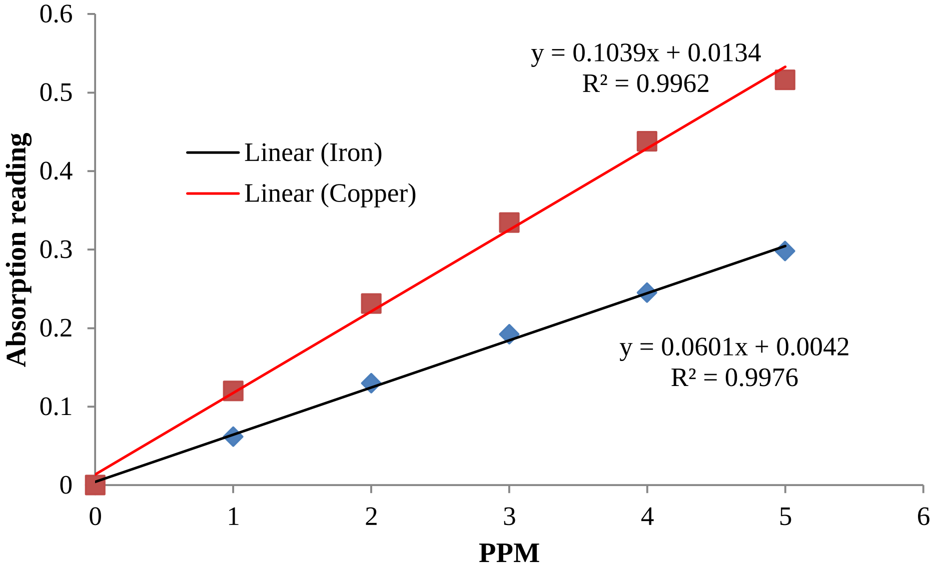


Figure 3.17 Calibration curve for AAS

The mass of metal padded on and retained by fabric samples weighing 10 g each are presented in Table 3.7. In considering these results, the following facts should be kept in mind: 1) a 10 g fabric sample padded with 5 g/l iron (II) sulfate picks up only 0.04

grams of the salt, which in turn contains a meagre 0.008 g of iron; and 2) a 10 g fabric sample padded with 15 g/l copper (II) sulfate picks up 0.12 g of salt, translated as 0.03 g of metal. It can be observed that both cotton and wool retained increasing quantities of copper or iron as the concentration of the corresponding salt was raised in the pad liquor. However, such increases were not in direct proportion. In the presence of dye, a significant increase in the mass of metal retained was observed for both mordants confirming the formation of a dye-metal-fibre complex as described earlier.

Table 3.7 Metal retained (mg) measured using AAS

Copper (II) sulfate (g/l)	**Metal (mg)**				
		Retained by			
	Applied by padding on 10 g fabric, 80% wet pick up	*Cotton*	*Cotton and dye*	*Wool*	*Wool and dye*
5	10.2	0.86		2.49	
10	20.4	1.29		8.87	
15	30.6	3.52	6.49	10.40	28.52
20	40.8	5.88		18.69	

Iron (II) sulfate (g/l)	**Metal (mg)**				
		Retained by			
	Applied by padding on 10 g fabric, 80% wet pick up	*Cotton*	*Cotton and dye*	*Wool*	*Wool and dye*
3	4.8	2.52		1.02	
5	8.1	5.22	6.12	2.88	6.04
10	16.1	5.78		4.07	
15	24.2	7.57		5.11	

The difference in optimum mordant concentration (5 g/l for iron (II) sulfate and 15 g/l for copper (II) sulfate) indicates that the dye reactivity varies according to the mordant. The observed optimum concentrations are much lower than the recommended concentration of 60 g/l mordant for meta-mordanting [94]. The low amount of mordant required for dyeing and the high metal retention percentage reduce effluent load.

When padding and exhaust dyeing are considered, there is a significant difference in the liquor ratio. Padding requires approximately 1:2 (calculated from 80% pick-up during padding of dye and mordant) while a ratio of 1:30 is recommended for exhaust dyeing. The mordant levels and time for dyeing are lower than the 5% OWM mordant levels and dyeing time of 45 minutes suggested for exhaust dyeing by the dye supplier. As mentioned earlier, the present study identified a significantly lower quantity of mordant as compared to that reported by other researchers. These observations are summarised in Table 3.8. Overall it is evident that padding is an attractive option as compared to exhaust dyeing using the natural dyes investigated.

Table 3.8 Comparison of dyeing process consumables (10 g fabric sample)

Dyeing process	**Exhaust**	**Padding [94]**	**Padding***
Water (ml)	300	20	20
Time (min)	45	20	20
Mordant (g)	0.50	0.48	0.12 or 0.04

* Padding parameters determined in this investigation

3.5.5 Fastness properties

Good fastness to rubbing, washing and light are desirable properties in dyed textiles. As evident from the test results shown in Table 3.9 all fastness ratings are 3-4 or better.

Table 3.9 Fastness testing results for pad-dyed cotton

Dye		**Thar (A. *catechu*)**		**Caspian (A. *nilotica*)**	
Mordant		$CuSO_4.5H_2O$ (15 g/l)	$FeSO_4.7H_2O$ (5 g/l)	$CuSO_4.5H_2O$ 15 g/l)	$FeSO_4.7H_2O$) (5 g/l)
Washing test		3–4	3–4	3–4	3–4
Light fading test		4–5	3–4	4–5	3–4
Rubbing test	*Dry*	5	5	5	5
	Wet	5	5	5	5

Both dyes, when mordanted using either copper (II) sulfate or iron (II) sulfate, exhibited excellent rubbing fastness. There was no staining of the white fabric under both dry and wet conditions. During washing, the colour did not bleed either into the liquor or onto the adjacent fabric. However, a colour tone change was observed after washing, leading to a grey scale rating of 3–4. This change may be attributed to long exposure (30 min) to a high temperature (60˚C) during standard washing. A similar change but of a temporary character was observed at the end of the light fading test. Samples subjected to testing for fastness to light regained their original tone of colour after conditioning at 20 ± 2°C and 65% RH for 24 hours. It is possible that at elevated temperatures one or more of the bond angles in the dye-mordant-cotton complex undergo changes, altering the shade. The change is reversible in the absence of excess moisture during light fading but becomes permanent when this restraint is removed during washing. Fading to light at 48 hours of exposure was rated 4–5 against blue wool standards.

The fastness results agree well with those obtained by Patel et al. [94]. Tannins, the main components of dyes derived from the Acacia family, are inherent mordants that are used to improve the fastness properties of other natural dyes. This factor combined with the metallic salts used in this study resulted in strong covalent bonds between cotton and the dye-mordant complex, leading to the robust fastness ratings observed. The results support the findings of Gupta [37], who postulates that the characteristics of mordants play a more important role for the fastness properties of natural dyes than the dyes themselves. Samples treated with copper (II) sulfate showed less significant colour change as opposed to those treated with iron (II) sulfate. This may be due to the more stable structure of the copper-dye-cotton complex.

3.6 Conclusions

Cotton fabric can be padded with natural dyes and a low mordant concentration to yield shades that are equivalent to those obtained by exhaust dyeing. The padded samples possessed acceptable rubbing, washing and light fastness properties. Post-mordanting is a better procedure than pre-mordanting or meta-mordanting when the levelness and depth of shade obtained are considered. Copper (II) sulfate and iron (II) sulfate as mordants produced beige and grey shades respectively with the same natural dye from the Acacia family. Each mordant-dye combination is unique in terms of the optimum amount of mordant required for the same amount of dye. The optimal mordant concentration was determined to be 15 g/l copper (II) sulfate and 5 g/l iron (II) sulfate respectively for 10 g/l dye. AAS results confirmed a definite increase in the quantity of metal retained by the dyed fabric as compared to mordanted fabric. FTIR analyses identified significant differences between the two dyes investigated; however, these differences diminished on forming complexes with iron or copper and cotton (dyed fabric). The difference seen in the reflectance curves may be attributed to variations in bond angle and orientation in the dyed fabric. The optimum process parameters, namely mordant concentration, process sequence and the post-mordanting technique, were adopted in the next stage where improvements to the padding of natural dyes were attempted.

Chapter 4

Plasma pretreatment for improving padding of natural dyes

4.1 Introduction

This chapter presents the investigations into one of the pathways of improving the dyeing process mentioned in Section 1.2.2.5. Atmospheric Pressure Plasma (APP) pretreatment has been applied to improve the pad-dyeing of natural dyes. The significance of APP is that it is a continuous process that does not require either water or chemicals [60, 143]. The following sections introduce plasma technology, describe the experimental procedures and discuss the results obtained.

4.2 Plasma technology

Plasma, also known as the fourth stage of matter, is defined as a collection of nearly equal numbers of positive and negative charges obtained by ionisation of a gas. This mixture of excited ions, molecules, electrons, neutrons, protons and free radicals (Figure 4.1) is highly reactive [144]. The plasma gas is ionised by addition of energy in the form of temperature or the application of a high electric field. Heat originated plasma, with a high volume of charged particles and gas densities, is described as ‘hot’ or thermal plasma and has temperatures above 700°C. Non-thermal or ‘cold’ plasma, generated by the application of a high electric field, exists at near room temperature and is better suited for treating textile materials [144, 145].

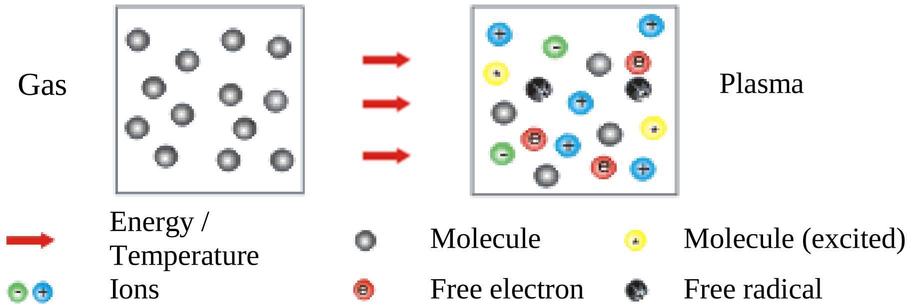


Figure 4.1 Schematic representation of plasma [144]

Shishoo [60] summarises the classification of cold plasma as low-pressure (vacuum) and atmospheric pressure, depending on the gas pressure at which the plasma is generated. The former, a mature technology developed in non-textile areas, operates at vacuum pressures between 10^{-2} and 10^{-3} millibars. The latter, operating at atmospheric pressures, is sub-divided into corona treatment, dielectric barrier discharge and glow discharge, based on shape and positioning of electrodes. The major disadvantages of the first two types are non-uniformity of treatment, the requirement for precise substrate positioning and low inter-electrode spacing (~1 mm). Glow discharge imparts uniform treatment by generating the plasma between two parallel-plate electrodes in an inert atmosphere.

Treatment by either vacuum or atmospheric pressure plasma yields comparable results in terms of the functionality achieved [145, 146]. Although APP for textiles is a fairly recent development, it is economical and convenient for continuous production as it avoids working under a vacuum [60]. A typical characteristic of all plasma treatment is that it affects only the surface (<1000 angstroms, 1 angstrom = 1 x 10^{-10}m) and leaves the bulk properties unaffected.

Desirable functionalities such as altered moisture relations (absorbance or repellence), antimicrobial property, soil repellence, stain resistance, soft handle and improved dyeing are widely achieved on textiles by wet finishing processes. Such processes employ a variety of chemicals [11]. Plasma pretreatment followed by wet finishing has been employed to impart similar functional finishes to textile materials with lesser amount of chemicals and in some cases without the use of chemicals or water [147-154]. The effect of plasma treatment may be altered by varying process parameters such as supply frequency, discharge power, treatment time, type and pressure of gas. For example oxygen or helium plasma increases moisture absorbance while fluorocarbon increases water repellence. Several surface phenomena such as adsorption, desorption, etching, cleaning, surface activation and cross-linking occur singly or in combination on exposure to plasma [154-156]. A concise comparison between traditional finishing and plasma treatment is given in Table 4.1 [60].

Table 4.1 Plasma treatment vs. traditional wet processing [60]

	Plasma processing	**Traditional wet chemistry**
Medium	No wet chemistry involved;. treatment by excited gas	Water based
Energy	Electricity – only free electrons heated (<1% of system mass)	Heat – entire system mass temperature raised
Reaction type	Complex, multi-functional and simultaneous	Relatively simpler, well established

Reaction location	Surface specific, unaltered bulk properties	Bulk of material is usually affected
Potential for new processes	High, rapidly developing field	Low technological growth
Equipment	Experimental, laboratory and prototype, rapid development	Mature, slow evolution
Energy consumption	Low	High
Water consumption	Negligible	High

Consistent with the above discussion, treatment of wool with plasma has been reported to affect the lipid layer and surface cuticle without changing the bulk properties. This results in higher wettability and increased dye up-take, leading to improvements in the depth of shade and evenness. The available literature relates only to different classes of synthetic dyes [157-159]. It has also been suggested that intrinsic dye hydrophilicity is a deciding factor in this improvement [160]. Hence atmospheric pressure plasma pretreatment of wool was expected to improve padding with natural dyes.

4.3 Equipment

4.3.1 Plasma machine

An atmospheric plasma treatment system APC 2000 (Figure 4.2), manufactured by Sigma Technologies International (Tucson, Arizona, USA), operating at ambient temperature, was used. Figure 4.3 shows the two aluminium electrodes mounted above a ceramic-coated aluminium electrode (in the form of a roller) to which the fabric (face side up) was attached using masking tape [161]. The operating frequency and roller speed were 90 kHz and 25 rpm respectively. The voltage range used was 1.8–2.2 kV with a maximum power input of 5 kW.

Figure 4.2 APC 2000 atmospheric plasma treatment system [161]

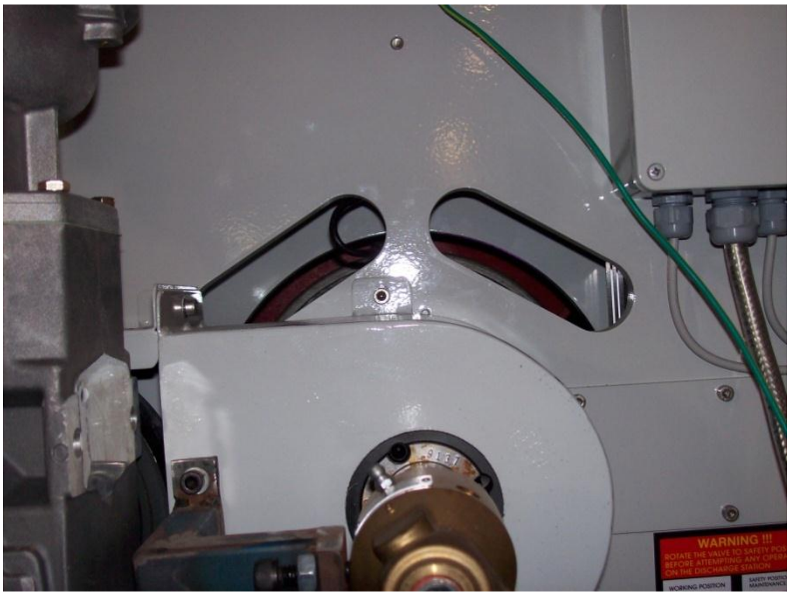


Figure 4.3 APC 2000 side view showing position of electrodes [161]

4.3.2 Padding mangle, steamer and dryer

The equipment described in Sections 3.2.1, 3.2.2 and 3.2.3 were used for padding, steaming and drying. The operating conditions were the same as adopted in Chapter 3.

4.4 Materials

The fabrics, mordant-dyes and required chemicals described in Sections 2.2.1.1, 2.2.1.2 and 2.2.1.3 were used in this investigation.

4.5 Methods

This section describes the plasma pretreatment and subsequent padding and evaluation processes.

4.5.1 Plasma pretreatment

The electrodes were thoroughly cleaned using ethanol to remove residual traces of glue and other debris. A fabric sample (wool or cotton) of size (40 cm x 40 cm) was attached to the roller electrode using masking tape. Care was taken to ensure that the attached fabric passed freely between the electrodes. Fabrics were treated with plasma for two exposure times of approximately 7 and 14 seconds based on earlier research [160]. Exposure time was calculated considering the number of passes through the plasma machine. Two plasma gases (100% helium and a mixture of 95% helium and 5% nitrogen) were evaluated. It was expected that the plasma generated from the mixture of gases would be more reactive. A flow rate of 14 litres per minute was used in both cases. In order to obtain a patterning effect by partially blocking the plasma, a white copy paper was applied as a mask (Figure 4.4). Treated samples were kept in a clean air-tight environment with minimum handling to prevent contamination prior to evaluation or padding.

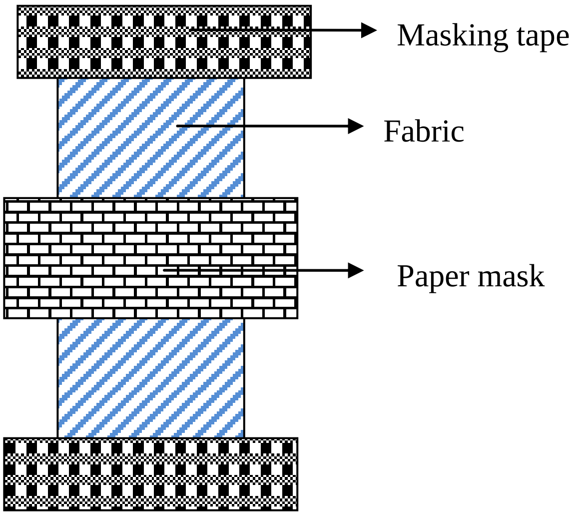


Figure 4.4 Schematic sample set-up for plasma treatment

4.5.2 Padding

Padding of cotton and wool fabric samples pretreated with plasma was carried out as described under Section 3.3.1. Post-mordanting and the optimum parameters determined in Chapter 3 and shown in Table 4.2 were adopted.

Table 4.2 Mordant concentration and sequence for padding with 10 g/l dye

Mordant	**$CuSO_4.5H_2O$**	**$FeSO_4.7H_2O$**
Concentration (g/l)	15	5
Dyeing sequence	Pad → Dry → Steam	Pad → Steam → Dry
Mordanting sequence	Pad → Steam → Dry	Pad → Steam → Dry

4.5.3 Evaluation

The wettability of untreated and plasma-treated fabrics was evaluated according to the methods described in Section 2.2.3.3. Dyed fabrics were conditioned prior to assessing their colour strength and fastness properties according to the procedures described in Section 2.2.3.

4.6 Results and discussion

4.6.1 Fabric wettability

It was observed that plasma-treated wool fabric instantaneously absorbed a drop of water. Similarly, wicking height in excess of 5 cm in the given time was measured for all plasma-treated wool fabrics. As evident from the data presented in Table 4.3, over identical periods of measurement, the wicking length appeared to be independent of plasma-gas type and treatment duration. In comparison, untreated wool showed a wicking length of 1.0 cm only. The above observations and results are in agreement with the findings of Sun and Stylios [151] and Shekar ad Bajpai [152] who report increased absorbency and wicking when wool was treated with plasma. Another study [160] exposed similar fabric to helium plasma, under conditions identical to the present investigation, and determined that a 1 second exposure to plasma was sufficient to make the surface hydrophilic. It was established that this was primarily due to surface modification only and did not involve removal of the fatty acid layer.

On the other hand, cotton did not display any substantial difference in absorbance or wicking between untreated and treated fabrics. This may be due to the intrinsic hydrophilicity of bleached and mercerised cotton, which is not significantly increased by plasma treatment.

Table 4.3 Wicking test results

Wicking height (cm)										
Fabric	Wool					Cotton				
Plasma gas	Nil[a]	He[b]		Mix[c]		Nil[a]	He[b]		Mix[c]	
Time		7 sec	14 sec	7 sec	14 sec		7 sec	14 sec	7 sec	14 sec
0.5 min	0.0	1.0	1.2	1.0	1.2	0.5	0.75	0.75	0.75	0.7
1 min	0.25	2.0	2.4	2.1	2.5	1.2	1.3	1.3	1.3	1.3
5 min	0.50	4.0	4.0	3.8	4.1	4.6	4.5	4.6	4.5	4.7
15 min	1.0	5.2	5.5	5.3	5.5	8.5	8.5	8.5	8.5	8.5

a – untreated, b – Helium (100%), c – Helium (95%) + Nitrogen (5%)

4.6.2 Effect of plasma treatment on shade obtained

Plasma-treated and untreated cotton and wool fabric samples were dyed with natural dyes derived from the Acacia family using the padding method and post-mordanting technique. Similar to the results reported in Chapter 3, mordanting with copper (II) sulfate resulted in a copper-beige shade while iron (II) sulfate yielded a yellowish-grey shade. A definite increase in the depth of shade was observed only on wool fabric for both plasma gases used, irrespective of the dye and mordant applied. The darkest shade was obtained when pure helium was used as the plasma gas and at 14 second exposure duration. Reflectance curves shown from Figure 4.5 through Figure 4.8 are evidence of the above.

Similar to the wicking behaviour, plasma pretreatment did not significantly improve the dyeing of cotton. In general, a more uniform dye distribution was visually observed on the surface of plasma-treated fabric (both wool and cotton) as compared to untreated fabric. This was confirmed by a less than 2% variation in the sum of the K/S values measured at 10 points across the sample.

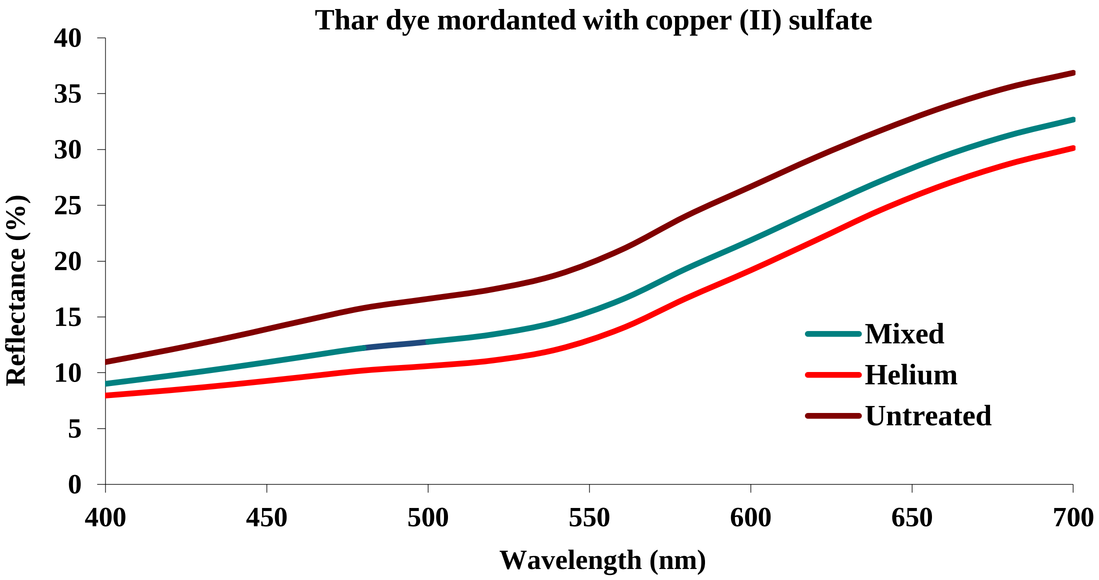


Figure 4.5 Effect of plasma gas on depth of shade
(fabric wool, exposure time 14 s, dye Thar, mordant copper (II) sulfate)

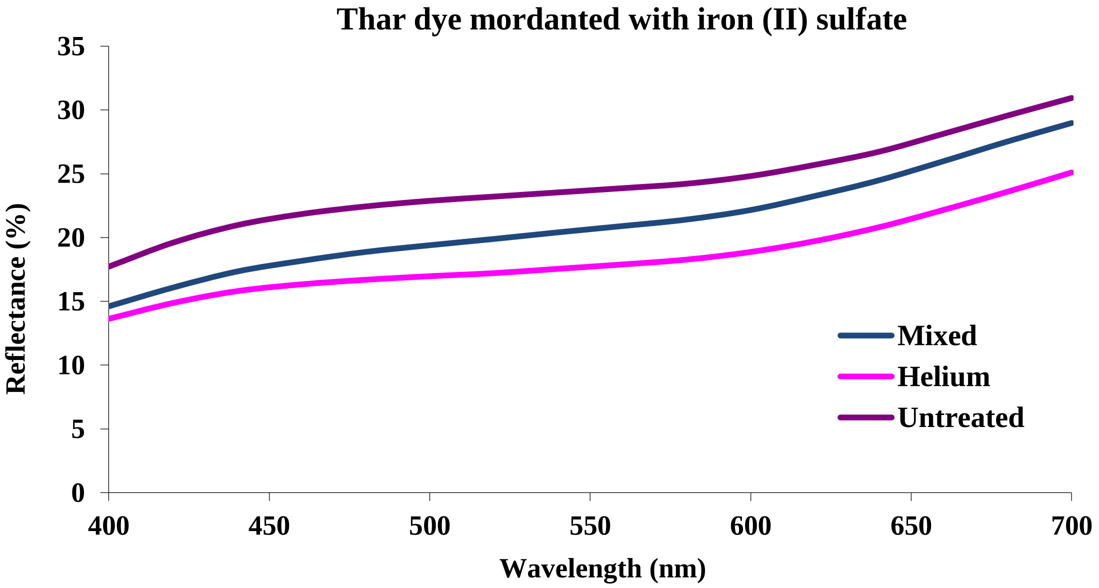


Figure 4.6 Effect of plasma gas on depth of shade
(fabric wool, exposure time 14 s, dye Thar, mordant iron (II) sulfate)

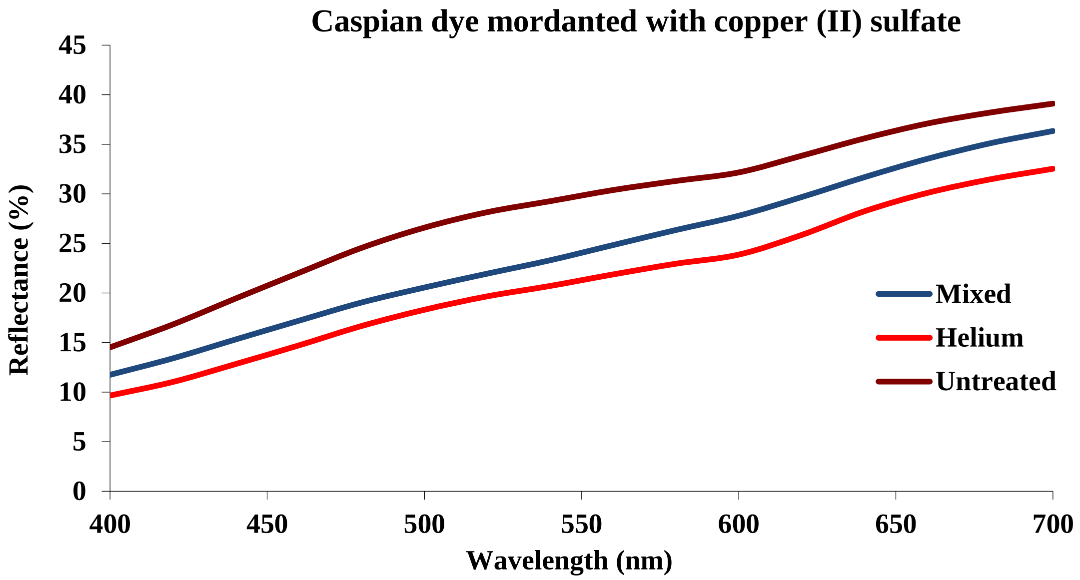


Figure 4.7 Effect of plasma gas on depth of shade
(fabric wool, exposure time 14 s, dye Caspian, mordant copper (II) sulfate)

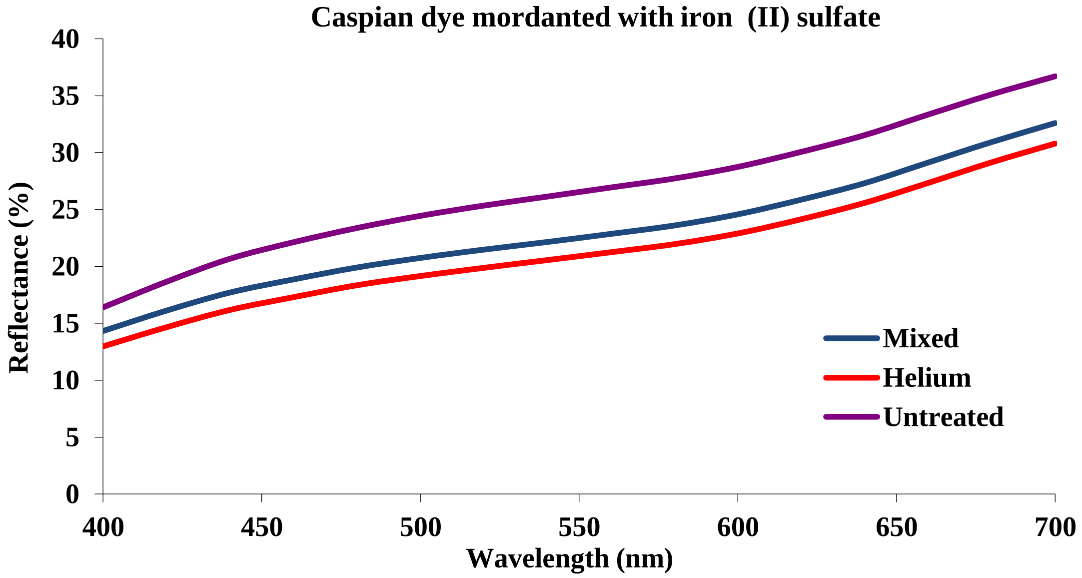
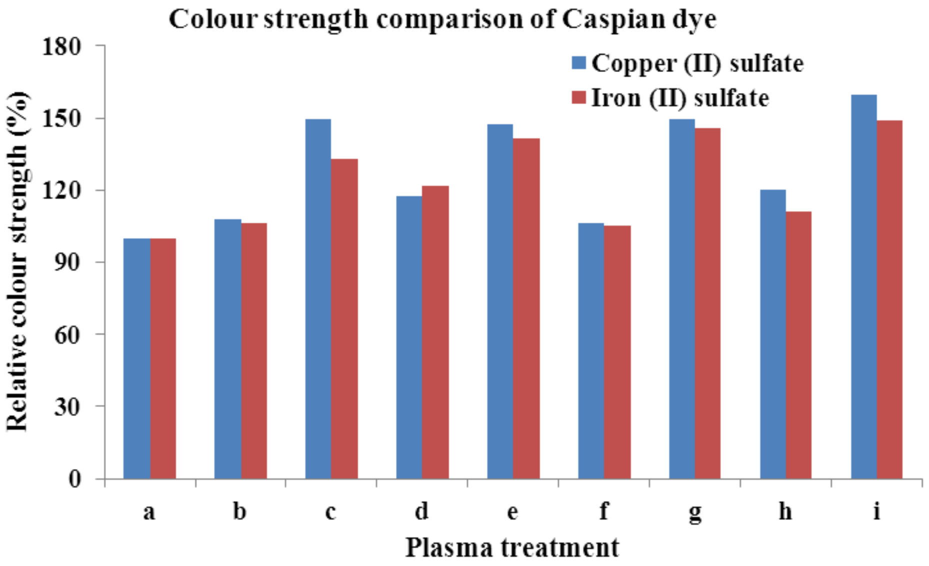


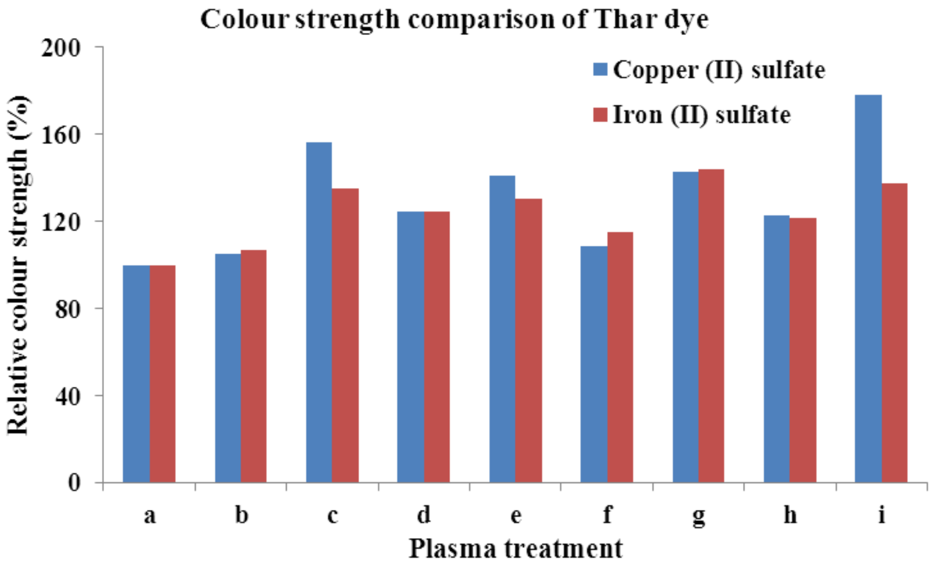
Figure 4.8 Effect of plasma gas on depth of shade
(fabric wool, exposure time 14 s, dye Caspian, mordant iron (II) sulfate)

Figure 4.9 and Figure 4.10 are graphical representations of the sum of the K/S values for wool fabrics dyed using the two natural dyes in individual combinations with the two mordants. The graphs bring out the effect of the composition of gas and duration of plasma treatment on the final shade obtained. They also include results regarding the outcomes of blocking the plasma using a paper mask. The value for samples dyed without plasma treatment was used as the benchmark (100%).



a) Untreated; b) 7 s mix masked; c) 7 s mix; d) 14 s mix masked;
e) 14 s mix; f) 7 s He masked; g) 7 s He; h) 14 s He masked; i) 14 s He

Figure 4.9 Effect of varying the plasma parameters on padding Caspian dye on wool fabric



a) Untreated; b) 7 s mix masked; c) 7 s mix; d) 14 s mix masked;
e) 14 s mix; f) 7 s He masked; g) 7 s He; h) 14 s He masked; i) 14 s He

Figure 4.10 Effect of varying the plasma parameters on padding Thar dye on wool fabric

An overall increase in depth of shade was observed as the exposure period increased irrespective of the gas used or dye-mordant combination. A treatment time of 14 seconds in plasma produced from pure helium resulted in an average increase of 60% in the depth of shade (Figure 4.9 and Figure 4.10 (i)). This could be attributed to sustained surface modification (etching) due to increased duration of plasma treatment. However, when treatment duration was increased to 14 seconds in plasma produced from the gas mixture, the increase in depth of shade was either marginal or reversed (Figure 4.9 and Figure 4.10 (c and e)). Apparently, as treatment time increased, the addition of nitrogen reduced the effect of the pretreatment. Similar trends, albeit of a lower proportion, are seen in the masked area as well. This indicates that the paper mask is only partially effective in blocking the plasma.

Generally, a higher increase in relative colour strength is seen when copper (II) sulfate is used as a mordant instead of iron (II) sulfate irrespective of plasma gas or dye. This could be due to the higher reactivity of the copper chelate with the plasma activated surface.

The multi-dentate structure of the polyphenolic dyes used possesses several hydroxyl groups that make them have properties similar to those of hydrophilic acid dyes. Consistent with an earlier publication [160], the observed enhancement in depth of shade on plasma treated fabrics confirms the hydrophilic nature of the dyes.

As mentioned earlier, the paper mask employed was able to partially block the plasma. When the fabric was padded, a tone-on-tone pattern (Figure 4.11) due to differential dyeing was obtained in a single step. This may be employed to simplify current printing processes. The novel patterning effects could be exploited by designers to cater to niche markets. A limitation was that the composite (mask and fabric) should pass unhindered between the electrodes during plasma treatment which restricts thick fabrics from being treated in this manner.

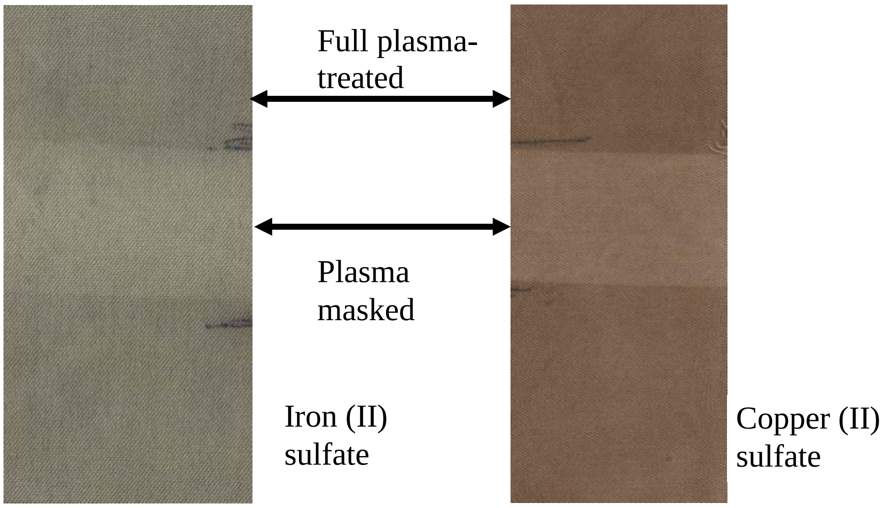


Figure 4.11 One-step patterning

4.6.3 Fastness properties

Plasma treatment improved the depth of shade but did not affect the fastness properties of the natural dyes under consideration. As can be seen from Table 4.4, the fastness properties of wool fabric dyed after plasma treatment are identical to those of cotton fabric without plasma treatment reported in Chapter 3 (Table 3.9). Depth of shade as well as fastness properties of cotton fabrics are not affected by plasma pretreatment. Hence the results are not presented here.

Table 4.4 Fastness properties of wool dyed after plasma treatment
(Plasma gas – Helium, treatment duration – 14 s)

Dye	**Thar (A. *catechu*)**				**Caspian (A. *nilotica*)**			
Mordant	$CuSO_4.5H_2O$ (15 g/l)		$FeSO_4.7H_2O$ (5 g/l)		$CuSO_4.5H_2O$ (15 g/l)		$FeSO_4.7H_2O$ (5 g/l)	
Washing test	3–4		3–4		3–4		3–4	
Light fading	4–5		3–4		4–5		3–4	
Rubbing	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
	5	5	5	5	5	5	5	5

4.7 Conclusions

Combining atmospheric pressure plasma treatment and padding enhances the process efficiency, quantified by the depth of shade obtained from a given dye concentration, of continuous application of natural dyes on wool. Plasma pretreatment provides a benign alternative to the existing wet-treatment methods for enhancing dye uptake on wool.

Compared to 7 s, 14 s exposure of wool fabric to plasma leads to an increase in the depth of shade obtained, highlighting the progressive surface modification of wool. The hydrophilic character of the natural dyes used is identified by their enhanced uptake by plasma-treated wool. In this case, copper (II) sulfate performs better than iron (II) sulfate as a mordant in terms of increasing the depth of shade. Partial blocking of plasma pretreatment that brings about differentiated dyeing may be used to produce one-step patterning effects aimed at niche markets. Apart from improving the levelness, plasma pretreatment did not significantly increase the depth of shade on cotton fabrics. The fastness properties of the dyed fabrics were unaffected by the pretreatment. The next chapter will be aimed at improving the padding of cotton with natural dyes.

Chapter 5

Improving dyeing performance by using chitosan in padding of natural dyes

5.1 Introduction

There are many approaches for increasing colour yield during dyeing. These could be simple changes to process parameters (such as temperature and time), pretreatment of the substrate and addition of auxiliaries [11, 12, 50]. The process gains popularity when the increase in colour yield is brought about by using a byproduct or waste product [78, 79, 162, 163].

Chitin is a byproduct of the seafood industry because it is abundantly present in the inedible shells of crustaceans such as crabs, shrimps and lobsters. It is also the second most widely present natural polymer next to cellulose. Chitosan is derived by de-acetylation of chitin [164]. The interaction between chitosan and textile dyes has been utilised in a variety of applications [163-168]. However, application of chitosan simultaneously with dye, especially by padding, has not been reported. This chapter details the work done to improve the padding of natural dyes by incorporating chitosan in the dye bath. A brief discussion of chitosan and its typical characteristics is followed by a description of the experiments and comprehensive analyses of the results obtained.

Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (de-acetylated unit) and N-acetyl-D-glucosamine (acetylated unit) [166]. As depicted in Figure 5.1, it is poly-cationic with three reactive groups, namely the amino (–NH_2) group at C-2 and the two hydroxyl (–OH) groups at C-6 and C-3 in each repeat unit. This poly-cationic character has been utilised in different areas, such as cosmetics, weight loss, health care, water treatment and textile dyeing [164, 168].

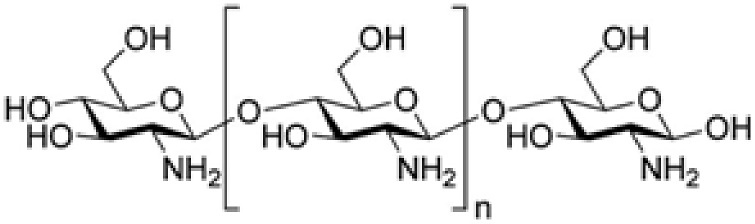


Figure 5.1 Schematic structure of chitosan [164]

5.1.1 Application of chitosan in dyeing

The characteristic of multiple reaction sites in chitosan has been utilised for the decolourisation of dyeing effluents by agglomeration [169, 170]. Alternately, the ability to agglomerate dyes has been used to improve the dye-ability of cotton and wool by pretreatment with chitosan. The mechanism proposed was that chitosan forms a film and increases the number of reaction sites on the substrates for dyes [168, 171]. An improvement in dye uptake leading to darker shades has been reported for both synthetic and natural dyes [96, 97, 163, 172-174]. Rippon [175] pretreated cotton fabric with chitosan to lower the differences in depth of shade between immature and mature fibres. Similar effects of chitosan pretreatment on damaged and undamaged wool have been reported by Davidson and Xue [174]. It should be noted that these dyeing studies applied chitosan in a separate step and primarily used the exhaust method of dyeing. Hence combining chitosan and dye in one-step pad-dyeing offers an unexplored research area.

5.1.2 Antimicrobial activity of chitosan

The use of chitosan has been known to impart a durable antimicrobial functionality to the textile substrate [96, 176, 177]. Such functionality is desirable because it avoids bad odours and occasional damage of textile caused by microbial growth. The antimicrobial activity of chitosan is generally attributed to interaction between the cationic chitosan and anionic cell surface of microbes. The interaction leads to extensive microbial cell surface alterations and damage, inhibiting metabolism and finally killing the microbe [176, 178, 179]. Chitosan acts as a biocide for some microbes and as biostatic for others [180]. The lowest amount of a substance required to inhibit microbial activity is termed the Minimum Inhibition Concentration (MIC). Chitosan has been reported to have an MIC of 0.05% [181]. Hence, including chitosan in the padding liquor of natural dyes is likely to impart antimicrobial features to the dyed fabric. Such an additional benefit would open specialty markets in medical textiles. Hence the antimicrobial effectiveness of the dyed fabric also needs to be evaluated.

5.2 Equipment

5.2.1 Padding mangle, curing chamber and dryer

The equipment described in Sections 3.2.1, 3.2.2 and 3.2.3 were used for padding, curing and drying. The operating conditions were the same as described earlier.

5.2.2 Antimicrobial testing

Sterile petri dishes, conical flasks and a thermostat oven were the main equipment utilised for this process.

5.3 Materials

A bleached and mercerised cotton fabric and the two mordant dyes described in Section 2.2.1.1 and Section 2.2.1.2 were used in this set of experiments. Chemicals listed in Table 2.2 were utilised according to the recipe employed. Chitosan from crab shells (Brookfield viscosity of 200 centipoise and degree of de-acetylation > 80%) was sourced from Sigma-Aldrich, Australia and used as received. As bacterial growth media, tryptone soya agar and nutrient broth, both from Oxoids, Australia, were used.

5.4 Methods

5.4.1 Padding

A 1% stock solution of chitosan was prepared in 1% acetic acid by stirring until a clear solution was obtained**.** The dissolved chitosan was incorporated into the padding liquor at 0.025%, 0.05%, 0.075% and 0.1% w/v concentrations. In continuation of the work reported in Chapter 3, padding liquor was prepared in accordance with the recipe furnished in Table 5.1. The notable difference was the omission of sodium alginate, because anionic sodium alginate has been reported to form a complex with cationic chitosan and this complex can hinder the dyeing process [182]. Optimal mordant concentrations, 15 g/l for copper (II) sulfate ($CuSO_4.5H_2O$) and 5 g/l iron (II) sulfate ($FeSO_4.7H_20$) as determined in Chapter 3, were used in this phase as well. Freshly prepared dye and mordant solutions were used for all the experiments.

Table 5.1 Padding liquor recipe incorporating chitosan

Chemical	**Concentration (g/l)**
Caspian (A. *nilotica*) or Thar (A. *catechu*)	10
Chitosan (w/v %)	0.025/0.05/0.075/0.1
Potassium sulfate	1

Cotton fabric (10 g) was padded using the 3 dip–3 nip technique at room temperature with 80% wet pick-up. As shown in Figure 5.2, curing or dry-baking at 130°C instead of steaming was adopted for the fixation of chitosan [183]. Post-mordanting (dye padding followed by mordant padding) was followed throughout the investigation. After padding with mordant, samples were cured at 100°C for 5 minutes. The next step was soaping off with 1 g/l anionic soap solution at boil for 20 minutes. The samples were finally rinsed in hot and cold water respectively and dried at 65°C.

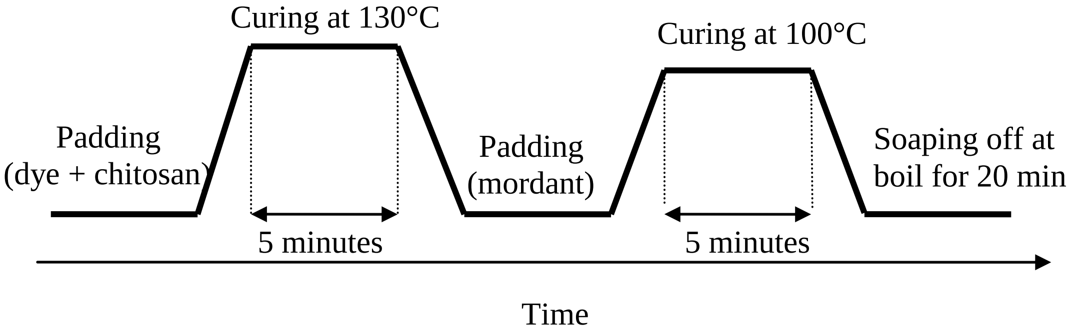


Figure 5.2 Line diagram of pad dyeing in the presence of chitosan

5.4.2 Evaluation

Procedures described in Section 2.2.3 were followed to measure the colour strength and fastness properties of conditioned dyed fabrics. In addition, the antimicrobial effectiveness was assessed according to the procedure given in Section 2.2.3.3. The dyes, in solution by themselves, were also evaluated to eliminate the possibility of inherent antimicrobial properties that may be attributed to some polyphenols [115].

5.5 Results and discussion

5.5.1 Shades obtained

The results were similar to those obtained previously for both Caspian and Thar dyes. Mordanting with copper (II) sulfate resulted in a beige shade while iron (II) sulfate yielded a grey shade, irrespective of the inclusion of chitosan. This is evident from the near-parallel reflectance curves (Figure 5.3 and Figure 5.4) for the two dyes. The lower curves obtained for the samples dyed in the presence of chitosan indicate a darker shade.

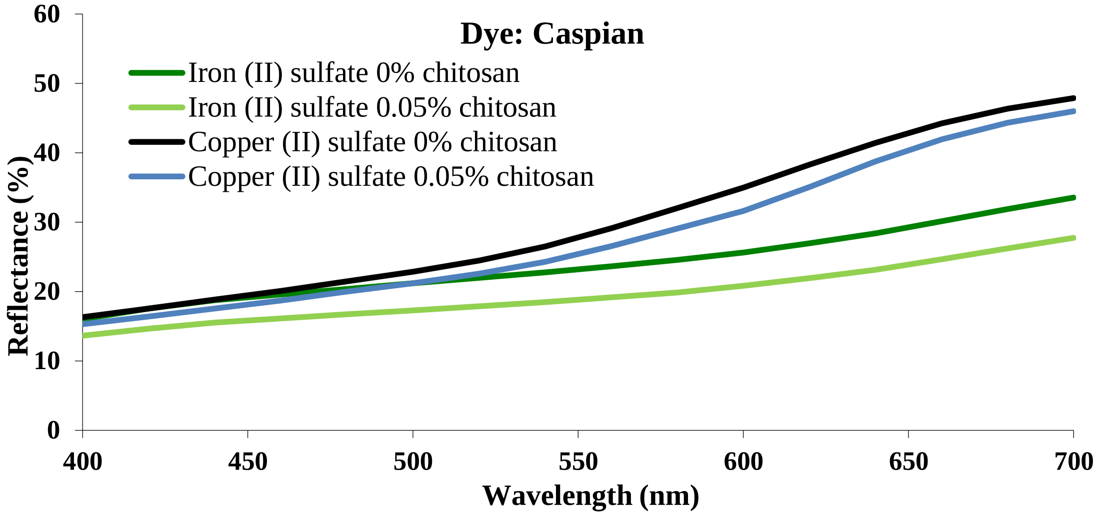


Figure 5.3 Reflectance curve for Caspian

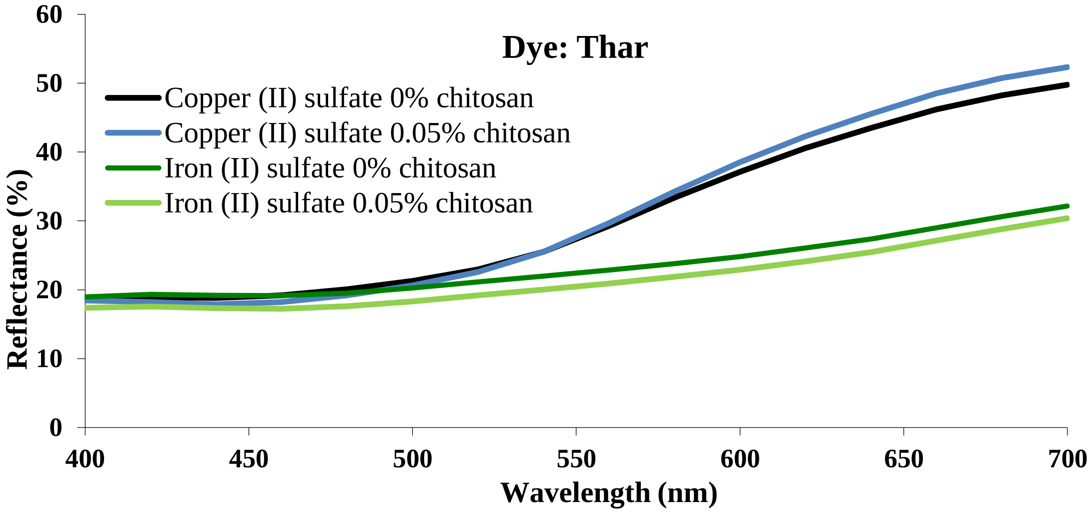


Figure 5.4 Reflectance curve for Thar

5.5.2 Effect of chitosan

Figure 5.5 and Figure 5.6 show shade cards that bring out the effect of adding chitosan to the padding liquor. In order to quantify the shades, the sums of the K/S values are depicted in Figure 5.7 and Figure 5.8, assuming the value obtained for fabric dyed without chitosan as the benchmark (100%).

It can be seen from the shade cards and graphs that the addition of chitosan to the dye liquor affected the depth of shade irrespective of the dye–mordant combination. In general, a uniform dye distribution was observed on the fabric padded in the presence of chitosan. Davidson and Xue [174] and Canal et al. [172] have reported similar levelness of shade in exhaust dyeing experiments conducted after pretreatment of fabric with chitosan. They attributed the evenness of shade to the film-forming characteristic of chitosan, which provided an increased number of reaction sites for the dye. Other researchers have exploited the film-forming feature in diverse areas [183-185]. However, this feature might have inhibited dye uptake during initial trials in this study when the fabric was pretreated with 0.05% chitosan followed by padding. It was likely that the low quantity of dye liquor taken up by the pretreated material was insufficient to overcome the chitosan film barrier and dye the fabric.

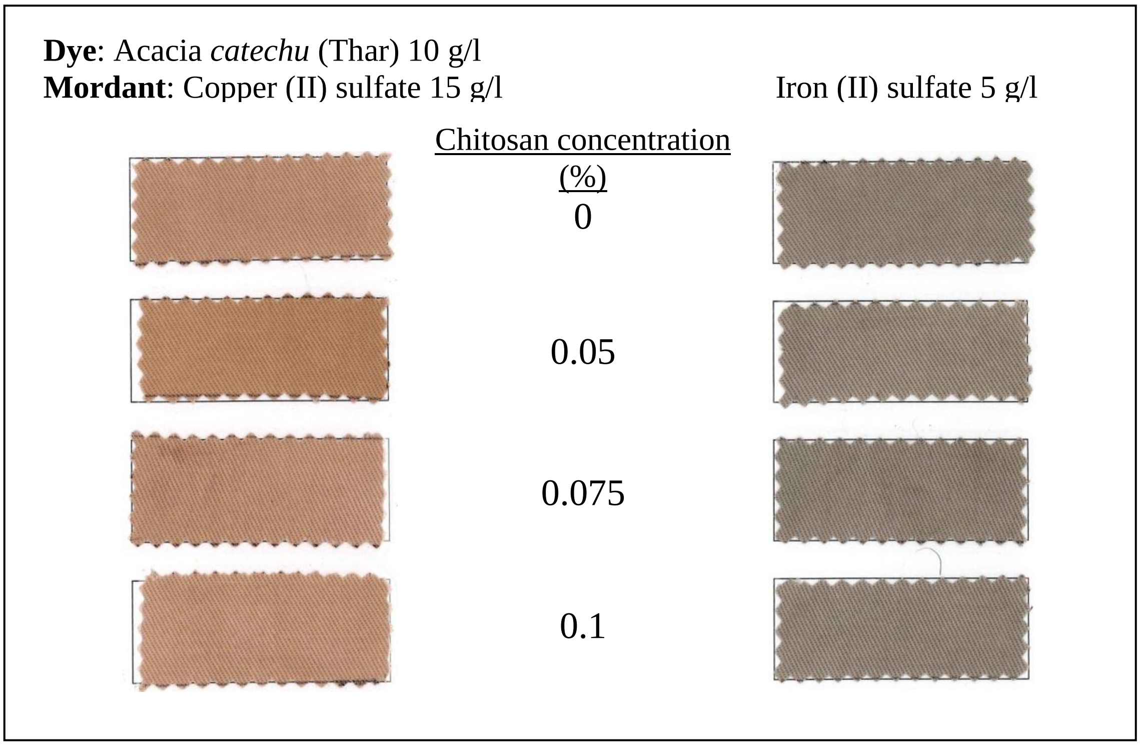


Figure 5.5 Shade card for Thar dye

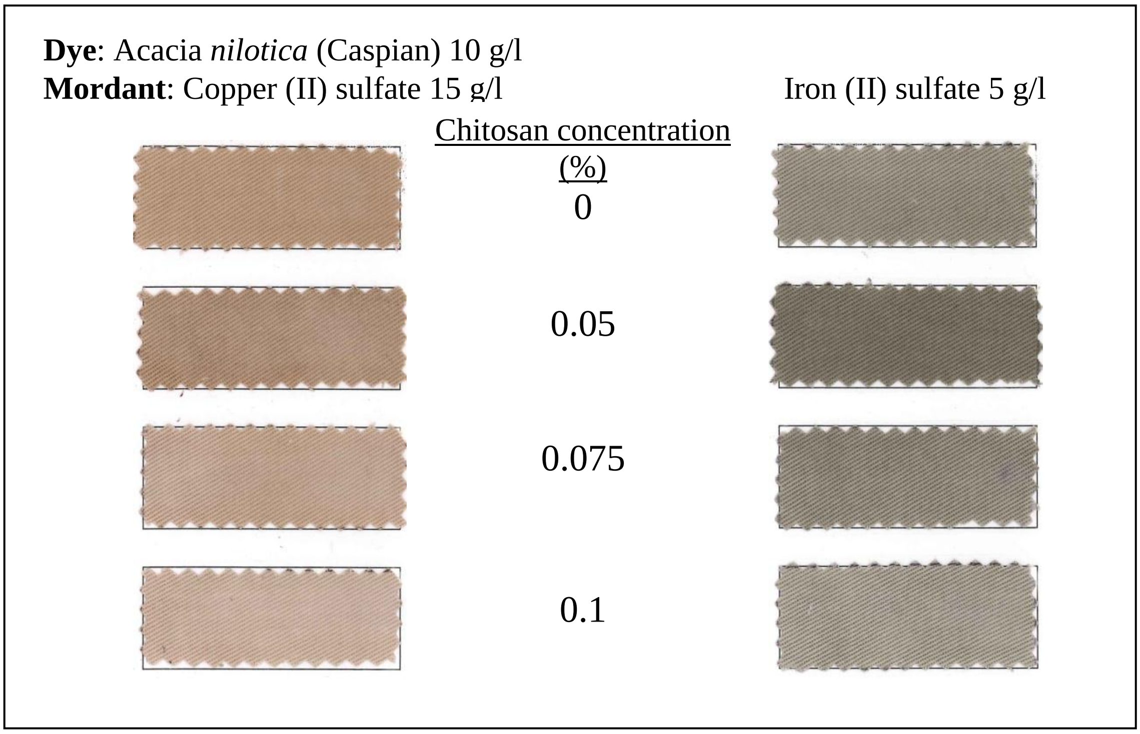


Figure 5.6 Shade card for Caspian dye

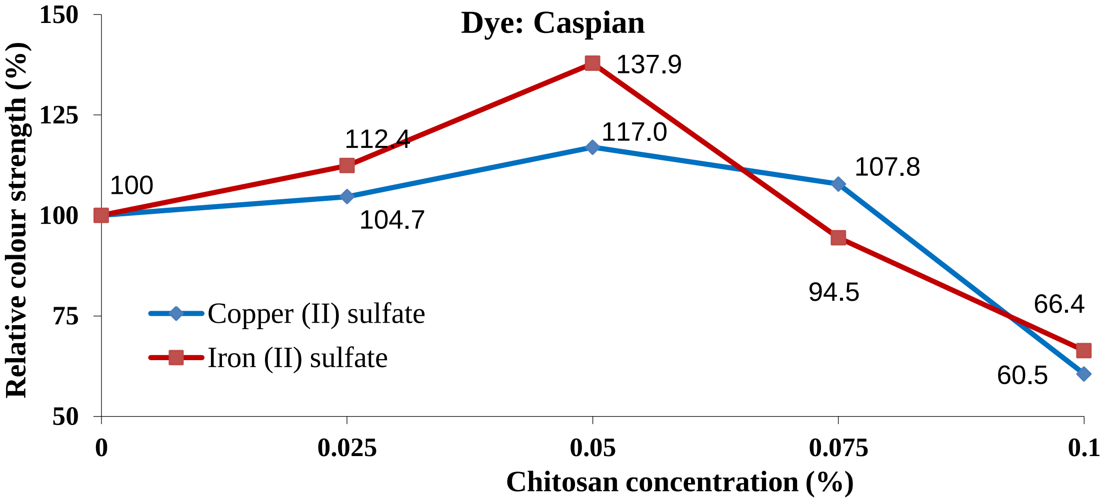


Figure 5.7 Comparison of sum of the K/S values for Caspian dye

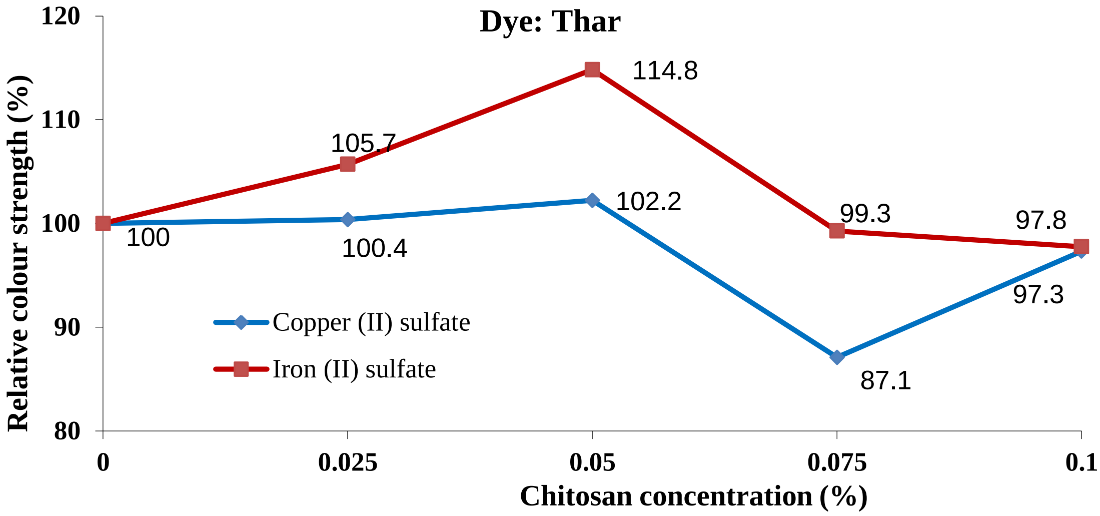


Figure 5.8 Comparison of sum of the K/S values for Thar dye

It can be observed from Figure 5.7 and Figure 5.8 that incorporating 0.05% chitosan in the dye liquor produced the darkest shades for both mordants in combination with either dye when compared to samples dyed without chitosan. Further additions of chitosan reduced the colour strength. The observations contradict earlier results of exhaust dyeing, where an increase in the amount of chitosan used in pretreatment produced a proportional increase in the depth of shade [171, 174, 175]. As suggested by Chenite et al. [186] and Hirano et al. [187], it is likely that the chitosan film formed a gel in the presence of excess water and extended process time, which are typical characteristics of exhaust dyeing. Such a gel would have been able to attract additional quantities of dye leading to the darker shades reported by earlier researchers [171, 174, 175].

While analysing the padding results, in addition to the film-forming characteristic of chitosan the competing affinities between chitosan-dye, chitosan-cotton and dye-cotton also have to be taken into consideration. If it is assumed that at low chitosan concentrations cotton has an equal affinity for both chitosan and dye, then the thin film of chitosan absorbed an additional quantity of dye, leading to the observed increase in depth of shade. When higher amounts of chitosan were added to the pad liquor, the cotton absorbed a relatively lower amount of dye. The absorbed chitosan formed a thicker film which, in spite of having absorbed more dye, could not be readily penetrated by the dye especially in the low volume of liquor picked up. The combined effect was reflected as the lower colour strength at higher concentrations of chitosan.

The difference between the two dyes, Caspian and Thar, determined by FTIR in Chapter 3 becomes prominent when the effect of chitosan in increasing the depth of shade is considered. On examining Figure 5.7 and Figure 5.8, it is clear that the depth of shade increased less for Thar as compared to Caspian. It is possible that the subtle variations between the dyes and the resultant complexes alter the interaction with chitosan.

The increase in depth of shade was more pronounced when iron (II) sulfate was the mordant as compared to copper (II) sulfate. This may be due to the increased affinity of chitosan for Fe^{++} as compared to Cu^{++} ions [188, 189], translated as an increased affinity for the dye-mordant complex.

5.5.3 Fastness properties

The fastness properties of the cotton fabric pad-dyed in the presence of 0.05% chitosan are consistent with those obtained earlier. The results given in Table 5.2 indicate that chitosan does not significantly affect the fastness properties of the natural dyes investigated.

Table 5.2 Fastness ratings of cotton fabric dyed with Acacia dye and 0.05% chitosan

Dye (10 g/l)		**Thar (A. *catechu*)**		**Caspian (A. *nilotica*)**	
Mordant		$CuSO_4.5H_2O$ (15 g/l)	$FeSO_4.7H_2O$ (5 g/l)	$CuSO_4.5H_2O$ (15 g/l)	$FeSO_4.7H_2O$ (5 g/l)
Washing test		3–4	3–4	3–4	3–4
Light fading		4–5	3–4	4–5	3–4
Rubbing	*Dry*	5	5	5	5
	Wet	5	5	5	5

5.5.4 Antibacterial evaluation results

In accordance with the test specifications in Section 2.2.3.4, the agar plates for the different dilutions for the control swatch were examined after incubation. The plates containing 10^0 and 10^1 times dilutions had uncountable colonies, while the plate with 10^3 times dilution had too few colonies. These plates were therefore discarded. The plate with 10^2 dilutions with 253 Colony Forming Units (CFU) was selected to compare the control and test swatches.

Both dyes, when tested on their own, were found to be inactive, with uninhibited growth of bacteria (>500 CFU) in the agar plates (Figure 5.9). This is in agreement with the results published by Singh et al. [101], who reported that the dyes derived from the Acacia family do not possess intrinsic antibacterial functionality.

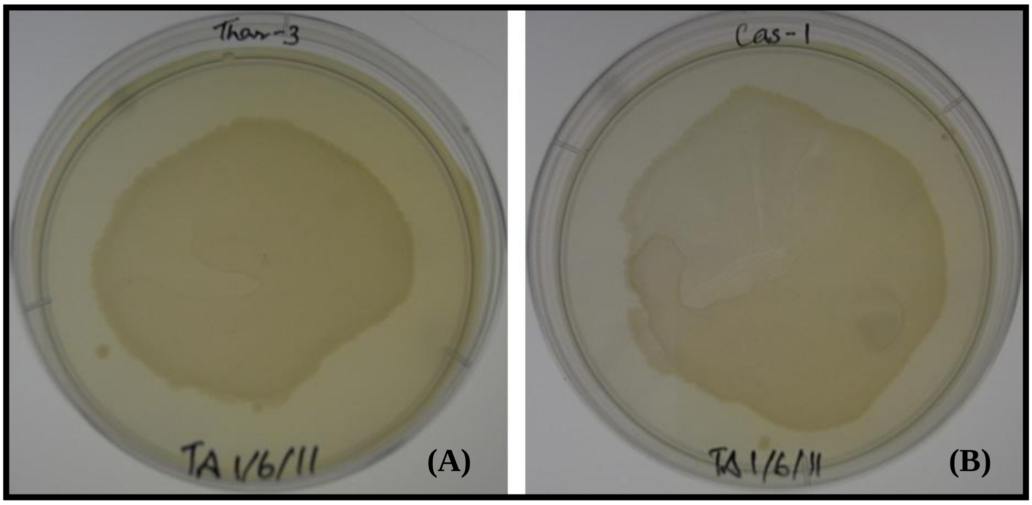


Figure 5.9 Bacterial growth on agar plates for Thar (A) and Caspian (B) dyes

All fabric samples pad-dyed in the presence of chitosan were completely effective against E. *coli*. The 10^2 dilutions from these samples did not show any bacterial colonies after incubation and thereby exhibited 100% reduction in CFU% as calculated by Equation 2.2.

$$\frac{(X-Y)}{X}\times 100\% \qquad \textbf{Equation 2.2}$$

where
X= average number of bacterial colonies in the agar plate from control
Y = average number of bacterial colonies in the agar plates from fabric dyed in the presence of chitosan

Figure 5.10 shows representative photographs of biocidal activity in the agar plates corresponding to the control fabric (A) with 253 CFU of E. *coli* and the test sample dyed in the presence of 0.05% chitosan (B) with no bacterial growth. The results are in agreement with earlier research, which reported antimicrobial properties of cotton fabrics treated first with chitosan by exhaust dyeing and then dyed by exhaust or padding methods [96, 176, 190, 191].The above results are summarised in Table 5.3.

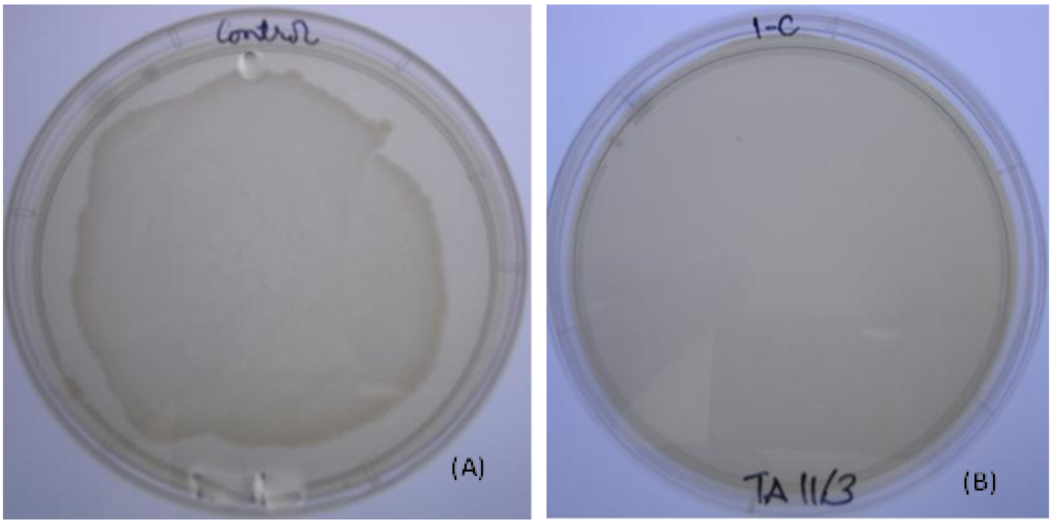


Figure 5.10 Agar plates control (A) and fabric dyed with Thar and 0.05% chitosan (B)

Table 5.3 Antimicrobial testing results

	Dye (10 g/l)		**Chitosan added to pad liquor (%)**	
	Caspian	Thar	0	0.05
Reduction in CFU (%)	0	0	Control	100

This study is the first reported instance where chitosan was applied simultaneously with the pad-dyeing liquor on cotton fabric to produce shades with acceptable fastness. The single-bath approach was probably rejected by earlier researchers because during exhaust dyeing chitosan agglomerated the dye in the dye bath and hindered colouration. This impediment was avoided in padding by 1) the low chitosan concentration employed; and 2) curing the fabric sample instead of steaming. The present findings are indicative of a simpler and more efficient process. Further, the excellent antimicrobial attributes acquired by the dyed fabric may be exploited in the specialty application area of medical textiles for use as bed linen.

5.6 Conclusions

This investigation demonstrates that chitosan could be utilised to improve dye uptake by cotton fabrics during padding with natural dyes. Incorporating 0.05% chitosan achieved a maximum increase of 37.9% in the depth of shade obtained from the Acacia plant family. Excess chitosan limited the reactivity between the dye-mordant complex and the fabric, consequently reducing the final colour yield. The propensity of chitosan to increase the depth of shade was more pronounced when iron (II) sulfate was the mordant. The fastness properties of the dyed fabrics were not affected by chitosan. All samples dyed in the presence of chitosan showed excellent antimicrobial properties. Thus such materials dyed in the presence of chitosan have the potential for application in medical textiles as hospital linen.

Chapter 6

Indigo dyeing and printing

6.1 Introduction

Indigo, the blue dye known since ancient times, is a widely known natural vat dye. Textile colouration using indigo involves a reversible reduction-oxidation process, mentioned in Section 1.2.1. A combination of sodium hydroxide (caustic soda) as alkali and sodium dithionite (sodium hydrosulfite or hydros) as reducing agent is widely employed in commercial production processes for indigo dyeing. Section 2.2.2.2 outlines the disadvantages of the above industrial process. In spite of the various alternatives developed for the reduction of indigo, scope for a simpler method exists. This chapter details the investigations into the use of chemicals having lesser impact on the environment in the indigo reduction process. The chemicals investigated are thiourea dioxide as the reducing agent and sodium carbonate as the alkali.

6.1.1 Thiourea dioxide (TUD)

TUD or formamidine sulfinic acid is an established reducing agent for vat and sulfur dyes. The use of TUD has been proposed for exhaust dyeing and printing with vat dyes especially for silk and cellulose acetate [192, 193]. At an alkaline pH of 11, a 1% solution of TUD has a reduction potential of (-965) mV as compared to (-800) mV for a similar solution of sodium dithionite [50, 194]. TUD is stable both as a solid and in aqueous solution up to 40°C and reaches full reduction potential at 100°C. The degradation products are less harmful as compared to those of sodium dithionite [113, 129, 195, 196]. The above features of TUD make it an attractive alternative to replace sodium dithionite.

6.1.2 Sodium carbonate

Sodium carbonate (washing soda or soda ash) is the sodium salt of carbonic acid. The textile processing industry uses it as a buffer to maintain alkaline conditions. Soda ash with its lower degree of alkalinity has a much reduced environmental impact as compared to sodium hydroxide [126, 197].

The following sections describe the methods adopted in colouring cotton fabrics using indigo that was reduced utilising the abovementioned chemicals. The effectiveness of the methods was evaluated further by comparing the results obtained from indigo of both natural and synthetic origins.

6.2 Equipment

6.2.1 Padding mangle, steamer and dryer

The equipment described in Sections 3.2.1, 3.2.2 and 3.2.3 was used for padding, steaming and drying. Steaming was carried out using saturated steam at 100°C and 100% RH. Various steaming durations were employed as indicated in later sections. The drying temperature was 65°C.

6.2.2 Printing

A Tiffany brand hand mixer (model number HM218) was used for blending the print paste. Table-top printing, simulating a 48T screen mesh, was achieved by employing a combination of a K-Bar hand coater and a number 2 (two) K-Bar (RK Print Coat Instruments), shown in Figure 6.1. The precision-wound steel-wire construction of the K-Bar allows only a specific quantity of print paste to be spread on a sample. This eliminates process variations such as squeegee pressure and quantity of print paste, the outcome being consistency and repeatability of the printing trials [198].

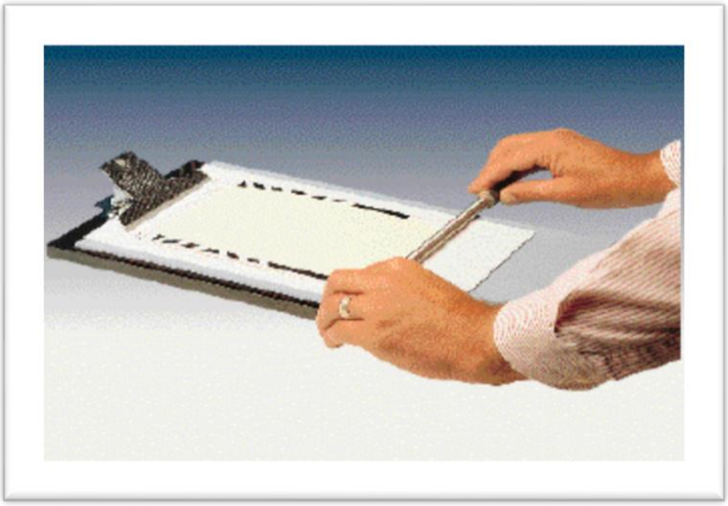


Figure 6.1 K-Bar hand coater [198]

6.3 Materials

Cotton fabric and indigo (natural and synthetic) as described in Section 2.2.1.1 and Section 2.2.1.2 were used in the experiments. Table 2.2 lists the other chemicals utilised in the recipes.

6.4 Methods

6.4.1 Indigo dyeing

Exhaust method

As a benchmark, cotton fabric was dyed using indigo (natural or synthetic) to a 1.5% depth of shade on the weight of material (OWM) according to the recipe and process suggested by Kraftkolour, the indigo dye supplier. A material-to-liquor ratio of 1:30 was used. Table 6.1 lists the constituents of the dye bath. The dye was dissolved (dispersed) using 30% of the calculated volume of water (at 35°C) resulting in a blue solution. The calculated amounts of sodium dithionite, sodium hydroxide and dextrose were added to this solution and mixed thoroughly. Dextrose, a reducing agent by itself, lowers the oxidation rate of sodium dithionite and served as a stabiliser for the reducing agent. The remaining 70% of water (at room temperature) was added and the dye solution was left undisturbed for 20 minutes to permit complete reduction (vatting) of the indigo. This was indicated by change of the solution colour from blue to pale yellow.

Table 6.1 Indigo exhaust dyeing recipe

Chemical	**Concentration (OWM)**	**Function**
Indigo	1.5%	Dye
Sodium dithionite	3.0%	Reducing agent
Dextrose	2.0%	Stabiliser
Sodium hydroxide	3.0%	Alkali

The fabric sample was immersed in the clear dye solution for 30 minutes. During that period, the dye bath was stirred continuously. Care was taken to ensure that the fabric remained completely immersed, to prevent premature oxidation. After 30 minutes, the fabric sample was taken out and squeezed to remove most of the dye liquor. This sample was allowed to oxidise in atmospheric air at ambient temperature for 5 minutes. Oxidation was recognised by a return of blue colour to the fabric. The blue fabric was re-entered into the dye bath and the above dyeing sequence repeated for a further 30 minutes. After a final oxidation of 10 minutes, the dyed fabric was treated in 2 grams per litre (g/l) solution of acetic acid to neutralise residual alkali. This was followed by soaping off, at boil for 20 minutes, in a 1 g/l standard soap solution. The dyed fabric sample was then rinsed sequentially in hot water and cold water. Final drying was carried out at 65°C.

Vat dyeing method

Dyeing was achieved by adapting the padding process usually employed for vat dyes, that is, pad (dye) → dry → pad (reducing chemicals) → steam → oxidise → (sour) → soaping off. The sequence is schematically depicted in Figure 6.2. Sodium dithionite was not suitable for this process because of its thermal instability. As mentioned earlier, TUD attains maximum reduction capability at 100°C and it has a slightly higher reduction potential than sodium dithionite [196, 199]. Hence TUD was selected as the alternate reducing agent.

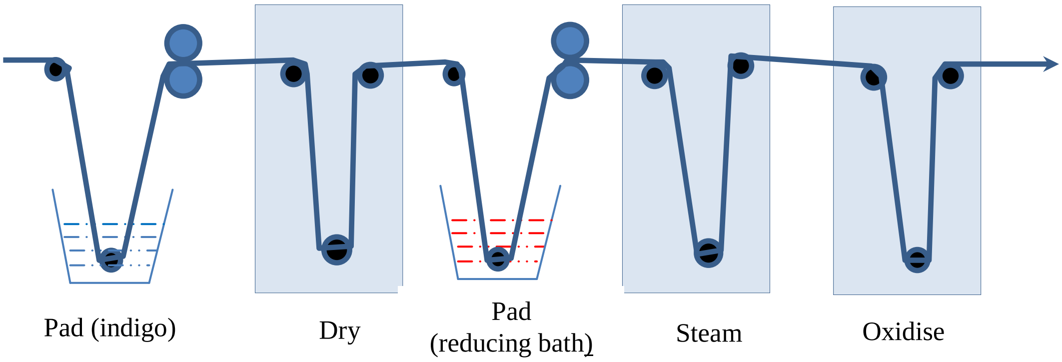


Figure 6.2 Modified vat pad-dyeing process

Dye liquor was prepared according to the recipe given in Table 6.2. A fresh solution of sodium alginate and Delinol VB/LU was made up and allowed to settle for three hours. This was necessary to ensure that the sodium alginate swelled and became completely effective. Indigo (natural or synthetic) at 16 g/l, approximating a nominal 1.5% shade, was made into a paste with warm water and dispersed in this solution. This ensured even dispersion of the dye. Fabric samples of 10 g each were padded with the above dispersion using the 3 dip–3 nip technique with 80% wet pick-up at room temperature. The padded fabric was dried at 65°C for approximately 2 hours and stored under clean conditions to avoid contamination. Drying facilitated pick-up during the subsequent chemical padding step.

Table 6.2 Pad liquor recipe

Chemical	**Quantity (g/l)**	**Function**
Indigo	16	Dye
Sodium alginate NVS	1	Anti-migrant
Delinol VB/LU	1	Dispersing agent

Developing step

Table 6.3 details the recipe for the two reduction baths evaluated in this study. The chemical ratios were based on equivalent requirements for exhaust dyeing. Dextrose served as a stabilising agent. Bath A introduced TUD as the reducing agent while in Bath B caustic soda was also replaced by sodium carbonate. The dried fabric, after padding with indigo, was padded with either Bath A or Bath B using 3 dip–3 nip technique with 80% wet pick-up. This was immediately followed by steaming at 100°C and 100% RH. Steaming durations of 30, 60 and 90 seconds were evaluated when padding in Bath A. Steaming duration was based on the industrial practices for padding of vat dyes, which usually involve a steaming duration of 30–60 seconds [11, 50]. The shortest steaming duration beyond which no significant increase in depth of shade became evident was selected as the ideal steaming time. This principle was the basis for increasing the steaming time evaluated to 2, 4 and 6 minutes when reduction was carried out using Bath B.

Table 6.3 Constitution of reducing chemical pad baths

Chemical	**Bath**	
	A (g/l)	**B** (g/l)
Dextrose	10	20
Thiourea dioxide	25	25
Sodium hydroxide	12.5	--
Sodium carbonate	--	10

On emerging from the steamer, the pale green samples (the colour of leuco indigo) were allowed to oxidise at ambient temperature in an open atmosphere for 5 minutes. Samples padded with Bath A were then soured in a 2 g/l solution of acetic acid to neutralise residual alkali. Neutralisation was not required when Bath B was used because of the lower alkalinity of soda ash. The next step was washing off in a 1 g/l solution of standard soap at the boil for 20 minutes. This was done to remove unfixed dye from the surface and promote dye aggregation inside the substrate. Dye aggregation improves fastness properties by enabling physical retention of the chemically non-reactive dye in cotton. Samples were then rinsed in hot and cold water, followed by oven drying at 65°C.

6.4.2 Printing with indigo

A combined flash-age pad-steam process was adopted in this study. Nishkam and Kasturiya [200] detail the flash-age process as one of the industrial processes for printing with vat dyes, where fabric is printed with a paste containing dye (indigo), dried and developed by passing through a reducing bath, followed immediately by flash-aging with super-heated steam (125–140°C and 100% RH) for 20–40 seconds. The pad-steam process is an alternate method where the fabric is printed using paste that contains metal salts such as sodium formaldehyde sulfoxylate in addition to dye, dried, padded in a reducing bath and immediately exposed to saturated steam for 5–10 minutes. It should be noted that in indigo printing the sodium or calcium or zinc salt of formaldehyde sulfoxylate is employed as the reducing agent due to the thermal instability of sodium dithionite [127]. Sodium hydroxide is the alkali generally employed. The major issues identified in regards to the above chemicals are the malodorous decomposition products especially of the zinc salt, and the care required in handling caustic soda.

In this research, a print paste containing indigo prepared as for the flash-age process and a reducing bath containing TUD were employed. The steaming for up to 10 minutes at 100°C employed in the pad-steam process was utilised to ensure that the TUD attained its full reduction potential. Similar to the dyeing trials, the effect of substituting sodium hydroxide by sodium carbonate as alkali was evaluated.

The print paste constituents and their functions are listed in Table 6.4. An alkali-stable coagulating thickener (Prisulon 1550S) was necessary to ensure the integrity of the printed pattern during developing. The print paste was prepared according to the following procedure. First, the thickener was mixed with about 80% of the total water using a hand-mixer and allowed to swell for 2 hours. Simultaneously,the dye and dispersing agent were made into a paste separately with the 20% balance of water. Next, the dye dispersion was added to the swollen thickener and thoroughly blended using the hand mixer to produce a homogenous print paste.

Table 6.4 Print paste recipe for indigo

Constituent chemicals	**Concentration (g/l)**	**Function**
Indigo	16	Dye
Delinol VB/LU	1	Dispersing agent
Prisulon 1550S	100	Coagulating thickener

A 10 cm x 25 cm cotton fabric sample, free of creases, was clamped onto the K-Bar hand coater. About 1 ml of print paste was placed at one end of the fabric and drawn down using a number 2 (two) K-Bar simulating a 48T screen mesh. As explained earlier, the K-Bar system standardised printing process variables. The printed sample was dried at 65°C for 15 minutes. The dried sample was developed by padding with a reducing bath followed by steaming according to the procedures described in Section 6.4.1.

The padding/printing process and the subsequent developing steps are schematically shown in Figure 6.3. These processes were carried out for both natural and synthetic indigo.

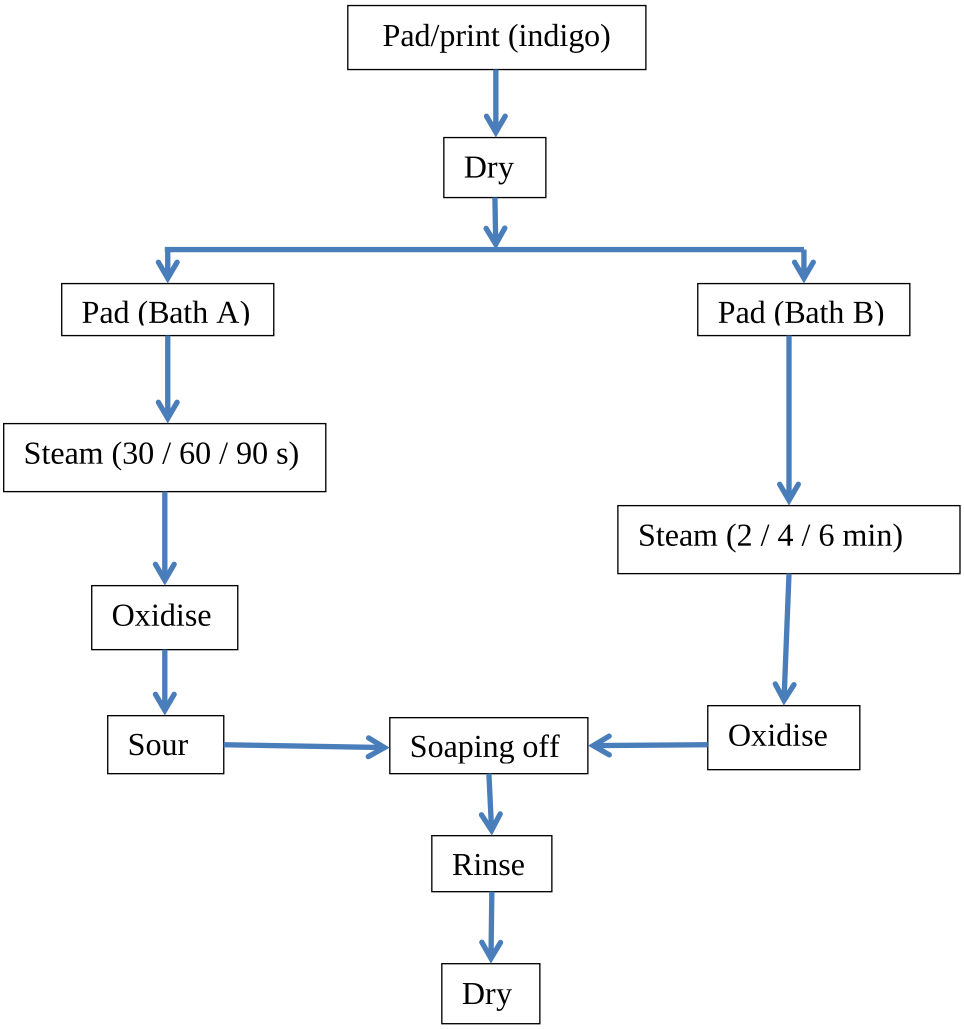


Figure 6.3 Schematic process sequence diagram

6.4.3 Evaluation

After conditioning for 24 hours under standard conditions of 65 ± 2% RH and 20 ± 2°C, the colour and fastness properties of the dyed/printed samples were measured according to the procedures set forth in Section 2.2.3. The equivalence of shade obtained between exhaust dyeing and padding was established. Comparison was made between shades obtained on the basis of the alkali used, the source of indigo and steaming duration.

6.5 Results and discussion

6.5.1 Dyeing

6.5.1.1 Shades obtained

The vat dyeing process sequence of pad (dye) → dry → pad (reducing chemicals) → steam → oxidise → soap → rinse → dry was found to be applicable for dyeing cotton fabric using both natural and synthetic indigo. Comparative reflectance curves of exhaust dyed and pad-dyed indigo (Figure 6.4 and Figure 6.5) identified a typical blue shade with maximum absorption wavelength (λ_{max}) of 660 nm in all cases. It should be noted that sodium dithionite was the reducing agent employed in exhaust dyeing, while it was thiourea dioxide during padding. Sodium dithionite could not be used in padding because of its thermal instability, mentioned earlier. For the padding results shown, both natural and synthetic indigo were reduced in the presence of sodium hydroxide (Bath A) and steamed for 60 s. The overlap of the curves indicates that the shades were of near-equal depth; in other words, TUD and sodium dithionite were equivalent reducing agents for indigo. A less than 5% variation among the triplicate trials confirmed the repeatability of the process.

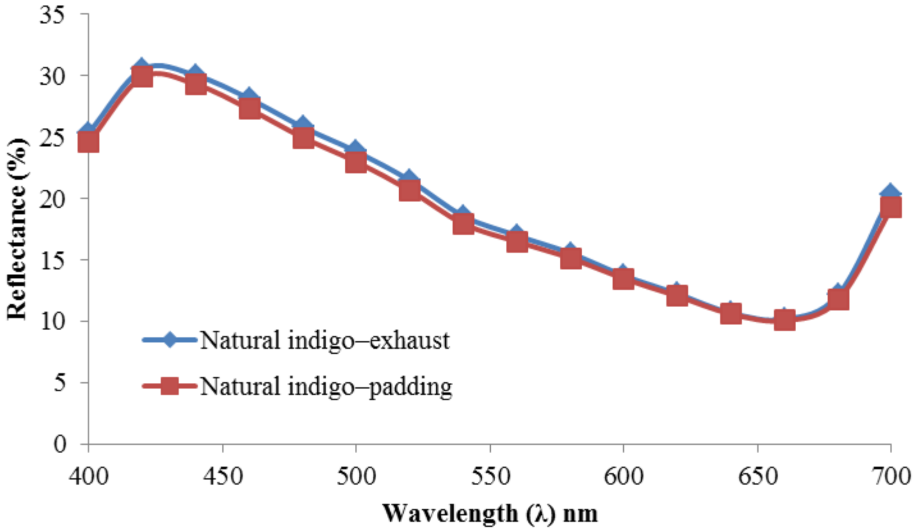


Figure 6.4 Comparison between exhaust dyeing and padding – natural indigo

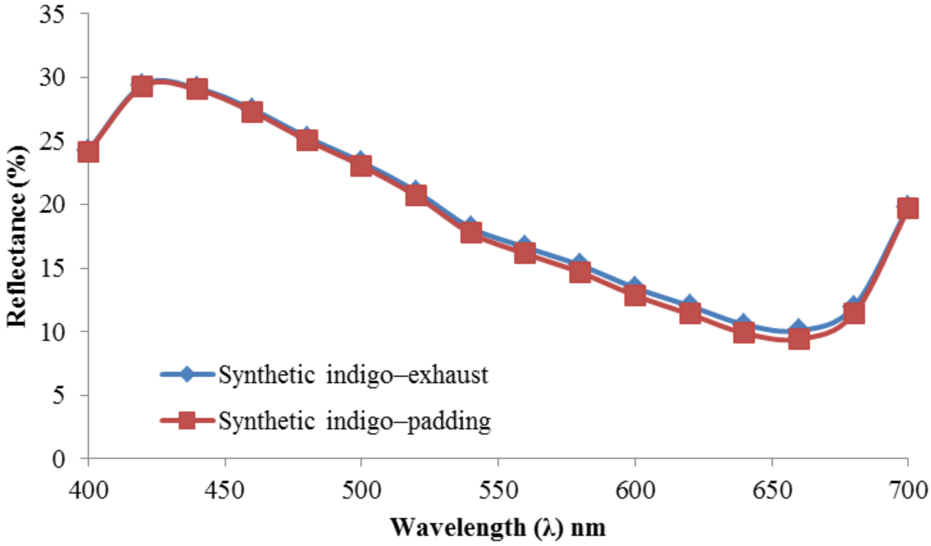


Figure 6.5 Comparison between exhaust dyeing and padding – synthetic indigo

Figure 6.6 compares reflectance curves for synthetic and natural indigo, both reduced using Bath A and steamed for 60 seconds. Once again the overlap of the curves represents an equivalence of shade. The marginal increase in absorption by synthetic indigo in the range of 570–660 nm indicates a slightly darker shade. This may be attributed to a higher degree of purity of the synthetic indigo [13, 112]. The results confirm that TUD functions as a reduction agent for both synthetic and natural indigo.

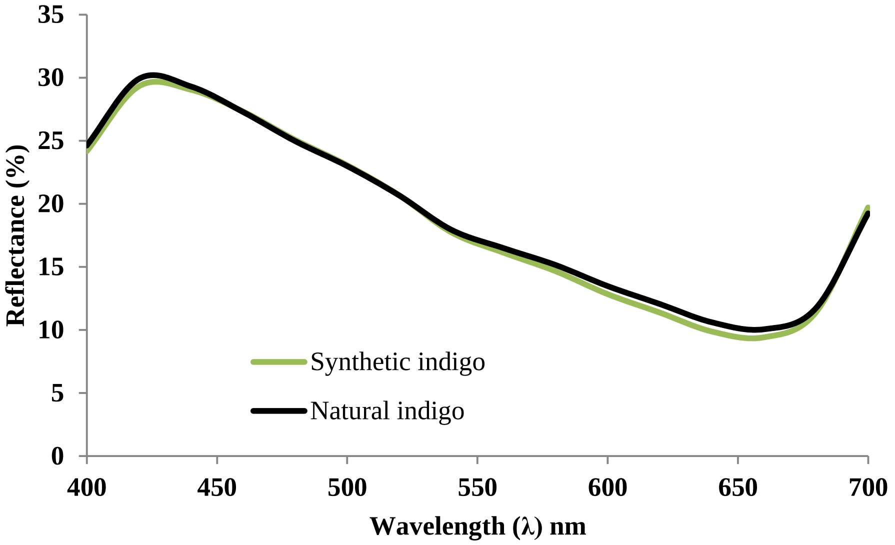


Figure 6.6 Reflectance curves – synthetic and natural indigo,
reduced in Bath A, steamed for 60 s

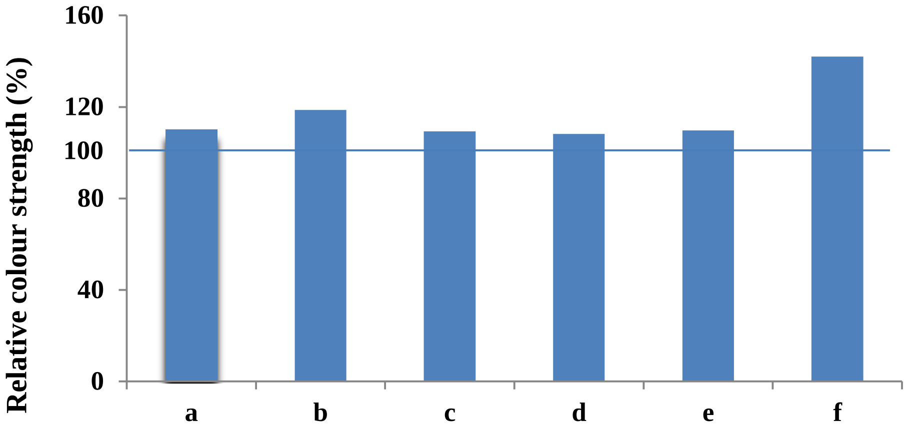
6.5.1.2 Effect of steaming time and alkali

All pad-dyed samples exhibited a pale yellow-green colour when exiting the steaming chamber. This indicated that the indigo had been reduced to its leuco-form. The samples regained a dark blue shade on oxidation. The final shade became apparent after soaping off wherein the unfixed dye was removed. When soda ash replaced caustic soda as the alkali, dyeing did not seem to occur until the steaming duration had been increased to 2 minutes. It is probable that a comparatively higher amount of energy was required to reduce indigo in the presence of sodium carbonate.

The K/S values at maximum absorption wavelength (λ_{max}) of 660 nm were compared to determine the effect of steaming time on the shade obtained by reducing indigo in either Bath A or Bath B. The value for 4 minutes steaming of the synthetic indigo–Bath B combination was assumed to be the benchmark (100% colour strength) in this thesis. Table 6.5 lists the numerical values for this comparison while Figure 6.7 and Figure 6.8 are graphic representations of the same.

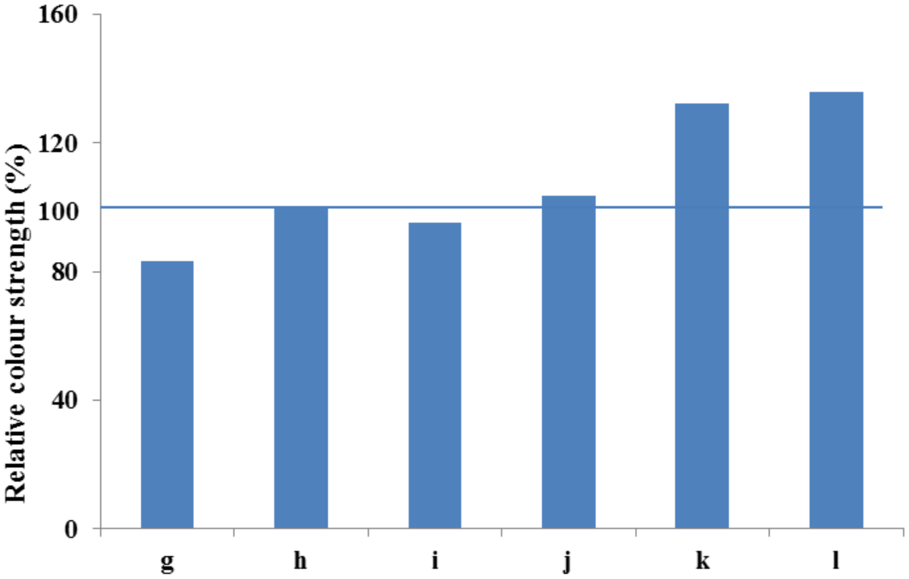
Table 6.5 Comparative colour strength that demonstrates effect of steaming time

Reducing bath	**Steaming time**	**Indigo source**	
		Synthetic	***Natural***
A (caustic soda + TUD)	30 seconds	110.3%	108.2%
	60 seconds	118.7%	109.7%
	90 seconds	109.3%	**142.0%**
B (soda ash + TUD)	2 minutes	83.4%	103.4%
	4 minutes	**100.0%**	132.1%
	6 minutes	95.1%	135.7%



a, b, c – synthetic indigo; d, e, f – natural indigo
and steamed for 30, 60, 90 s respectively

Figure 6.7 Effect of steaming duration on colour strength (reduced in Bath A)



g, h, i – synthetic indigo, j, k, l – natural indigo
and steamed for 2, 4, 6 minutes respectively

Figure 6.8 Effect of steaming duration on colour strength (reduced in Bath B)

The combination of synthetic indigo and sodium hydroxide resulted in the darkest shade at a steaming time of 60 seconds, while it was 4 minutes with sodium carbonate. The first combination yielded a shade that was darker by 18.7%. This was in agreement with Etters [123] and Blackburn et al. [116], who postulated that a higher amount of indigo would be absorbed by cotton at the higher alkalinity resulting from caustic soda. Such an increased absorption was probably caused by the swelling of cotton in the presence of sodium hydroxide. In both cases an increase in steaming time irreversibly reduced (over-reduced) the indigo, which resulted in a lighter shade. This was consistent with the publications of Chakraborty et al. [50, 117, 201].

Table 6.5 shows that natural indigo gave the darkest shades at steaming durations of 90 seconds and 6 minutes for combinations with sodium hydroxide (Bath A) and sodium carbonate (Bath B) respectively. Consistent with the results for synthetic indigo, dyeing in the presence of sodium hydroxide produced a slightly darker shade. The necessity for a longer steaming duration may be explained by the fact that natural indigo is not as pure as its synthetic counterpart [116]. The increased steaming time ensured that sufficient energy was available for the indigo isomers to be reduced.

The lower crystallinity of natural indigo [116] probably facilitated a higher degree of reaction with the reducing agent and resulted in the relatively darker shades observed. A solubility test was conducted to attest to the lower crystallinity (in turn a lower particle size) of natural indigo. One (1) gram of indigo (natural or synthetic) was dissolved in 100 ml of water. The solutions were vacuum-filtered and the solids remaining after filtration were dried and weighed accurately. This weight was compared to the initial weight (1 gram) of dye added. It was determined that 95% of synthetic indigo remained insoluble while it was only 80% for natural indigo. This confirmed that natural indigo is more soluble than synthetic indigo.

The reflectance curves for natural indigo reduced in the presence of either sodium hydroxide (Bath A) or sodium carbonate (Bath B) as depicted in Figure 6.9 indicate near-equivalent shades. This confirms that cotton can be dyed using indigo by the pad → steam process with a combination of sodium carbonate and TUD. Etters [123] has reported similar shade equivalency for indigo dyed in the presence of a mixture of sodium hydroxide and sodium carbonate as alkali. The work in this thesis is the first instance where sodium hydroxide has been totally replaced, although with the requirement for a longer steaming time.

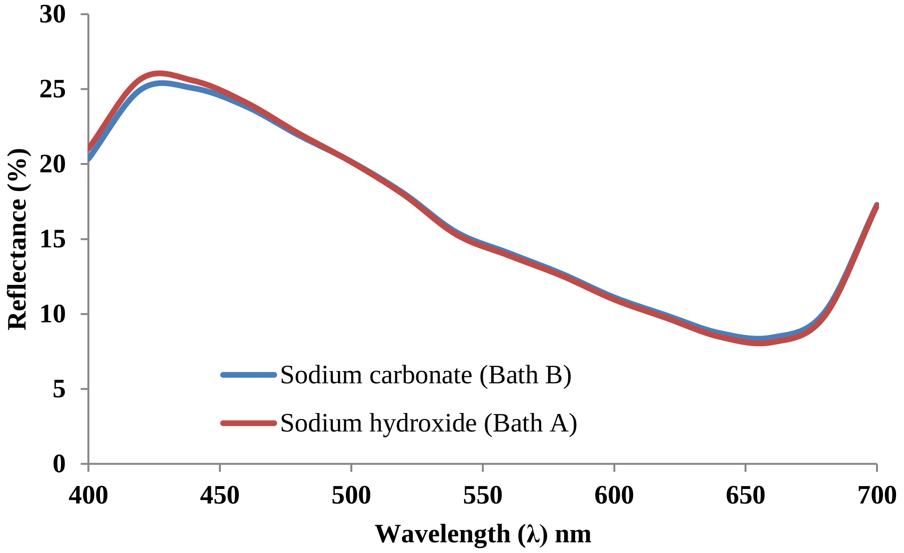


Figure 6.9 Reflectance curves natural indigo (Bath A 90 s and Bath B 6 min)

By employing TUD, the release of sulfur dioxide and other toxic byproducts of oxidation of sodium hydrosulfite into the atmosphere can be avoided. This makes the process easy to control and friendly to the operators and the environment. These aspects are further enhanced by the use of sodium carbonate instead of caustic soda, which increases safety in handling and reduces disposal load.

6.5.1.3 Fastness properties

The fastness ratings of the indigo-dyed cotton fabrics are summarised in Table 6.6. The results reported are for those process combinations that yielded the darkest shades. All samples exhibited excellent fastness to light, with an average rating of 4–5 against blue wool standards after 48 hours of exposure to simulated sunlight. This is in agreement with the light fastness results of indigo reported by other researchers [202, 203]. Washing test results indicate a colour change of average to good with ratings ranging from 3.5 to 4.5. Staining of the nylon and acetate components of the adjacent multi-fibre fabric (rated at 3 to 3.5) indicates that the dye released into the wash liquor behaved like a disperse dye, as put forth by Etters [123]. Dry rubbing fastness was better than wet rubbing, being rated as good to very good (4 to 4.5) as against average to good (3 to 4). The dyed samples had a rating of 5 when tested for fastness to perspiration under both acid and alkaline conditions. There was no change of original colour or staining of the adjacent fabric. These results confirmed that the fastness properties of indigo are not affected by the reducing agent or alkali employed during dyeing.

Table 6.6 Fastness testing results (dyeing)

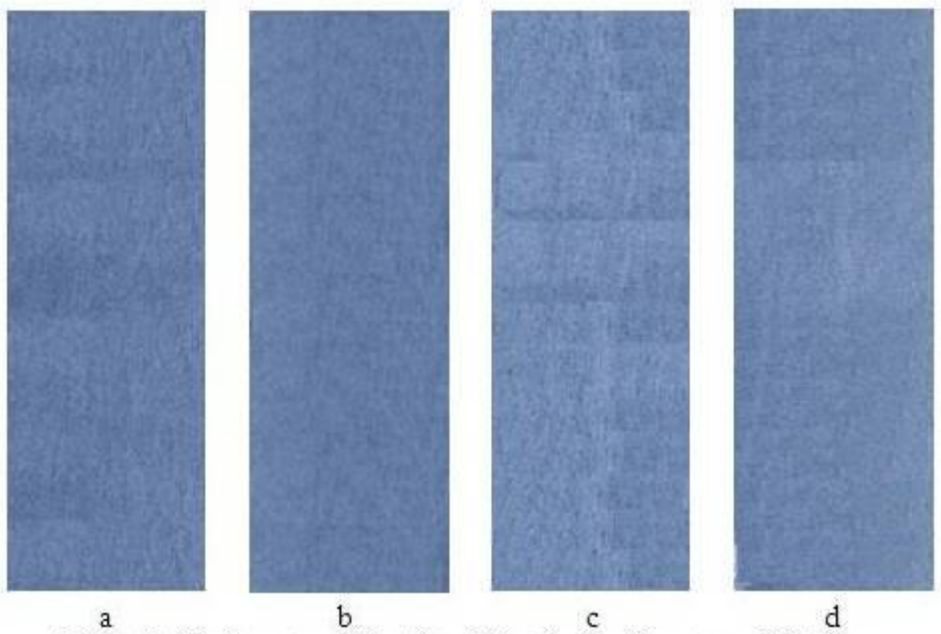
		Natural indigo		**Synthetic indigo**	
Reducing bath		Bath A	Bath B	Bath A	Bath B
Steaming duration		90 seconds	6 minutes	60 seconds	4 minutes
Fading to light		4.5	5	5	5
Washing (colour change)		3.5	4.5	4.5	4
Washing (staining)	Nylon	3.5	3	3.5	3
	Acetate	3.5	3	3	3.5
Perspiration	Acid	5	5	5	5
	Alkaline	5	5	5	5
Rubbing	*Dry*	4.5	4	4.5	4
	Wet	3	4	3.5	4

Bath A - Sodium hydroxide and TUD
Bath B - Sodium carbonate and TUD

6.5.2 Printing

6.5.2.1 Shades obtained

Printing with indigo was achieved by a combined flash-age pad-steam process as described earlier. The printed indigo was solubilised by employing either a) an alternate reducing agent (TUD) in the presence of caustic soda as alkali; or b) TUD in combination with an alternate alkali followed by steaming. Similar to dyeing, all printed samples were pale-yellow in colour after steaming. This was proof that the indigo had been reduced. As can be observed from Figure 6.10, the samples acquired the typical blue shade of indigo after oxidation.



(a) Synthetic indigo steamed for 60 s (b) Synthetic indigo steamed for 90 s
(c) Natural indigo steamed for 60 s (d) Natural indigo steamed for 90 s

Figure 6.10 Printed indigo reduced using Bath A (TUD + caustic soda)

The reflectance curves depicted in Figure 6.11 brought out the 80% lighter shade produced by natural indigo as compared to synthetic indigo. Further, the close overlap of the curves for the two steaming durations (60 and 90 seconds) indicated that the longer duration did not significantly improve the final shade for both natural indigo and synthetic indigo reduced using Bath A.

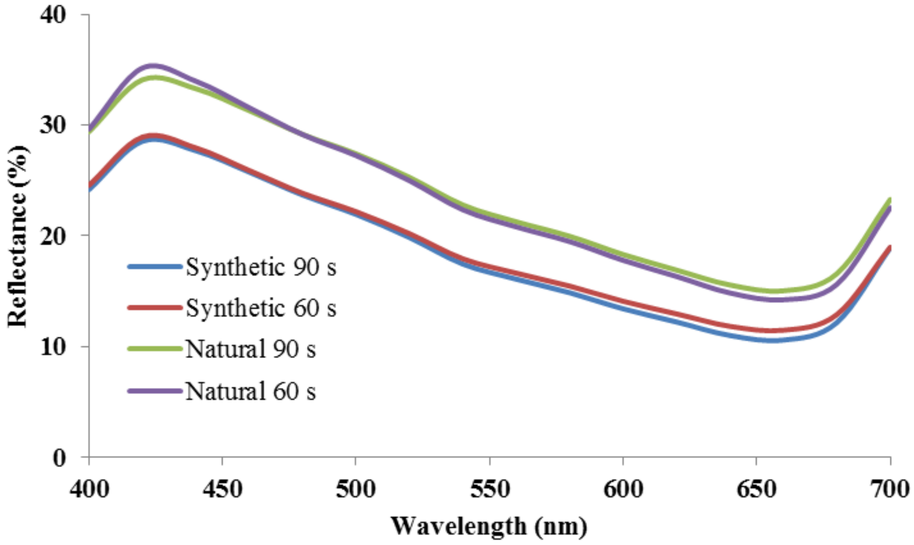


Figure 6.11 Reflectance curves comparing print shades from synthetic and natural indigo reduced using Bath A

The evident contrast between the printing and dyeing results for indigo may be attributed to the higher degree of crystallinity of synthetic indigo [204] and the role of the thickener (Prisulon 1550S). The less crystalline natural indigo was probably bound intimately with the thickener as compared to synthetic indigo, and hence after being reduced could not readily migrate to the fabric. This resulted in lighter shades from natural indigo. In the additional 30 seconds of steaming time, the overall stability of the print paste may have prevented any additional quantity of the leuco-compound from being absorbed by the fabric. Further extension of steaming time caused dye degradation, which proved detrimental to the final shade.

6.5.2.2 Effect of alkali and steaming duration

The reflectance curves displayed in Figure 6.12 show that the shade obtained when caustic soda was replaced by sodium carbonate was lighter by approximately 15%. In addition, the colour strength relationship between natural and synthetic indigo was retained, that is, natural indigo produced only 80% of the shade of synthetic indigo. Although the duration of steaming affected the final shade, the trend observed disagreed with that of dyeing. The darkest shade for synthetic indigo reduced in the presence of sodium carbonate was obtained at a steaming time of 6 minutes, whereas 2 minutes were sufficient for natural indigo. During pad-dyeing, when sodium carbonate was employed as the alkali, natural indigo yielded the darkest shade at a steaming time of 6 minutes while it was 4 minutes for synthetic indigo. All other steaming durations consistently produced a lighter shade in the case of printing.

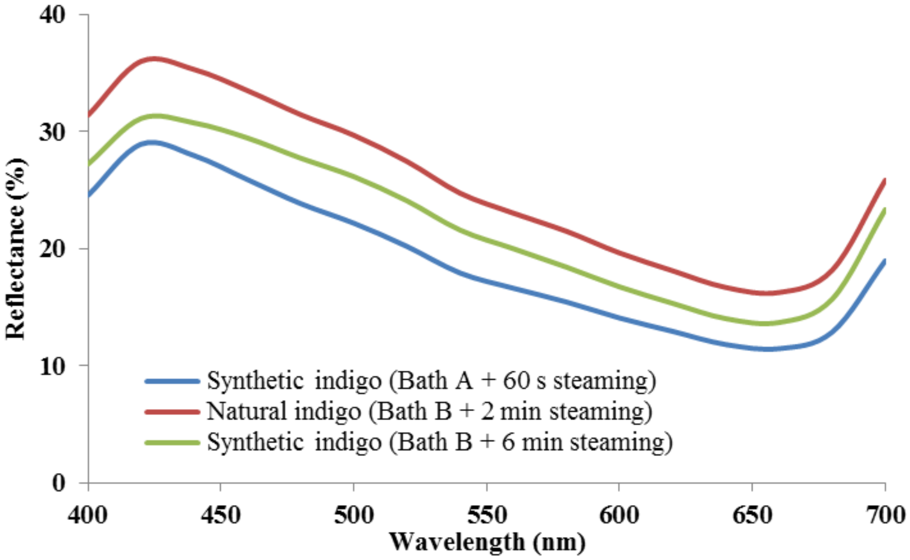


Figure 6.12 Effect of alkali on indigo printing

The results highlight the role of the thickener in deciding the final shade in these experiments. The thickener (Prisulon 1550 S) has an inherent pH of 9–11.5 [205]. Caustic soda would raise the alkalinity and facilitate increased uptake of the leuco-indigo. When steaming time was extended, the reduction of indigo became irreversible, and resulted in poor colour yield [50]. Sodium carbonate, a milder alkali, has a pH approximately equal to that of the thickener and so would maintain the integrity of the print paste hindering colour transfer into the substrate. The use of a lower thickener concentration would affect print paste rheology and thereby pattern definition [205]. On the other hand, steaming time of 6 minutes gave the darkest shades with synthetic indigo reduced in the presence of soda ash, probably because the available extra energy was able to promote additional dye migration.

6.5.2.3 Evaluation of fastness

The typical fastness properties of indigo were evident for all samples, as shown in Table 6.7. The darker samples, resulting from synthetic indigo, showed greater colour change (fading) on exposure to artificial sunlight or rubbing. This could be due to the fact that small changes in lighter shades are not readily apparent as compared to a similar change in darker shades. All samples performed well in the test for fastness to perspiration with a rating of 5, indicating no change in colour and no staining of adjacent multi-fibre fabric. Washing fastness yielded ratings of 3.5 to 4.5. The nylon and acetate components of the adjacent multi-fibre fabric were stained and rated at 3 to 3.5, similar to those for dyeing. The fastness ratings agree with the earlier dyeing results and it can be concluded that the alkali or reducing agent does not affect the fastness properties of indigo during printing.

Table 6.7 Fastness testing results (printing)

Reducing bath	**Bath A**		**Bath B**	
Indigo source	Synthetic	Natural	Synthetic	Natural
Steaming time	60 s	60 s	6 min	2 min
Fading to light	4	4.5	4.5	5
Washing	3.5	4.5	4	4.5

Perspiration	Acid	5	5	5	5
	Alkaline	5	5	5	5
Rubbing	*Dry*	4	4.5	4	4.5
	Wet	3	4	3.5	4

Bath A - Sodium hydroxide and TUD
Bath B - Sodium carbonate and TUD

6.6 Conclusions

The results of this investigation prove that the pad/print (dye) → dry → pad (reduction chemicals) → steam → oxidise process can be employed to dye or print cotton with either natural or synthetic indigo. Thiourea dioxide is able to replace sodium dithionite (sodium hydrosulfite) as a reducing agent for indigo. Similarly sodium carbonate served as an alternate for sodium hydroxide although at the cost of added steaming time. This was the first instance where both reducing agent and alkali were replaced during indigo colouration. It should be noted that process parameters using the alternate chemicals have not been optimised, that is, the lowest amount of chemicals required to reduce a given concentration of indigo has not been determined.

In the dyeing process, the steaming time required to yield the darkest shade for synthetic indigo reduced in the presence of sodium hydroxide was found to be 60 seconds, while it was 90 seconds for natural indigo. When sodium hydroxide was replaced by sodium carbonate as the alkali, steaming time was increased to 4 and 6 minutes for synthetic and natural indigo respectively. In the above dyeing experiments, natural indigo gave about 20% darker shade than synthetic indigo. This may be attributed to the lower crystallinity of the former.

A combined flash-age pad-steam method was used for printing with either natural or synthetic indigo on cotton. Thiourea dioxide proved to be a viable reducing agent. In contrast to dyeing, natural indigo yielded a 20% lighter shade than the synthetic indigo. The use of sodium carbonate, although effective in replacing sodium hydroxide, was not able to produce an equivalent depth of shade. The steaming time required to yield the darkest shade for indigo reduced in the presence of sodium hydroxide was determined to be 60 seconds. However, when sodium carbonate was used as the alkali, the steaming time had to be increased to 6 and 2 minutes for synthetic and natural indigo respectively. The shade obtained and optimum steaming time was affected by: a) the stability of thickener to alkali; and b) the interaction of dye with the thickener. Alternate thickeners that address these issues may be investigated in the future.

The use of thiourea dioxide or the additional replacement by sodium carbonate did not affect the fastness ratings of the dyed or printed samples. The ratings for the common desirable properties of light fading, washing, rubbing and perspiration were acceptable for textiles coloured using indigo.

The impact of the extended steaming duration is an important factor to be considered prior to adopting the methods developed above on a commercial scale. On the whole, the use of thiourea dioxide and sodium carbonate for reducing indigo during colouration by padding may be considered as a sustainable advancement.

Chapter 7

Conclusions

7.1 Introduction

This chapter summarises the conclusions from the investigations into understanding the compatibility between natural dyes and continuous colouration processes. Based on the information found, further work could be undertaken to increase the level of knowledge regarding the performance and application of selected natural dyes using present-day colouration technology.

7.1.1 Padding of mordant dyes

It has been found that mordant dyes of natural origin are compatible with the padding process for dyeing of cotton and wool fabrics. An in-depth evaluation was conducted of pre-mordanting, post-mordanting and simultaneous mordanting techniques. Of the three techniques, post-mordanting produced the most level dyeing as well as the darkest shades in the present study. The combination of mordant and dye is unique in terms of the shade produced, processing sequence and dye-to-mordant ratio.

It was confirmed that, metal from the mordant chelate with the dye and textile material forming a covalent bonded complex. Quantitative assessment of the actual mass of metal retained from the mordant may be used to optimise padding recipes. Each dye-mordant combination has an individual ideal ratio and requires a unique process sequence. The same dye can yield different shades in combination with different metals. It was established that, the metal influences the bonds of the complex to such an extent that similar complexes are formed from different dyes. It should be noted that, the quantity of metal retained by the dyed fabrics was within the standard limits recommended by international organizations such as Oekotex.

When compared with current available literature, it was found that, for the dyes and mordants investigated, a low dye-to-mordant ratio was sufficient to produce deep and level shades at the examined concentration of dye. This fact combined with the low material-to-liquor ratio, as compared to the requirements for exhaust dyeing, make padding the process of choice for large scale production.

7.1.2 Improving padding of mordant dyes

Atmospheric pressure plasma pretreatment improves the wettability and dye uptake of wool. At treatment duration of 7 seconds, plasma generated from pure helium was equally effective as that from a mixture of helium and nitrogen in increasing the depth of shade obtained. When the treatment duration was increased to 14 seconds, the presence of nitrogen decreased the effect of plasma. Longer treatment in helium plasma results in darkest shades although a definite trend is yet to be established. Selective exposure to plasma can be employed to create tone-on-tone patterns on wool in a single step by padding. Apart from increasing the evenness of shade, the effect of plasma pretreatment was not significant on cotton.

The present work, of adding chitosan to the pad liquor and increasing the depth of shade on cotton, is the first published report on the simultaneous application of chitosan and natural dye by padding. The amount of chitosan that produces the desired result has to be carefully determined because excess chitosan reduces the shade obtained. As an added benefit, the use of chitosan imparts an antimicrobial character to the dyed fabric. While chitosan has medical applications in absorbable sutures and wound dressing materials, its use in general medical textiles has not been fully explored. It is hoped that the present work will stimulate research into application of fabrics dyed in the presence of chitosan in hospital bed linen.

The shades obtained from both improvement techniques bring out the influence of mordant in the bonding characteristics of the dye-mordant-textile complex. The increase in depth of shade varies according to the mordant employed.

7.1.3 Indigo colouration

This thesis is the first to report on the complete replacement of the chemicals used to reduce indigo, the most important among all the available natural dyes. The research is unique in that, cotton was dyed, using indigo reduced by the alternate chemicals, by employing a modified commercial vat dye padding process.

Natural indigo is commonly used for producing traditional fabrics. Although a variety of application methods are used by the craft industry, reduction of indigo is achieved by the traditional fermentation method across the globe. The textile manufacturing sector employs sodium dithionite as reducing agent in the presence of sodium hydroxide for indigo colouration. In this research an alternate reducing agent, thiourea dioxide, has been evaluated for reducing indigo in the presence of either sodium hydroxide or sodium carbonate.

Cotton fabric can be dyed by both natural and synthetic indigo, reduced by either of the above alternate chemical combinations, employing a modified commercial vat-dye padding process of pad (dye) → dry → pad (reducing chemicals) → steam. The use of sodium carbonate as the alkali while reducing indigo results in a near equivalent shade to that produced in the presence of sodium hydroxide. The drawback is that a longer duration of steaming is necessary.

Similar to dyeing, printing with indigo is a traditional art with its own variety of processes. The common factor is the use of alkali-stable thickeners to ensure pattern integrity. As may be expected, the characteristics of print-paste thickener influences the shade obtained. In the present investigation, the thickener did not permit sodium carbonate to be as effective as sodium hydroxide and the result was a lighter shade produced in the presence of the former. In comparison to dyeing, the duration of steaming to obtain the darkest shade was also affected.

The difference in crystallinity between natural and synthetic indigo affects the depth of shade obtained. The less crystalline natural indigo produces a darker shade during dyeing. However, in printing, the lower crystallinity increases the interaction with the thickener hindering migration of the leuco-indigo to the fabric and thereby produces lighter shades.

In all cases irreversible reduction (over-reduction) of indigo results in light shades and has to be avoided. This generally occurs by steaming for longer than necessary duration.

The overall outcome is that natural dyes are compatible with continuous dyeing processes. The synergistic effect of a renewable dye source and the efficiency of present day colouration processes would make commercial colouration using natural dyes sustainable. The above conclusions indicate areas for further research of which some are listed below.

7.2 Further work

7.2.1 Increasing the scale of experiments

The above experiments could be conducted on an industrial scale to determine economic and environmental impact. This would require shade cards of varying depths of shade with their individual process parameters. Further, the wide variety of natural dyes offers enormous scope for developing new shades in combination with different mordants. In the large scale trials, plasma pretreatment or the addition of chitosan in the pad liquor could be evaluated individually or in combination to enhance process efficiency.

7.2.2 Analysis of dye-metal-textile complex

Investigations into the structure of the metal chelates using FTIR and 2D-IR would yield better understanding of the bonds modified or created during dyeing. Such knowledge could be used in engineering an optimised dyeing process and recipe.

AAS analysis could be utilised to quantitatively analyse the metal retaining capacity of polyphenols by themselves or in combination with different textile substrates. The results could be applied in diverse fields such as filtration, separation and pollution control (for absorbing dissolved metals)

.

7.2.3 Effects of chitosan

Exhaust dyeing incorporating chitosan in the dye bath is a prospective area of investigation. The antimicrobial efficacy of fabrics pad-dyed in the presence of chitosan could be evaluated against other strains of microbes. Keeping in mind the possible application of hospital bed linen, the wash durability of the antimicrobial character could also be investigated.-

7.2.4 Indigo colouration

The present work on padding of indigo could be extended by determining the lowest amount of the alternate chemicals required for a given range of shade depths. The study could be broadened by verifying the degree of dye diffusion into the fabric. Alternate thickeners compatible with sodium carbonate as the alkali could be evaluated for indigo printing.

References

[1] M. Nicholson, *The new environmental age*: Cambridge Univ. Press, 1987.

[2] P. Bansal and K. Roth, "Why companies go green: a model of ecological responsiveness," *Academy of Management Journal*,pp. 717–36, 2000.

[3] D. Esty and A. Winston, *Green to gold: How smart companies use environmental strategy to innovate, create value, and build competitive advantage*: Wiley, 2009.

[4] G. Walsh, L. Bahner and W. Horning, "Toxicity of textile mill effluents to freshwater and estuarine algae, crustaceans and fishes," *Environmental Pollution Series A, Ecological and Biological*, vol. **21** (3) pp. 169–79, 1980.

[5] M. Ajmal and A. Khan, "Effects of a textile factory effluent on soil and crop plants," *Environmental Pollution Series A, Ecological and Biological*, vol. **37** (2) pp. 131–48, 1985.

[6] P. Kaushik, V. Garg and B. Singh, "Effect of textile effluents on growth performance of wheat cultivars," *Bioresource Technology*, vol. **96** (10) pp. 1189–93, 2005.

[7] R. Reid, "Go green – a sound business decision (part 1)," *Journal of the Society of Dyers and Colourists*, vol. **112** (4) pp. 103–05, 1996.

[8] M. Abrar, Z. Tian and X. Deng, "Exploration of niche market and innovation in organic textile by a developing country," *International Journal of Business and Management*, vol. **4** (2) p. 10, 2009.

[9] B. J. Agrawal, "Commercial viability for colouration of nylon substrate with natural vegetable dyes," presented at the RMUTP International Conference: Textiles & Fashion, Bangkok, Thailand, 2012.

[10] T. Bechtold and R. Mussak, *Handbook of natural colorants*: Wiley, 2009.

[11] A. D. Broadbent, *Basic principles of textile coloration*: Society of Dyers and Colourists, 2001.

[12] M. Clark, "Fundamental principles of dyeing," in *Handbook of textile and industrial dyeing*. vol. 1, M. Clark, Ed., Woodhead, 2011.

[13] J. Balfour-Paul, *Indigo*, 2 ed. London: Archetype Publications, 2006.

[14] E. Trotman, *Dyeing and chemical technology of textile fibres*, 6 ed.: Charles Griffin, 1984.

[15] H. Zollinger, *Color chemistry: syntheses, properties, and applications of organic dyes and pigments* 3rd rev. ed. Wiley-VCH, 2003.

[16] B. Burdett, "The Colour Index: The past, present and future of colorant classification," *Journal of the Society of Dyers and Colourists,* vol. **98** (4) pp. 114–20, 1982.

[17] Freedonia-group, "World dyes and organic pigments – Industry forecasts for 2013 & 2018 Report," 2009.

[18] AATCC, *AATCC test methods and evaluation procedures*. USA, 2012.

[19] Standards-Australia. (2012, 21 September). *Standards Australia*. available: http://www.standards.org.au/Pages/default.aspx

[20] S. Burkinshaw, "Application of dyes," in *The chemistry and application of dyes,* D. Waring and G. Hallas, Eds., Plenum Press, 1991.

[21] J. J. Hummel, *The dyeing of textile fabrics*: Cassell, 1898.

[22] W. S. Perkins, *Textile coloration and finishing*: Carolina Academic Press, 1996.

[23] D. M. Nunn, *The dyeing of synthetic-polymer and acetate fibres*: Dyers Co. Publications Trust, 1979.

[24] C. Hawkyard, *Synthetic fibre dyeing*: Society of Dyers and Colourists, 2004.

[25] R. Chavan, "Environemtally friendly dyes," in *Handbook of textile and industrial dyeing*. vol. 1, M. Clark, Ed., Woodhead, 2011.

[26] K. Ramakrishna, "Into the golden era of natural and vegetable dyes," *Colourage,* vol. **46** pp. 29–30, 1999.

[27] R. Mussak and T. Bechtold, "Natural colorants in textile dyeing," in *Handbook of natural colorants*, R. Mussak and T. Bechtold, Eds., Wiley, 2009.

[28] D. Cardon, *Natural dyes*: Archetype London, 2007.

[29] B. Patel, "Natural dyes," in *Handbook of textile and industrial dyeing*. vol. 1, M. Clark, Ed., Woodhead, 2011.

[30] M. Gulrajani and D. Gupta, *Natural dyes and their application to textiles*: Department of Textile Technology, Indian Institute of Technology, 1992.

[31] N. Bhattacharyya, *Natural dyes for textiles and their eco-friendly applications*: IAFL Publications, 2010.

[32] G. Fereday, *Natural dyes*. British Museum Press, 2003.

[33] S. Bhattacharya and A. Shah, "Metal ion effect on dyeing of wool fabric with catechu," *Coloration Technology,* vol. **116** (1) pp. 10–12, 2000.

[34] C. Bird, *The theory and practice of wool dyeing*, 3 ed.: The Society of Dyers and Colourists, 1963.

[35] C. Giles, "The mechanism of the mordanting of animal fibres," *Journal of the Society of Dyers and Colourists,* vol. **60** (11) pp. 303–15, 1944.

[36] G. Nalankilli, "Application of tannin in the colouration of textiles," *Textile Dyer & Printer,* vol. **30** (27) pp. 13–15, 1997.

[37] D. Gupta, "Fastness properties of natural dyes – Part I: Introduction and review of literature," *Colourage,* vol. **46** (7) pp. 35–38, 1999.

[38] A. Cribb and J. Cribb, *Useful wild plants in Australia*: Collins, 1981.

[39] A. Dyer, *Dyes from natural sources*: Bell, 1976.

[40] S. Ratnapandian, S. Fergusson and L. Wang, "Application of acacia natural dyes on cotton by pad dyeing," *Fibers and Polymers,* vol. **13** (2) pp. 206–11, 2012.

[41] S. Agarwal. (2011, 19 December). *History, chemistry and application of indigo dyes*. available: http://www.denimsandjeans.com/denim/manufacturing-process/history-chemistry-and-application-of-indigo-dye/

[42] A. Buhler, "Indigo dyeing among primitive races," *Ciba Review,* vol. **85** p. 4, 1951.

[43] W. A. Vetterli, "The history of indigo," *Ciba Review,* vol. **85** p. 6, 1951.

[44] M. Melo, "Missal blue: anthocyanins in nature and art," in *21st meeting on dyes in history and archaeology*, 2002, pp. 10–12.

[45] E. Saidman, A. Yurquina, R. Rudyk, M. Molina and F. Ferretti, "A theoretical and experimental study on the solubility, dissolution rate, structure and dipolar moment of flavone in ethanol," *Journal of Molecular Structure: THEOCHEM,* vol. **585** (1) pp. 1–13, 2002.

[46] M. Gulrajani, D. Gupta, V. Agarwal and M. Jain, "Studies on natural yellow dyes. Part 3. Quinones - henna, dolu," *Indian Textile Journal,* vol. **102** (6) p. 76, 1992.

[47] E. Haslam, *Chemistry of vegetable tannins*: Academic Press, 1966.

[48] R. Adrosko and M. Furry*, Natural dyes and home dyeing (formerly titled: Natural dyes in the United States)* vol. 281: Dover, 1971.

[49] A. K. Samanta and P. Agarwal, "Application of natural dyes on textiles," *Indian Journal of Fibre & Textile Research,* vol. **34** (4) pp. 384–99, 2009.

[50] J. Chakraborty, *Fundamentals and practices in colouration of textiles*: Woodhead, 2010.

[51] D. Lewis, *Wool dyeing*: The Society of Dyers and Colourists, 1992.

[52] G. Nair, "Methods and machinery for the dyeing process," in *Handbook of textile and industrial dyeing*. vol. 1, M. Clark, Ed., Woodhead, 2011.

[53] K. Hunger, *Industrial dyes*: Wiley-VCH, 2007.

[54] G. Nair and S. Pandian, "ITMA ASIA + CITME 2008 Shanghai," *Colourage,* vol. **55** (9) pp. 8–32, 2008.

[55] J. Shore, *Cellulosics dyeing*: The Society of Dyers and Colourists, 1995.

[56] J. Aspland, "Reactive dyes and their application," *Textile Chemist and Colorist,* vol. **5** pp. 31–36, 1992.

[57] G. Krichevsk and I. Movshovich, "Use of methods of heterogeneous chemical kinetics and non-equilibrium thermodynamics for the quantitative evaluation of the rate of fixation of reactive dyes by fibrous materials 1," *Textile Research Journal,* vol. **40** (9) pp. 793–802, 1970.

[58] B. Gebert, W. Saus, D. Knittel, H. Buschmann and E. Schollmeyer, "Dyeing natural fibers with disperse dyes in supercritical carbon dioxide," *Textile Research Journal,* vol. **64** (7) pp. 371–74, 1994.

[59] W. Saus, D. Knittel and E. Schollmeyer, "Dyeing of textiles in supercritical carbon dioxide," *Textile Research Journal,* vol. **63** (3) pp. 135–42, 1993.

[60] R. Shishoo, *Plasma technologies for textiles*: Woodhead, 2007.

[61] P. Senthilkumar, P. Umashankar and B. Sujatha, "Ultrasonic dyeing of cotton fabric with neem leaves," *Indian Textile Journal,* vol. **112** (6) p. 15, 2002.

[62] V. Tiwari and P. S. Vankar, "Unconventional natural dyeing using microwave and sonicator with Alkanet root bark," *Colourage,* vol. **48** (5) p. 25, 2001.

[63] P. S. Vankar, R. Shanker, S. Dixit, D. Mahanta and S. Tiwari, "Sonicator dyeing of modified cotton, wool and silk with Mahonia napaulensis DC and identification of the colorant in Mahonia," vol. 27, ed, 2008, pp. 371–79.

[64] J. Park, "Carpet dyeing in the 1990s," *Journal of the Society of Dyers and Colourists,* vol. **109** (3) pp. 92–96, 1993.

[65] R. Wang, W. Jiang, S. Li, H. Yang, Y. Dong and Y. Fu, "Application research on infrared drying in silk re-reeling process," *Textile Research Journal,* vol. **82** (13) pp. 1329–36, 2012.

[66] J. Chakraborty, "An overview of dye fastness testing," in *Handbook of textile and industrial dyeing*. vol. 1, M. Clark, Ed., Woodhead, 2011.

[67] H. Lee, G. Chen and P. Yue, "Integration of chemical and biological treatments for textile industry wastewater: a possible zero-discharge system," *Water Science and Technology,* pp. 75–83, 2001.

[68] K. Ranganathan, K. Karunagaran and D. Sharma, "Recycling of wastewaters of textile dyeing industries using advanced treatment technology and cost analysis–Case studies," *Resources, Conservation and Recycling,* vol. **50** (3) pp. 306–18, 2007.

[69] C. Levi-Strauss. (2010, 18 December). *Recycling and consumer care*. available: http://www.levistrauss.com/sustainability/product/re-use

[70] K. Gilbert and D. Cooke, "Dyes from plants: Past usage, present understanding and potential," *Plant Growth Regulation,* vol. **34** (1) pp. 57–69, 2001.

[71] G. Dalby, "Greener mordants for natural coloration," *Journal of the Society of Dyers and Colourists,* vol. **109** (1) pp. 8–9, 1993.

[72] B. Patel, B. Agarwal and H. Patel, "Dyeing of nylon with Babool bark extract," *Textile Asia,* vol. **33** pp. 34–42, 2002.

[73] N. Memon, "Textile finishing: Increased demand for eco-friendly products," *Pakistan Textile Journal,* vol. **59** pp. 46–47, 2010.

[74] D. Gupta, S. Khare and A. Laha, "Antimicrobial properties of natural dyes against Gram-negative bacteria," *Coloration Technology,* vol. **120** (4) pp. 167–71, 2004.

[75] K. Ranganathan and G. Lakshmi, "Growing preference for natural dyes," *Textile Magazine,* vol. **47** (3) pp. 85–86, 2006.

[76] J. Dean, *Wild colour*: Octopus, 1999.

[77] B. Mohanty, K. Chandramouli and H. Naik, *Natural dyeing processes of India*: Calico Museum of Textiles, 1987.

[78] T. Bechtold, R. Mussak, A. Mahmud-Ali, E. Ganglberger and S. Geissler, "Extraction of natural dyes for textile dyeing from coloured plant wastes released from the food and beverage industry," *Journal of the Science of Food and Agriculture,* vol. **86** (2) pp. 233–42, 2006.

[79] N. Meksi, W. Haddar, S. Hammami and M. Mhenni, "Olive mill wastewater: A potential source of natural dyes for textile dyeing," *Industrial Crops and Products,* vol. **40** (0) pp. 103–09, 11// 2012.

[80] M. Nerurkar, C. Meena and N. Khurana, "Microbial dyes: The undisputed natural dyes," *Journal of the Textile Association,* vol. **71** (6) pp. 338–39, 2011.

[81] F. Alihosseini, "Biosynthesis of colorants from microorganisms and their application on textile materials," PhD Thesis, University of California, Davis, 2009.

[82] X. Han, W. Wang and X. Xiao, "Microbial biosynthesis and biotransformation of indigo and indigo-like pigments," *Chinese Journal of Biotechnology,* vol. **24** (6) pp. 921–26, 2008.

[83] G. Han, H. Shin and S. Kim, "Optimization of bio-indigo production by recombinant E. coli harboring fmo gene," *Enzyme and Microbial Technology,* vol. **42** (7) pp. 617–23, 2008.

[84] D. Hill, "Is there a future for natural dyes?," *Review of Progress in Coloration and Related Topics,* vol. **27** (1) pp. 18–25, 1997.

[85] Anonymous, "Alps Industries successfully completes R&D project on eco-friendly natural dyes," *Colourage,* vol. **48** (12) pp. 69–71, 2001.

[86] I. Flint, *Eco colour: botanical dyes for beautiful textiles*: Murdoch Books, 2008.

[87] R. Chavan, "Revival of natural dyes – a word of caution to environmentalists," *Colourage,* vol. **42** p. 27, 1995.

[88] R. Chavan, "Eco-fibres and eco-friendly textiles," *Textile Magazine,* vol. **43** (1) p. 61, 2001.

[89] M. Gulrajani, "Natural dyes - Part I. Present status of natural dyes," *Colourage,* vol. **46** (7) p. 19, 1999.

[90] M. Kumaresan, P. Palanisamy and P. Kumar, "Application of eco-friendly natural dye on cotton using combination of mordants," *Indian Journal of Fibre and Textile Research,* vol. **37** (2) pp. 194–98, 2012.

[91] T. Bechtold, A. Turcanu, E. Ganglberger and S. Geissler, "Natural dyes in modern textile dyehouses – how to combine experiences of two centuries to meet the demands of the future?," *Journal of Cleaner Production,* vol. **11** (5) pp. 499–509, 2003.

[92] P. Vankar, "Chemistry of natural dyes," *Resonance,* p. 7, 2009.

[93] P. Vankar and R. Shanker, "Ecofriendly ultrasonic natural dyeing of cotton fabric with enzyme pretreatments," *Desalination,* vol. **230** pp. 62–69, 2008.

[94] B. Patel, B. Agarwal and H. Patel, "Novel padding technique for dyeing babool dye on cotton," *Colourage,* vol. **50** (1) pp. 21–26, 2003.

[95] R. Mongkholrattanasit, J. Kryštůfek and J. Wiener, "Dyeing and fastness properties of natural dyes extracted from eucalyptus leaves using padding techniques," *Fibers and Polymers,* vol. **11** (3) pp. 346–50, 2010.

[96] V. Giridev, J. Venugopal, S. Sudha, G. Deepika and S. Ramakrishna, "Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye," *Carbohydrate Polymers,* vol. **75** (4) pp. 646–50, 2009.

[97] S. Kittinaovarat, "Using chitosan for improving the dyeability of cotton fabrics with mangosteen rind dye," *J. Sci. Res. Chula. Univ,* vol. **29** (2) p. 10, 2004.

[98] M. Gulrajani, R. Srivastava and M. Goel, "Colour gamut of natural dyes on cotton yarns," *Coloration Technology,* vol. **117** (4) p. 225, 2001.

[99] D. Gupta, "Fastness properties of natural dyes - Part II: Effect of chemical structure on light fastness," *Colourage,* vol. **46** (8) pp. 41–46, 1999.

[100] D. Cristea and G. Vilarem, "Improving light fastness of natural dyes on cotton yarn," *Dyes and Pigments,* vol. **70** (3) pp. 238–45, 2006.

[101] R. Singh, A. Jain, S. Panwar, D. Gupta and S. Khare, "Antimicrobial activity of some natural dyes," *Dyes and Pigments,* vol. **66** (2) pp. 99–102, 2004.

[102] D. Gupta, A. Jain and S. Panwar, "Anti-UV and anti-microbial properties of some natural dyes on cotton," *Indian Journal of Fibre & Textile Research,* vol. **30** (2) pp. 190–95, 2005.

[103] B. Glover, "Are natural colorants good for your health or are synthetic ones better?," *Book of Papers, National Technical Conference of AATCC,* pp. 229–34, 1993.

[104] L. Angelini, S. Tozzi and N. Nassi Di Nasso, "Differences in leaf yield and indigo precursors production in woad (Isatis tinctoria L.) and Chinese woad (Isatis indigotica Fort.) genotypes," *Field Crops Research,* vol. **101** (3) pp. 285–95, 2007.

[105] P. Guinot, A. Rogé, A. Gargadennec, M. Garcia, D. Dupont, E. Lecoeur, et al., "Dyeing plants screening: an approach to combine past heritage and present development," *Coloration Technology,* vol. **122** (2) pp. 93–101, 2006.

[106] S. Ratnapandian, L. Wang, S. Fergusson and M. Naebe, "Effect of atmospheric plasma treatment on pad-dyeing of natural dyes on wool," *Journal of Fiber Bioengineering and Informatics,* vol. **4** (3) pp. 267–76, 2011.

[107] R. Haller, "The history of indigo dyeing," *Ciba Review,* vol. **85** p. 7, 1951.

[108] V. Prideaux, *A handbook of indigo dyeing*: Search Press, 2003.

[109] G. Sandberg, *Indigo textiles: Technique and history* A & C Black Lark Books, 1989.

[110] M. Fox and J. Pierce, "Indigo–Past and present," *Textile Chemist and Colorist,* vol. **22** (4) pp. 13–15, 1990.

[111] P. Garcia-Macias and P. John, "Formation of natural indigo derived from woad (Isatis tinctoria L.) in relation to product purity," *Journal of Agricultural and Food Chemistry,* vol. **52** (26) pp. 7891–96, 2004.

[112] H. Mercer. (2010, 19 December). *Indigo blue dye: Not only blue – some interesting facts*. available: http://www.denimsandjeans.com/denim/manufacturing-process/indigo-blue-not-only-blue-some-interesting-facts/

[113] U. Baumgarte, "Developments in vat dyes and in their application 1974–1986," *Review of Progress in Coloration and Related Topics,* vol. **17** (1) pp. 29–38, 1987.

[114] T. R. New, *A biology of Acacias*: Oxford University Press, 1984.

[115] R. Hemingway and P. Laks, *Plant polyphenols: synthesis, properties, significance*: Springer, 1992.

[116] R. S. Blackburn, T. Bechtold and P. John, "The development of indigo reduction methods and pre-reduced indigo products," *Coloration Technology,* vol. **125** (4) pp. 193–207, 2009.

[117] R. Chavan and J. Chakraborty, "Dyeing of cotton with indigo using iron (II) salt complexes," *Coloration Technology,* vol. **117** (2) pp. 88–94, 2001.

[118] S. Ratnapandian, S. Fergusson, L. Wang and R. Padhye, "An innovative approach to indigo dyeing," in *TBIS 2012 Textile Bioengineering and Informatics Symposium,* Ueda, Japan, 2012.

[119] S. Ratnapandian, S. Fergusson, L. Wang and R. Padhye, "Sustainable developments in printing cotton fabrics with indigo," in *The 88th Textile Institute World Conference,* Shah Alam, Malaysia, 2012.

[120] T. Dawson and C. Hawkyard, "A new millennium of textile printing," *Review of Progress in Coloration and Related Topics,* vol. **30** (1) pp. 7–20, 2000.

[121] P. Floud, "The English contribution to the early history of indigo printing," *Journal of the Society of Dyers and Colourists,* vol. **76** (6) pp. 344–49, 1960.

[122] J. Etters, "Quality control of cotton denim in indigo dyeing," *American Dyestuff Reporter,* vol. **81** (3) pp. 17–24, 1992.

[123] J. Etters, "Indigo dyeing of cotton denim yarn: correlating theory with practice," *Journal of the Society of Dyers and Colourists,* vol. **109** (7-8) pp. 251–55, 1993.

[124] Fisher-Scientific. (2008, 14 January). *MSDS _ Sodium hydrosulfite*. available: https://fscimage.fishersci.com/msds/01503.htm

[125] M. Božič and V. Kokol, "Ecological alternatives to the reduction and oxidation processes in dyeing with vat and sulphur dyes," *Dyes and Pigments,* vol. **76** (2) pp. 299–309, 2008.

[126] W. New, "Sodium hydroxide, pellets: sc-203387 search datasheet| MSDS," 2012.

[127] J. Provost, "Discharge and resist printing – a review," *Review of Progress in Coloration and Related Topics,* vol. **18** (1) pp. 29–36, 1988.

[128] A. Roessler, D. Crettenand, O. Dossenbach, W. Marte and P. Rys, "Direct electrochemical reduction of indigo," *Electrochemica Acta,* vol. **47** (12) pp. 1989–95, 2002.

[129] Fisher-Scientific. (2008, 20 January). *Thiourea dioxide - MSDS*. available: http://fscimage.fishersci.com/msds/67987.htm

[130] K. Butts. (2011, 17 Jan). *What you see is what you get!* available: http://www.techexchange.com/library/Database%20Preparation%20for%20Successful%20Computer%20Color%20Matching.pdf

[131] J. Robinson, "Atomic absorption spectroscopy," *Analytical Chemistry,* vol. **32** (8) pp. 17–29, 1960.

[132] Perkin-Elmer. (2005, 05 February). *FT-IR Spectroscopy: Attenuated Total Reflectance (ATR)*. available: http://www.utsc.utoronto.ca/~traceslab/ATR_FTIR.pdf

[133] J. Schuttlefield and V. Grassian, "ATR–FTIR Spectroscopy in the undergraduate chemistry laboratory. Part I: Fundamentals and examples," *Journal of Chemical Education,* vol. **85** (2) p. 279, 2008.

[134] F. Zhang, D. Zhang, Y. Chen and H. Lin, "The antimicrobial activity of the cotton fabric grafted with an amino-terminated hyperbranched polymer," *Cellulose,* vol. **16** (2) pp. 281–88, 2009.

[135] A. Ali, S. Ali, H. Saleem and T. Hussain, "Effect of tannic acid and metallic mordants on the dyeing properties of natural dye extracted from Acacia nilotica bark," *Asian Journal of Chemistry,* vol. **22** (9) pp. 7065–69, 2010.

[136] S. Ali, "Evaluation of cotton dyeing with aqueous extracts of natural dyes from indigenous plants," PhD Thesis, Department of Chemistry, University of Agriculture, Pakistan, 2007.

[137] E. Norkus, J. Vaiciuniene and D. Virbalyte, "Interaction of copper (II) with cellulose pulp," *Chemija (Vilnius) T,* vol. **13** pp. 75–84, 2002.

[138] S. Ajiboye and D. Brown, "Electron spin resonance study of soluble copper (II)–cellulose complexes," *Journal of the Chemical Society, Faraday Transactions,* vol. **86** (1) pp. 65–68, 1990.

[139] I. Ignat, I. Volf and V. I. Popa, "Characterization of extractives from some raw materials processed by biorefining," presented at the COST meeting, Paris, 2011.

[140] C. Shi, Y. Dai, Q. Liu, Y. Xie and X. Xu, "The FT-IR spectrometric analysis of the changes of polyphenol oxidase II secondary structure," *Journal of Molecular Structure,* vol. **644** (1) pp. 139–44, 2003.

[141] M. Khalil, N. Demirdöven and A. Tokmakoff, "Coherent 2D IR spectroscopy: molecular structure and dynamics in solution," *The Journal of Physical Chemistry,* vol. **107** (27) pp. 5258–79, 2003.

[142] I. Noda, "Two-dimensional infrared (2D IR) spectroscopy: theory and applications," *Applied Spectroscopy,* vol. **44** (4) pp. 550–61, 1990.

[143] Z. Cai and Y. Qiu, "Dyeing properties of wool fabrics treated with atmospheric pressure plasmas," *Journal of Applied Polymer Science,* vol. **109** (2) pp. 1257–61, 2008.

[144] P. Muguntharajan and R. Saminathan, "Plasma finishing of textiles helps solve many practical problems," *Textile Magazine,* vol. **50** (4) pp. 60–68, 2009.

[145] Y. J. Hwang, "Characterization of atmospheric pressure plasma interactions with textile/polymer substrates," PhD Thesis, North Carolina State University, 2003.

[146] A. Ceria, F. Rombaldoni, G. Rovero, G. Mazzuchetti and S. Sicardi, "The effect of an innovative atmospheric plasma jet treatment on physical and mechanical properties of wool fabrics," *Journal of Materials Processing Technology,* vol. **210** (5) pp. 720–26, 2010.

[147] S. Sadova, L. Lapchik, O. Paigrt and V. Kalouskova, "Action of low-temperature plasma on wool surfaces (English)," *Izvestiya Vysshikh Uchebnykh Zavedenii, Tekhnologiya Tekstil'noi Promyshlennosti,* (6) p. 64, 1983.

[148] A. Ulesova, A. Grechko and S. Sadova, "Continuous dyeing of wool fabric containing polyamide fibre and modified by plasma glow discharge," *Fibre Chemistry,* vol. **40** (2) pp. 143–46, 2008.

[149] T. Wakida, S. Tokino, S. Niu, M. Lee, H. Uchiyama and M. Kaneko, "Dyeing properties of wool treated with low-temperature plasma under atmospheric pressure," *Textile Research Journal,* vol. **63** (9) pp. 438–42, 1993.

[150] T. Wakida, S. Cho, S. Choi, S. Tokino and M. Lee, "Effect of low temperature plasma treatment on color of wool and nylon 6 fabrics dyed with natural dyes," *Textile Research Journal,* vol. **68** (11) pp. 848–53, 1998.

[151] D. Sun and G. Stylios, "Effect of low temperature plasma treatment on the scouring and dyeing of natural fabrics," *Textile Research Journal,* vol. **74** (9) pp. 751–56, 2004.

[152] R. Shekar and S. Bajpai, "Effect of oxygen plasma on woollen fabric properties," *Indian Journal of Fibre & Textile Research,* vol. **25** (3) p. 229, 2000.

[153] R. Deshmukh and N. Bhat, "Pretreatments of textiles prior to dyeing: Plasma processing," in *Textile Dyeing,* P. Hauser, Ed., ed: InTech, 2011.

[154] H. Karahan and E. Özdoğan, "Improvements of surface functionality of cotton fibers by atmospheric plasma treatment," *Fibers and Polymers,* vol. **9** (1) pp. 21–26, 2008.

[155] M. Subbulakshmi, Hansraj and N. Kasturiya, "Effect of plasma on fabrics," *Indian Textile Journal,* vol. **109** (1) pp. 12–16, 1998.

[156] H. Höcker, "Plasma treatment of textile fibers," *Pure Appl. Chem,* vol. **74** (3) pp. 423–27, 2002.

[157] C. Kan, K. Chan, C. Yuen and M. Miao, "The effect of low-temperature plasma on the chrome dyeing of wool fibre," *Journal of Materials Processing Technology,* vol. **82** (1–3) pp. 122–26, 1998.

[158] C. Kan and C. Yuen, "Plasma technology in wool," *Textile Progress,* vol. **39** (3) pp. 121–87, 2007.

[159] M. Lehocký and A. Mráček, "Improvement of dye adsorption on synthetic polyester fibers by low temperature plasma pre-treatment," *Czechoslovak Journal of Physics,* vol. **56** pp. B1277–B1282, 2006.

[160] M. Naebe, P. G. Cookson, J. Rippon, R. P. Brady, X. Wang, N. Brack, et al., "Effects of plasma treatment of wool on the uptake of sulfonated dyes with

different hydrophobic properties," *Textile Research Journal,* vol. **80** (4) pp. 312–24, 2010.

[161] M. Naebe, "Personal communication – Plasma machine particulars," ed, 2012.

[162] A. Shams-Nateri, "Reusing wastewater of madder natural dye for wool dyeing," *Journal of Cleaner Production,* vol. **19** (6–7) pp. 775–81, 2011.

[163] Y. Shin and D. Yoo, "Green chemistry in natural dyeing: Application of chitosan for dyeing protein/cellulose blend fabric," *J. Chitin Chitosan,* vol. **15** (3) pp. 136–40, 2010.

[164] P. Sanford, "Chitosan: commercial uses and potential applications," in *Chitin and chitosan,* G. Skjak-Braek, T. Anthonsen and P. Sanford, Eds., ed: Elsevier, 1989, pp. 51–69.

[165] Y. Shin and D. Yoo, "Use of chitosan to improve dyeability of DP-finished cotton (II)," *Journal of Applied Polymer Science,* vol. **67** (9) pp. 1515–21, 1998.

[166] S. Lim and S. Hudson, "Application of a fibre-reactive chitosan derivative to cotton fabric as a zero-salt dyeing auxiliary," *Coloration Technology,* vol. **120** (3) pp. 108–13, 2004.

[167] R. Liu and H. Tang, "Oxidative decolorization of direct light red F3B dye at natural manganese mineral surface," *Water Research,* vol. **34** (16) pp. 4029–35, Nov 2000.

[168] N. Majeti and R. Kumar, "A review of chitin and chitosan applications," *Reactive and Functional Polymers,* vol. **46** (1) pp. 1–27, 2000.

[169] G. Crini and P.-M. Badot, "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature," *Progress in Polymer Science,* vol. **33** (4) pp. 399–447, 2008.

[170] E. Guibal and J. Roussy, "Coagulation and flocculation of dye-containing solutions using a biopolymer (Chitosan)," *Reactive and Functional Polymers,* vol. **67** (1) pp. 33–42, 2007.

[171] D. Knorr, "Dye binding properties of chitin and chitosan," *Journal of Food Science,* vol. **48** (1) pp. 36–37, 1983.

[172] J. Canal, C. Rodriguez, G. Caballero and M. Julia, "Chitosan boosts dyeing efficiency," *International Dyer,* vol. **183** (2) p. 16, 1998.

[173] D. Gupta and A. Haile, "Multifunctional properties of cotton fabric treated with chitosan and carboxymethyl chitosan," *Carbohydrate Polymers,* vol. **69** (1) pp. 164–71, 2007.

[174] R. Davidson and Y. Xue, "Improving the dyeability of wool by treatment with chitosan," *Journal of the Society of Dyers and Colourists,* vol. **110** (1) pp. 24–29, 1994.

[175] J. A. Rippon, "Improving the dye coverage of immature cotton fibres by treatment with chitosan," *Journal of the Society of Dyers and Colourists,* vol. **100** (10) pp. 298–303, 1984.

[176] S. Lim, "Synthesis of fiber-reactive chitosan derivative and its application to cotton fabric as an antimicrobial finish and a dyeing-improving agent,," PhD Thesis, North Carolina State University, 2002.

[177] S. Lim and S. Hudson, "Application of a fiber-reactive chitosan derivative to cotton fabric as an antimicrobial textile finish," *Carbohydrate Polymers,* vol. **56** (2) pp. 227–34, 2004.

[178] D. Raafat, K. Von Bargen, A. Haas and H. Sahl, "Insights into the mode of action of chitosan as an antibacterial compound," *Applied and Environmental Microbiology,* vol. **74** (12) pp. 3764–73, 2008.

[179] E. Rabea, E. Mohamed, C. Stevens, G. Smagghe and W. Steurbaut, "Chitosan as antimicrobial agent: applications and mode of action," *Biomacromolecules,* vol. **4** (6) pp. 1457–65, 2003.

[180] S. Islam, S. Ratnapandian, R. Padhye and L. Wang, "Sustainable colouration of cotton fabrics utilising chitosan and natural dyes," presented at the The 8th Asia Pacific Conference on Sustainable Energy & Environmental Technologies APCSEET, Adelaide, Australia, 2011.

[181] H. No, N. Young Park, S. Ho Lee and S. Meyers, "Antibacterial activity of chitosans and chitosan oligomers with different molecular weights," *International Journal of Food Microbiology,* vol. **74** (1) pp. 65–72, 2002.

[182] L. Becherán-Marón, C. Peniche and W. Argüelles-Monal, "Study of the interpolyelectrolyte reaction between chitosan and alginate: influence of alginate composition and chitosan molecular weight," *International Journal of Biological Macromolecules,* vol. **34** (1–2) pp. 127–33, 4// 2004.

[183] S. Islam, "Development of automotive textiles with anti-odour/anti-microbial properties," Masters Thesis, Fashion and Textiles, Royal Melbourne Institute of Technology University, Melbourne, 2008.

[184] A. Sezer, F. Hatipoglu, E. Cevher, Z. Oğurtan, A. Bas and J. Akbuğa, "Chitosan film containing fucoidan as a wound dressing for dermal burn healing: Preparation and in vitro/in vivo evaluation," *AAPS PharmSciTech,* vol. **8** (2) pp. E94–E101, 2007.

[185] M. Cervera, J. Heinämäki, K. Krogars, A. Jörgensen, M. Karjalainen, A. Colarte, et al., "Solid-state and mechanical properties of aqueous chitosan-amylose starch films plasticized with polyols," *AAPS PharmSciTech,* vol. **5** (1) pp. 109–14, 2004.

[186] A. Chenite, C. Chaput, D. Wang, C. Combes, M. Buschmann, C. Hoemann, et al., "Novel injectable neutral solutions of chitosan form biodegradable gels in situ," *Biomaterials,* vol. **21** (21) pp. 2155–61, 2000.

[187] S. Hirano, S. Kondo and Y. Ohe, "Chitosan gel: a novel polysaccharide gel," *Polymer,* vol. **16** (8) p. 622, 1975.

[188] S. Lee, F. Mi, Y. Shen and S. Shyu, "Equilibrium and kinetic studies of copper (II) ion uptake by chitosan-tripolyphosphate chelating resin," *Polymer,* vol. **42** (5) pp. 1879–92, 2001.

[189] Y. Lee and W. Lee, "Degradation of trichloroethylene by Fe (II) chelated with cross-linked chitosan in a modified Fenton reaction," *Journal of Hazardous Materials,* vol. **178** (1–3) pp. 187–93, 2010.

[190] A. Parize, M. Heller, V. Favere, M. Laranjeira, I. Brighente, G. Micke, et al., "Impregnation of chitosan microspheres with the natural dye curcuma," *Latin American Journal of Pharmacy,* vol. **28** (1) pp. 19–26, 2009.

[191] S. Houshyar and S. Amirshahi, "Treatment of cotton with chitosan and its effect on dyeability with reactive dyes," *Iranian Polymer Journal,* vol. **11** pp. 295–302, 2002.

[192] H. A. Lubs, "Process for reducing vat dyestuffs," USA Patent 2,164,930, 1939.

[193] P. Krug, "Thiourea dioxide (Formamidinesulphinic acid) A new reducing agent for textile printing," *Journal of the Society of Dyers and Colourists,* vol. **69** (13) pp. 606–11, 1953.

[194] Oxford-Technologies-Australia. (2006, 01 February). *Thiox – Product information sheet*. available: http://www.oxfordtech.net.au/sitebuilder/commercial/files/161/thiox-pds.pdf

[195] U. Baumgarte, "Vat dyes and their application," *Review of Progress in Coloration and Related Topics,* vol. **5** (1) pp. 17–32, 1974.

[196] U. Baumgarte and H. Schlüter, "A modern look at continuous dyeing with vat dyes," *Book of Papers, National Technical Conference of AATCC,* pp. 85–94, 1984.

[197] D. Ash, "All-clear soda ash – MSDS," 2012.

[198] R. P. Instruments. (2012, 21 December). *K Hand Coater*. available: http://www.rkprint.co.uk/?page_id=10

[199] T. Hussain. (2007, 19 December). *Important considerations in dyeing with vat dyes*. available: http://textilescience.blogspot.com/2007/11/important-considerations-in-dyeing-with.html

[200] A. Nishkam and N. Kasturiya, "Vat printing of cotton fabric," *Colourage,* vol. **35** (11) p. 23, 1988.

[201] J. Chakraborty, G. Dhiman and P. Singh, "Differential coloured effects on denim garments," *Asian Textile Journal,* vol. **19** (4) pp. 63–69, 2010.

[202] S. Grierson, D. Duff and R. Sinclair, "The colour and fastness of natural dyes of the Scottish Highlands," *Journal of the Society of Dyers and Colourists,* vol. **101** (7–8) pp. 220–28, 1985.

[203] T. Padfield and S. Landi, "The light-fastness of the natural dyes," *Studies in Conservation,* vol. **11** (4) pp. 181–96, 1966.

[204] L. Rudkin, *Natural dyes*: A & C Black, 2007.

[205] CHT. (2012, 15 March). *Printing auxilliaries*. available: http://www.saewoo.com/Auxiliaries02/Auxiliaries02-18.htm