

Effects of Cotton Structure and Surface Interactions on Dye Uptake

by

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Preface

The dyeing of cotton is influenced by chemical and physical interactions between dyes and the substrate, many of which are not well understood. It is believed that dyeability variation is caused by differences in the fibre structure and/or surface chemistry due to growth environment, genetic variety, or dyeing pretreatment conditions. However little work has been done to determine if this is the case. In this work the effects on dyed appearance of structural and processing differences, along with other fibre traits such as colour and fineness, will be investigated to determine the real cause of colour variation. This project aims to investigate those fibre properties affecting dye uptake, particularly those relating to the fibre surface chemistry and cellulosic structure.

Chapter 1 of this document provides an overview to the objectives of this project, along with a review of the literature discussing the structure and surface chemistry of cotton, the cotton dyeing process, and cotton fibre properties influencing dyeability. The objectives and desired outcomes of this work are then presented in the context of the literature review. Chapter 2 outlines the experimental methodology used in this project. Chapters 3-7 detail the individual experiments, along with the experimental results obtained and a discussion of their significance. Chapter 3 looks at the dyeability of cotton fibre samples with similar properties, namely maturity and micronaire. Chapter 4 examines the effects of variety on dyed appearance, which is expanded on in chapter 5 with a study of growth location. Chapter 6 determines the effect of storage conditions on cotton dyeability, particularly humidity. Chapter 7 investigates the influence of various pretreatments, such as scouring and bleaching, on cotton dyeability. Chapter 8 gives a conclusion, as well as recommendations for future work.

Definition of Key Terms

Barré – unintentional repetitive horizontal streaks in fabric occurring due to physical, optical, or colour differences in the yarns used in its construction.

Chromophore – the chemical group in a dye, or naturally occurring within a fibre responsible for its colour.

Enzyme – a protein produced by an organism that acts as a catalyst for a specific chemical reaction.

Fineness – the linear density, or mass per unit length of a cotton fibre, expressed in micrograms per metre (called millitex (mtex)).

Greige – describes an unfinished woven or knitted fabric which has not been bleached or dyed.

Lustre – describes the level of sheen of a fibre, yarn, or fabric.

Maturity – the degree of secondary wall thickening of a cotton fibre, expressed as a dimensionless ratio.

Micronaire – a measure of the specific surface area of a cotton fibre, and an indirect measure of air permeability.

Module – a compressed mass of cotton bolls with a protective plastic covering, used as a means of temporary storage between picking and ginning.

Moisture content – the weight of water in a material expressed as a percentage of the total weight of the material.

Saponification – a chemical reaction in which an ester, generally a fatty acid, is hydrolysed by an alkali to form a carboxylic acid and an alcohol.

Sequesterant – a substance used to isolate metal ions by the formation of chelate complexes

Substantivity – describes the attraction between a dye in solution and a fibre.

Trash – extraneous plant matter contaminating cotton fibre such as leaves and stems.

Warp – the yarns held in the loom in weaving of fabric.

Weft – the yarn that is passed through the weft yarns in weaving of fabric.

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1. Introduction

Cotton is the most widely used natural fibre in the textile industry, accounting for 32.9% of world apparel fibre consumption in 2010 (Food and Agriculture Organization of the United Nations and International Cotton Advisory Committee, 2013). Over the last few decades there has been a steady decline in the percentage of textiles made from cotton with a corresponding rise in synthetic materials (Taylor, 2000). Use of synthetic fibres over natural fibres is advantageous to textile manufacturers as there is no reliance on crops, they are often cheaper, and chemical alteration of fibre properties is easier. From a consumer point of view, synthetic fibres are appealing again for their cheaper price, and for fabric properties such as wrinkle resistance, durability, ease of laundering, quick drying, moisture wicking, and softness. It is therefore vital for the cotton industry that fibre properties influencing textile processing be optimised to remain competitive with synthetic fibres in the textile market.

Dyeing is an important step in textile processing, imparting colour to the product. Dyeing is influenced by complex chemical and physical interactions between the dyestuff and the substrate. In the dyeing of cotton there are many influencing factors related to both dyes and the properties of the cotton fibre itself including the affinity of the dye for the fibre, dye type, size of the dye molecules, the application process, pretreatments prior to dyeing, fibre surface chemistry, and the internal cellulosic structure of the fibre. Accordingly, dyeing is subject to many sources of shade variation which must be carefully regulated to ensure shade repeatability. Off shade dyeings can lead to issues in later processing such as barré in fabrics. In some cases shade variation can be fixed with further dyeings but can sometimes result in whole batch losses, with both situations being costly for

dyehouses. Despite the level of care taken in dyeing there are still instances where cotton dyeing is off shade for no clear reason (Gordon et al., 2004). Two fibres with seemingly identical properties can exhibit very different dyeing behaviour. Shade variation has been observed between fibres of the same genetic variety grown in different regions (Gordon et al., 2002).

This project aimed to increase understanding of the dyeing behaviour of cotton fibre by answering the following questions:

1. Why do cotton fibres that are nominally the same in terms of fibre properties differ in dyed appearance?
2. What are the key factors related to fibre properties and processing of cotton textiles that affect dyeability?
3. Is there an effective method to directly assess the dyeability of cotton fibre?

To answer these questions a range of factors with the potential to influence dyeability, related to both the fibre and production processes, were examined. It has been well established that certain fibre properties, such as maturity and micronaire, effect dyeability. These properties were be studied, as well as other fibre-related factors thought to influence dyeing such as cotton variety and growth environment. The impact of various processing steps such as storage conditions and pretreatments on dyeing behaviour was also investigated as these may induce changes to the fibre structure or surface chemistry.

Increased knowledge of the chemical and physical interactions between dyes and the cotton fibre will help give a greater understanding of cotton fibre dyeability, and in doing so improve the quality of the end product, whether it be fibre, yarn or fabric. The ideal outcome of this project would be identification of fibre structural traits that

affect dye uptake, which may lead to improvements in the way mills and dyehouses assess cotton dyeability.

1.1 Cotton Growth

Each cotton fibre is a single seed hair, harvested from four domesticated species of plant in the genus *Gossypium*. Plants of one species, *Gossypium hirsutum*, are the source of over 90% of cotton produced globally. This species is commonly referred to as Upland cotton. Another species, *Gossypium barbadense*, makes up another 8% of cotton fibre and is known for producing long, fine fibres. The other two domesticated species, *Gossypium arboreum* and *Gossypium herbaceum*, are not widely cultivated and commercially grown only in India and Pakistan.

Cotton is an annual summer crop, preferentially growing in hot climates with low humidity (Cotton Australia, 2014). Cotton is grown in approximately 100 countries worldwide, with the three largest cotton producers being India, China and the United States (Cotton Australia, 2016c). The three largest exporters of cotton are the United States, India and Brazil (Cotton Incorporated, 2016b). The majority of cotton mill consumption is by developing countries such as China and India, accounting for over half of all cotton consumption globally (Cotton Incorporated, 2016b).

Cotton fibres are harvested from a seed pod known as a boll. It takes 4–5 months for a cotton plant to grow from seed to boll opening. Cotton flower buds develop a few weeks after plants grow, with flowers opening a few weeks after that. The day of flowering is known as anthesis, with fibre development often described in days post-anthesis (dpa). Cotton fibre development occurs in four overlapping stages; initiation, elongation, secondary wall deposition, and maturation (Figure 1.1, (Lee et

al., 2007)). The initiation stage of development starts when the flowers open, marking the start of fibre growth. The fibres extend longitudinally during the elongation stage, with final fibre length reached at 21–35 dpa. It is also during this stage that the outer layers of the fibre develop, establishing fibre diameter. Secondary wall deposition commences at around 21 dpa, continuing for 3–6 weeks. At maturity the bolls open, exposing the cotton fibres to the elements and drying them out.

Once mature the cotton bolls are harvested. Nowadays this is mostly done mechanically but is still done by hand in some parts of the world. One drawback of mechanical harvesting is that the immature bolls on the plant are also harvested, which can affect dye uptake. The bolls are then ginned to separate the fibre from the seed, and the fibres packed into bales for transport to mills or export.

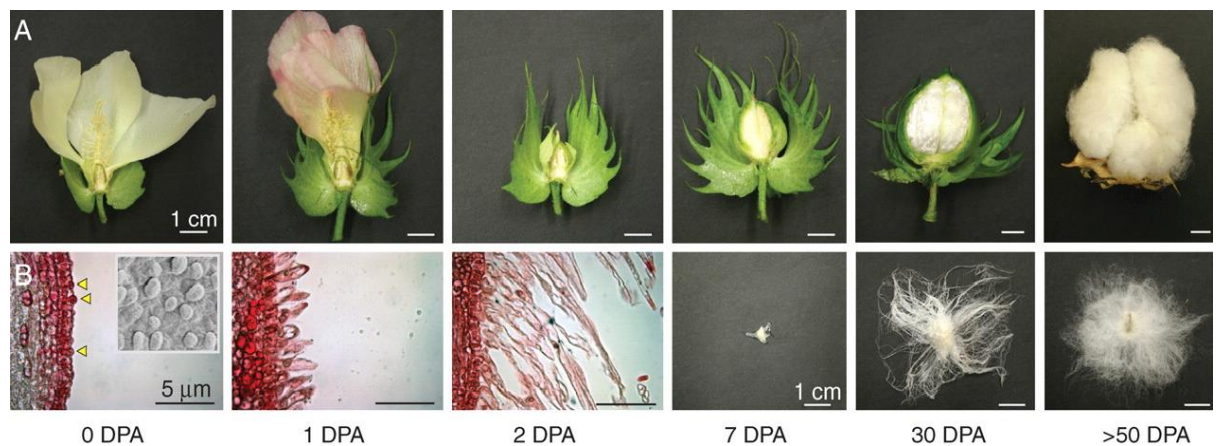


Figure 1.1: Cotton fibre development from initiation (0 dpa) to maturation (50+ dpa)

(adapted from Lee, Woodward and Chen 2007).

1.1.1 The Australian Cotton Industry

Australia is a relatively minor cotton producer, ranking 8th worldwide in 2014/2015, producing 2.6 million bales (as opposed to India, currently the world's largest producer, with 26.8 million bales) (Cotton Incorporated, 2016b). The record for cotton production in Australia was 5.3 million bales in the 2011/2012 season (Cotton

Australia, 2016a). High yields were also obtained in the 2012/2013 and 2013/14 seasons, with 4.6 million and 4.1 million bales produced respectively (Cotton Incorporated, 2016b). However, the vast majority of Australian cotton is exported, making it the 4th largest exporter globally, therefore it is economically important that quality is constantly improving to remain competitive in overseas markets (Long et al., 2010, Cotton Incorporated, 2016b). Of the 99% of Australian cotton that is exported, nearly 68% of this goes to China (Cotton Australia and Cotton Research and Development Corporation, 2014). In Australia, cotton is primarily grown in Southern and Central Queensland, and in Northern New South Wales. However the last decade has seen a large increase in cotton production in Southern New South Wales. The cotton that is grown is of a very high quality, attracting a premium price, giving Australian cotton a global reputation that needs to be maintained (Cotton Australia, 2016a). Australian cotton has a particularly strong reputation in terms of strength, length, colour, and low trash content (Gordon et al., 2004).

1.2 Cotton Structure

Despite much research into the structure of cotton fibre much is still unknown, particularly at a highly detailed level. Cotton is about 95% cellulose with the remaining 5% consisting of noncellulosic materials such as proteins, waxes, sugars, and metal ions. Cotton fibre has a layered structure, with each layer having its own unique properties contributing to overall fibre traits (Figure 1.2, (Wakelyn et al., 2007)).

The outermost layer of the cotton fibre is the cuticle, a waxy layer coating the fibre. As well as wax, other surface chemical components present in this layer include sugars, salts, pectins, and metal ions (Wakelyn et al., 2007). The cuticle protects the fibre, acting as a waterproof coating.

Intermingled with the cuticle is the primary cell wall; it is not uncommon for these two layers to be regarded as one (Etters, 1999, Maxwell et al., 2003). This layer consists mostly of cellulose, and noncellulosic materials including pectins, waxes and proteins (Maxwell et al., 2003). The cellulose is arranged in fine strands forming a network of capillaries. The combined cuticle and primary wall contribute only around 1% of the total fibre thickness (Etters, 1999)

A lacy network of cellulose microfibrils, called the winding layer, separates the primary and secondary cell walls. Although regarded as the first layer of the secondary wall, or the S1 layer, it differs in structure from both the primary wall and the remaining secondary wall layers with the cellulose strands aligned at a different angle.

The secondary cell wall is composed almost entirely of cellulose, and makes up 90% of the total fibre weight (Heine and Hocker, 1995). The bulk of the cotton fibre is found in the second or S2 layer of the secondary cell wall. After the fibre diameter is established during elongation the secondary wall cellulose is deposited in layers of tightly packed cellulose strands.

The final or S3 layer of the secondary wall separates the S2 layer from the hollow lumen in the centre of the fibre, and is accordingly referred to as the lumen wall. During growth the lumen is filled with protoplast which dries up on boll opening, leaving a hollow bean-shaped cavity.

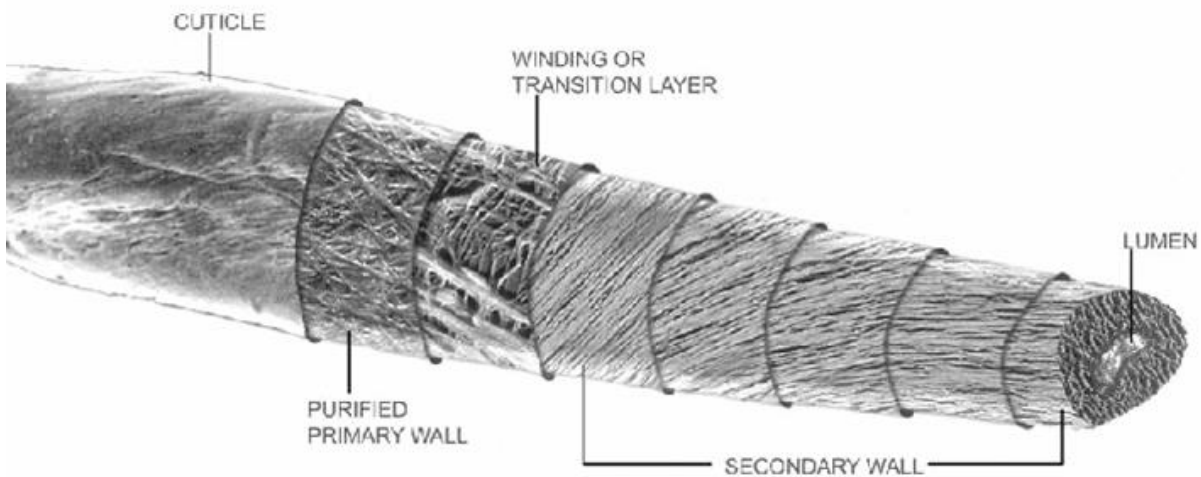


Figure 1.2: The layered structure of the cotton fibre (Wilton Goynes (Wakelyn et al., 2007)).

1.2.1 Cotton Cellulose

Cotton fibre is composed almost 95% of pure cellulose. Cellulose is a polymer of D-glucopyranose units, an isomer of glucose, joined together in unbranched chains by $\beta(1\rightarrow4)$ -glycosidic bonds (Figure 1.3). The repeated unit of the chain is cellobiose, formed from two glucose molecules. The number of glucose units linked together to form the cellulose chain is described as the degree of polymerisation. In cotton fibre the degree of polymerisation ranges on average from 10,000–15,000 glucose units. Each chain has a reducing end with a free hemiacetal group, and a non-reducing end with an alcohol group.

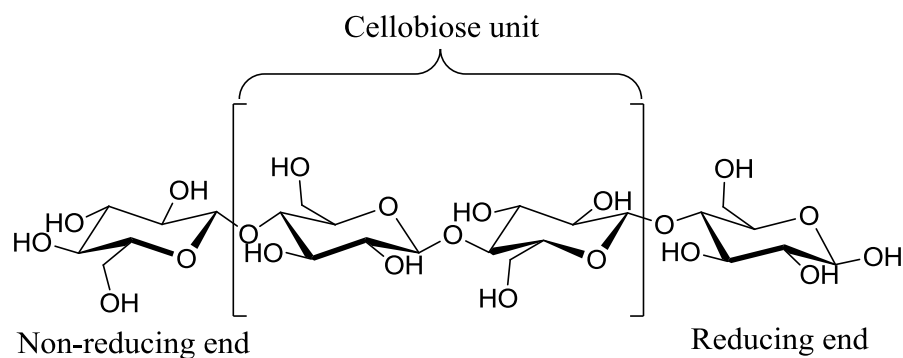


Figure 1.3: The structure of cellulose chain.

The chains of cellulose are held together by hydrogen bonds between the hydroxyl groups on adjacent chains (Figure 1.4, (Zhou and Wu, 2012)). The cellulose chains are arranged into crystalline strands known as microfibrils, which are further arranged into the cellulosic layers of the cotton fibre.

Cotton fibre contains two types of cellulose, crystalline and amorphous, in various ratios depending on genotype and maturity (Figure 1.4, (Zhou and Wu, 2012)). On average cotton fibre is estimated to contain 70% crystalline cellulose and 30% amorphous cellulose. The amorphous regions are distributed regularly along the cellulose microfibrils, with the transition between crystalline and amorphous regions thought to be gradual (Bertran and Dale, 1986, Zhou and Wu, 2012).

Crystalline cellulose has a highly ordered, tightly packed structure with a near parallel arrangement of microfibrils. The hydrogen bonds holding the chains together are most extensive in these regions. This combination of tight structure and strong intermolecular bonds prevents many reagents, including water and consequently dye solutions and dyeing auxiliaries, from penetrating the intracrystalline regions of cellulose, with only the surface of crystalline regions being accessible (Ciolacu et al., 2011). The more the microfibrils are compacted, the greater the extent of

intermolecular bonding between them, and the lower the accessibility (Wakelyn et al., 2007).

Amorphous cellulose has no definite crystalline form. Regions containing amorphous cellulose are more accessible to water and other substances, with many reagents only able to penetrate amorphous regions. Accordingly, amorphous cellulose is sometimes referred to as accessible cellulose. Amorphous cellulose also contains a greater number of free hydroxyl groups available for water absorption and chemical reaction (Bertran and Dale, 1986). The primary cell wall has a higher proportion of amorphous cellulose than the secondary cell wall. Hence, immature fibres are more accessible than mature fibres due to having a greater ratio of amorphous cellulose. However, immature fibres also have a smaller total cellulose content due to less developed secondary cell walls, so there is a smaller available surface area for dyes to bind to and they don't hold colour as well (Smith, 1991).

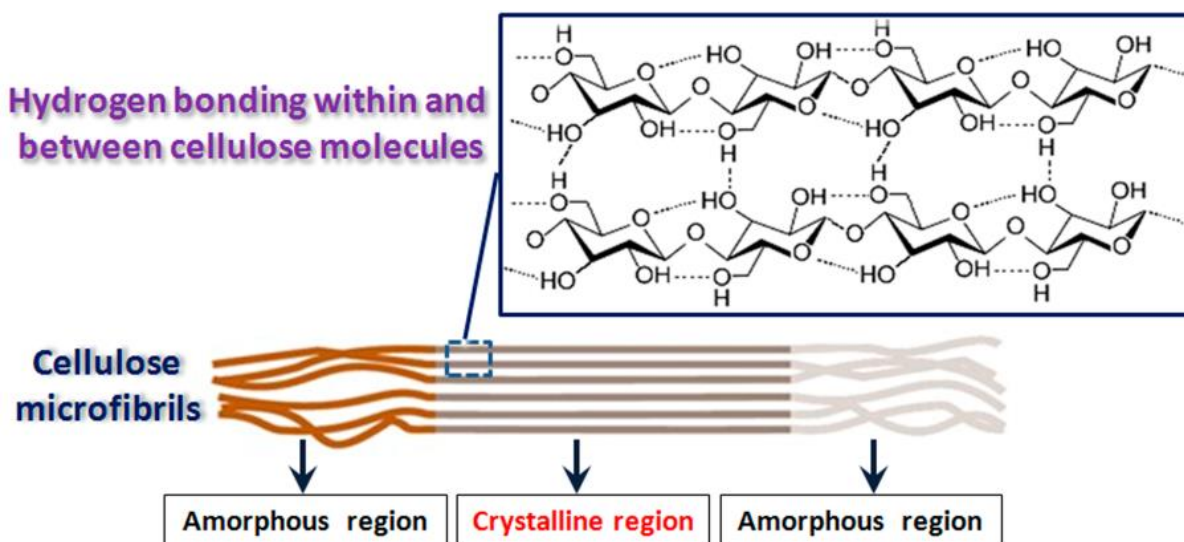


Figure 1.4: Hydrogen bonding between cellulose chains and the differential arrangement of cellulose microfibrils in amorphous and crystalline regions (Zhou and Wu, 2012).

1.2.2 Cotton Surface Chemistry

The outer layers of the cotton fibre, the cuticle and the primary cell wall, contain various noncellulosic compounds, making up nearly 4% of the cotton surface (Buchert et al., 2001). Most apparent of these are waxes, but there are also pectins, xyloglucans and other sugars, and various amino acids, proteins, organic acids, and inorganic salts. Residues of noncellulosic plant material can also be found inside the lumen. All of these compounds can have a marked effect on cotton fibre processing. In relation to dyeability the most significant noncellulosic compounds are waxes and pectins.

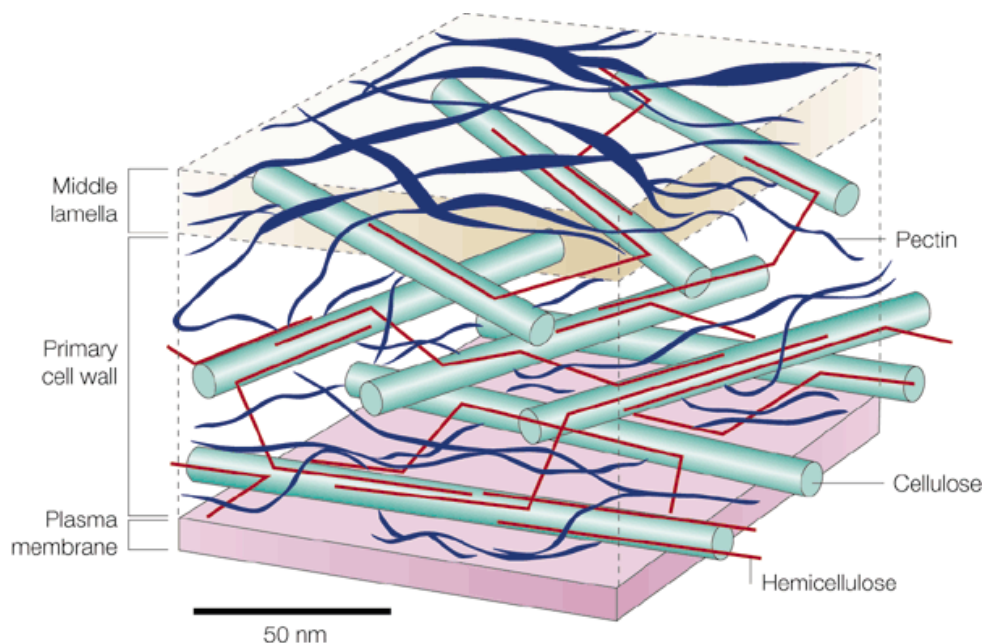
Cotton wax consists of a mixture of high molecular weight long-chain saturated fatty acids and alcohols, resins, hydrocarbons (both saturated and unsaturated), sterols, and sterol glucosides (Wakelyn et al., 2007). Wax has the greatest effect on dyeability as it acts as an impermeable barrier, preventing water and dye molecules from penetrating the fibre. Cotton is hence scoured before dyeing to remove the wax and other noncellulosic impurities, but despite this a residual waxy layer sometimes remains (Mitchell et al., 2005).

Levels of cotton wax are influenced by both genetic and environmental factors. A 2002 study by Gordon *et al.* found statistically significant variation in cotton wax content between fibres of the same variety grown in different regions, highlighting environmental effects on cotton development. Some cottons in this study that suffered heat or water stress during growth were found to have lower micronaire values. Additionally, the composition of cotton wax was not uniform, with some of the stressed cottons having high concentrations of a wax containing high levels of hydrocarbon which could not be removed easily by conventional scouring methods (Gordon et al., 2002).

It is thought the presence of wax may be beneficial in mechanical processing of cotton, such as spinning, by acting as a natural lubricant, reducing fibre breakage. However, work by Cui *et al.* (2002) found no significant correlation between wax content and fibre breakage. This work found wax to be significantly correlated with micronaire but no other fibre property (Cui *et al.*, 2002). This was backed up the following year in work by Gamble (2003). This work also found an inverse relationship between micronaire and pectin content, and linear relationships between micronaire and salt and sugar contents (Gamble, 2003).

Hemicelluloses are estimated to make up approximately 1.4% of the cotton surface (Buchert *et al.*, 2001). Hemicelluloses are polysaccharides with a backbone structurally similar to that of cellulose, but unlike cellulose may contain residues other than glucose. Additionally, the chain lengths of hemicelluloses are shorter and may be branched. Hemicelluloses also have a more amorphous structure, making them more reactive to reagents. Types of hemicelluloses found in cotton include pectin and xyloglucan.

Pectin is a generic term used to describe a family of polysaccharides containing 1,4- α -D-galacturonic acid, including homogalacturonans, rhamnogalacturonans, and substituted galacturonans. Pectin acts as a cement, binding the noncellulosic surface components of cotton within the cellulosic matrix of the primary cell wall (Figure 1.5, (Smith, 2001)), as well as partially contributing to the hydrophobic character of the cuticle and primary wall (Etters, 1999).



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Figure 1.5: Generic structure of a plant primary cell wall (Smith, 2001).

1.3 Dyeing of Cotton Textiles

Cotton has been used in textiles as early as 3000 BC and dyed for just as long. Historically natural dyes were used such as plant and animal extracts, and mineral pigments. The first synthetic dyes were developed in 1856 by Sir William Henry Perkin, triggering a boom in dye manufacture (Aspland, 1992a). Nowadays there are many types of dyes available for use on cotton textiles including vat, direct, sulphur, azoic and reactive dyes. Dyes may be registered with the Colour Index, signified by the letters “C.I”, which is a database of dyes and pigments published by the Society of Dyers Colourists (SDC) and the American Association of Textile Chemists and Colourists (AATCC). Dyes are classified by both a C.I. Generic Name and a C.I. Constitution Number. The C.I. Generic Name describes the class of the dye, its colour, and the order in which it was registered e.g. C.I. Reactive Yellow 135. The C.I. Constitution Number is used to classify the dye by its chemical structure e.g. C.I.

24925 designates a diazo dye. A C.I. Constitution number is only assigned if the chemical structure of the dye has been disclosed for publication.

1.3.1 Types of Dyes

This section introduces the main types of dyes used in the dyeing of cotton textiles.

1.3.1.1 Direct Dyes

Direct dyes have previously been quite popular due to their ease of application and full range of available shades but recent years have seen a shift towards other dye classes, particularly reactive dyes. Direct dyes are water soluble anionic dyes that are drawn in to the substrate on addition of electrolyte to the dyebath (Aspland, 1991).

Once the dye molecules have entered the fibres they are held by intermolecular forces including Van der Waals interactions and hydrogen bonds. The dye molecules are relatively large with a long and flat shape, allowing them to lie parallel to the cellulose chains. The large size of the molecules also increases the substantivity between the dye and the fibre by increasing the number of intermolecular bonds that can form. The Goldthwaite differential dye test, a method formerly used for measuring cotton maturity, involves dyeing of fibres with C.I. Direct Red 81 and C.I. Direct Green 26. Immature fibres preferentially take up the green dye, while more mature fibres have a higher affinity for the red. This suggests molecular structure can have an influence on dye uptake and diffusion, and therefore dye performance, particularly for fibres with differing maturities (Cheek and Wilcock, 1988). Direct dyes can have good light fastness but may not produce the most vibrant results, and generally have poorer wash fastness than other dye types used on cotton (Aspland, 1991).

1.3.1.2 Vat Dyes

Vat dyes are among the oldest type of dyes known. The most common vat dye is the indigo used to colour denim, however nowadays synthetic indigo is used over natural indigo (Aspland, 1992c). Vat dyes work via a reduction-oxidation reaction. The dye is sold as a water insoluble pigment which is solubilised on addition of a reducing agent. The fabric is added to the dyebath and on exposure to air or an oxidising agent the dye reverts to the water-insoluble form inside the fibre.

Vat dyes typically have high fastness properties, especially wash fastness and transference (Aspland, 1992c). A notable exception to this is indigo, most commonly used in manufacturing of denim, which is known for poor wash and rub fastness properties. This is not due to the chemistry of the dye but rather the dyeing method used to apply it. Consumer demand for denim fabrics with a worn appearance necessitates ring dyeing, so called due to the ring seen when a dyed yarn is cross-sectioned (Chequer et al., 2013). The dye is applied in a concentrated layer on the yarn surface, impeding dye penetration into the yarn and resulting in poor fastness properties (Chequer et al., 2013). Gradual wear leads to exposure of the undyed core of the yarn which contributes to the classic worn denim appearance (Chequer et al., 2013). This effect also comes from the twill weave method used in the construction of denim fabric in which the dyed warp yarns are woven over multiple undyed weft yarns, with the exposed weft yarns giving the appearance of white flecks in the fabric. The abrasion resistance of indigo can be improved with treatment of the fabric.

Some vat dyes can react with light causing accelerated fibre degradation, known as photochemical tendering. One theory explaining this degradation suggests the light converts the dye into an excited state allowing it to continually withdraw

electrons from the fibre while remaining in its oxidised form due to oxygen exposure from the air (Baumgarte, 1974). Another theory proposes the formation of a highly active singlet oxygen species is responsible for the tendering (Baumgarte, 1974). Particularly known for this degradation are some yellow, orange, and brown shades, and certain dye combinations (Chakraborty, 2010).

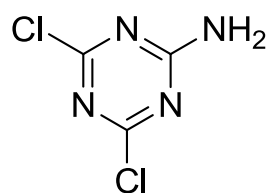
1.3.1.3 Sulphur Dyes

Sulphur dyes are another popular type of dye due to their low price and good wash fastness. Sulphur black is a particularly common dye due to its cost and depth of colour (Aspland, 1992b). Application of sulphur dyes is similar to that of vat dyes, with colouration occurring by a reduction then oxidation reaction; however oxidizing agents may be required to return the dye to an insoluble form. Some colours are not available as sulphur dyes and rub fastness can be poor. As sulphur dyes are also reductive dyes they can also cause photochemical tendering (Shenai and Rao, 1973).

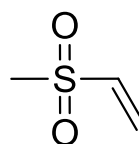
1.3.1.4 Reactive Dyes

Reactive dyes first appeared on the market in 1956 and since then have become increasingly popular in the textile industry, particularly in the dyeing of cellulosic fibres for which they are now the most commonly used dye type. Reactive dyes are a class of dye that form covalent bonds with the substrate, chemically binding them to it. Covalent bonds are much stronger than the intermolecular forces that hold other dyes.

The two major reactive groups in commercial reactive dyes are the chlorotriazine and vinyl sulfone groups (Figure 1.6) (Buschle-Diller and Traore, 1998). Dyes may be monofunctional or bifunctional, with the later containing two reactive groups which may be the same or different.



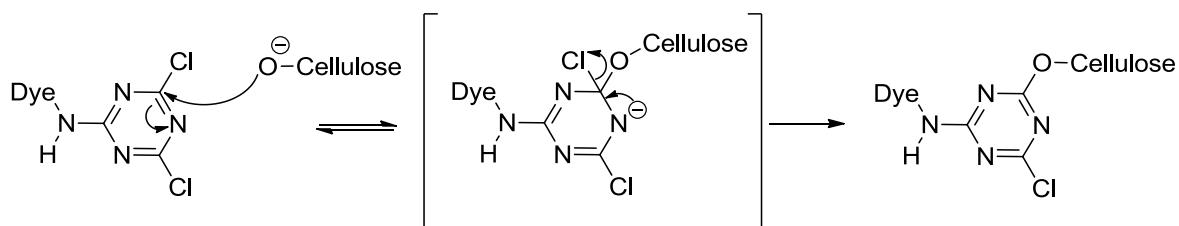
a. The structure of a dichlorotriazine group.



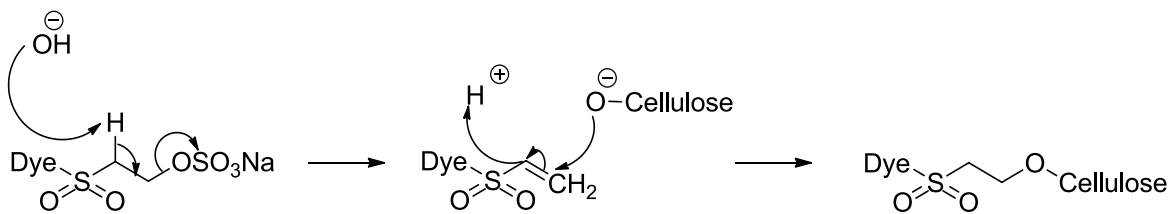
b. The structure of a vinyl sulfone group.

Figure 1.6: The structure of a dichlorotriazine group (a.), and a vinyl sulfone group (b.).

The reaction between the dyestuff and the cotton fibre proceeds via a different mechanism for each reactive group. For the chlorotriazine group, the reaction occurs by nucleophilic substitution, forming an ether bond with hydroxyl groups on the cellulose (Figure 1.7.a.). For the vinyl sulfone group, the reaction proceeds by nucleophilic addition, creating an ester (Figure 1.7.b.). The dye initially has a sulfatoethylsulfone group, becoming the vinyl sulfone form on elimination of a bisulfate anion.



a. The nucleophilic substitution mechanism of chlorotriazine dyes.



b. The nucleophilic addition mechanism of vinyl sulfone dyes.

Figure 1.7: The mechanism of the reaction between cotton fibre and chlorotriazine dyes (a.), and vinyl sulfone dyes (b.).

Chromophoric groups used in reactive dyes include anthraquinone, phthalocyanine, formazin, oxazine and azo groups, with the latter estimated to make up around 66% of reactive dyes (Bhatti et al., 2012).

Reactive dyes are known for having low levels of dyebath exhaustion, with fixation rates generally in the range of 50–80% (Khatri et al., 2015). Typically, reactive dye molecules are smaller in size than other dye types (such as direct dyes) and therefore have a lower affinity for the cotton fibre as fewer intermolecular bonds form. Accordingly, larger amounts of salt may be required to improve dye affinity for the fibre by negating charge repulsion between them. The high salt content together with poor dye exhaustion rates raises environmental concerns about dyebath effluent. Some low salt reactive dyes have a larger molecular size and therefore enhanced substantivity by intermolecular attraction. These dyes have been developed to reduce the reactive dye effluent problems however they still only have 80% fixation rates (Ciba Specialty Chemicals Inc., 1995). In addition to their low substantivity, reactive dyes can also undergo hydrolysis with water as they are designed to bond with the hydroxyl groups of cotton cellulose. If dye molecules react with water they then cannot react with the cotton fibre, resulting in further dye loss.

Hydrolysed dye must be thoroughly washed off to prevent fastness issues. Reactive dyes typically have good wash fastness and light fastness, and a full range of shades is available (Aspland, 1992a). Compared to other dye classes reactive dyes can have longer processing times and be more costly, however prices have fallen with their increasing popularity. As they are important in dyeing of cotton, reactive dyes will be the main focus for this project.

1.3.1.5 Azoic Dyes

Azoic dyes are a class of dyes produced by reaction of a diazo compound with a coupling compound, which is typically an alkali soluble naphthol, phenol, or aromatic amine. The reaction occurs as a two-step process within the fabric. First the coupling compound is absorbed into the fibre from alkaline solution. The substrate is then treated with a solution containing the diazo compound in salt form which reacts with the coupling compound, producing the dyed colour. This step is performed at low temperatures (0–5°C), requiring the dyebath to be cooled with ice. Azoic dyes are not commonly used these days as the application process is costly. Azoic dyes are known for their particularly bright colours and high wash fastness but can have poor rub fastness if not properly applied. Excess coupling compound must be completely removed as it will react with the diazo compound to form dye on the surface of the cotton, which will not wash off easily but will readily rub off.

1.3.1.6 Azo Dyes

Azo dyes are a class of dyes containing an insoluble azo group ($R-N=N-R'$) as the chromophore. Azo dyes are the most common type of dye on the market today, accounting for 60–70% of dyes (Chequer et al., 2013). As well as textiles azo dyes also see use in many other industries, including food, cosmetics, pharmaceuticals, and paints. Some of the advantages offered by azo dyes include comparatively cheap

and easy synthesis, structural diversity, high molar absorptivity, and good to excellent wash fastness and light fastness (Chequer et al., 2013). Azo dyes may be applied as direct, vat, or reactive dyes. A small number of azo dyes can break down to form carcinogenic aromatic amines and hence are banned in some markets. Although the manufacture and application of these particular azo dyes has declined drastically regulation is critical to prevent them entering the environment via wastewaters, and to ensure any products on the market containing them do not exceed safe levels (30 ppm under European regulations).

1.3.2 Dyeing Procedure

Cotton may be dyed in fibre, yarn or fabric forms. The process is slightly different for each dye class but the basic stages remain the same. These are pretreatment, dyeing, and finishing.

Pretreatment can involve multiple steps including singeing, desizing, scouring, bleaching, and mercerisation. Singeing is performed on yarns and fabrics to burn off stray fibres not tightly bound in the yarn or fabric. The fabric is lightly brushed to raise the loose fibres before being rapidly passed over a heated plate or open flame. Desizing is done to remove starches and other sizes that may have been applied to the yarn or fabric in previous processing steps and involves treatment with amylase enzymes, oxidising agents, or acids. Scouring is performed to remove cotton wax and other impurities that may inhibit dyeing. Traditionally scouring is done under alkaline conditions, using strong sodium hydroxide solutions at high temperatures. Bleaching further removes impurities from cotton, particularly those that may have caused discolouration or yellowness, with the aim to improve dyeing results by providing a uniform base. Bleaching of cotton is typically done using hydrogen peroxide at high temperatures. Mercerisation is a chemical process

designed to swell cellulosic fibres, improving dye affinity and luster. Mercerisation involves treatment of yarn or fabric in a highly concentrated sodium hydroxide bath (>15%, usually around 22%) under tension, followed by neutralisation in an acid bath. Mercerisation is not a routine step in cotton pretreatment and is most commonly used for embroidery and crochet yarns, with some use in clothing.

For all dye types, dye uptake occurs in three stages which are surface adsorption, fibre penetration, and internal migration. Surface adsorption describes the initial take up of dye from the liquor and ensuing distribution over the fibre surface. During the fibre penetration stage the dye diffuses into the fibre. The dye spreads throughout the entire fibre in the migration stage. Some dye types require additional fixation steps to anchor the dye inside the fibre. For reactive dyes, as used in this project, the dyeing procedure is commonly broken down into three steps: exhaustion, fixation, and washing off. During exhaustion the dye is taken up by the substrate to its maximum capacity. Cotton fibres become negatively charged when immersed in water due to ionization of the hydroxyl groups of cellulose, and consequently repel dyestuffs which are predominantly anionic. Salt is added to the bath to help increase dye exhaustion onto the substrate by negating the charge repulsion. The lower the fibre affinity of the dye the more salt is required. Other reagents such as wetting agents and sequesterants may also be added at the start of dyeing to assist the process. Typically, the dye is added at room temperature and the dyebath gradually heated to dyeing and fixation temperature. In the fixation stage the covalent bonds between the dye and the fibre form. An alkali, such as sodium hydroxide or soda ash, is added to the dyebath, which converts the hydroxyl groups on the cotton cellulose to the reactive anionic form. The addition of alkali triggers a shift in equilibrium between the dye in the substrate and in the bath. When equilibrium is reached all free

dye molecules have been bound to the substrate or have hydrolysed in the bath, and no further increase in colour depth occurs. The final step of the process, washing off, requires all unfixed, hydrolysed dye to be removed from the substrate. This can be a lengthy process, depending on the substantivity of the dye, requiring washes at various temperatures and possibly further scouring.

Finishing involves chemical or mechanical treatments of the dyed substrate to improve appearance, texture, or performance (Shamey and Hussein, 2005). Chemical treatments may be used to impart properties such as resistance to wrinkles, water, odours, and fire, as well as enzyme treatments to defuzz the fabric or yield special effects such as stonewash look denim. Examples of mechanical finishes include pre-shrinking of fabrics, brushing, pressing, singeing, and shearing to remove loose threads.

1.3.3 Issues in Dyeability

Over time large volumes of research have been done on cotton dyeability, yet there is still much scope for process improvement. Perhaps the biggest impact on cotton dyeing came with the development of the first synthetic dyes in the 19th century, with many more following in subsequent years. Also of note for the dyeing of cellulosic fibres such as cotton is the development of fibre reactive dyes in the 1950's offering greatly improved fastness properties. Much of the research into cotton dyeability throughout the 20th century focused on improving cotton dyeability by chemical modification of the fibre, whereas more modern research has looked at pretreatments to enhance dyeability such as cationisation. Since the 1990's there has been a big increase in studies looking at the environmental impacts of cotton dyeing, which is still one of the key issues in dyeability today. Another area of research of importance

with today's consumer driven economy is identification of sources of shade variation in an effort to ensure consistent dyeing.

1.3.3.1 Environmental Issues

Environmental issues in dyeing revolve around water consumption, energy consumption, and dyeing effluent. Dyeing can be a very inefficient process with several wet processing steps required from initial pretreatment to washing off, all of which use water and energy. Research is being done to increase productivity of dyeing, reducing the amount of water and energy required, by looking toward process alterations such as one-bath multi-step processes and lower water dyeings utilising other solvents such as supercritical fluids (Eren et al., 2009, Presa and Tavcer, 2009, Ozcan et al., 1998).

Many chemicals are involved in the dyeing process including harsh alkaline pretreatments, bleach, dyes, and salts. A lot of research has been carried out regarding the plausibility of replacing chemical scouring and bleaching with enzyme-based bioscouring treatments using enzymes such as cellulases and pectinases. Although many studies have shown the potential of bioscouring on a laboratory scale (Li and Hardin, 1997, Kim et al., 2006, Kalantzi et al., 2009), these treatments have not been widely implemented in industry. Kalantzi *et al.* (2009) put this down to higher cost, longer treatment times, incomplete removal of waxes, and some limitations in dyeing of darker shades. Issues dyeing lighter shades compared to conventional scouring have also been reported when dyeing on unbleached fabrics, yet this can be reduced by bleaching (Losonczi et al., 2004).

Polluted wastewaters from dyehouses can be of serious environmental concern, particularly in developing countries. It is estimated that during the dyeing

process 10–50% of the dye is lost to the environment (Chequer et al., 2013). Residual dye in waters can pose a hazard to both humans and animals (particularly fish) because of the high toxicity and mutagenicity of some dyes, as well as affecting aquatic plant growth due to colour in the water reducing light transmittance (Akbari et al., 2002). Azo dyes are particularly concerning in this regard as they are not readily removed from wastewaters, with some dyes potentially being metabolized in the body of both animals and humans to form carcinogenic aromatic amines (Chequer et al., 2013).

As well as dye, these waters also contain other potentially harmful chemicals including detergents, surfactants, and other additives. Work has been done to remediate dye effluent removing some of the chemicals and allowing it to be recycled utilising methods such as coagulation/flocculation, nanofiltration, and bioremediation by bacterial consortiums (Akbari et al., 2002, Avlonitis et al., 2008, Phugare et al., 2011, Khouni et al., 2011). Also of environmental concern is the large amounts of salt often required to increase the affinity of cotton fibre for the dyestuff which can increase salinity in waterways, harming aquatic life. Methods are being developed for low or salt-free dyeing including the synthesis of novel dyes and chemical modification of the cotton fibres (Zheng et al., 2012, Dehabadi et al., 2013).

1.3.3.2 Shade Variation

Shade variation is a major problem faced by dyehouses. Although care is taken to replicate dyeing procedure, repeatability is not the only source of variation. Shade differences are also an expensive problem, costing both time and money to fix, and potentially causing whole batch losses (Smith, 1991). A 1992 report by Cooper and Taylor found variation in dyeability to be greatest in raw cotton fibre, decreasing with each stage of processing, and recommended that different colour standards be

used at each stage accordingly. However, quantification of fibre dyeability variation is not straight forward, with the same paper noting that some dyestuffs appear more sensitive to fibre variability than others (Cooper and Taylor, 1992). There are many fibre related sources of shade variation which will be discussed in the next section. Additionally there are reports of cotton, that is the same in terms of fibre properties, dyeing off shade for no explicable reason (Gordon et al., 2004). There are currently no testing methods designed to rapidly assess dyeability of raw cotton samples (Gordon et al., 2004, International Trade Centre, 2007).

1.4 Fibre Properties Affecting Dyeability

Cotton fibre is classed to sort it into quality grades which are reflected in the price paid to the grower. Previously classing was done by hand and by eye but nowadays is mostly done instrumentally. Cotton is most commonly graded by high volume instrument (HVI™), manufactured by Uster Technologies AG, Switzerland. The HVI™ system gives measures of length, strength, uniformity, micronaire, colour, and trash content. As HVI™ is the standard classification system for cotton in most countries, these parameters are also the ones used by mills and dyehouses in the selection of cotton samples to purchase from growers. Fibre properties are determined by the cotton genotype, growth environment, and interactions between them, as well as the metabolic rate of the plant during development (Bradow and Davidonis, 2000). Properties such as length, strength and fineness are for the most part determined by genetics but environmental factors can influence overall fibre quality (Bradow and Davidonis, 2000). The most important fibre properties in relation to dyeability are colour and micronaire. Discolouration of cotton can arise from numerous causes, potentially indicating fibre quality issues which may affect dyeability. Micronaire is closely related to maturity. Micronaire and maturity are

considered the major parameters affecting shade and are used to predict dyeability of cotton accordingly.

1.4.1 Colour

Naturally white cotton may become discoloured during growth due to factors such as weather conditions, microbial or insect damage, and disease. Additionally, cotton fibre contains trace amounts of metal ions which are absorbed from soil. Higher concentrations of calcium and magnesium have been found to correlate with increased fibre yellowness (Millington et al., 2015). Fibre discolouration can also arise from poor moisture and temperature conditions during storage. Colour variation in cotton fibre may suggest variation in other physical properties that may also have an effect on processing and quality of the end product and result in a lower market value (Cui et al., 2014, Matusiak and Walawska, 2010). Discolouration due to fibre deterioration can affect the ability of cotton to take up dyes and other treatments (Matusiak and Walawska, 2010). Discolouration can sometimes be reduced or eliminated by bleaching, minimising its impact on dyeability. Work by Bradow and Bauer in 1998 found growth environment to be the main influence on colour of both raw and dyed cotton fibres. Temperature was a big influence with higher ambient temperatures correlating with increased whiteness and decreased yellowness in raw fibre (Bradow and Bauer, 1998a). The same paper found that although genotype did not have a significant influence on the colour of raw fibre, it did affect the colour and shade of dyed fabrics (Bradow and Bauer, 1998a).

Raw fibre colour is measured instrumentally using the HVI™ system in terms of yellowness (+b) and reflectance (Rd). Yellowness gives a measure of the level of pigmentation of the cotton based on the yellow/blue (+b/-b) axis in the CIE LAB colour space, which will be discussed further in Section 2.5. Reflectance is a measure

of brightness and is important to the overall appearance of cotton in terms of lustre. Immature fibres appear duller than mature fibres as their shape does not reflect light as efficiently (Gordon et al., 2004). Australian cottons have been reported to be less lustrous than some African cottons and therefore appear duller (Gordon et al., 2004).

Cotton colour is also checked against grade standards by a classer. If the classer grade and the HVI™ grade are not in accord, the colour grade assigned by the classer is used. Disagreements in colour grade generally result from differences in how man and machine process colour. A classer examines a larger sample area than a machine and is not influenced by irregularities such as trash and spots (Xu et al., 1998). However the classers perception of colour is also influence by another parameter, redness (+a), which is not measured by the HVI™ colourimeter (Xu et al., 1998). Work by Xu, Fang, and Watson (1998) found redness to contribute 10–33% to overall cotton chroma, with recommendations made that measurement of redness be added to instrumental cotton colour grading. A 2010 study by Matusiak and Walawska found agreement between classer and HVI™ grading of cotton grown outside the USA (central Asia) to be insufficient. They suggest that HVI™ may not be the best measure for this property and an alternative method is needed (Matusiak and Walawska, 2010). Ultimately the colour of fibres, yarns, and fabrics will be visually scrutinised, hence instrumental methods of determining fibre colour should be correlated with the human eye (Bradow and Davidonis, 2000).

1.4.2 Micronaire

Micronaire is a measure of the specific surface area of a fibre determined by measuring the air permeability of a constant mass of cotton fibres that is compressed to a fixed volume (Cotton Incorporated, 2014). Micronaire is a function of maturity and fineness, with maturity referring to the degree of cell wall thickening and

fineness referring to linear density of the fibre. The formal unit of micronaire is $\mu\text{g}/\text{inch}$ however micronaire values are seldom cited with units. The acceptable range of micronaire values for Upland type cotton is between 3.5–4.9, with fibres between 3.7–4.2 attracting a premium price and fibres above or below the acceptable range being sold at a discounted rate. Higher micronaire fibres tend to be coarse, and accordingly are limited in processing to coarser yarns. Low micronaire cotton fibres are more prone to breaking and tangling. The latter is particularly problematic as it can lead to the formation of neps; tangled clumps of fibres which may also contain foreign matter such as trash or seed coat fragments. Neps are problematic as they lead to imperfections and irregularities in yarns and fabrics. Neps often appear resistant to dyeing and may appear in fabrics as pale or white specks. This is primarily an optical effect as neps typically have thinner fibre cell walls, allowing light to pass more readily (Cheek and Wilcock, 1988). A low micronaire value may result from immaturity or genetic fineness, whereas high micronaire can result from coarseness or thicker, more developed secondary cell walls; hence relying on micronaire alone is an insufficient method of quantifying maturity (Paudel et al., 2013). Micronaire is one of the two factors most heavily influencing dyeability of cotton, with studies conducted at the International Centre for Textile Research recommending cotton fibre to be used in fabrics from multiple sources varying by no more than 0.2 micronaire units to avoid dyeability issues such as streaking (Chellamani et al., 2001).

1.4.3 Maturity

Maturity has a greater influence on fabric appearance and defects than any other fibre property. Maturity is not a chronological term but rather an expression of cell wall thickness. Fibre maturity can be described as the thickness of the secondary cell wall

in relation to the fibre diameter. Maturity is expressed as a maturity ratio which has a maximum value of 1.2, with values greater than 0.85 being considered as mature. Maturity is tested based on the ASTM standard D1442-06 by either the sodium hydroxide swelling method or polarised light microscopy method (ASTM International, 2013).

Immature fibres behave differently to mature fibres which consequently causes differences in dyed appearance (Figure 1.8, (Bange et al., 2009)). In immature fibres the secondary cell wall cellulose, which is the part of the cotton fibre that primarily takes up dye, is under developed causing the fibres to accept dye differently (Smith, 1991). Shade variation is also influenced by chemical differences in immature fibres which can affect affinity for dye stuffs, and optical effects due to different reflectance properties. This is highlighted in the Goldthwaite differential dye test, a method formerly used for measuring cotton maturity. The test involves dyeing of fibres with C.I. Direct Red 81 and C.I. Direct Green 26, with immature fibres preferentially taking up the green dye and more mature fibres having a greater affinity for the red dye.

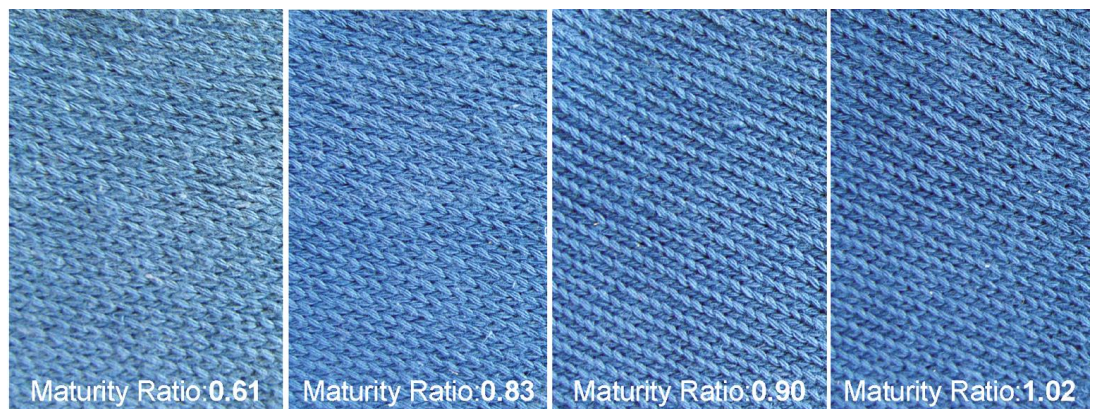


Figure 1.8: Shade variation between cottons of different maturities dyed in the same dyebath (Bange et al., 2009).

Several types of defects in dyed fabrics result from immature fibres including poor shade repeatability, piece-to-piece shading, filling bands, warp streaks, and barré (Smith, 1991). These problems can generally be controlled by measures such as fibre blending, separation of fibres from different sources, or adjusting dyeing recipes to compensate for the immature fibre (Smith, 1991). Within a fabric, dyed appearance is dependent not only on the average maturity of the fibres, but also the distribution of immature fibres. Localised areas with immature fibres can appear as white specks which may not be correctable (Smith, 1991). Both bulk and localised defects in dyed fabrics can be very costly to manufacturers.

Maturity has been well studied, as may be expected by the dramatic impacts on quality of the end product caused by this property. A paper by Smith (1991) acknowledged that although maturity is related to fibre properties influencing dye uptake, such as secondary wall thickness and fineness, it does not give a direct indication of dyeability, with the exception of dyeing defects directly related to immature fibres such as barré and white specks. This paper states that other properties, such as order, crystallinity and morphology, may be equally important if not more so than maturity in regards to dyeability (Smith, 1991). Bradow *et al.* did a series of studies in the late 90's – early 00's on environmental effects on cotton development. Maturity was found to be quite sensitive to growth environment, particularly temperature, regardless of whether genotype was taken into consideration (Bradow *et al.*, 1996b). Further work from this group found relationships between maturity and both yarn elongation percentage and dye uptake (Bradow and Bauer, 1998a). They emphasise the need for reliable maturity testing for prediction of dye defects related to individual immature fibres, and not bulk fibre properties, suggesting that further modeling of effects of growth environment on

maturity is required (Bradow et al., 1996a). The need to review maturity testing procedures in terms of dyeability is also demonstrated in work by Pellow *et al.* (1996) which showed fine fibres that would be rejected by mills on the basis of high micronaire to uptake dye more successfully than lower micronaire fibres. In this case the high micronaire of the fibres was related to high maturity and not coarseness (Pellow et al., 1996). In the late 2000's CSIRO developed the Siromat instrument, which uses polarised light microscopy to directly measure maturity. This instrument was found to give strong predictions of dye shade variation, even between fibres with high maturity ratios (within the range of 0.90–0.98) (Gordon et al., 2008). This work found there to be shade variation between dyed fibres with as little as 0.05 units maturity difference (Gordon et al., 2008).

1.4.4 Fineness

The term fineness can refer to a number of different aspects of the cotton fibre. Biologically speaking, fineness refers to the perimeter of the cotton fibre. More commonly however, fineness refers to the linear density, or mass per unit length of a cotton fibre. This property is expressed in millitex, or micrograms per metre. Finer fibres can improve performance properties of yarns and fabrics due to having a greater number of fibres within the yarn cross-section but may be more susceptible to breakage and tangling. In addition, fabrics and yarns made from finer fibres have enhanced lustre as they have more reflective surfaces per unit area (Bradow and Davidonis, 2000). Typically, finer fibres have lower micronaire values but this is not necessarily always true, with some fine fibres having higher micronaire values due to higher maturity (Pellow et al., 1996).

1.4.5 Cotton Variety

Evidence of domestication of cotton has been dated back as early as 7000 years ago. Nowadays commercially grown cotton fibre is harvested from four domesticated species of plant in the genus *Gossypium*. The two most widely grown species are *Gossypium hirsutum* and *Gossypium barbadense*. Less widely cultivated are *Gossypium arboreum* and *Gossypium herbaceum*, which are only commercially grown in India and Pakistan. There are also hybrid cotton varieties being produced, predominantly in India and China, by crossing two species together. The majority of cotton varieties currently available are developed using biotechnology, with up to 99% of Australian cotton and 60% of all cotton produced worldwide having genetically modified traits (Cotton Australia, 2016b). Although primarily implemented to reduce insecticide use on crops, transgenic cotton varieties have also helped improve fibre quality (Cotton Australia, 2016b).

Gossypium hirsutum, commonly referred to as Upland cotton, is the source of over 90% of cotton produced globally. Upland cotton varieties typically have a micronaire between 3.0 and 5.5, and a fibre length of 1–1.25 inches (25.4–31.8 mm) (Cotton Incorporated, 2014). Upland cotton is classed on the basis of HVI™ properties such as length, length uniformity, strength, micronaire, and colour. Length and strength are predominantly determined by variety whereas colour and micronaire are heavily influenced by environmental effects.

Another species, *Gossypium barbadense*, makes up another 8% of cotton fibre and is known for producing long, fine fibres. This species is often referred to as Extra Long Staple (ELS) cotton or, more commonly, Pima cotton. The minimum fibre length for ELS cotton fibres is 1.375 inches (34.9 mm), with some fibres exceeding lengths of 1.6 inches (40.6 mm) (Cotton Incorporated, 2014). Due to its

longer length, higher length uniformity, and higher strength Pima cotton typically attracts a higher price than Upland cotton. Yet despite these advantages over Upland cotton production levels of Pima cotton are much lower due to the extensive crop management and specific environmental conditions required for growing, as well as lower yields (International Trade Centre, 2007). Pima cotton has a yellower colour than Upland cotton, requiring a different grading system for colour (Cotton Incorporated, 2013). However other properties are measured by HVI™ as they are for Upland cotton. A study comparing two methods of yarn ring-spinning using three cotton varieties showed Pima cotton to have a greater colour depth than organic or Upland cottons, irrespective of the spinning process used (Wan et al., 2010). The spinning method was also found to have an effect on dyed colour, with the low twist method showing a greater depth of shade (Wan et al., 2010). Although the authors attributed this to the lower twist factor allowing dye to penetrate the yarn more readily, it is more probable that this is not related to dye uptake but rather an optical effect due to the different spinning methods scattering light in different ways.

1.4.6 Growth Environment

Growth environment is a major source of variation in terms of cotton fibre properties. Cotton is grown in a range of environments globally from the humid climates of Asia and South America, to the drier conditions of Australia and the USA. Additionally growing conditions within a location can vary from year to year and it is suggested that environmental stresses, such as heat stress and water stress, are the main cause of annual variation in cotton yields (Singh et al., 2007). Growth environment is a major factor in raw fibre colour, with higher air temperatures being linked to whiter cotton (Bradlow and Bauer, 1998a). Higher growing temperatures also accelerate maturation, but may result in lower yields as boll shedding and

reduction in boll size can occur (Singh et al., 2007). A study by Conaty et al. (2012) aimed to determine the optimum leaf temperature for cotton development under Australian growing conditions. This work found the optimum plant temperature to be 28°C, which is comparable with previous estimates from the high plains of Texas, but noted that yields began to suffer when the average canopy temperature exceeded 28°C (Conaty et al., 2012). Overnight temperature also has an effect on cotton development, with cooler night temperatures found to reduce micronaire (Pettigrew, 2001). Sunlight is important for fibre development, with shaded plants showing reduced micronaire and maturity caused by a reduction in photosynthetic activity (Pettigrew, 2001). Water stress may also reduce rates of photosynthesis and consequently cause lower micronaire values (Pettigrew, 2001). Water stress can also cause reduced yields due to development of fewer bolls and boll shedding. Growth environment can also have an effect on the composition of cotton wax, which is the main noncellulosic compound on the fibre surface affecting dyeability. Work by Gordon, Church and Evans (2002) found variation in wax content between cotton fibres of the same variety when grown in different regions. Some of the cotton grown in this study suffered heat or water stress during growth resulting in lower micronaire values, and some samples having wax containing high levels of hydrocarbon which was not easily removed with conventional scouring processes (Gordon et al., 2002).

1.5 Cotton Processing and Effects on Dyeability

In the transition from the bale to finished, dyed fabric cotton fibre undergoes many stages of processing. Cotton may be stored in mills for long periods of time before being made into yarns and fabrics. In turn, yarns and fabrics must be pre-treated to

remove surface chemicals and undesirable pigmentation prior to dyeing. Each of these steps can have an effect on the dyed appearance of cotton.

1.5.1 Storage Conditions

After being picked cotton fibre may sit in a module for a period of time before ginning. At picking, seed-cotton ideally has a moisture content between 6.5–8%. If the moisture content of cotton is too high when picked it can cause ginning problems and may have an increased rate of microbial growth. The ginned cotton is then sold to mills, where cotton bales may be stored for extended periods of time before being processed into yarns and fabrics. In turn, yarns and fabrics may sit in dyehouses before being scoured and/or bleached and dyed. The majority of mills and dyehouses are located in Asian countries with hot, humid climates. Microbes, which have the potential to damage cotton fibres, thrive in warm, moist conditions which could be causing dyeability issues. Storage of cotton at moisture contents above 9% has been seen to cause brittleness and high short fibre contents attributed to bacterial degradation (Fleming and Thaysen, 1920). Work by Fleming and Thaysen (1920) found cotton to be more susceptible to bacterial degradation during different stages of fibre processing. In this experiment cotton samples of various grades were wetted and left at room temperature to determine how long it would take to observe visible fibre damage. A cotton waste sample with a bacterial content of 1 million organisms per gram showed damage after 5 days, whereas a freshly picked cotton boll with a bacterial content of 20,000 organisms per gram didn't show damage for 20 days. Heat has also been shown to degrade cellulosic fibres, with minimal effect below 100 °C but rapid increases in rates of degradation above this temperature (Orr et al., 1954). However an increase in degradation rate is seen when heating occurs in the presence of moisture up to almost 100% humidity, at which point exclusion of

oxygen reduces degradation (Orr et al., 1954). It is therefore recommended that cotton be stored at very low or very high humidity levels to prevent degradation (Orr et al., 1954). Further cotton storage recommendations were given by Cooper and Taylor (1992) with the suggestion that yarn deliveries be used in rotation as variation in dyeability between batches increases over time. Although this work predominantly looks at variation due to the source of the yarn, degradation of the cotton could also be a factor of long-term dyeability variation. Recommendations are also made that the dyeability be assessed prior to processing when yarns from multiple sources are to be combined (Cooper and Taylor, 1992).

1.5.2 Yarn and Fabric Production

Yarn and fabric production is another source of variation within textile production with potential to influence dyeability. Cotton yarn production is a multi-step process. Ginned cotton is taken to spinning mills where the bales are arranged in a laydown. The fibres are blended to uniformly mix the different bales then cleaned to remove trash. The cleaned fibres are then put through a carding machine in which the fibres are aligned and separated into a fine web, which is then drawn through a funnel to form a loose rope called a sliver. The slivers are then blended together in a process called drawing. The drawn sliver will sometimes be combed to reduce short fibre content and remove trash, making the sliver finer and more uniform. The extra processing step in production of combed yarn also means combed yarns are more expensive than carded yarns. Finally the sliver is drawn out into a finer strand in a process known as roving before being spun. The most common type of spinning used today is ring spinning, in which the roving assembly is drawn out and twisted on a rotating spindle before being wound onto a bobbin. Other spinning processes used include rotor spinning and air-jet spinning. Yarns are then either woven or knitted

into cotton fabrics. Work by Cooper and Taylor (1992) found dyeability variation to decrease with increased levels of processing from fibre to fabric, with the greatest level of variation seen at the bale level. Fabric construction and yarn count were also found to affect dyeability (Cooper and Taylor, 1992). Wan, Kan and Choi (2010) compared the dyeability of fabrics produced from conventional ring-spun yarn and low-twist yarn made using a torque-free ring-spinning process. Yarns were produced from Upland, Pima, and organic cotton varieties. Two reactive dyes were used, one with a single reactive group and one with two reactive groups. The torque-free ring-spun yarns had better colour yields than the conventionally spun yarns which was credited to the lower twist factor enabling easier dye penetration (Wan et al., 2010). It is likely that this observation was unrelated to dye uptake but rather an optical effect due to the different spinning methods scattering light in different ways. However a greater depth of shade was also seen using the dye with two reactive groups, and using the Pima cotton (Wan et al., 2010). A study by Ashraf, Hussain and Jabbar (2014) looked at the effects of fibre and yarn characteristics on dyeability of woven cotton fabrics with vat dyes. It was found that cotton fabrics made from combed yarns gave better colour depth, as well as finer yarns with lower twist levels (Ashraf et al., 2014). It was also observed that cotton with higher reflectance values have a lighter dyed appearance (Ashraf et al., 2014). This work highlighted the importance of yarn consistency within fabrics to avoid defects such as streaks and barré. Yarn fineness, source, type, and twist level were all identified as properties affecting dyeability, and therefore potential causes of such problems (Ashraf et al., 2014). Yarn hairiness may indirectly affect the appearance of dyed fabrics as loose fibres may become tangled during processing, causing pilling and surface roughness. Cellulase enzymes are commonly used to smooth the surface of cotton fabrics by

cleaving the cellulose in loose fibres, however on dyed fabrics their activity can be impeded by dye molecules (Buschle-Diller and Traore, 1998) This is particularly true for reactive dyes, which form covalent bonds with the cotton cellulose (Buschle-Diller and Traore, 1998).

1.5.3 Pretreatment

Cotton textiles may undergo a range of pretreatments prior to dyeing including singeing, desizing, scouring, bleaching, and mercerization. Scouring and bleaching are the most common treatments and have the greatest influence over dyed appearance. Raw cotton must be scoured prior to dyeing to remove the waxy cuticle layer and other surface chemicals which may act as a barrier to dyes. Bleaching may be required to remove undesired pigmentation, produced due to growing or storage conditions, prior to dyeing.

1.5.3.1 Scouring

Cotton is scoured prior to dyeing primarily to remove the waxy cuticle layer on the surface, which acts as a waterproof barrier inhibiting dyeing. Scouring also removes other noncellulosic compounds which may affect cotton dyeing, such as pectin, proteins, ash, and hemicelluloses (Jordanov and Mangovska, 2009). Traditionally scouring is done at high temperatures under alkaline conditions, using strong sodium hydroxide solutions. The removal of the wax is facilitated by saponification of the waxes on the surface by the alkali. Other alkalis such as sodium carbonate may also be used. The scouring solution may also contain other reagents such as detergents, wetting agents, and sequesterants. Many rinses are often required to thoroughly remove the scouring solution, with acetic acid often added to neutralise the alkali. The relatively harsh conditions can cause damage to the cotton fibres if not properly controlled. This process consumes a lot of water and energy, and is a main

contributor of organic pollutants in textile effluent (Etters, 1999). Hence there is a growing research trend towards bioscouring with enzymes including cellulases and pectinases. Enzyme treatments are designed to be a gentler method of scouring cotton with a lesser environmental impact due to lower water use and fewer chemicals required. However, these treatments are not currently commercially viable in terms of time and cost effectiveness.

1.5.3.2 Bleaching

Bleaching is done to further remove impurities from cotton, particularly pigmentation causing discolouration or yellowness which may lead to differential results in the end product. Bleaching provides a uniform white base and helps ensure dyeing is even. Bleaching is especially important in dyeing of pale shades. Bleaching of cotton is typically done using hydrogen peroxide at high temperatures under alkaline conditions. Scouring and bleaching are able to be performed in a single process, minimizing labor and water requirements. Bleaching can be done at lower temperatures, however lengthy incubation times may be required. Cotton bleaching may also be performed using sodium hypochlorite, however it is used much less commonly. Byproducts of sodium hypochlorite bleaching include toxic chlorinated organic compounds which may end up in wastewaters and consequently this method has ceased in many countries due to environmental concerns. It is also a harsher treatment than hydrogen peroxide bleaching. Like scouring, research is being done into finding alternative bleaching methodologies such as enzyme treatments to minimise environmental impacts and fibre damage (Eren et al., 2009).

1.6 Analysis of Structural and Surface Properties of Cotton Fibre

There are many methods of instrumental analysis available for the characterisation of cotton fibre. Different methodologies are used for different aspects of the fibre including internal structure, surface morphology, chemical composition, and colour.

1.6.1 Structural Analysis

Cotton fibre contains two different types of cellulose, crystalline and amorphous. Crystalline cellulose has a highly ordered structure, whereas amorphous cellulose has no defined crystalline form and consequently is much more accessible to water and aqueous reagents such as dyes. Cotton is generally estimated to be made up of 70% crystalline cellulose and 30% amorphous cellulose, however proportions vary depending on genotype and maturity. Measuring the crystallinity of cotton cellulose can be useful in dyeability studies as it often correlates well to fibre accessibility. A range of methodologies may be used to analyse the internal structure of cotton and other cellulosic fibres. The primary method of structural analysis used in this work was x-ray diffraction, which is described in the following section. Another method of gaining structural information of polymers is by differential scanning calorimetry (DSC), which is a method of determining physical changes in a polymer sample with temperature.

1.6.1.1 X-ray Diffraction

One method which can be used to study the structure of cotton fibre is x-ray diffraction (XRD). When x-rays contact a crystalline substance they are diffracted, producing a characteristic scattering pattern. This scattering pattern can be used as a method of characterisation and identification of crystalline materials. Cellulose can form four crystalline forms, cellulose I-IV, each producing characteristic scattering patterns due to the shape of the repeating crystalline unit and organisation of the

cellulose chains. Cotton fibre is naturally in the cellulose I form but can be converted to other forms on chemical treatment, such as the transformation to cellulose II on alkaline mercerisation. For cotton fibre XRD provides a direct method of determining the degree of crystalline order (Teeaar et al., 1987). Structural change in cotton fibre during development has been assessed using XRD (Hu and Hsieh, 1996). The effects of various treatments and chemical modifications in cotton and other cellulosic materials have also been thoroughly studied (Zhao et al., 2007, Cao and Tan, 2005, Lewin and Roldan, 1971).

Synchrotrons may be used similarly to XRD for high resolution structural analysis, with x-rays generated at a much higher intensity than laboratory sources allowing faster measurement, and measurement of smaller samples. A synchrotron is a form of particle accelerator that moves electrons at high speeds. A magnetic field is applied to the electrons which forces them to change direction, resulting in emission of electromagnetic radiation which can be captured in beamlines and utilised experimentally. Notably, synchrotron x-rays were utilised in the work of Nishiyama, Langan and Chanzy (2002) studying the structure of cellulose. In this work synchrotron x-ray and neutron diffraction data were combined to determine the crystal structure, molecular structure, and hydrogen bonding system within cellulose I β , the main form of cellulose in higher plants (Nishiyama et al., 2002).

1.6.2 Surface Characterisation

Chemical treatments such as scouring change the surface properties of cotton fibre by removing noncellulosic compounds from the outer layers of the fibre, improving cellulose accessibility and therefore affecting dyeability. The primary means of characterizing the surface morphology of fibres and other materials is microscopy. There are many different microscopy techniques used in textile characterization, with

each one revealing different information about the sample surface. Often a combination of techniques will be utilised to create a fuller picture of the overall sample properties. The primary method used in this project to characterize the surface of cotton is scanning electron microscopy, which is described in the following section. Other methods include atomic force microscopy (AFM) which gives topographical information, transmission electron microscopy (TEM) which can give morphological and structural information at a near atomic level, and confocal laser scanning microscopy which can give information about the surface and layer thickness in polymers.

1.6.2.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a commonly used method for imaging the surface morphology of samples, among numerous other applications. The sample is hit with a concentrated beam of electrons, causing x-rays and electrons to be ejected from the sample which are collected by a detector and composed into an image. One downside of SEM in the study of cotton fibres is that it cannot distinguish between crystalline and amorphous regions of cellulose. However SEM is very useful for surface characterisation of chemically treated cotton fibre, with many studies using SEM to evaluate the effects of treatments including acid hydrolysis and enzymatic scouring (Zhao et al., 2007, Wang et al., 2006). Other complementary techniques may be used alongside SEM to create a more detailed picture of the sample. For example, the topographical information given by AFM may provide useful supplementary data to SEM images (Wang et al., 2006).

1.6.3 Chemical Characterisation

The chemical composition of cotton is quite complex, especially in regards to dyeing. On the outer surface of the fibre are an array of noncellulosic compounds,

such as waxes and pectins, which act as a waterproof coating. This limits accessibility of water and chemical reagents to the internal layers of the fibre and therefore affects dyeability. Inside the fibre the cellulosic structure of cotton places limitations on the ability of dyes to penetrate the fibre. It is the hydroxyl groups on the surface of the cellulose with which reactive dyes form covalent bonds. Cellulosic structure may be altered by chemical treatments such as enzymatic or acid hydrolysis. Although not used in the present work, there are many ways of assessing the chemical composition of cotton including methods studying chemical bonding of the cellulosic structure, and those used for quantitative and qualitative analysis of the noncellulosic surface compounds. Vibrational spectroscopic techniques such as Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy can give a fingerprint spectrum of the sample, which is comprised of peaks and troughs characteristic of the movements of the particular molecular bonds present. These techniques have been used previously to track changes in the chemical composition of cotton fibre during development and following chemical modifications designed to enhance dyeability (Wang and Lewis, 2002, Lewis and Lei, 1991, Selvam and Sundrarajan, 2012, Xiao et al., 2007, Abidi et al., 2010). Similarly, nuclear magnetic resonance (NMR) spectroscopy can be used to produce a characteristic spectrum based on interaction of the nuclei of atoms within a sample, most commonly hydrogen and carbon, with an applied electromagnetic field. Methods of chemical extraction, such as soxhlet extraction, may be used for quantitative and qualitative analysis of the noncellulosic components of cotton fibre. These methods typically involve removing the noncellulosic components of the fibre with a solvent which is then evaporated, and the remaining products analysed.

1.6.4 Analysis of Colour

The ability to accurately measure and assess colour is crucial to studies of dyeability, whether by comparing the colour of dyed samples or by tracking dyebath absorption. Cotton colour is also important prior to processing as the colour grading of raw fibre, in terms of reflectance and yellowness, is a factor of quality assessment and pricing in textile markets. The primary method used to analyse the colour of cotton in this work, both before and after dyeing, was colourimetry which is described in the following section. The colour of the dye liquor can also be analysed using UV-visible spectroscopy, which enables the concentration of coloured solutions to be determined. This is utilised for purposes such as studying the influence of various additives on dye bath exhaustion and detection of potentially harmful dyes in textile wastewaters (Pineiro et al., 2004, Hamlin et al., 1999).

1.6.4.1 Colourimetric Analysis

Colourimetry is used to analyse the difference in colour between two samples, whether they be raw, scoured, bleached or dyed. Measuring after dyeing allows determination of dyeing differences, whilst measuring before dyeing allows calculation of dyeability relative to fibre colour. The science of colourimetry is designed to quantify and objectively describe colour, based on perception by the human eye. Colourimetric analysis involves measurement of a range of parameters relating to how the colour of the sample is perceived. Examples of colour spaces used include CIE XYZ, which assesses colour based on the response of the three different cone cells in the eye (L which responds to red, M which responds to green, and S which responds to blue), and CIE LAB which is designed to approximate the human vision response to lightness, red/green balance, and blue/yellow balance. CIE LAB has widely replaced CIE XYZ as it is based on an x,y,z plot, making it much

easier to understand. Colourimetry can aid in identifying cotton samples with differential dyeing characteristics as it can distinguish between smaller colour differences than the human eye.

1.7 Gaps in the Literature

Fibre properties such as micronaire, length, and strength are used in both the classing and pricing of cotton fibre, and in fibre selection by mills. Micronaire and maturity are two closely related fibre properties known to have large effects on dyeability, as illustrated in the above literature review by the volume of dyeability studies focusing on these properties. Accordingly, care is taken to keep fibre properties consistent during processing. Yet despite this level of care there are still incidences of cotton fibres with near identical properties exhibiting quite different dyeing behaviour. It is possible that the drastic effects caused by maturity and micronaire may have overshadowed the importance of other properties to dyeability, necessitating further study. It has been acknowledged that although maturity does influence dye uptake it does not give a direct indication of dyeability and other properties, such as order, crystallinity and morphology, may be equally important in regards to dye uptake (Smith, 1991). Chapter 3 details an experiment with the aim to see if a dyeability difference could be seen within sample sets with controlled maturity and micronaire ranges in an effort to identify other properties which may influence dye uptake. In the experiments detailed throughout Chapters 4–7 maturity and micronaire will be held constant where possible to minimise the impact by those properties as a source of dyeing variation.

Fibre properties may be influenced by both environmental and varietal factors. Colour and maturity, which greatly affect dyeability, are primarily environmentally related properties. Other properties such as length and strength are

due to variety. Cotton species has been known to affect colour, but little work has been done studying dyeability differences between varieties of the same species. Chapter 4 outlines a dyeability study of seven different cotton varieties, of which six were Upland and one was Pima. The experiment was designed to determine if a difference in dye uptake could be seen between both samples of different varieties within the same species, and between samples of different species. As well as having consistent maturity, these samples were all grown in the one location, negating differences caused by growth environment.

The effects of growth environment on cotton fibre properties have been well studied, however only a small amount of this work has extended into dyeability. Further, little work has been done directly comparing the dyeability of samples from different growth locations and climates. Chapter 5, following on from the work in Chapter 4, compares the dyeability of samples with consistent maturity grown in both a single location, and grown in three different growing regions with vastly different climates. This study aimed to determine the level of variation in dye uptake in cotton samples grown in a range of environments.

Dyeability variation may also result from storage and processing conditions post-harvest. Many cotton mills are located in Asia, a region with largely hot and humid climates. Moisture is known to have detrimental effects on cotton fibre properties, which in turn affects processing performance. However most of the work done in this area is outdated, or is focused on other processing stages such as ginning rather than dyeability. Chapter 6 features a study on dyeability of cotton samples after being held under moist, humid conditions for various time frames. This study was designed to simulate conditions seen in some mills with the aim of determining whether storage under such conditions induces changes in the cotton which in turn

affects dyeing behaviour. The work was completed with a generic greige cotton fabric to ensure consistent fibre properties between samples.

Both mechanical and chemical processing steps can affect dyeability. Chemical pretreatments, such as scouring and bleaching, are key steps in the dyeing process. Scouring is essential for removing the waxy cuticle layer on the cotton fibre surface which acts as a waterproof barrier preventing dye penetration. Bleaching is particularly important for removing undesired pigmentation in the dyeing of pale shades. Although there has been a lot of research done in this area, much of it has been more focussed on lessening the harshness of these treatments to reduce fibre damage and environmental impacts. If dyeability is considered, it is generally for the purpose of comparing the effectiveness of conventional and alternative treatments. There have not been many extensive studies on how variations on conventional treatments affect dyed colour. The work presented in Chapter 7 outlines studies of both scouring and bleaching, with the aim to determine how differential pretreatments prior to dyeing may affect shade. The studies were designed using treatment matrices considering variables such as reagent concentrations, treatment time, and temperature. The work was completed with a generic greige cotton fabric to ensure consistent fibre properties between samples.

1.8 Research Aims

This project aims to build on the current knowledge of the dyeing behaviour of cotton presented in the literature review by uncovering the reasons why cotton fibre that is nominally the same in terms of HVITM properties may differ in dyed appearance. In answering the research questions presented in the introduction it is hoped that a greater understanding of dyeing behaviour of cotton can be obtained.

2. General Experimental Methodology

This section details the general experimental methodology used throughout this project. Methodology specific to individual experiments is detailed with the relevant experiments in chapters 3–7.

2.1 Scouring

Scouring was done using a laboratory rotary dyeing machine. Three different rotary dyeing machines were used throughout this work; SDM2-140 rotary dyeing machine (Fong, Hong Kong), H24-C rotary dyeing machine (Rapid, Taiwan), and Datacolor AHIBA IR Pro (Datacolor, USA). Scouring was performed in a solution of 1.0 g/L NaOH (Sigma Aldrich, Australia), 1.0 g/L Leonil JDZ (Achroma, Switzerland), and 2.0 g/L Hostapal FAZ (Achroma, Switzerland). The samples were scoured for 1 hr at 90 °C, followed by a warm rinse, and a cold rinse. The cotton was then spun to remove excess water in a MSE Basket 300 centrifuge (MSE, UK), and further dried in a 105 °C oven for 10 mins.

2.2 Dyeing

Dyeing was done using a laboratory rotary dyeing machine eg. SDM2-140 rotary dyeing machine (Fong, Hong Kong), H24-C rotary dyeing machine (Rapid, Taiwan), or Datacolor AHIBA IR Pro (Datacolor, USA). Dyeing was carried out using 0.1% w/w reactive dyes (Cibacron Green LS-3B, Procion Yellow HE-3G, Procion Yellow HE-6G, Procion Blue HERD, Procion Orange H-2R) (Cibacron dyes: Huntsman, Australia, Procion dyes: Kiri Industries Limited (KIL), India). Samples were added to 70 g/L NaCl solution (Sigma Aldrich, Australia) with 0.5 g/L Albaflow FFW (Huntsman, Australia) added as a wetting agent and 1.0 g/L Verolan NBO (Rudolf Atul Chemicals Ltd, India) added as a sequesterant. For the Cibacron dye only 30 g/L of NaCl was required. The dye liquor was held at 30 °C for 10 mins, before dye

was added. The temperature was raised to 90 °C (2 °C/min) and held for 30 mins. The bath was then cooled to 70 °C (2 °C/min) before 10.0 g/L soda ash (Sigma Aldrich, Australia) was added and the bath held for 35 mins (Figure 2.1). The dyed samples were rinsed in cold water, spun dry using a MSE Basket 300 centrifuge (MSE, UK), and then further dried in a 105 °C oven for 10 mins.

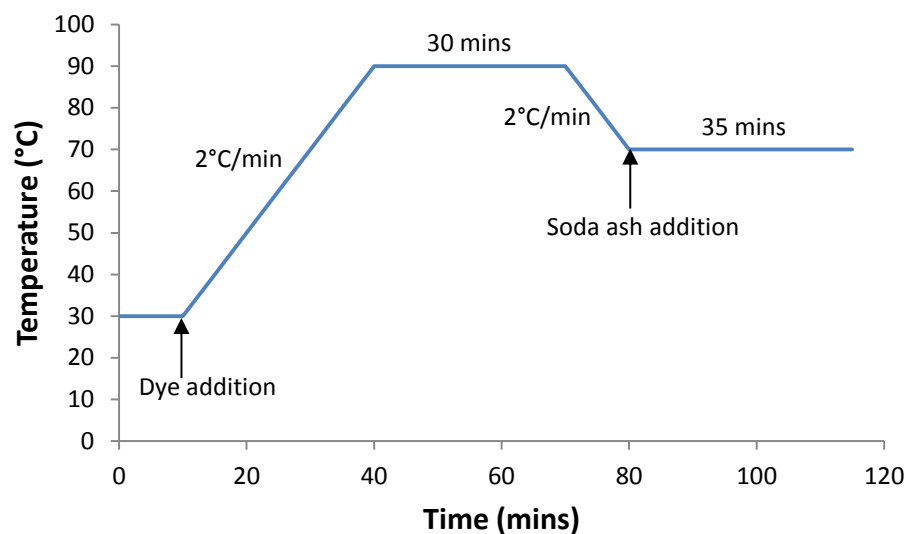


Figure 2.1: The temperature profile of the dyeing method.

2.3 Colourimetry

Colour was measured using a Gretag Macbeth Color-Eye 7000A UV/Vis reflectance spectrophotometer (X-rite, USA) using the D65 light source and a 10° collection angle with the spectral component included. Fabrics were measured using the large (25.4 mm) aperture, folded in half twice to eliminate interference from background light. Fibres were measured using the small (10.0 mm x 7.5 mm) aperture (placed in cuvettes, 0.512g +/- 0.005, cubes to make density equal). Samples were conditioned 24 hrs under standard conditions i.e. 20°C and 65% relative humidity prior to colour measurement. Colour was measured in the CIELAB colour space from the average of 3 readings of L* (lightness, 0 = white, 100 = black), a* (+a = red, -a = green), and b*

((+b = yellow, -b = blue) values. ΔE values were calculated to appraise colour differences between samples using the formula below:

$$\Delta E = \sqrt{(\Delta L^*{}^2 + \Delta a^*{}^2 + \Delta b^*{}^2)}$$

From these calculations the ΔE values can be used to show the extent of the colour difference between two samples (Table 2.1) (Electronics for Imaging Inc.). The colour scheme used in Table 2.1 will be used throughout the experimental chapters to designate the degree of colour difference of the samples.

Table 2.1: ΔE values and their corresponding colour differences (Electronics for Imaging Inc.).

ΔE	Meaning
0–1	Normally invisible difference
1–2	Very small difference, only obvious to trained eye
2–3.5	Medium difference, also obvious to untrained eye
3.5–5	Obvious difference
>5	Very obvious difference

Difference in lightness ΔL^* were calculated using the following formula:

$$\Delta L^* = \sqrt{(L^*{}_{1} - L^*{}_{2})^2}$$

Where, depending on the comparison $L^*{}_{1}$ represents raw or scoured fabric and $L^*{}_{2}$ represents scoured or dyed fabric.

Mean values were calculated using the following formula:

$$\bar{x} = \frac{\sum x}{n}$$

Standard deviations were determined using the following formula:

$$s = \sqrt{\frac{\sum(x - \bar{x})^2}{n - 1}}$$

Standard error of the mean was calculated using the following formula:

$$SE_{\bar{x}} = \frac{s}{\sqrt{n}}$$

2.4 X-ray Diffraction

X-ray diffraction patterns were recorded using a PANalytical X'Pert Pro MRD XL (PANalytical, The Netherlands). The diffracted intensity of Cu K α radiation ($\lambda = 1.54$ Å; 40.0 kV and 30.0 mA) was measured in 2θ range between 5° and 40° . Zero background sample holders were used to minimise noise in the diffraction pattern. The diffraction patterns were analysed using OriginPro 2017 (OriginLab, USA). Peaks were resolved by Gaussian deconvolution. The area under the deconvoluted peaks was determined using the software. From this data the ratio of amorphous cellulose to crystalline cellulose was calculated as a percentage of the total peak area.

2.5 Scanning Electron Microscopy

Cotton fabric samples were imaged using a Zeiss Supra 55 VP FEG SEM (Carl Zeiss, Germany) or LEO 1530 FEG SEM (Carl Zeiss, Germany). Samples were coated with gold using a Leica EM ACE600 high vacuum sputter coater (Leica

Microsystems, Germany) to improve the conductivity of the samples and thus the image quality.

3. Micronaire and Maturity

Cotton mills select fibre on the basis of similar high-volume instrument (HVI™) properties, which include micronaire, fibre length, and strength. Yet there are still incidences of cotton fibres with near identical properties exhibiting quite different dyeing behaviour. Micronaire and maturity are two closely related fibre properties renowned for their effects on dyeability and accordingly have been well researched. However it has been acknowledged that although maturity does influence dye uptake it does not give a direct indication of dyeability, and that other properties, such as order, crystallinity and morphology, may be of equal significance (Smith, 1991).

Micronaire is a function of fibre fineness and maturity which gives a measure of the specific surface area of cotton fibres. Micronaire is measured from the air permeability of compressed fibres using the HVI™ system. The acceptable range of micronaire values for Upland cotton is between 3.5–4.9 units, with fibres between 3.7–4.2 units attracting a premium price. Cotton fibres with micronaire values outside the acceptable range are sold at a discounted rate. High micronaire fibres are often coarse, resulting in coarser yarns. Low micronaire fibres are more prone to breakage and tangling during processing, which may result in defects in yarns and fabrics. Micronaire is the HVI™ property most associated with dyeability. Studies from the International Centre for Textile Research recommend blends of fibres vary by no more than 0.2 units to avoid dyeing defects such as streaking (Chellamani et al., 2001).

Maturity of cotton fibre is not a chronological measurement, but rather a description of secondary cell wall thickness expressed as a ratio. Maturity is tested based on the ASTM standard D1442-06 by either the sodium hydroxide swelling method or polarised light microscopy method (ASTM International, 2013). A cotton

fibre with a maturity ratio of 0.85 or above is considered mature, with 1.2 being the maximum value for maturity ratios. It is the secondary cell wall of cotton which primarily accepts dyes. Immature fibres consequently take up dyes differently to mature fibres due to their less developed secondary cell walls. Immature fibres may also have different surface chemical properties which may influence dye affinity, and different reflectance properties which may change optical perceptions of colour (Smith, 1991). The differential dyeing behaviour of immature fibres can cause a range of dyeing defects including poor shade repeatability, piece-to-piece shading, filling bands, warp streaks, and barré (Smith, 1991). Dyeing has been shown to be quite sensitive to variation in maturity, with colour differences observed when maturity ratios differ by 0.05 or more units (Gordon et al., 2008).

This chapter details the experimental methodology used in studies of the dyeability of two sets of fibres with near identical properties. The aim was to determine whether a dyeability difference could be observed within samples with controlled maturity and micronaire ranges. As the dramatic effects on dyed colour of these properties have been well documented it is possible that there are fibre properties influencing dyeability which may otherwise have been overlooked. Dyeings were performed in competitive dyebaths to assess whether any of the samples took up dye preferentially. Variation in dye uptake within the samples could serve as an indicator of other fibre properties having an effect on dyeability. Section 3.1 details a dyeing trial to determine if dyeability differences could be observed within each of the sample sets. Section 3.2 investigates if there is a change in dye uptake when the two samples sets are combined in the same dyebath.

3.1 Fibre Dyeing Trial of Two Individual Cotton Sets

A dyeing trial was designed to determine if there was an observable difference in dyeability between cotton samples with similar properties. This experiment aimed to select samples exhibiting differential dyeing behaviour for analysis of the fibre structure and surface chemistry. The hypothesis was that there may be key differences in the structural and chemical properties of the cotton fibre effecting dyeability aside from the routinely measured HVI™ properties. Differential dye uptake between samples with similar HVI™ properties may serve as an initial indication of such differences and following analysis could provide a starting point for further investigation of other factors affecting dyeability.

3.1.1 Experimental Methodology

3.1.1.1 Sample Selection and Preparation

Upland cotton fibre samples were selected on the basis of similar HVI™ properties, particularly maturity and micronaire. The selected samples were unreleased CSIRO breeding lines grown in north-western NSW in the 2010/2011 cotton season. Two sets of five samples were collected, one ranging from micronaire values 3.6–3.9 with maturity values of 0.83–0.85 and the other with micronaire values from 4.8–5.1 and maturity values of 0.88–0.89 (Table 3.1 and Table 3.2). The samples were cleaned twice using an SLD 102 Shirley Analyser MK II (Shirley Developments Limited, UK).

Table 3.1: HVI™ data of the low micronaire sample set.

Sample ID	Length (in)	Strength (gf/tex)	Micronaire	Maturity	Fineness
1022-10	1.16	28.8	3.7	0.84	163
1024-45	1.17	30.4	3.9	0.85	168
1031-1	1.19	29.8	3.6	0.83	170
1031-6	1.16	31.7	3.7	0.84	169
1031-36	1.15	31.7	3.6	0.84	168

Table 3.2: HVI™ data of the high micronaire sample set.

Sample ID	Length (in)	Strength (gf/tex)	Micronaire	Maturity	Fineness
1066-3	1.20	32.8	4.9	0.88	178
1066-4	1.19	33.4	5.1	0.89	193
1066-8	1.19	32.8	4.8	0.88	189
1066-10	1.23	32.4	5.0	0.89	185
1066-61	1.22	35.0	5.1	0.89	199

3.1.1.2 Scouring and Dyeing

Scouring and dyeing were both done using an Ahiba Turbomat 1000 Laboratory Dyeing Machine (Datacolor, USA). Scouring was performed as detailed in Section 2.1, using 10.0 g quantities of cotton fibre per pot in the dyeing machine in 200 ml of solution.

Dyeing was carried out using 1% w/w Cibacron reactive dyes (Cibacron Green LS-3B, Cibacron Blue LS-3R, and Cibacron Red LS-6G) (Hunstman, Australia) by the migration method 90/70 °C as per the manufacturer's instructions (Ciba Specialty Chemicals Inc., 1995). To increase the dye affinity for the fibre 15.0 g/L of NaCl (Sigma Aldrich, Australia) was added. Also added to the dye liquor was 0.5 g/L Albaflow FFW (Hunstman, Australia) used as a wetting agent and 1.0 g/L Verolan NBO (Rudolf Atul Chemicals Ltd, India) added as a sequesterant to chelate metal ions, which may cause discolouration and unevenness. To raise the dyebath pH at the beginning of the fixation stage 3.0 g/L Soda ash (Sigma Aldrich, Australia) was added, with an additional 7.0 g/L added 10 mins later as patchiness can occur if pH is raised too quickly. The dyed samples were rinsed in cold water, spun dry using a MSE Basket 300 centrifuge (MSE, UK), and then further dried in a 105 °C oven for 30 min.

The baskets of the dyeing machine were packed with 0.5 g +/- 0.01 quantities of each sample in a set (totalling 2.5 g of fibre), separated by layers of 100% polyester organza fabric (Figure 3.1). This fabric was chosen as it would not take up dyes designed for cellulosic materials and would allow the dye liquor to pass through easily while keeping the samples separate.

The dyebath was prepared to an initial volume of 350 ml, giving a 140:1 liquor ratio. The long liquor ratio was not ideal but there was limited flexibility in this due to small sample sizes and the volume of dye liquor required in the pot to cover the basket and allow circulation of the dye liquor. Dyeings were performed in triplicate for each sample set using all three dye colours.

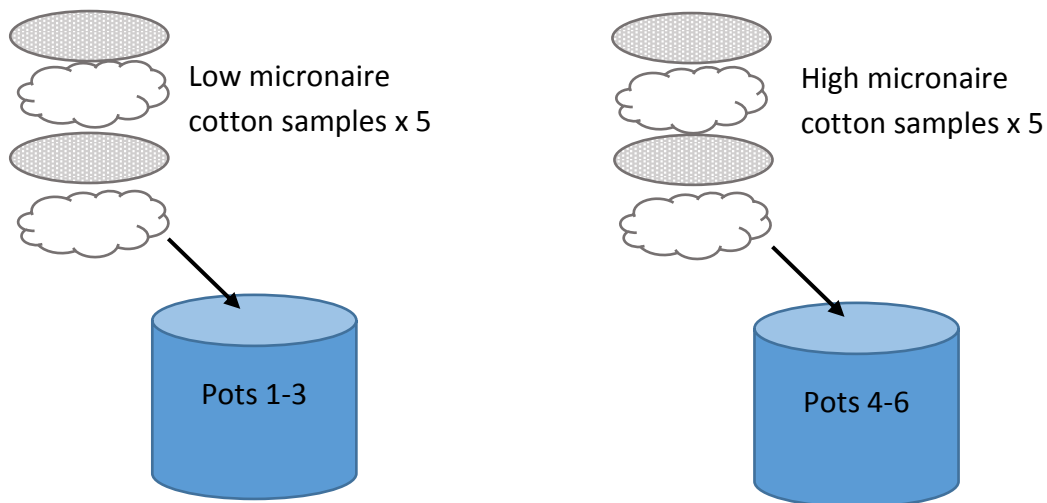


Figure 3.1: The experimental set up of the fibre dyeing.

3.1.1.3 Colourimetry

Colourimetry was performed as detailed for fibre samples in Section 2.3. Colour was measured before scouring, after scouring, and after dyeing to observe the level of colour difference between samples at each stage of the dyeing process.

3.1.2 Results and Discussion

Two sets of five Upland cotton samples were chosen on the basis of HVI™ properties. Of particular interest were maturity and micronaire due to their proven influence on dyeability. Fibre strength was also a consideration as this property could be an indication of crystallinity differences between fibres. The low micronaire set was visibly yellower than the high micronaire samples.

The cotton samples were scoured individually under alkaline conditions to remove the surface wax layer prior to dyeing. The cotton was thoroughly dried prior to dyeing to ensure the mass of each sample going into the dyebath was accurate. Minimal colour difference could be identified between the scoured samples with the naked eye.

The fibres were dyed competitively to determine whether each sample within a set had similar dyeability due to having similar properties. The idea behind this was if a sample within a set took up dye more or less readily than the other samples in the bath it would differ in dyed appearance. Dyeing was performed at a 1% dye concentration as subtle shade variations can be difficult to see between darker colours produced at higher concentrations. The dyes used were Cibacron LS reactive dyes. These dyes are designed to have a greater affinity for cellulose than other reactive dyes, and therefore require less salt to pull the dye into the fibre which is advantageous in terms of cost and environmental impact. However the chemical structure of these dyes is heavily patent protected so it is difficult to examine in depth the interactions between the cotton fibre structure and the molecular structure of the dye. It is believed that the majority of this series are bi-functional monofluorotriazine dyes with unknown linker groups (Choudhury, 2006, Zollinger, 2003). The increased affinity for cellulose is thought partly to be due to a large, flat dye molecule with a greater number of hydrogen bonding sites (Choudhury, 2006).

The dyeings were carried out using three different dye colours; a blue, a red and a green. The blue dye produced a relatively uniform shade across both sample sets with even coverage and no colour difference observable with the naked eye. The red dye gave obviously patchy results in both sample sets, ranging from bright red to burgundy shades within individual samples. A later dyeing using a cotton sample outside the sample sets used in the current work gave similar results. It is not known whether this was related to the dyeability of the fibre, uneven flow in the dyebath, or due to contamination at some stage of the dyeing process. The green dye gave even coverage and showed a difference in shade between the sample sets, with the low

micronaire sample set visibly lighter than the high micronaire set. This is similar as to what was seen in the raw fibre colour.

Raw, scoured, and dyed fibre colour was measured for each sample in both sets. For the raw and scoured samples ΔE values were calculated from L^* , a^* and b^* values obtained from the average of 4 reads of a single fibre sample (Table 3.3). For the dyed samples the average of L^* , a^* and b^* values measured from each of the three replicates were taken and used to calculate ΔE values (Tables 3.4 and 3.5). Sample 1022-10 was used as the reference for the raw and scoured samples. For the low micronaire set both samples 1022-10 and 1031-36 were used as references. Samples 1066-3 and 1066-61 were used as references for the high micronaire set. The raw sample ΔE values suggest a medium level of colour difference between the low micronaire and high micronaire sample sets which decreases upon scouring to minor or invisible differences. These values are in agreement with the colour difference which could be seen with the naked eye within the samples. The values from the blue dyeing showed no visible difference in the low micronaire set, with minor differences in the high micronaire set. The values for the red dyeing in the low micronaire set indicate little to no visible colour difference, with small to medium differences in the high micronaire set. Although these results have been presented no solid conclusions should be drawn from them due to the unevenness mentioned previously. The values for the green dyed samples in both the low and high micronaire sets indicate no visible difference from the reference samples, however there was a visible colour difference between the two sets.

Table 3.3: ΔE values calculated for the raw and scoured fibre samples from 1022-10.

Sample ID	ΔE Raw	ΔE Scoured
1024-45	0.742	1.203
1031-1	0.343	1.296
1031-6	0.153	0.744
1031-36	1.528	1.027
1066-3	2.041	1.766
1066-4	2.664	0.544
1066-8	2.381	0.763
1066-10	2.663	1.214
1066-61	2.615	1.254

Table 3.4: ΔE values for the low micronaire set calculated from 1022-10 (a.) and 1031-36 (b.).

a. ΔE values calculated using 1022-10 as the reference.

Sample ID	ΔE Blue	ΔE Red	ΔE Green
1024-45	0.609	1.911	0.415
1031-1	0.429	1.570	0.205
1031-6	0.434	1.408	0.374
1031-36	0.808	1.032	0.609

b. ΔE values calculated using 1031-36 as the reference.

Sample ID	ΔE Blue	ΔE Red	ΔE Green
1022-10	0.808	1.029	0.607
1024-45	1.032	0.957	0.805
1031-1	0.584	0.599	0.440
1031-6	0.465	0.454	0.255

Table 3.5: ΔE values for the high microneaire set calculated from 1066-3 (a.) and 1066-61 (b.).

a. ΔE values calculated using 1066-3 as the reference.

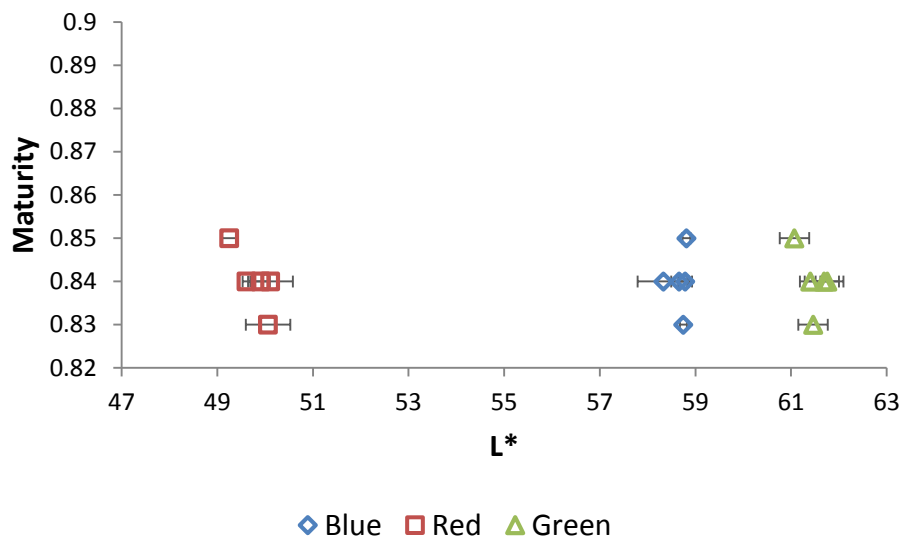
Sample ID	ΔE Blue	ΔE Red	ΔE Green
1066-4	2.162	2.562	0.745
1066-8	0.736	0.698	0.227
1066-10	0.063	1.534	0.480
1066-61	1.258	0.882	0.740

b. ΔE values calculated using 1066-61 as the reference.

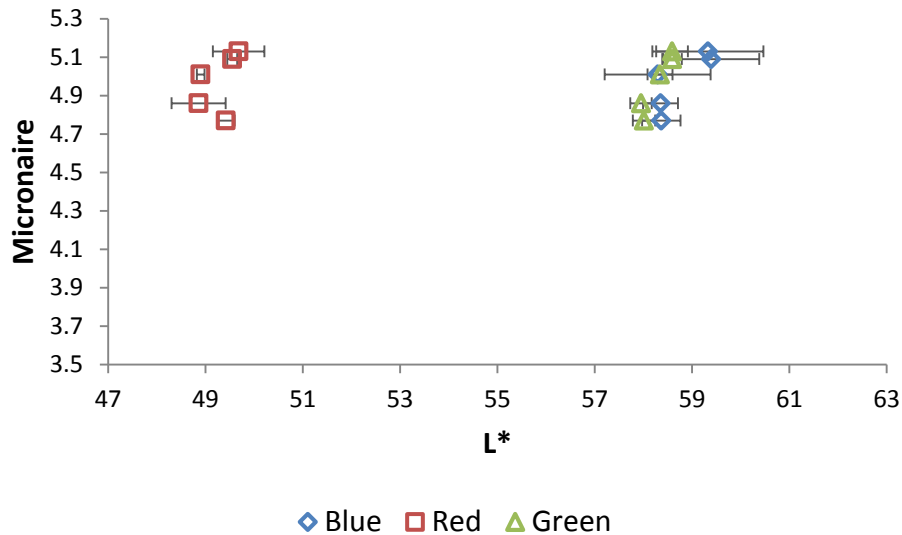
Sample ID	ΔE Blue	ΔE Red	ΔE Green
1066-3	1.258	0.882	0.740
1066-4	1.139	2.867	0.619
1066-8	1.032	0.889	0.607
1066-10	1.258	2.091	0.695

The colour difference observed between the low micronaire and high micronaire sets when dyed with the green dye could be due to a number of reasons. Firstly it is of note that a similar colour difference was seen in the raw fibre colour, which could mean the base colour of the fibre is a factor. Another possible cause of the colour variation is fibre structural differences between the two sets. The high micronaire samples have slightly higher maturity values, and therefore greater amounts of secondary wall cellulose in the fibres. As this is the part of the fibre which primarily takes up dye, the high micronaire fibres may appear darker. However differences in maturity of the magnitude seen between the sample sets typically do not cause quite as dramatic a colour difference. Optical effects due to differences in cross sectional size may also have an effect on colour. The smaller cross-section of the low micronaire set could mean they reflect light differently, giving them a lighter appearance than the high micronaire set. Other potential sources of colour variation relate more to the dye itself. As the dyeing was done at a low concentration miniscule differences in the amount of dye going into the bath could affect the colour. One possibility looked at was the intensity of the dye in terms of standard depth, which refers to the percentage of dye required to produce a particular depth of shade. However according to the manufacturer the green dye required more dye to produce the standard depth than some of the other colours used in this experiment, so very small weighing inaccuracies should not produce such a large difference. Another possibility is due to pipetting error when adding the dye to the bath. As accurate as the operator may be there will always be residual dye solution remaining in the pipette that may be transferred into the next dye pot, which will never be at a constant volume.

To see if any trends could be observed between dyed appearance and fibre properties L^* values for the dyed samples were plotted against maturity and micronaire (Figure 3.2). A large shift in L^* values is seen in the green dyed samples between the two sets, which is particularly noticeable when looking at the values in relation to those of the blue dyed samples. The low micronaire samples were lighter than the blue samples while the high micronaire set was much closer in shade to the blue, if not slightly darker. The trend is seen across the plots for both fibre properties due to the strong influence of maturity on micronaire. Less mature fibres typically have lower micronaire values.



a. Plot of maturity against L^* for the low micronaire set.



d. Plot of micronaire against L* for the high micronaire set.

Figure 3.2: Maturity (a. and b.) and micronaire (c. and d.) plotted against L* to identify dyeability trends.

It is possible that the colour difference seen in the green dyed samples could be related to differences in maturity and micronaire values between the sets. However the maturity range across both sets is still quite close so it is unusual to have such a large difference in dyed appearance, especially when the blue dyed samples were so close in colour. It may be possible that there is some relation to the raw fibre colour, where a similar difference in ΔE values was also seen. The L* values recorded for the raw and scoured samples were plotted against maturity (Figure 3.3). In both the raw and scoured colour the L* values in the low micronaire set were spread over a greater range than in the high micronaire set. The scoured L* values lay across a much broader range than those for the raw fibre, most likely due to differential interactions of each fibre type with the scouring solution.

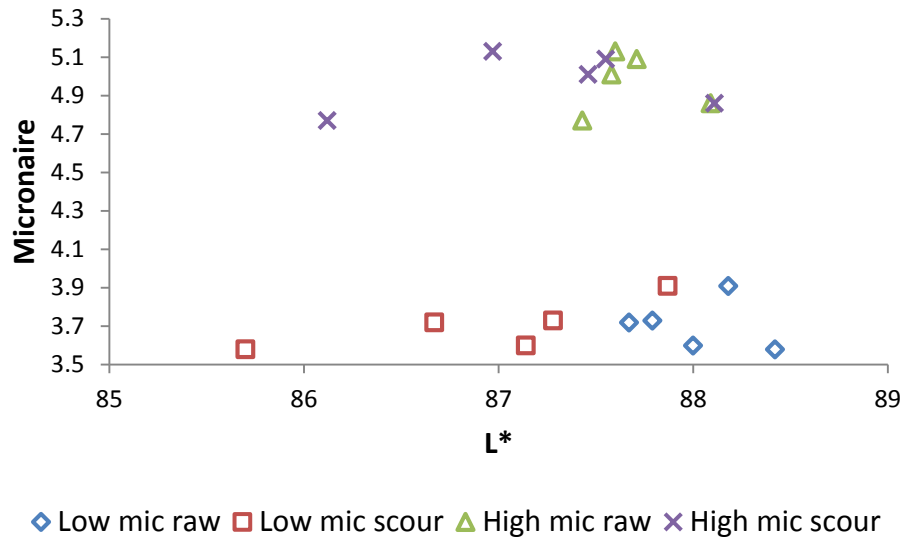


Figure 3.3: L* values for the raw and scoured fibre samples plotted against micronaire.

As the dyeings in this experiment were carried out in separate dye pots, this cannot be eliminated as the source of colour variation between the samples. Accordingly, further experiments are needed to properly determine the source of colour variation in these samples. Dyeing of the sample sets in the same pot would allow direct comparison of colour between the two sets and reduce colour difference due to variation between dyebaths.

3.1.3 Conclusion

A set of low micronaire cotton samples and a set of high micronaire cotton samples were dyed in separate pots with three dyestuffs. Although both the blue and green dyes gave level dyeing, the green dye yielded a shade difference between the high micronaire and low micronaire sets that was consistent over the entirety of the samples. Minimal significant shade variation was observed within the two sample sets. This difference in dyeability may be due to differences in maturity and micronaire between the two sets, which are known to cause shade variation.

However it could also be related to the raw fibre colour, where a similar difference in ΔE values was observed. As the samples were dyed in separate dye baths this may also be a source of this variation. Further experiments are needed with the samples dyed in the same pot.

3.2 Fibre Dyeing Trial of Two Combined Cotton Sets

In the previous section of this chapter dyeing of two cotton sample sets with similar properties in separate dye pots under the same conditions showed no significant colour difference within each set. However there was shade variation observed between the two sets. It was uncertain whether this was related to the fibre properties or the experimental design. A further experiment was therefore designed to determine whether a colour difference could be observed if samples from both sets were combined with in the same dyebath. Differences in dye uptake between the samples, whether from the same or different sets, could indicate key differences in the structural and chemical properties of the cotton fibre affecting dyeability aside from the routinely measured HVI™ properties.

3.2.1 Experimental Methodology

3.2.1.1 Sample Selection and Preparation

Samples were selected and prepared as in Section 3.1.1.1.

3.2.1.2 Scouring and Dyeing

Scouring and dyeing were performed as in Section 3.1.1.2 using Cibacron Green LS-3B (Huntsman, Australia). The baskets of the dyeing machine were packed with 0.5 g +/- 0.01 quantities of each sample from both sets (totalling 5.0 g of fibre), separated by layers of 100% polyester organza fabric (Figure 3.4). The dyeing was performed in triplicate. The dyebath was prepared to an initial volume of 350 ml,

giving a 70:1 liquor ratio. A control pot was prepared using 5 samples selected from both sets (140:1 liquor ratio).

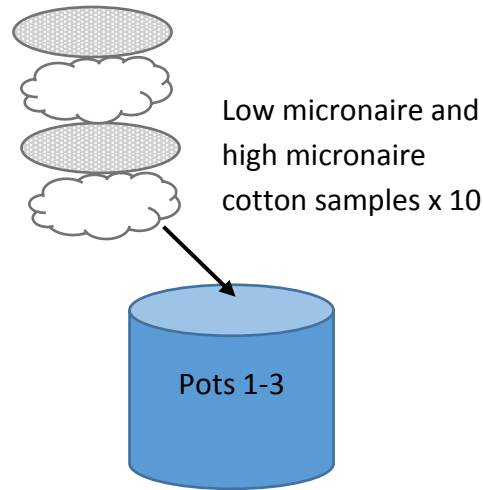


Figure 3.4: The experimental set up of the fibre dyeing.

3.2.1.3 Colourimetry

Colourimetry was performed as detailed for fibre samples in Section 2.3.

3.2.2 Results and Discussion

The cotton samples were scoured individually to remove the surface wax layer prior to dyeing. The fibres were dyed competitively to determine if there were differences in dyeability between the samples. If a sample within a set took up dye more or less readily than the other samples in the bath it would differ in dyed appearance. Dyeing was performed using Cibacron Green LS-3B as it was the only dye that gave level dyeings and obvious colour differences between the sets in the dyeing of the individual sample sets. Dyeing was performed at a 1% dye concentration as subtle shade variations can be difficult to see between darker colours produced at higher concentrations. The dye coverage was even but unlike the previous trial, where the sample sets were dyed in separate baths, there was no particularly noticeable difference in shade observable by the naked eye.

Although no visible difference was obvious, colourimetric measurement indicated subtle shade differences only visible to a trained eye (Table 3.6). The ΔE values were calculated from the average of the three replicate samples using 1022-10 as a reference. Colourimetry showed there to be similar levels of colour difference within the samples dyed in the control pot and their corresponding samples dyed at the shorter liquor ratio, with the exception of 1066-4 which showed a larger difference from the reference in the control pot (Table 3.7).

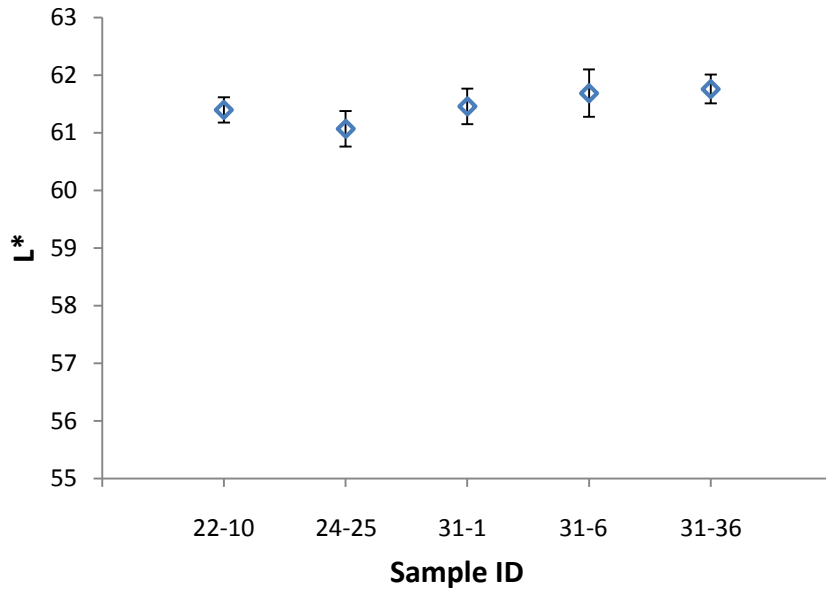
Table 3.6: ΔE values calculated when both sample sets dyed together from 1022-10.

Sample ID	ΔE
1024-45	0.331
1031-1	0.256
1031-6	0.317
1031-36	0.253
1066-3	0.765
1066-4	1.185
1066-8	0.905
1066-10	1.099
1066-61	1.371

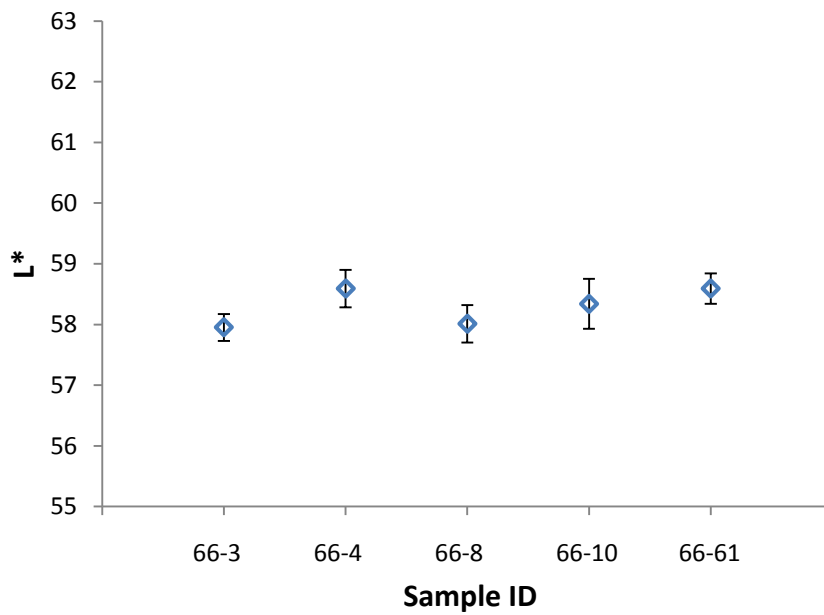
Table 3.7: ΔE values calculated between samples dyed in a control pot from 1022-10.

Sample ID	ΔE
1031-1	0.462
1066-3	0.650
1066-4	0.494
1066-61	1.395

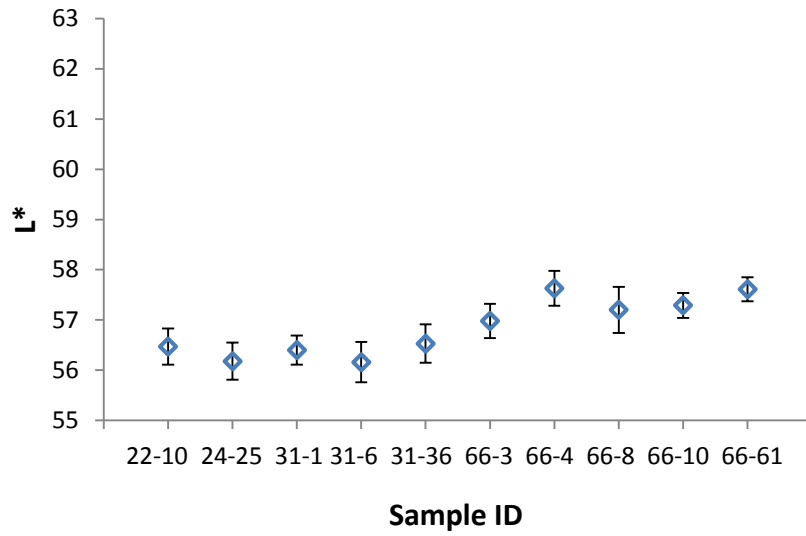
A plot was made of each colour space parameter (L^* , a^* , and b^*) against the samples when dyed both as separate sets (see Section 3.1 for experimental details) and with the sets combined (Figure 3.5). This was designed to determine if there were any observable trends in the individual colour parameters within the sets. When the sets were dyed separately the lower micronaire set appeared lighter than the higher micronaire set. It is unknown whether this was due to the dyeing properties of the fibres themselves or due to experimental error causing differences in the dyeing. Although there were only subtle differences in shade between the two sets, when dyed in the same dyebath the lower micronaire set was slightly darker (Figure 3.5.a.–c.). However, the trends in the fibre colour parameters a^* (red-green) and b^* (yellow-blue) remained relatively constant for both dyeings (Figure 3.5. d.–i.).



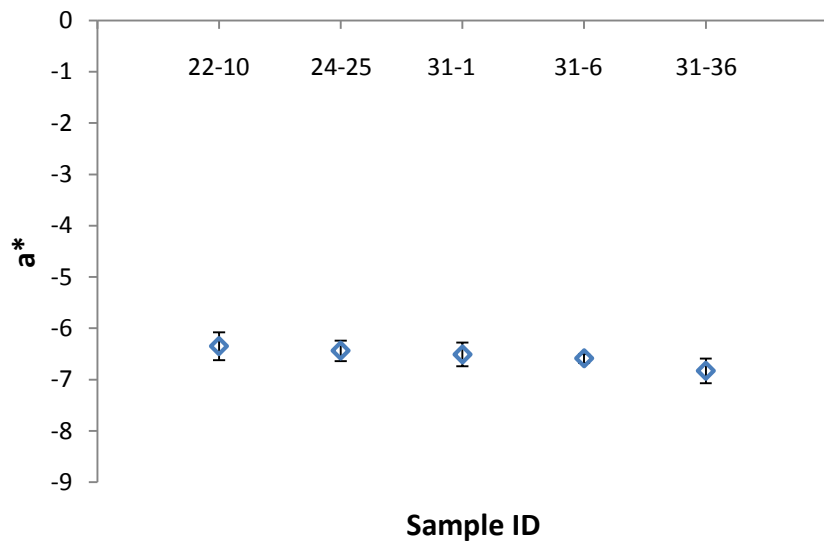
a. Plot of L^* (lightness) against sample ID for the low micronaire set dyed separately.



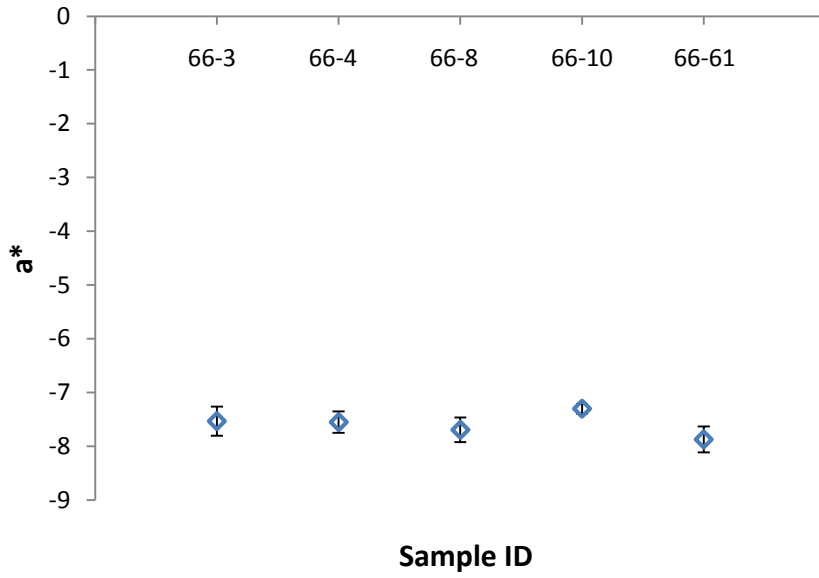
b. Plot of L^* (lightness) against sample ID for the high micronaire set dyed separately.



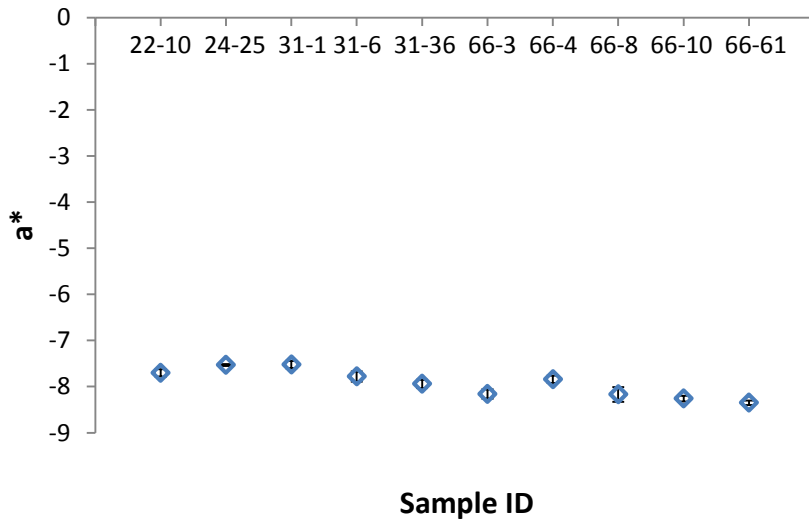
c. Plot of L* (lightness) against sample ID when sets dyed together.



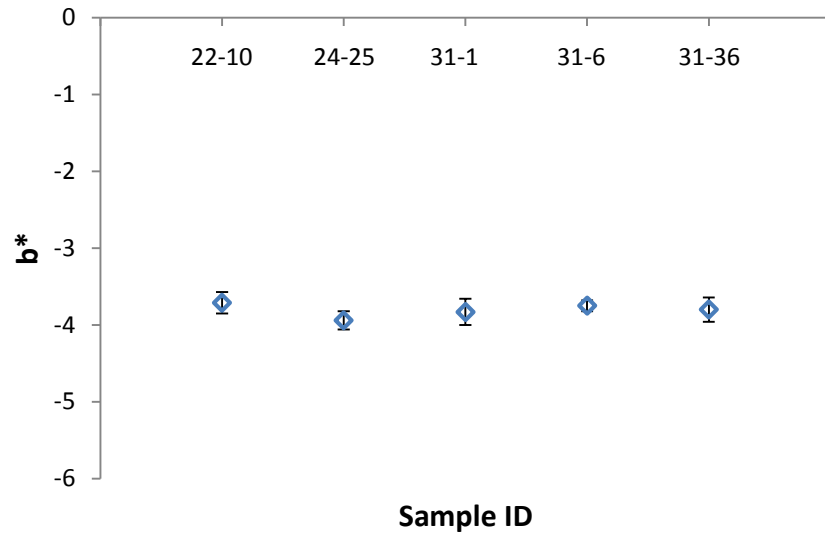
d. Plot of a* (red-green) against sample ID for the low micronaire set dyed separately.



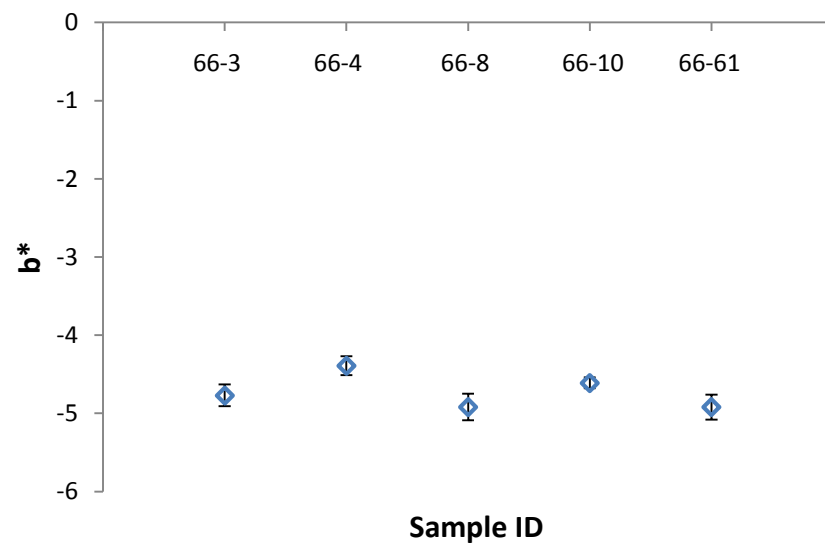
e. Plot of a^* (red-green) against sample ID for the high micronaire set dyed separately.



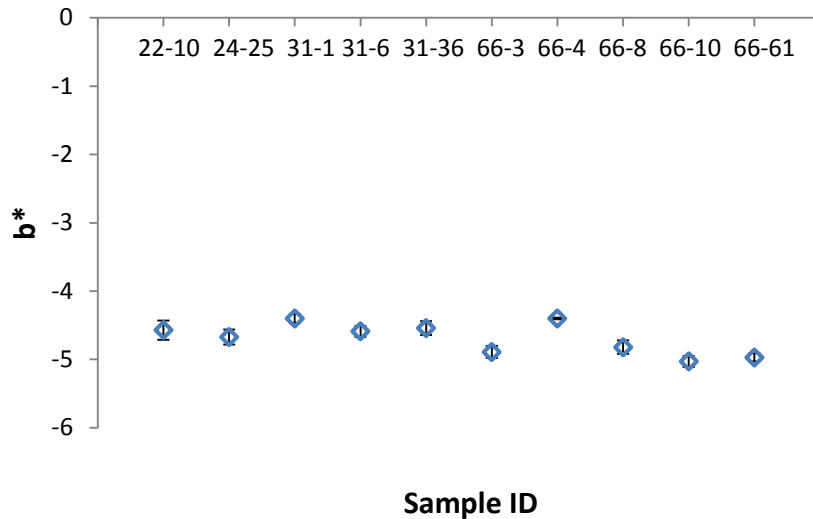
f. Plot of a^* (red-green) against sample ID when sets dyed together.



g. Plot of b^* (yellow-blue) against sample ID for the low microneaire set dyed separately.



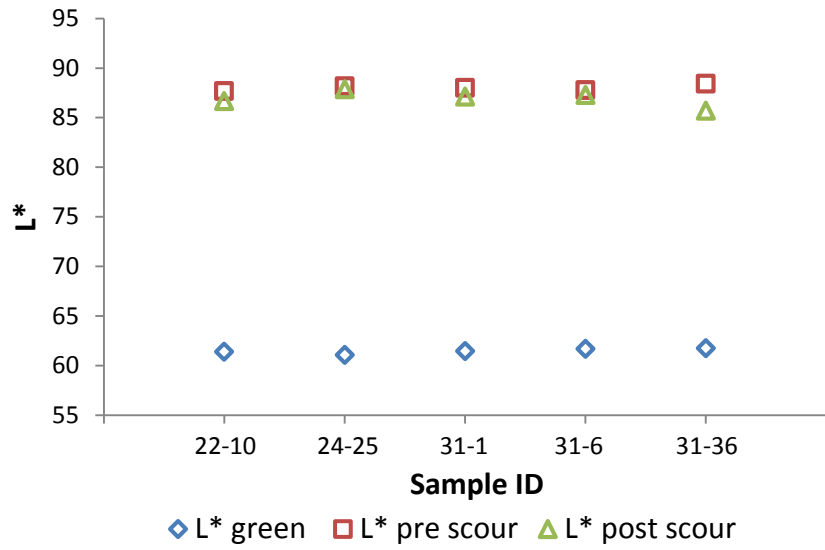
h. Plot of b^* (yellow-blue) against sample ID for the high microneaire set dyed separately.



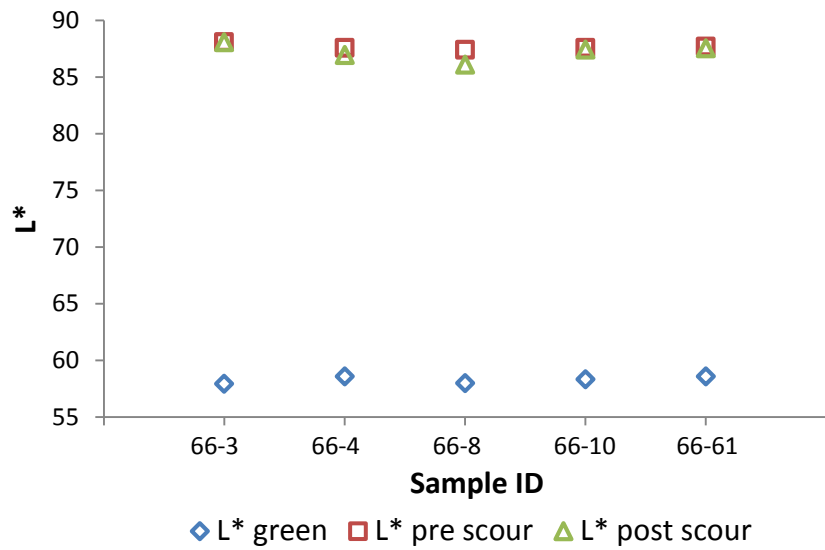
i. Plot of b^* (yellow-blue) against sample ID when sets dyed together.

Figure 3.5: Plot of the colour space parameters L^* (a.–c.), a^* (d.–f.), and b^* (g.–i.) against the samples when dyed both separately and combined.

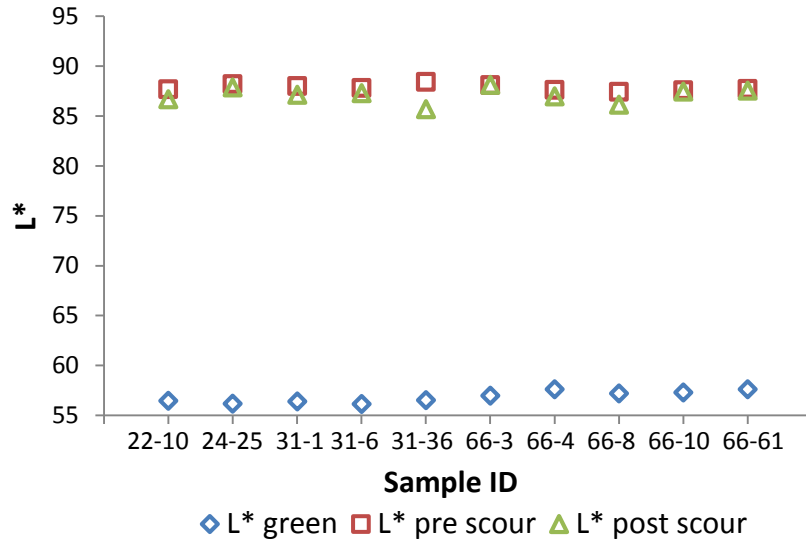
This is also different to what was seen in the raw fibre colour, where the high micronaire set was darker (Table 3.3). To see if any trends could be observed in dyed colour relative to the base colour, the colour parameters for the raw and scoured fibres were plotted against the samples alongside the dyed colour (Figure 3.6). When the sets were dyed together the difference in colour between the samples followed a similar trend across the raw, scoured, and dyed colour (Figure 3.6.c., f., and i.). These same trends could be seen between the samples dyed in separate baths, but were not as clear.



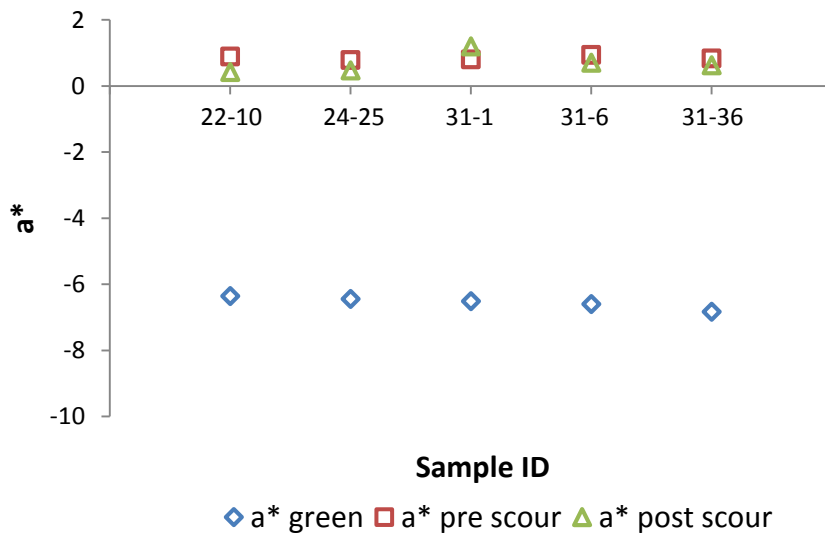
a. Plot of L* (lightness) against sample ID for the low micronaire set dyed separately.



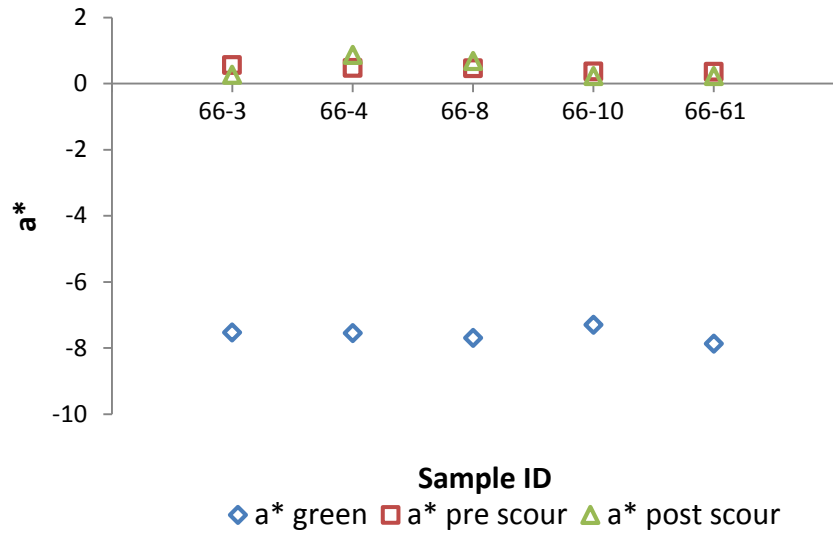
b. Plot of L* (lightness) against sample ID for the high micronaire set dyed separately.



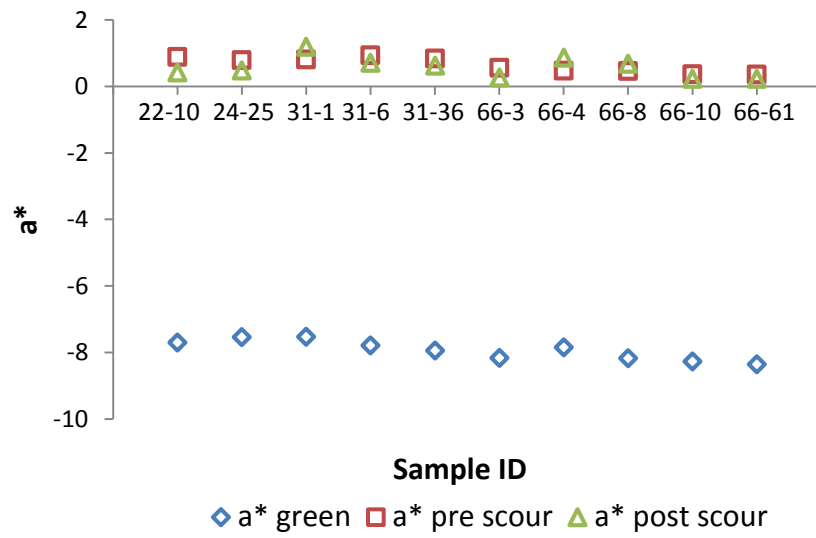
c. Plot of L* (lightness) against sample ID when sets dyed together.



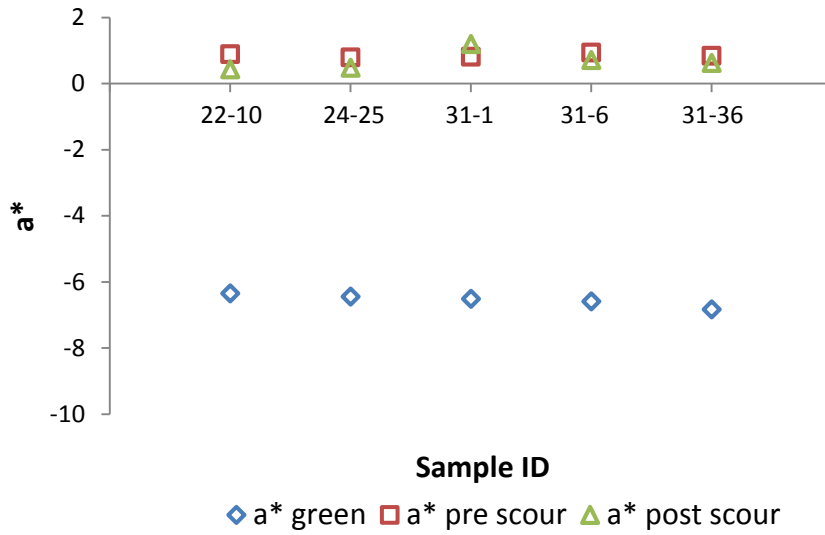
d. Plot of a* (red-green) against sample ID for the low micronaire set dyed separately.



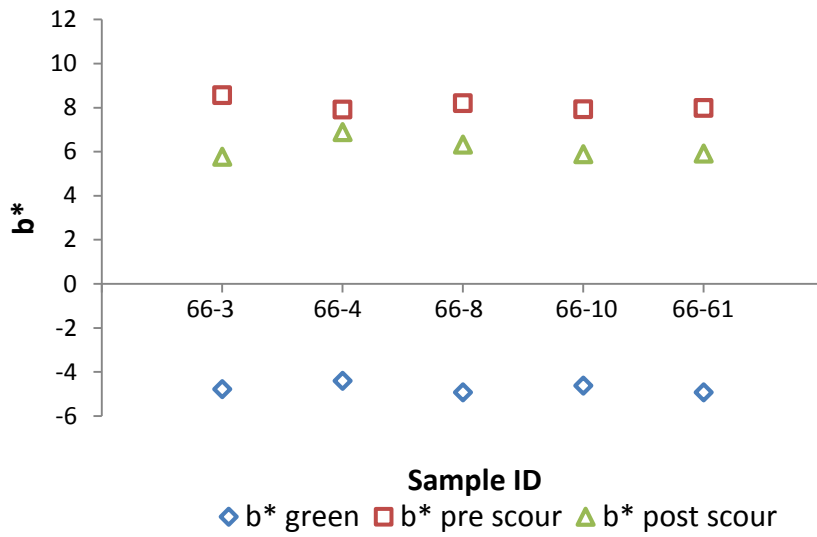
e. Plot of a* (red-green) against sample ID for the high micronaire set dyed separately.



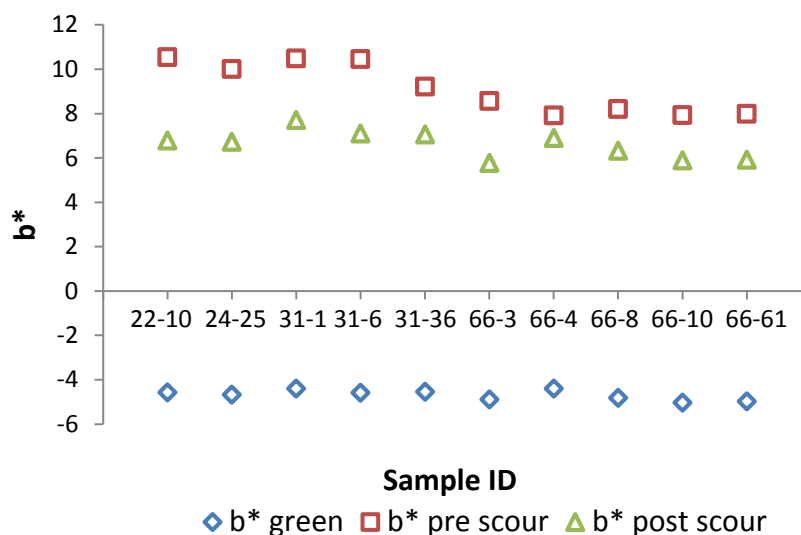
f. Plot of a* (red-green) against sample ID when sets dyed together.



g. Plot of b^* (yellow-blue) against sample ID for the low micronaire set dyed separately.



h. Plot of b^* (yellow-blue) against sample ID for the high micronaire set dyed separately.



i. Plot of b^* (yellow-blue) against sample ID when sets dyed together.

Figure 3.6: Plot of the colour space parameters L^* (a.–c.), a^* (d.–f.), and b^* (g.–i.) against the samples when dyed both separately and combined, alongside the values obtained for the raw and scoured samples.

The observed differences in dyeing behaviour between this and the previous experiment may be due to a number of reasons. One explanation may be that there is a variation in dyeing kinetics between the sample sets due to differences in fibre structure. The higher micronaire sample set may have a higher maximum dye uptake but the lower micronaire set may have a faster rate of dye uptake and would therefore preferentially absorb dye in a competitive bath. Dyeing kinetics may be related to fibre structural differences, such as the variation in maturity and micronaire between the sets. It must also be considered that the difference in dyed colour could be due to measurement inaccuracies or pipetting error causing dyebath variation, as in the previous experiment the sample sets were dyed in separate dyebaths. Further work in this area would be necessary to identify the source of variation, however it was not carried out in this project. Examples of this could include a dyeing where the liquor is periodically sampled to measure the concentration of dye over time, and

instrumental analysis of the fibre structure such as x-ray diffraction to measure crystallinity or transmission electron microscopy to image a cross-section of the internal fibre structure.

3.2.3 Conclusion

A set of low micronaire cotton samples and a set of high micronaire cotton samples were combined and dyed in the same dyebath. Minimal significant shade variation was observed within the two sample sets, however there was shade difference between the two sets with the low micronaire set appearing darker. This is in contrast to the dyeing of the individual sample sets in which the high micronaire set appeared darker. The observed colour difference may be due to differential dyeing kinetics due to structural differences between the cotton fibre sets, or could have been caused by measurement and pipetting differences during dyeing.

3.3 Overall Conclusion

Dyeing of a set of low micronaire cotton samples and a set of high micronaire cotton samples in separate dye baths with Cibacron Green LS-3B showed minimal significant shade variation within the two sample sets but an obvious shade difference between the two sets with the high micronaire set appearing darker. This difference in dyeability could be due to differences in maturity and micronaire between the two sets, or related to the raw fibre colour in which there was a similar difference in ΔE values.

The experiment was repeated, this time with the two sample sets dyed in the same dyebath. Again, minimal significant shade variation was observed within the two sample sets but there was shade difference between the two sets. However in this dyeing the low micronaire set appeared darker. Although there may be differential

dyeing kinetics between the sample sets, with the low micronaire set preferentially taking up dye in the competitive dyebath, it is also possible the differences seen between the two dyeings was due to experimental error.

If the colour difference was caused by differential dyeing kinetics, it is likely this would be due to structural and chemical differences between the sample sets. While the above experiments potentially show such differences between the sample sets, no further analysis was done in this work. It would be of interest in future work to determine exactly the source of variation between the sets. The remainder of the experiments in this project focus on identifying particular sources of variation in fibre properties which may impact on the dyeing of cotton fibre.

4. Variety

Commercially grown cotton fibre is harvested from four domesticated plant species in the genus *Gossypium*. Over 90% of cotton produced worldwide is from the species *Gossypium hirsutum*, which is more commonly referred to as Upland cotton. Upland cotton varieties generally have micronaire values between 3.0 and 5.5, and fibre lengths of 1–1.25 inches (25.4–31.8 mm) (Cotton Incorporated, 2014). The second most grown species, *Gossypium barbadense*, accounts for another 8% of global cotton production. This species of cotton is often referred to as Extra Long Staple (ELS) cotton or, more commonly, Pima cotton. Typically, the minimum fibre length of Pima cotton fibre is 1.375 inches (34.9 mm), with some fibres exceeding lengths of 1.6 inches (40.6 mm) (Cotton Incorporated, 2016a). As well as being a longer fibre, Pima cotton also has superior strength and fineness compared to Upland cotton, and accordingly attracts a higher price in textile markets. However considerably less Pima cotton is produced due to specific climate requirements for growth and overall lower yields (International Trade Centre, 2007).

Fibre properties of both Upland and Pima cotton are measured using the high-volume instrument (HVI™) system, which measures fibre properties including length, strength, and micronaire. Cotton colour is also measured using the HVI™ instrument for both Upland and Pima cotton, however different colour grading systems must be applied as Pima cotton is naturally more yellow in colour (Cotton Incorporated, 2013). Length and strength are predominantly determined by variety whereas micronaire and colour, for both raw and dyed fabrics, are heavily influenced by environmental effects. However, it has been shown that while genotype does not significantly affect raw fibre colour, it does influence both the colour and shade of dyed fabrics (Bradow and Bauer, 1998b). Varietal differences in fibre properties may

translate to shade variation in dyeing. Variation in structural properties such as length and strength may indicate differential amounts of secondary wall cellulose in the fibre, which is where the majority of dye is taken up. Variety may also influence the ratio of crystalline to amorphous cellulose within the fibre, with fibres containing a higher percentage of amorphous cellulose having a greater accessibility to dyes and therefore a greater uptake. Differences in dyeing behaviour have been shown between Upland and Pima cotton varieties, however there has been limited work studying dyeability between cotton varieties of the same species (Wan et al., 2010).

This chapter details the experimental methodology used in an investigation of the dyeability of seven cotton varieties, of which six were Upland and one was Pima. This selection of samples allowed comparison of dyeability both within varieties of a single species, and between different species. The range of maturity ratios in the samples was controlled and the samples all originated from the one growth location in an effort to negate the effect on dyeability of other properties. Section 4.1 details a dyeing trial using five different dyes to determine if dyeability differences could be observed within the sample set. This is followed on in the experiments outlined in Sections 4.2 and 4.3 which take a closer look at the dyeing behaviour of selected samples, based on performance in the first dyeing.

4.1 Fabric Dyeing Trial of Seven Cotton Varieties

A dyeing trial was designed to see if there was any observable difference within a series of cotton samples with similar properties. Fabric samples were selected over fibre samples for easier separation of samples during dyeing and simpler colour measurement. Differential dye uptake between fabric samples with similar HVI™ properties could serve as an initial indication of other structural and chemical differences affecting dyeability, necessitating further investigation into fibre

properties. The fabric samples were dyed competitively with the idea being that if a sample took up dye more or less readily than the other samples in the bath it would differ in dyed appearance. Additionally, the fabric samples were of different varieties but all came from a single growth location during one cotton season, allowing examination of varietal effects on dyed appearance of cotton independent of environmental variation.

4.1.1 Experimental Methodology

4.1.1.1 Sample Selection and Preparation

A set of fourteen fabric samples knitted from seven different cotton varieties (6 Upland cottons and 1 Pima variety) were chosen on the basis of HVI™ properties, particularly maturity and micronaire. Fibre strength was also a consideration as this property could be an indication of crystallinity differences between fibres. The cotton samples used in these fabrics were grown in the 2007/2008 growing season at the Australian Cotton Research Institute (ACRI), located in Narrabri, NSW (30.3°S 149.8°E) (Long et al., 2013). The plots the samples were grown in were randomised, with 2 replicates of each variety. Micronaire values ranged from 3.97–4.48 for the Upland cottons, with the Pima variety having a micronaire value of 3.4 (Table 4.1). From these samples 20 tex carded yarns were prepared (see Long et al. (2013, pp. 752–753) for details of yarn manufacture). These yarns were knitted into single knit jersey fabrics on a Falmac 30 inch diameter circular knitting machine with a 24 gauge cylinder (Falmac Machinery (Tianjin) Ltd., China). The fabrics had a cover factor of 1.32. The weight of each fabric was determined by Australian Standard 2001.2.13 (Standards Association of Australia, 1987). In this method fabrics are first conditioned for 24 hrs in a standard atmosphere. Five samples of the same size are then cut from the conditioned fabric, which was done in this work using a circular

cutter with an area of 86.55 cm². The cut samples are weighed and the mass per unit area is calculated using the formula:

$$m_{ua} = \frac{m}{a}$$

Where a is the area of the sample in square metres and m is the mass in grams. The values for each of the five samples are then used to calculate the mean mass per unit area, expressed in grams per square metre. This value can then be used to calculate the size of a fabric piece needed for a specific mass. For each dyeing 2.0 g +/- 0.1 cotton samples were used.

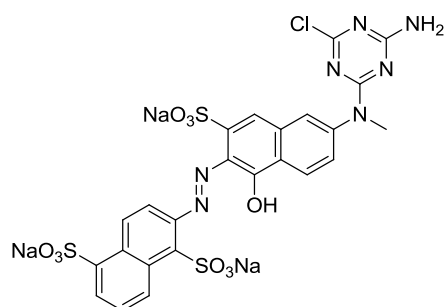
Table 4.1: HVI™ data of the fabric sample set.

Sample	Variety	Length (in)	Strength (gf/tex)	Micronaire	Maturity	Fineness
1	Sicot 71BR	1.177	29.4	4.48	0.87	187
2	Sicot 71BR	1.185	29.6	4.42	0.87	182
3	Sicot 70BRF	1.208	28.7	4.12	0.86	169
4	Sicot 70BRF	1.206	29	4.12	0.86	166
5	CHQX12B	1.272	32.5	3.99	0.87	177
6	CHQX12B	1.26	32.1	4.19	0.87	168
7	CHQX90	1.241	31.5	3.97	0.86	162
8	CHQX90	1.234	30.6	4.08	0.86	160
9	CHQX377	1.221	33	4.2	0.87	159
10	CHQX377	1.223	32.5	4.3	0.87	153
11	Sicala 350B	1.306	31.8	4.22	0.88	167
12	Sicala 350B	1.3	31.8	4.32	0.87	168
13	Sipima 280	1.408	46	3.45	0.87	144
14	Sipima 280	1.412	46.4	3.4	0.87	140

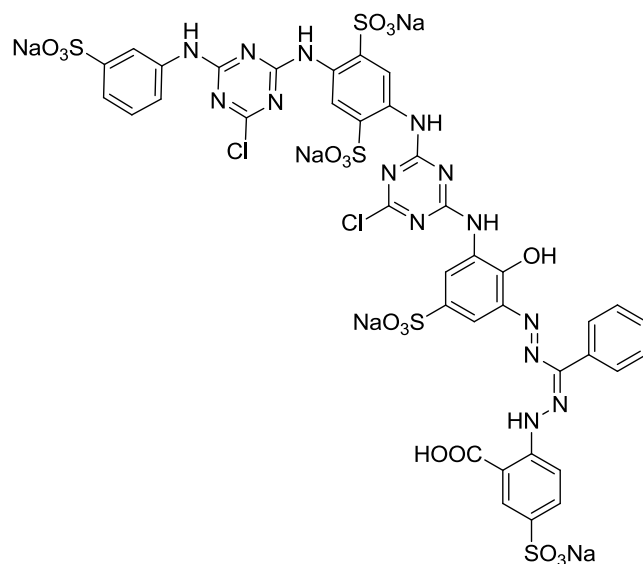
4.1.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. A rotary dyeing machine was deemed more suitable for this work than the Ahiba

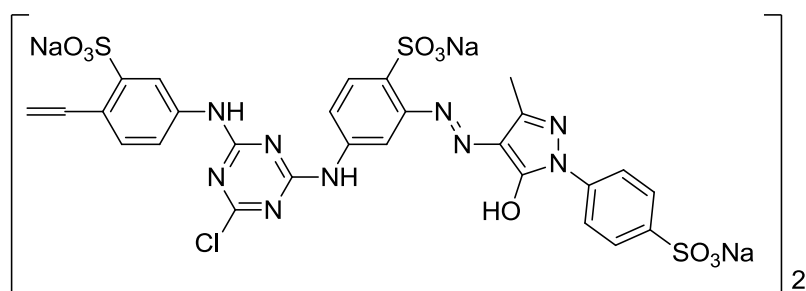
Turbomat 1000 Laboratory Dyeing Machine used previously as the flow of the Ahiba dyeing machine was not sufficient to evenly penetrate several layers of fabric and the fabric samples were too small to dye on a spindle. Dyeing could also be done at a much lower liquor ratio than in the Ahiba dyeing machine. The dyes used in this trial were predominantly Procion H and HE series reactive dyes (Figure 4.1). Four dyes were chosen on the basis of molecular structure with an emphasis on features such as size, number of reactive groups, and number of solubilising groups. The dyes chosen were Procion Orange H-2R, Procion Blue HE-RD, Procion Yellow HE-3G, and Procion Yellow HE-6G. It was of interest to know the chemical structure of the dyes to determine whether factors such as molecular size and the number of functional groups were impacting on dyed appearance. The chemical structures of the Cibacron LS series dyes, as used in the previous fibre dyeing trials, are heavily patent protected so it is difficult to examine in depth the interactions between the cotton fibre structure and the molecular structure of the dye. One of the Cibacron dyes, Cibacron Green LS-3B, was still used as it produced the most level dyeings and noticeable results in the fibre dyeing trials.



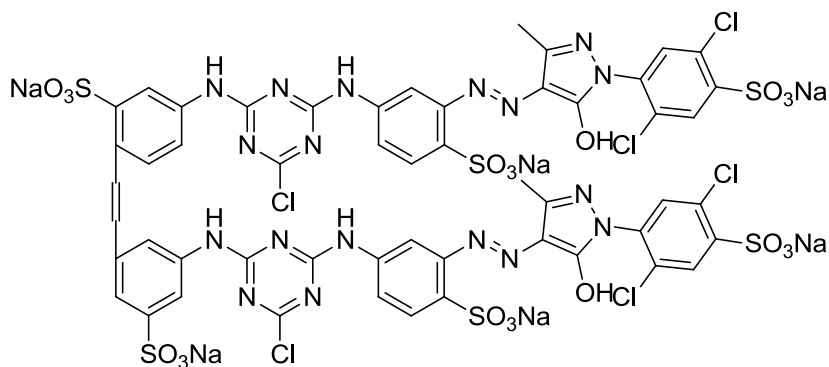
a. The structure of Procion Orange H-2R



b. The structure of Procion Blue HE-RD



c. The structure of Procion Yellow HE-3G



d. The structure of Procion Yellow HE-6G

Figure 4.1: The structure of the Procion reactive dyes used in this project.

Dyeing was performed at a 0.1% dye concentration as subtle shade variations can be difficult to see between the darker colours produced at higher concentrations.

Due to the change in dyes, a greater concentration of salt was required in the dyebath

to increase dye affinity for the fabric (30.0 g/L for Cibacron compared to 70.0 g/L for Procion). The Cibacron LS series of dyes is formulated to have a greater fibre affinity at a lower salt concentration than traditional cotton reactive dyes, reducing environmental impacts and costs. The “LS” stands for “low salt”.

Samples of each of the 14 cotton fabrics were dyed with each of the 5 dyestuffs. In each pot of the dyeing machine were placed 7 cotton samples (total fabric weight 14.0 g). The dyebath was prepared to an initial volume of 150 ml, giving approximately an 11:1 liquor ratio.

4.1.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before scouring, after scouring, and after dyeing to observe the level of colour difference between samples at each stage of the dyeing process.

4.1.2 Results and Discussion

The cotton samples were scoured under alkaline conditions to remove the surface wax layer prior to dyeing. There was little to no difference visible with the naked eye within the Upland samples both unscoured and scoured. There was an obvious difference between the Upland and Pima varieties which became even more pronounced after scouring with the Pima variety developing orange tones.

Initially dyeing was done in an Ahiba Turbomat 1000 Laboratory Dyeing Machine (Datacolor, USA) with the fabrics arranged to give as little overlap as possible. The Ahiba dyeing machine was effective for the fibre dyeing trials as the small, porous fibre samples allowed the dye liquor to pass through easily and separation of the fibres was simply done with a layer of organza mesh fabric. However when dyeing fabric samples in this machine both scouring and dyeing

produced uneven results and were still subject to the high liquor ratio issues experienced in the fibre dyeing trials (see Section 3.1.1.2). The samples used were not large enough to place on a spindle and although it was attempted to layer the fabric as thinly and evenly as possible the folded, compacted fabric samples were not as readily permeable as the fibre samples.

The remainder of the scouring and dyeing work was done using a rotary dyeing machine eg. SDM2-140 rotary dyeing machine (Fong, Hong Kong). Unlike the Ahiba dyeing machine, which uses a pumping system to move liquids throughout the pot, this was a tumble dyeing machine with the movement of the dye liquor and fabric sample in the pot coming from mechanical movement of the dye pots. The smaller size sealed pot and mechanical rotation also allowed the use of a lower liquor ratio. While the fibre samples were done at an average liquor ratio of 140:1 the fabric samples in this experiment were done using an 11:1 liquor ratio. This liquor ratio is closer to that used in industry where colour variation has been observed.

Dyeings were carried out using all five of the dyes. For the most part coverage was consistently on shade and even, though there were some incidences of patchiness with the darker shades, particularly the green dye which had performed best in the fibre dyeing trials. There was minimal shade variation observable by the naked eye within the Upland cotton varieties, though a difference was very noticeable between the Upland and Pima varieties. This difference was least noticeable using the orange dye due to the orange tones that developed in the Pima cotton samples upon scouring.

Colour was measured for each sample before scouring, after scouring, and after dyeing. For each parameter (L^* , a^* and b^*) of the raw and scoured samples the

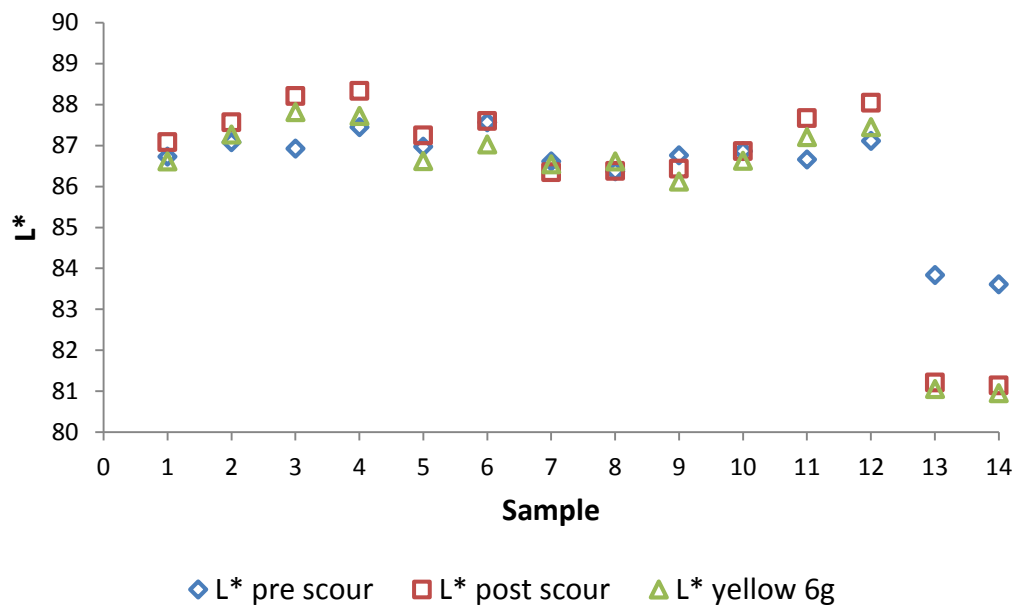
average values of five replicates were taken and used to calculate ΔE values (Table 4.2). The ΔE between the scoured and dyed samples was calculated from a single sample. Sample 1 was used as the reference. The average ΔE between raw samples was 0.77 within the Upland varieties, corresponding to an almost invisible difference, and 3.32 from the Upland to the Pima samples, indicating an obvious difference (see Table 2.1). After scouring, the average ΔE between Upland samples was 0.96, again corresponding to a difference so small a trained eye would struggle to see, and 7.17 from the Upland to the Pima samples, indicating an extremely obvious difference. After scouring the orange tone evident in the Pima fabrics produced a correspondingly large increase in the a^* parameter (red/green), along with a decrease in lightness. For each of the dye colours used there was little to no shade variation within the Upland samples but again substantial variation between the Upland and Pima samples. The smallest difference in shade between the Upland and Pima samples was seen with the green and orange dyes. The green dye was the darkest of the five and as such could be giving more coverage to subtle differences in shade whereas the two yellow dyes, which were the lightest, showed the greatest difference. Less difference may have been observed in the orange dyed samples due to the previously mentioned orange tones developed after scouring. Often a small change in hue is more noticeable than a change in depth, so an orange base colour is more likely to produce a hue change in a yellow, green, or blue dyed fabric than it is in an orange or red. The orange dye was also by far the smallest in terms of chemical structure so may be more readily able to penetrate the cotton fibre.

Table 4.2: ΔE values calculated from sample 1 between raw, scoured, and dyed cotton fabric.

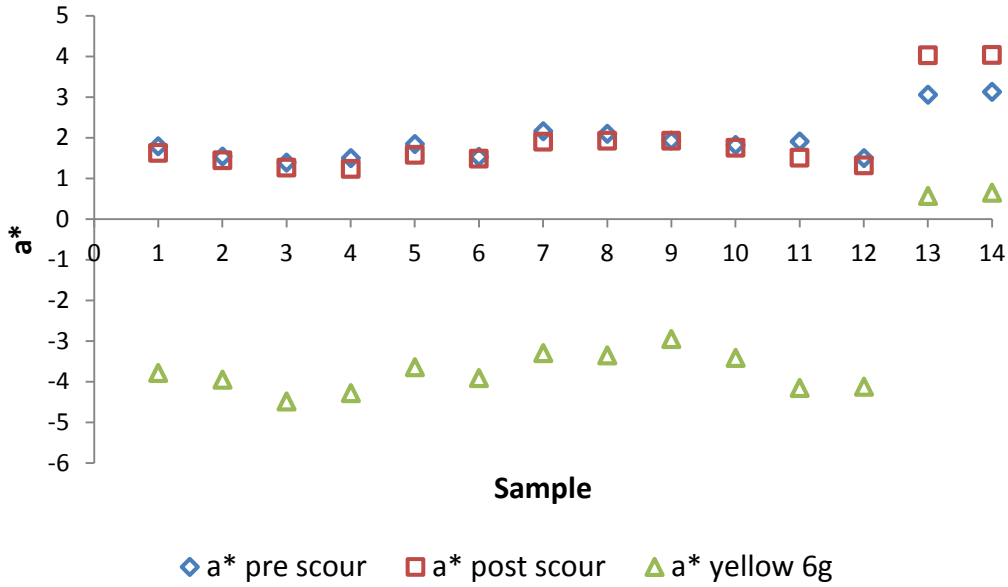
Sample	ΔE Raw	ΔE Scoured	ΔE Yellow 3G	ΔE Yellow 6G	ΔE Blue	ΔE Orange	ΔE Green
2	0.712	0.540	0.554	0.710	0.801	0.413	0.741
3	0.761	1.239	0.952	1.596	1.695	1.474	0.275
4	1.109	1.355	1.106	1.446	1.187	0.548	0.418
5	0.574	0.361	0.440	0.471	0.558	0.852	1.667
6	1.269	0.534	0.232	0.752	1.103	0.413	0.418
7	0.503	0.820	0.770	1.326	1.072	1.868	1.041
8	0.664	0.836	1.018	1.09	0.539	1.218	1.279
9	0.200	0.858	1.186	1.928	1.406	1.395	1.307
10	0.409	0.352	0.906	1.113	0.534	0.837	0.331
11	0.529	0.620	0.971	0.762	1.289	0.447	2.194
12	0.846	1.071	0.387	1.668	0.894	0.364	1.634
13	3.186	7.116	7.656	8.204	7.353	5.679	5.270
14	3.444	7.219	7.162	8.474	6.951	5.970	5.838

As the cotton samples were scoured but unbleached, the colour parameters L^* , a^* and b^* were plotted against the sample ID numbers to see if any minor colour differences were evident (Figure 4.2). There were no consistent trends observed in L^* , while the a^* and b^* values for the scoured and dyed samples followed a similar trend to that of the raw fabric base colour. Whilst only the results for Procion Yellow HE-6G are presented, all dye colours showed similar trends.

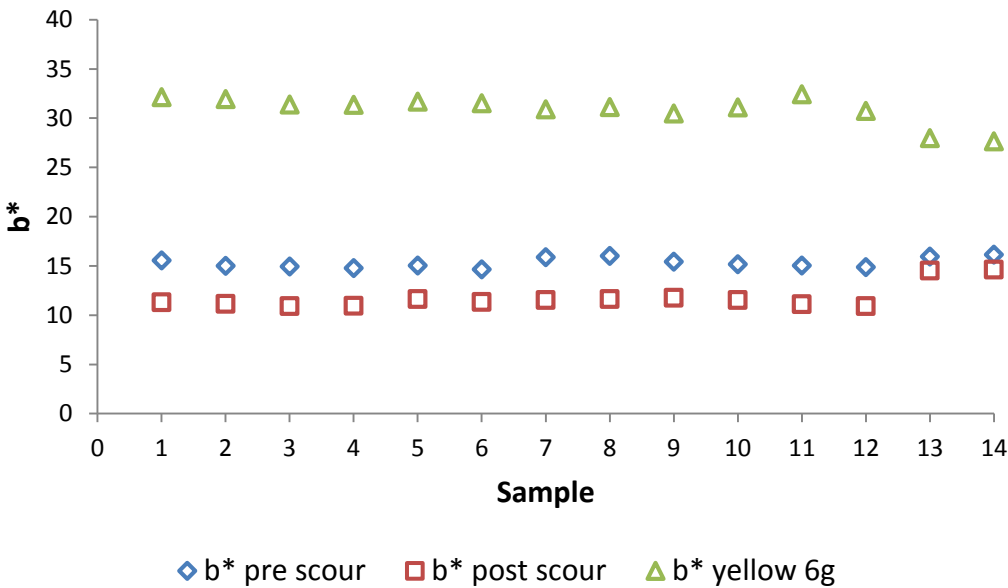
Selected samples were identified as having slightly different dyeing behaviour to other samples with similar properties, predominantly on the basis of the L^* values measured. These samples showed considerable variation in dyed colour lightness in relation to the raw fabric base colour, with some appearing lighter and some darker, and were chosen for further dyeing experiments. Samples 4-8 showed considerable variation within the L^* values in relation to each other for each stage of the dyeing process which was not seen in the a^* or b^* values. These samples were also some of the closest within the set in terms of fibre properties such as maturity and micronaire. The variation in dyeing behaviour within varietal pairs was also of interest. Sample pairs 3-4 and 11-12 showed substantial variation in L^* , a^* and b^* values despite being of the same cotton variety, with samples 7-8 being the sample pair with the most consistent dyeability.



a. Plot of lightness (L^*) against the cotton fabric samples pre scour, post scour, and dyed with Procion Yellow HE-6G.



b. Plot of red-green ($+a^*/-a^*$) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.



c. Plot of yellow-blue ($+b^*/-b^*$) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.

Figure 4.2: Cotton fabric samples plotted against colour parameters L^* (a.), a^* (b.) and b^* (c.) to identify dyeability trends and base colour differences.

4.1.3 Conclusion

A set of 14 cotton samples of 7 different cotton varieties were dyed competitively with five dyestuffs. Minimal significant shade variation was observed within the Upland cotton samples, however there were obvious shade differences between the Upland and Pima varieties. While the a^* and b^* values were consistent within the set, the L^* values showed considerable variation in relation to the base colour.

Despite this, it was thought overall variation in dyeability was related to base colour differences. Some samples were selected for further analysis as they showed slight differences in dyeability despite having very similar properties.

4.2 Dyeability of Five Cotton Samples from Three Varieties

In the previous section of this chapter, the dyeing trial undertaken to determine the dyeability of different cotton varieties with similar properties showed minimal significant difference in dye uptake within 12 Upland cotton samples from 6 varieties. There was an obvious colour difference between the Upland samples and two Pima cotton samples. The fabric samples all came from a single growth location during one cotton season, allowing examination of varietal differences which may affect dyed appearance of cotton independent of variation caused by growth environment. In most cases colour change could be attributed to the difference in the raw fabric base colour, however some samples warranted further analysis due to some minor differences in dyeing behaviour observed. Five fabric samples of three cotton varieties particularly stood out as they showed considerable variation in L^* , with some dyed samples appearing brighter and some appearing duller than the base colour (Figure 4.3). This difference was seen despite the samples having similar fibre properties and base colour. The same level of difference was not observed in the a^* or b^* parameters. This section details a further set of dyeings which were undertaken

to ensure that the samples were exhibiting this difference, and that it was not due to experimental or colourimeter error. Variation in dye uptake may potentially indicate intrinsic structural or chemical differences between the samples, necessitating further investigation into which fibre properties may be the cause.

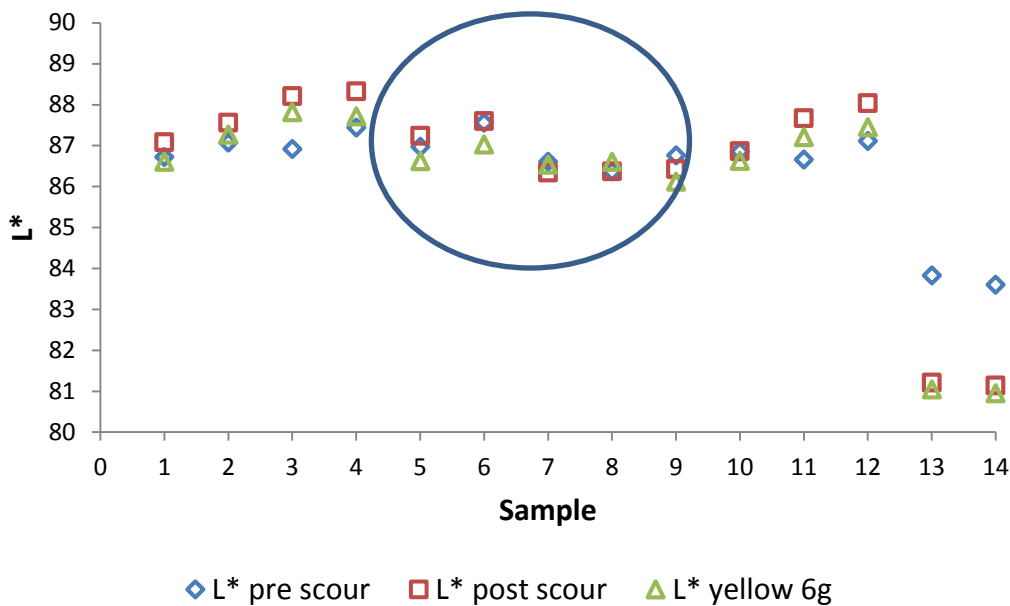


Figure 4.3: The samples selected for further analysis based on variation in dyed colour in relation to the base colour.

4.2.1 Experimental Methodology

4.2.1.1 Sample Selection and Preparation

Cotton fabric samples 4–8 were selected based on performance in the experiments detailed in Section 4.1. Details for the fibre properties are given in Table 4.3. Yarn and fabric preparation details for these samples can be found in Section 4.1.1.1.

Table 4.3: Fibre and colour properties of the fabric samples selected for the second fabric dyeing trial.

Sample	Micronaire	Maturity	Fineness
4	4.12	0.86	166
5	3.99	0.87	177
6	4.19	0.87	168
7	3.97	0.86	162
8	4.08	0.86	160

4.2.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. Samples of each of the 5 cotton fabrics were dyed in 5 replicates with each of the 5 dyestuffs.

For each dyeing 2.0 g +/- 0.1 fabric samples were used, with five samples per dye pot (total fabric weight 10.0 g). The dyebath was prepared to an initial volume of 150 ml, giving a 15:1 liquor ratio.

4.2.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before scouring, after scouring, and after dyeing to observe the level of colour difference between samples at each stage of the dyeing process.

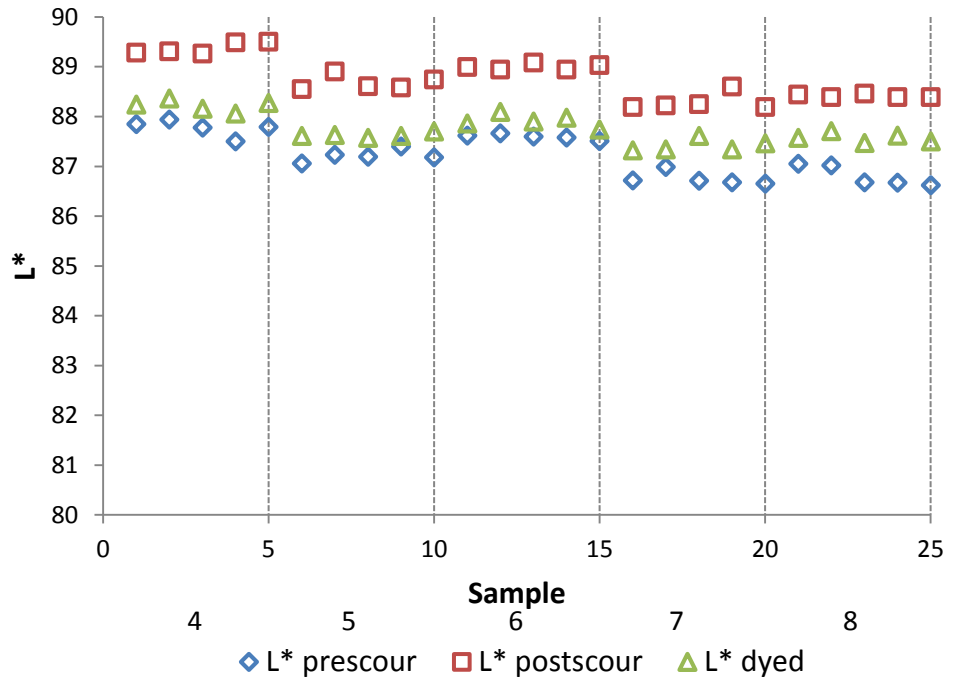
4.2.2 Results and Discussion

In the previous experiment it was observed that the recorded L* values for the dyed fabric colour were different in relation to the base colour, with some samples appearing lighter and some darker. This second dyeing was designed to determine the extent of variation in the L* values. Five samples from three cotton varieties were

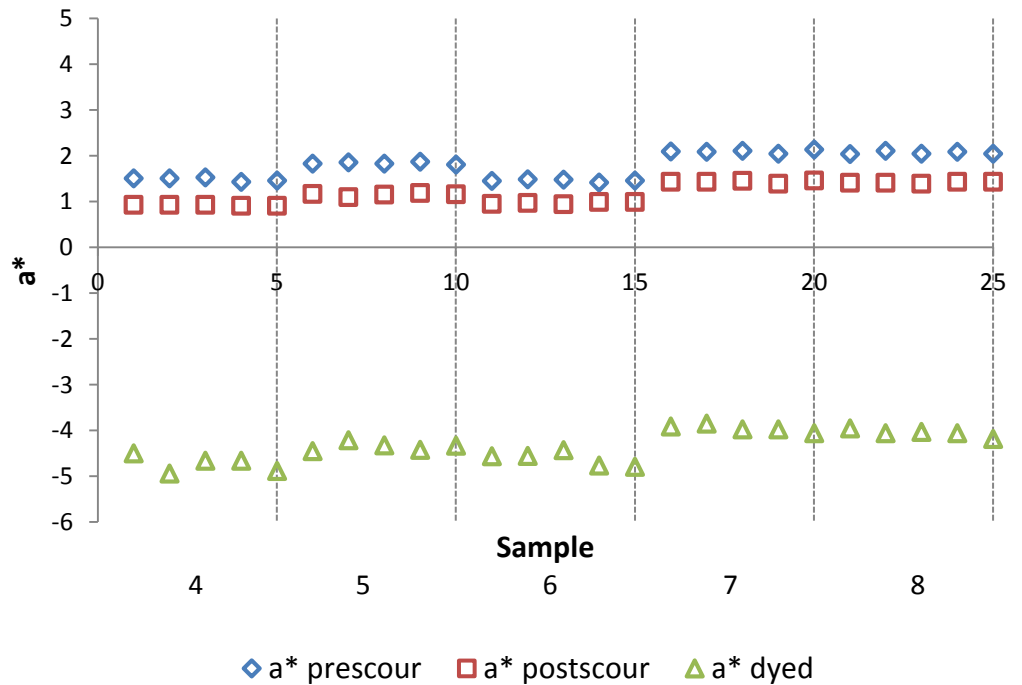
selected as they showed considerable variation in the first experiment despite having quite similar fibre properties.

The cotton samples were scoured under alkaline conditions prior to dyeing. There was little to no colour difference visible with the naked eye between the samples both unscoured and scoured. Dye coverage was predominantly on shade and even, with some minor patchiness in the darker shades. There was minimal shade variation observable by the naked eye within the samples.

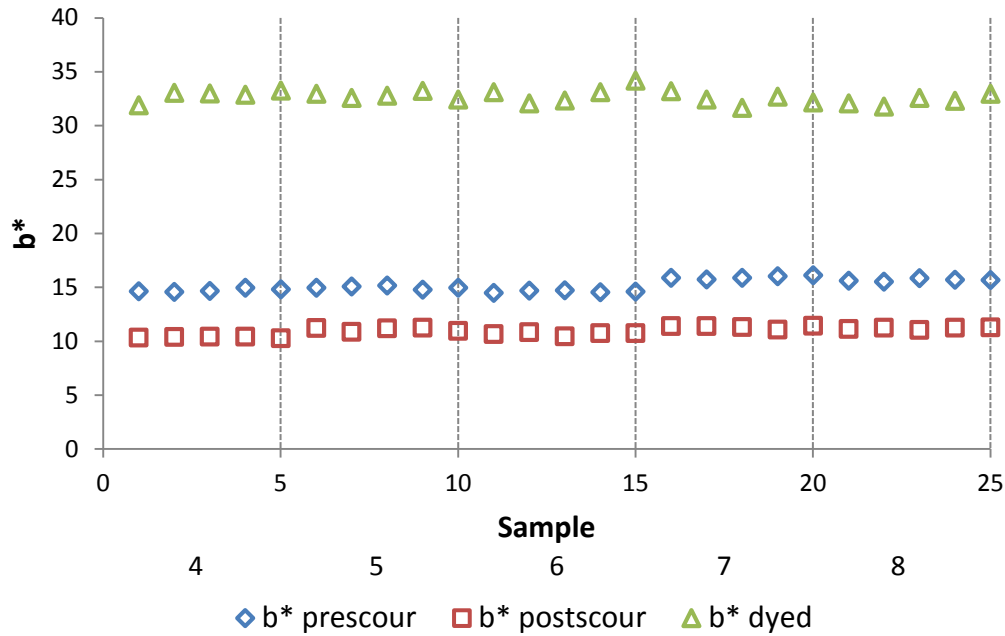
Colour was measured for each sample before scouring, after scouring, and after dyeing. The colour parameters L^* , a^* and b^* were plotted against the sample ID numbers to see if the minor colour difference observed in the previous experiment was evident (Figure 4.4). The results seen were quite different from those reported in Section 4.1. For all colour parameters the colour difference in the scoured and dyed fabric colour followed a similar trend to that of the base colour. This has previously only been observed in the a^* and b^* values. The variation in relation to the base colour seen in the previous experiment was not observed in this second dyeing, with all dyed samples appearing slightly lighter than the raw fabric (see Figure 4.2 and Figure 4.4). While sample pair 7 and 8 seem nearly identical, samples 5 and 6 show a slight, though still invisible, colour difference. This could be due to small differences in micronaire and fineness within the pair. This same difference was seen in the first experiment, however the variation was greater. It was of interest to determine the extent of variation between sample pairs and accordingly a third dyeing experiment was designed, studying sample pairs exhibiting the most and least colour difference.



a. Plot of lightness (L^*) against the cotton fabric samples pre scour, post scour, and dyed with Procion Yellow HE-6G.



b. Plot of red-green ($+a^*/-a^*$) against the cotton fabric samples pre scour, post scour, and dyed with Procion Yellow HE-6G.



c. Plot of yellow-blue (+b*/-b*) against the cotton fabric samples pre scour, post scour, and dyed with Procion Yellow HE-6G.

Figure 4.4: Cotton fabric samples plotted against colour parameters L* (a.), a* (b.) and b* (c.) to identify dyeability trends and base colour differences.

A possible explanation for the colour differences in relation to the base colour seen in the previous experiment could be weighing or pipetting inaccuracies between the two pots used for the dyeing. As the level of colour difference between the samples is already quite small, very minor variations in the dye quantity could cause a difference. Another potential cause is instrumental error in the colorimeter. Because the shade variation between the samples is miniscule, the error in the instrument may be greater than the colour difference. The measurements from each of the five sample replicates are provided in the above graphs (Figure 4.4) rather than a mean value to show the level of colour variation between dyeings. This highlights the difference between dyeings for unscoured, scoured, and dyed colour. The effect on colour measurement of instrumental error is discussed further in Section 4.3.

4.2.3 Conclusion

Five fabric samples of three cotton varieties were selected for further dyeing experiments as previous work showed variation in lightness, with some dyed samples appearing brighter than the raw fabric base colour and some duller. Minimal significant difference in dye uptake could be observed with the naked eye. The minor differences in dyed appearance observed were attributed to the fabric base colour. The variation in L^* seen previously was not observed in this set alluding to the possibility that other factors may be influencing the difference observed.

4.3 Dyeability of Three Cotton Sample Pairs

In the first section of this chapter, the dyeing trial undertaken to determine the dyeability of different cotton varieties with similar properties showed minimal significant difference in dye uptake within 12 Upland cotton samples from 6 varieties. A colour difference was observed between the Upland samples and two Pima cotton samples. The fabric samples originated from the same growth location during one cotton season, allowing examination of differences in fibre properties related to variety which may affect dyed appearance of cotton independent of variation due to environmental factors. In most cases colour change could be attributed to the difference in the raw fabric base colour, however some samples warranted further analysis due to some minor differences in dyeing behaviour observed. Sample pairs of three cotton varieties were selected as showing the most (samples 3-4 and 11-12) and least variation (samples 7-8) in the parameters L^* , a^* and b^* within the Upland samples (Figure 4.5). Variation in dye uptake may potentially indicate intrinsic structural or chemical differences between the samples, necessitating further investigation into which fibre properties may be the cause.

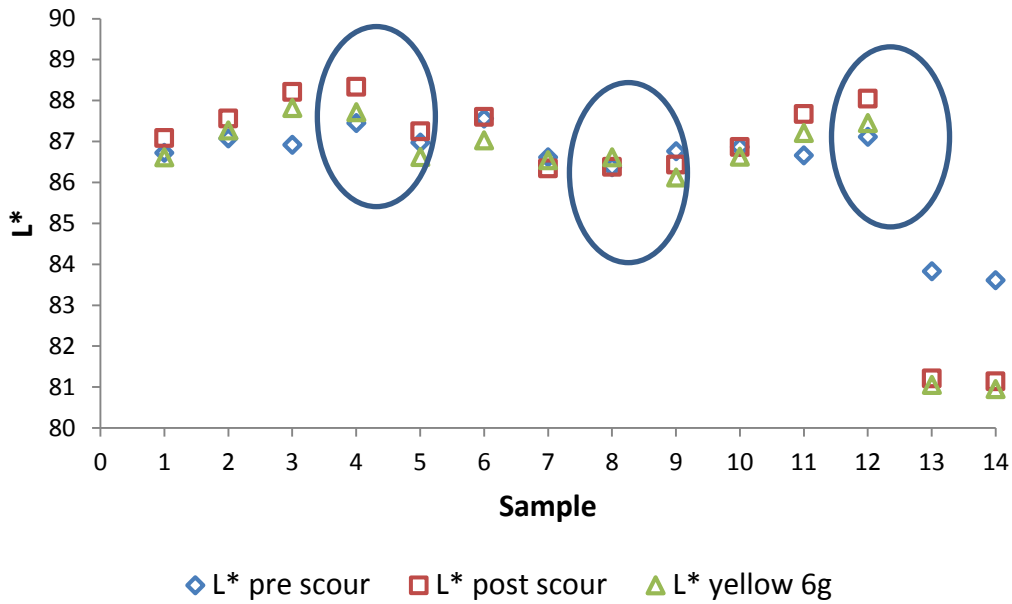


Figure 4.5: The samples pairs selected for further analysis based on variation in dyed colour in relation to the base colour.

4.3.1 Experimental Methodology

4.3.1.1 Sample Selection and Preparation

Cotton fabric sample pairs 3-4, 7-8, and 11-12 were selected based on performance in the experiments detailed in Section 4.1. Details for the fibre properties are given in Table 4.4. Yarn and fabric preparation details for these samples can be found in Section 4.1.1.1.

Table 4.4: Fibre and colour properties of the fabric samples selected for the third fabric dyeing trial.

Sample	Micronaire	Maturity	Fineness
3	4.12	0.86	169
4	4.12	0.86	166
7	3.97	0.86	162
8	4.08	0.86	160
11	4.22	0.88	167
12	4.32	0.87	168

4.3.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. Samples of each of the 6 cotton fabrics were dyed in 3 replicates with Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). For each dyeing 2.0 g +/- 0.1 fabric samples were used, with six samples per dye pot (total fabric weight 12.0 g). The dyebath was prepared to an initial volume of 150 ml, giving approximately a 13:1 liquor ratio.

4.3.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before scouring, after scouring, and after dyeing to observe the level of colour difference between samples at each stage of the dyeing process.

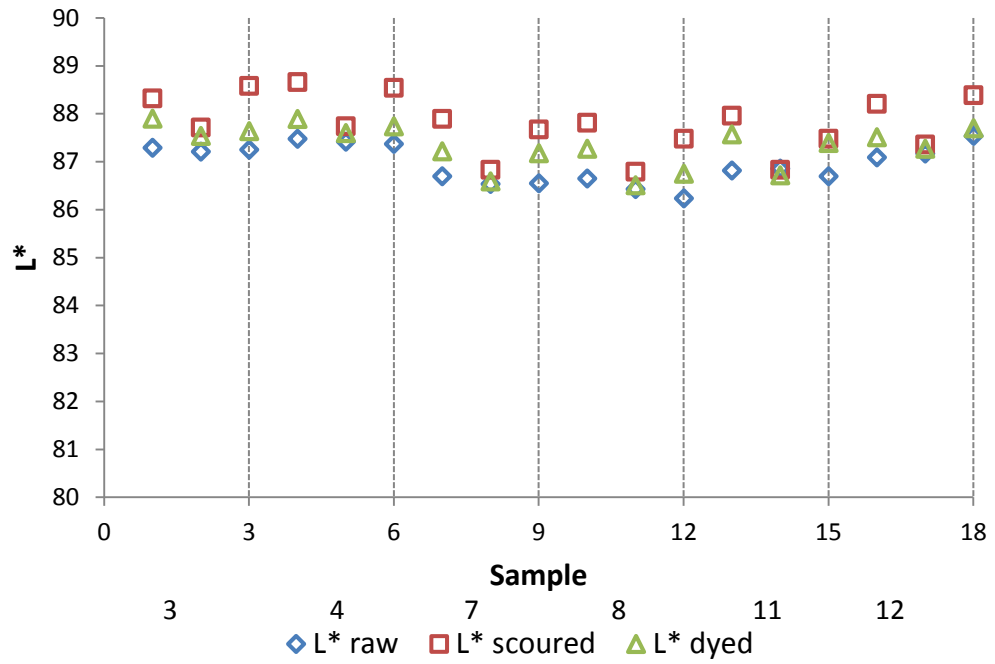
4.3.2 Results and Discussion

In the first experiment of this chapter it was observed that the recorded L* values were different in relation to the base colour, with some samples appearing lighter and some darker. A second dyeing with the aim to determine the extent of variation in the

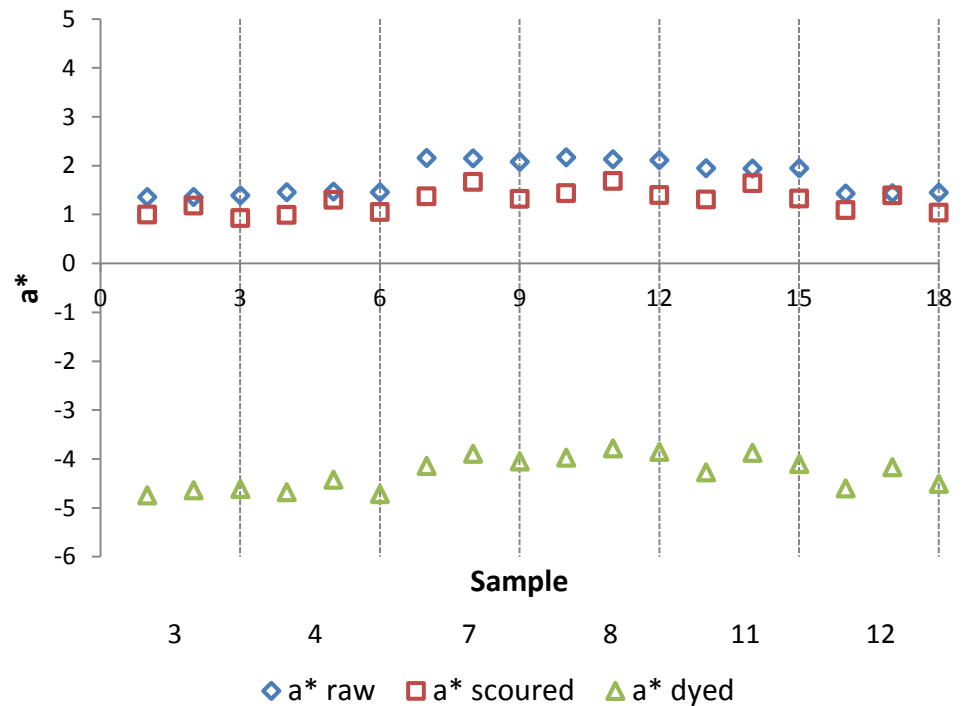
L* values did not show the same difference. However it was still of interest to determine the level of variation in L* between samples pairs. Three sample pairs were chosen due to the variation they exhibited in the initial dyeing.

The cotton samples were scoured under alkaline conditions prior to dyeing. There was little to no colour difference visible with the naked eye between the samples both unscoured and scoured. The dyeing was on shade and even, with minimal shade variation observable by the naked eye within the samples.

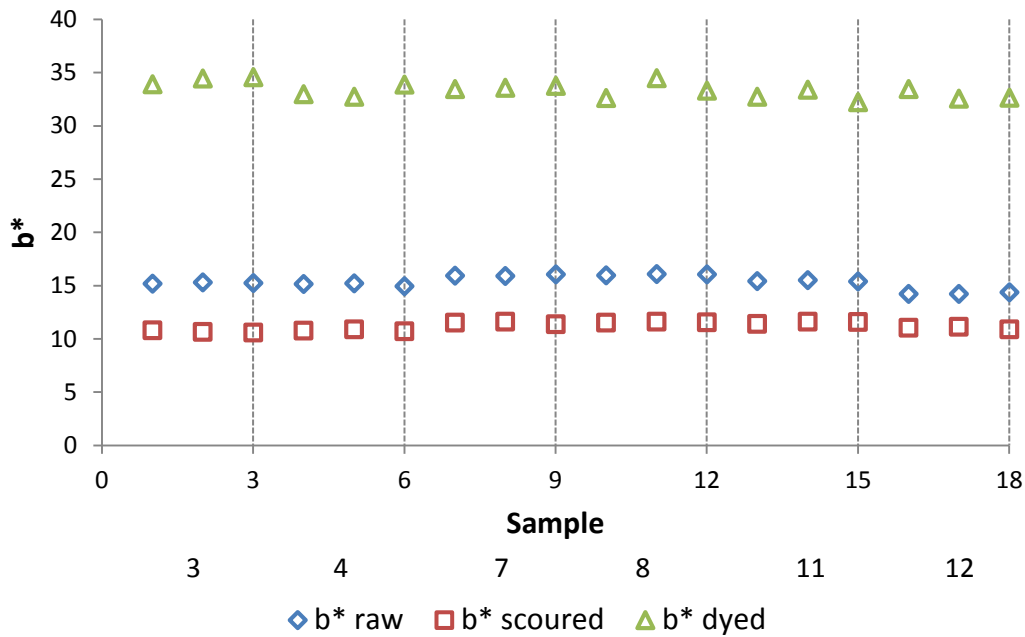
Colour was measured for each sample before scouring, after scouring, and after dyeing. The colour parameters L*, a* and b* were plotted against the sample ID numbers to see if the minor colour difference observed was due to dyeing or variation in the base colour (Figure 4.6). For each sample one replicate recorded a slightly lower L* value in the scoured colour, indicating a darker colour, which persisted through dyeing. This suggests some small measurement or other experimental error may have occurred during scouring. Overall, samples 7 and 8 were once again quite close to each other, yet there were small colour differences between the other two sample pairs. It is of note that samples 3 and 4 show a slight colour difference despite having the most similar fibre properties of all the pairs used in this series of experiments. The results seen were inconsistent both with the primary fabric dyeing (Figure 4.2) and within the replicated sample pairs (Figure 4.4). It was thought that this variation could be due to the instrumental error level within the colourimeter being greater than the very small colour difference between the samples.



a. Plot of lightness (L^*) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.



b. Plot of red-green ($+a^*/-a^*$) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.

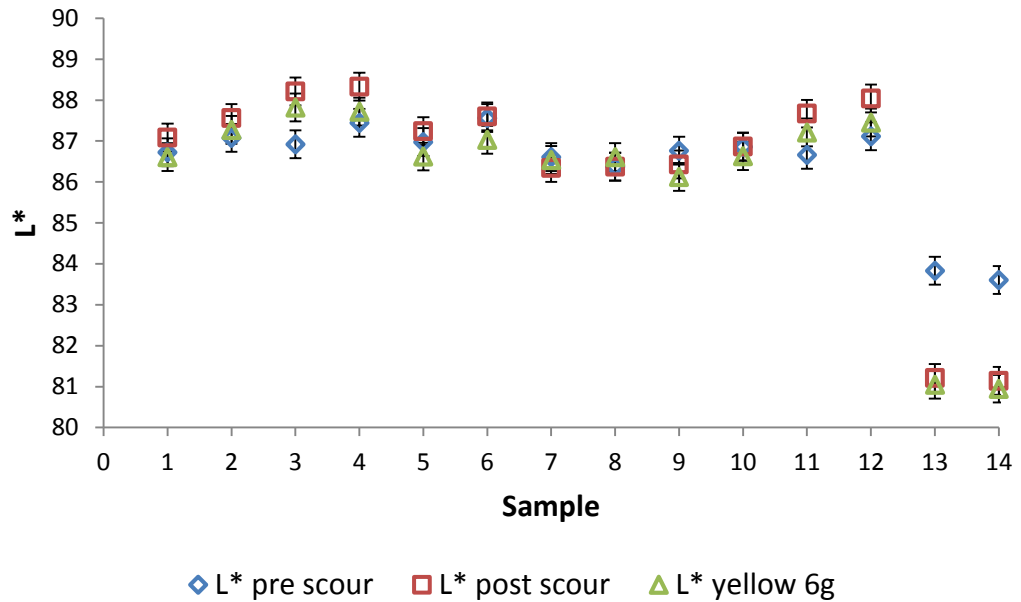


c. Plot of yellow-blue (+b*/-b*) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.

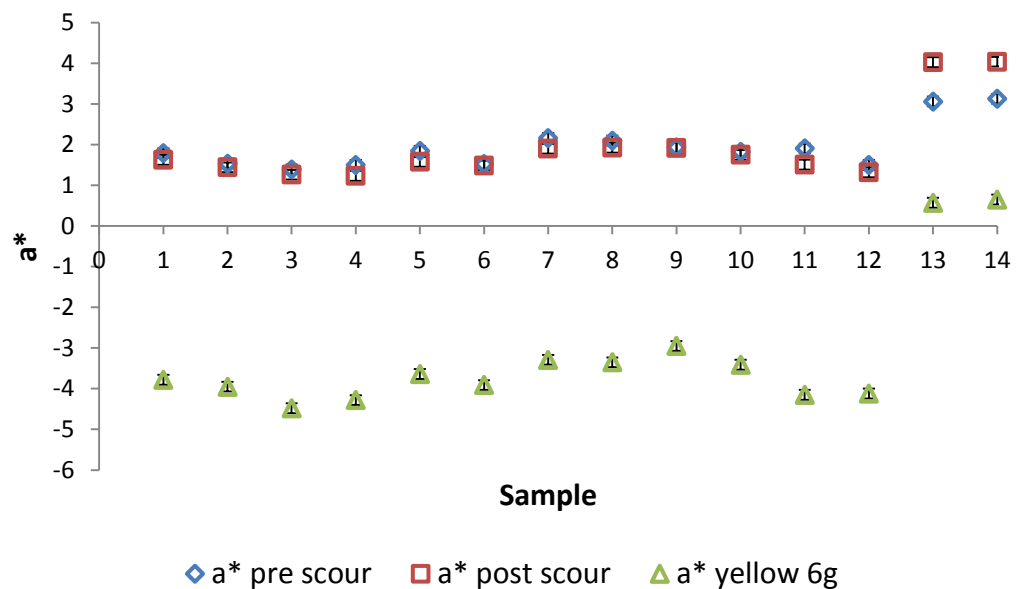
Figure 4.6: Cotton fabric samples plotted against colour parameters L* (a.), a* (b.) and b* (c.) to identify dyeability trends and base colour differences.

As the results of both this and the previous secondary dyeing trial were inconsistent with the initial fabric dyeing trial, the level of error within the colour measurement was examined. The data from the first experiment was revisited as these measurements showed the largest variation. Error bars were applied to the plots of L*, a* and b* on the basis of the raw sample colour as replicate values were only recorded for these samples (Figure 4.7). The standard deviation was calculated for the five measures of each sample. The average standard deviation was then determined and error bars applied at two standard deviations. Assuming the samples are normally distributed, 95% of values would be expected to lie within this range. While there was little to no overlapping of error bars seen in a* or b*, there was considerable overlap seen in the L*. This may explain why the colour of the dyed

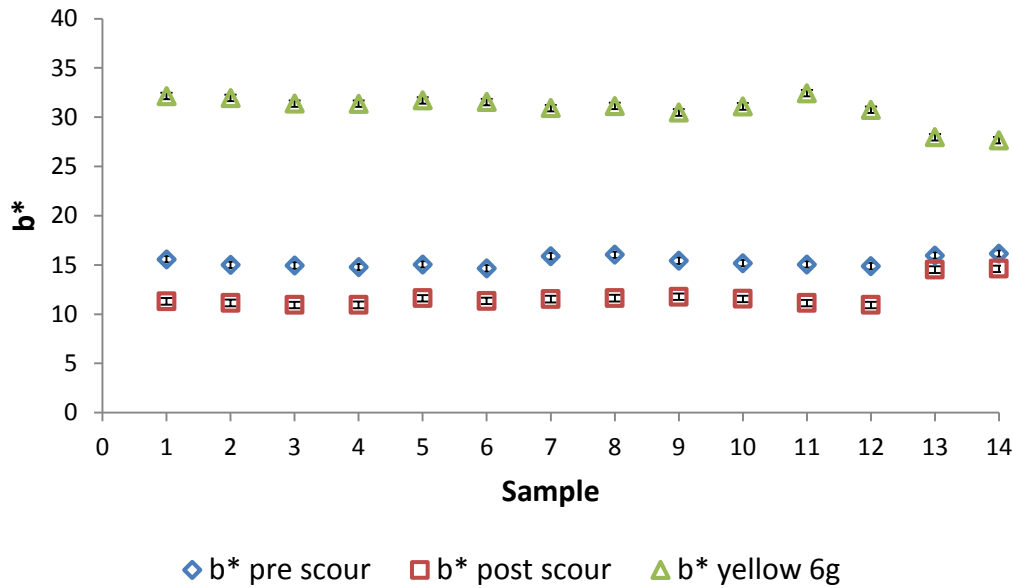
and scoured samples in relation to the base colour is very similar for a^* and b^* , but there is variation in the L^* values, with some dyed samples appearing lighter and some darker than the raw fabric.



a. Plot of lightness (L^*) against the cotton fabric samples pre scour, post scour, and dyed with Procion Yellow HE-6G.



b. Plot of red-green ($+a^*/-a^*$) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.



c. Plot of yellow-blue (+b*/-b*) against the cotton fabric samples prescour, post scour, and dyed with Procion Yellow HE-6G.

Figure 4.7: Cotton fabric samples plotted against colour parameters L* (a.), a* (b.) and b* (c.) with error bars applied to assess the level of instrumental error.

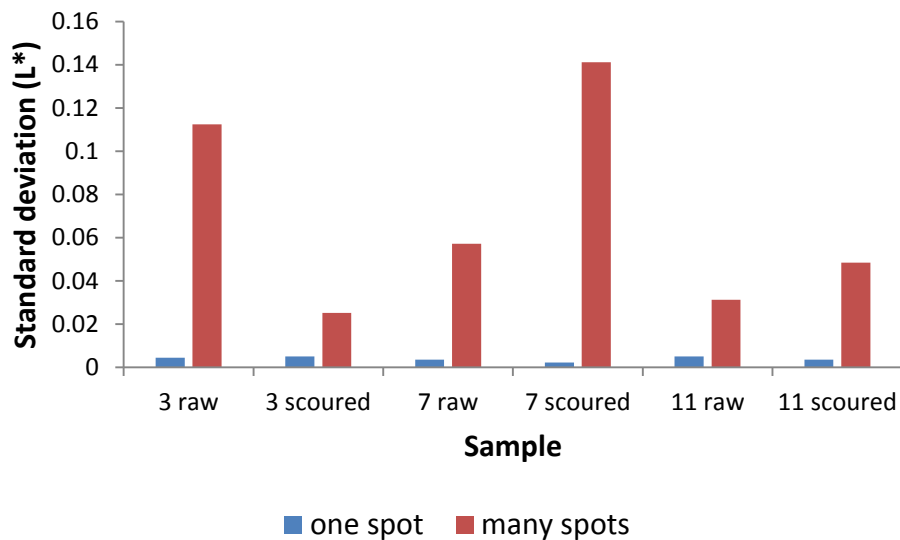
A test was designed to more specifically determine the level of instrumental error in the colourimeter. Colour measurement was performed on samples from 3 cotton varieties (samples 3, 7, and 11) as both raw and scoured fabrics. Each sample was measured (single readings) 20 times in one spot, and 20 times in multiple spots on the fabric.

For each set of measurements the average and standard deviation was taken (Table 4.5 and Figure 4.8). For the L* parameter the measurements taken in a single spot gave an average standard deviation of 0.004 whereas the average standard deviation for the samples measured in multiple spots was 0.069. Similar results were seen for the a* and b* parameters in the measurements taken at a single spot, though in multiple spots a* had a standard deviation of 0.037 and b* had the highest standard deviation of 0.12. Assuming the measurements have a normal distribution,

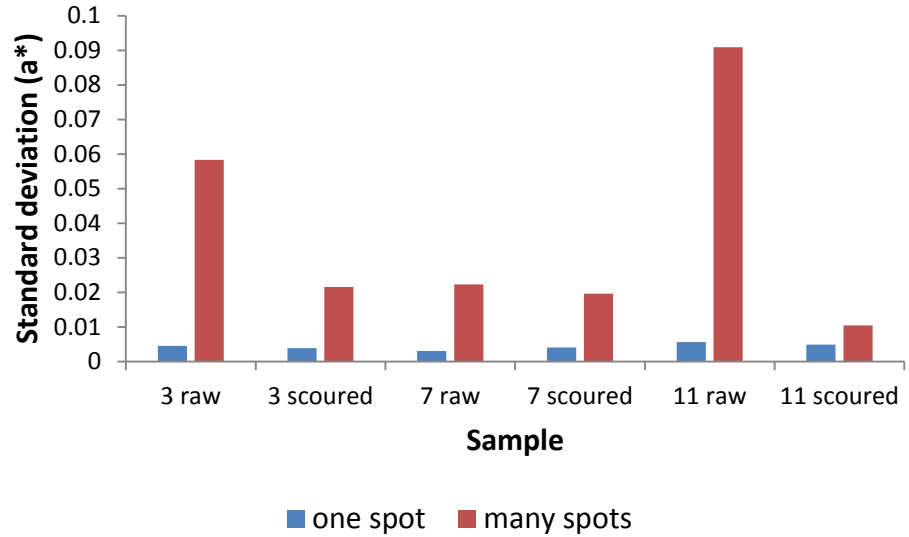
99.7% of the data would be expected to fall within three standard deviations of the mean. This implies that for L* differences as large as 0.21 may be observed in either direction from the mean. For a* differences up to 0.11 may be seen, and for b* up to 0.36. The standard deviation values were used to calculate the standard error of the mean for each parameter over the usual three readings taken per sample, giving values of 0.04 for L*, 0.02 for a*, and 0.07 for b*. Although these numbers are small they are large enough to influence the calculations of ΔE values, especially when dealing with very slight colour differences. As the colour differences seen in this work were so small, the error in the colorimeter was often equal to or greater than the colour difference seen. From these results the only significant colour differences seen in this work were between the Upland and Pima samples. Based on this it is evident that variety within a cotton species has little to no effect on dyeability when samples are grown in the one location.

Table 4.5: The average and standard deviation values for the raw and scoured samples used to calculate the standard error of means.

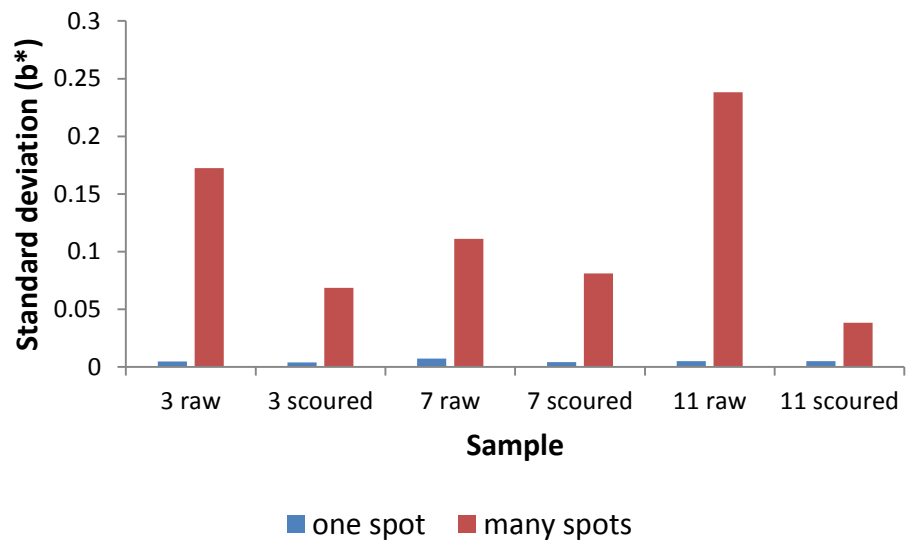
	L* one spot	L* many spots	a* one spot	a* many spots	b* one spot	b* many spots
3 raw	87.42	87.35	1.44	1.53	14.83	14.96
3 scoured	89.28	89.27	0.69	0.71	9.80	9.77
7 raw	86.74	86.68	2.09	2.12	15.69	15.78
7 scoured	88.24	88.40	1.18	1.15	10.91	10.79
11 raw	87.50	87.47	1.54	1.60	14.29	14.40
11 scoured	88.86	88.90	0.83	0.82	10.17	10.18
Average SD	0.004	0.069	0.004	0.037	0.005	0.118
SE of mean	0.002	0.039	0.003	0.021	0.003	0.068



- a. The standard deviation in L* values for samples measured in one spot vs samples measured in many spots.



b. The standard deviation in a^* values for samples measured in one spot vs samples measured in many spots.



c. The standard deviation in b^* values for samples measured in one spot vs samples measured in many spots.

Figure 4.8: A comparison of the L^* (a.), a^* (b.), and b^* (c.) values measured in one spot and measured in many spots.

4.3.3 Conclusion

Six cotton samples from three cotton varieties were selected for further dyeing experiments as they represented the sample pairs showing the most and least difference in dyeability. Minimal significant difference in dye uptake could be observed with the naked eye. The measurements of colour obtained were inconsistent with either of the previous two dyeings. A test was conducted to determine the level of error within the colorimeter. Although the level of instrumental error was small, it was sufficient to influence calculation of ΔE values. As the colour differences seen between the Upland samples were very small, the error in the colorimeter was often equal to or greater than the observed colour difference. As the only significant colour differences seen within this chapter were between the Upland and Pima samples, it is apparent that variety within a cotton species has little to no effect on dyeability when samples are grown in a single location.

4.5 Overall Conclusion

A dyeing of 14 cotton samples of 7 different cotton varieties showed minimal significant shade variation within the Upland cotton samples, however there were obvious shade differences between the Upland and Pima varieties.

Some samples from this initial dyeing were chosen for further dyeings as they demonstrated slight differences in dyeability. Five samples of three cotton varieties showed variation in lightness in relation to the raw fabric base colour which could not be replicated. A further six cotton samples were selected as being the three cotton variety pairs showing the most and least difference in dyeability. The colour measurements taken were inconsistent with either of the previous two dyeings.

Due to the inconsistency in results between the initial dyeing and the smaller secondary dyeings a test was performed to determine the level of instrumental error in the colourimeter. The level of instrumental error was found to be equal to or greater than the colour difference seen within many of the Upland samples, making it difficult to state whether the level of colour difference was statistically significant.

Overall the observed variation in dyeability was attributed to base colour differences as it was predominantly consistent with that seen in both the raw and scoured fabric colours. Due to the relationship seeming to occur between dyed colour and raw fabric colour no further analysis of the structure or surface chemistry was performed. As the cotton varieties were all grown in the one location the observed results suggest that varietal difference within a species has little to no effect on dye uptake.

5. Growth Location

Cotton is produced in approximately 100 countries worldwide and is grown under a diverse range of climates accordingly. Regions such as Asia and South America can be quite humid whereas conditions in the USA and Australia tend to be drier.

Additionally, growing conditions within a location can vary annually.

The effects of growing conditions on fibre properties have been well studied, and environmental factors found to be a major source of variation in terms of cotton fibre properties. While many of these fibre properties do influence dye uptake, little of this work has extended into cotton dyeability. Further, little work has been done directly comparing the dyeability of samples from different growth locations and climates. Growth environment is a major factor in the colour of both raw and dyed cotton. Higher growth temperatures have been linked to increased whiteness and decreased yellowness in raw fibre (Bradow and Bauer, 1998b). Australian cottons have been reported to be less lustrous than some African cottons, resulting in a duller appearance of dyed fabrics (Gordon et al., 2004). Lustre is influenced by the cross-sectional shape of the cotton fibre, which is in turn related to maturity. Maturity has been shown to be accelerated by higher temperatures, however reduced boll sizes and boll shedding can also result (Singh et al., 2007). Water stress may also cause boll shedding, as well as reduced micronaire (Pettigrew, 2001). Both heat and water stress can also alter the content and composition of cotton wax, which in turn may affect dyeability as wax must be removed prior to dyeing (Gordon et al., 2002).

This chapter details the experimental methodology used in studies of the effect of cotton growth location on dyeability. The work initially follows on from Chapter 4 with further examination of dyeing behaviour of cotton fabrics made from fibres grown in one location in Section 5.1. This work extends to a comparison of

dyeing behaviour between cotton fabrics made from fibres grown in one location and grown in different locations in Section 5.2. This is followed by a more in depth analysis of the dyeability of 10 cotton samples originating from three different countries with vastly different climates in Section 5.3. In all dyeings, sample sets were selected due to their similar maturity ranges.

5.1 Small Scale Dyeing of a Banded Fabric Prepared from Australian Cotton

In the previous fabric dyeing trials (see Chapter 4) no significant colour difference could be observed with the naked eye, and instrumental measures of colour difference were inconclusive. It was thought that any colour difference was less than or equal to instrumental error. A ΔE value of 1.0 or greater may be observable to the human eye. While colour differences greater than this value were recorded instrumentally in the previous chapter, no difference could be seen visually within the Upland samples. This could indicate that the results were affected by colourimetric error. Stripe knitted samples, where different cotton samples are directly adjacent to each other in a fabric, can allow the eye to distinguish colour differences far better than between samples placed on top of each other as effects such as shadows or layer change which may obscure differences are eliminated. This dyeing trial was designed to see if a difference in dyeability could be observed with the naked eye within the same series of cotton samples used in the previous chapter when combined into a single fabric. The fabric was to be knitted with bands of each cotton variety, allowing an easy visual comparison of colour between samples. Differential dye uptake between fabric samples with similar HVITM properties could serve as an initial indication of other structural and chemical differences affecting dyeability. As the cotton samples were of different varieties but came from a single

growth location during one cotton season, examination of varietal effects on dyed appearance of cotton could be done independent of environmental variation.

5.1.1 Experimental Methodology

5.1.1.1 Sample Selection and Preparation

Cotton yarn samples were selected on the basis of similar HVI™ properties, particularly maturity and micronaire due to their proven influence on dyeability. Single knit jersey fabric was knitted on a Lawson Hemphill Fibre Analysis Knitter with a 24 gauge cylinder (Lawson-Hemphill, USA) using 20 tex yarns, both combed and carded, from the 7 cotton varieties used in the previous fabric dyeing trials detailed in Chapter 4 (see Table 4.1 for cotton fibre properties, see Long et al. (2013 pp. 752–753) for details of yarn manufacture). A total of 27 yarns was used, as one sample was not available in the 20 tex yarn (sample 23). The fabric was knitted in a 10” diameter sock with 4.0 cm bands of each yarn. The fabric had a cover factor of 1.32. For each dyeing 12.0 cm x 4.0 cm pieces of fabric were cut, giving three cottons per sample piece, weighing on average 0.6 g. This size allowed side by side comparison between samples but prevented tangling of the fabric which may have occurred with longer samples.

5.1.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. The dyes used were Procion Orange H-2R, Procion Blue HE-RD, and Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). The pots of the dyeing machine were packed with one set of either the combed or carded yarn fabric samples, totalling around 4.0 g of fabric. The dyebath was prepared to an initial volume of 150 ml, giving approximately a 38:1 liquor ratio.

5.1.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3, however the small (10.0 mm x 7.5 mm) aperture was used. Samples were measured in a single layer on both sides of the fabric. Colour was measured only after dyeing.

5.1.2 Results and Discussion

The cotton samples were scoured under alkaline conditions to remove the surface wax layer prior to dyeing. There was little to no difference visible with the naked eye within the Upland samples both unscoured and scoured. The same differences observed previously between the Upland and Pima varieties were again evident with pronounced differences after scouring with the Pima variety developing orange tones.

Three dyes (Procion Orange H-2R, Procion Blue HE-RD, and Procion Yellow HE-6G) were chosen on the basis of performance in previous dyeings, and the molecular structure of the dyes (see Figure 4.1). The dyes represented a range of molecular sizes, with varying numbers of reactive sites and solubilizing groups. Each dye gave even coverage, however little to no shade variation could be seen visually within the Upland cottons. There was a noticeable difference between the Upland and Pima varieties. As observed in past dyeings the dye structure again seemed to have little effect on dyeability.

The colour of the dyed fabric samples was measured as in the previous trials. Multiple readings were taken for many of the cotton varieties as the fabric was cut in an overlapping manner. Table 5.1 shows an example of the typical results seen for half of the samples dyed with the yellow dye. The colourimetric measurements indicated large variations from one fibre sample to another, which is contrary to what

could be seen with the naked eye. No differences were observed visually within the fabric strips, with the exception of the colour difference between the Upland and Pima varieties. The size of the dyed samples limited folding of the fabric which gives a thicker sample, preventing measurement of the backing material through the fabric. This combined with the small measurement aperture size would have contributed to the large variance between visual and colorimetry results. Due to large variation seen within the measurements no conclusive information could be drawn from them.

Table 5.1: ΔE values calculated from sample 1 for the banded fabric dyed with Procion Yellow HE-6G.

Sample	ΔE
2	1.163
3a	1.207
3b	2.721
4	4.269
5a	2.020
5b	3.888
6	4.654
7a	2.831
7b	2.705
8	3.000
9a	3.292
9b	3.930
10	3.701
11a	3.958
11b	1.118
12a	0.998
12b	3.221
13a	4.615
13b	4.984
14	5.434

5.1.3 Conclusion

Dyeing of a fabric with knitted bands of the same yarns used in the varietal studies (Chapter 4) showed no visually obvious shade variation between the Upland cotton samples. Three dyestuffs were used, representing a range of molecular structures, yet there was no notable differences in dyeability between them. There was a notable difference between the Upland and the Pima cotton varieties. Instrumental analysis of the fabric colour was different to that observed visually however colourimetry results were compromised due to sample and measurement aperture size.

5.2 Small Scale Dyeing of a Banded Fabric Prepared from Cotton of Multiple Origins

In previous dyeing experiments using small fabric samples produced from individual cotton varieties no significant differences in dyed appearance could be observed visually. Additionally, instrumental measures of colour difference were found to give inconclusive results as the colour difference was less than or equal to instrumental error.

A further dyeing trial was designed to see if a difference in dyeability within the same series of cotton samples could be observed with the naked eye when combined into one fabric. In the previous experiment, dyeing of a banded fabric containing 7 cotton varieties grown in a single location showed no significant visible or instrumentally measured colour differences. The exception to this was the colour difference observed between the Upland and Pima cotton samples, which was attributed to fabric base colour (Section 5.1).

A second dyeing experiment was designed using the same varieties along with additional cotton samples from multiple growth origins. These additional yarns

were made from fibre selected from 10 bales out of a laydown in a commercial cotton mill. A bale laydown is an assemblage of cotton bales to be combined throughout mill processing. The bales are selected on the basis similar HVI™ properties with the aim to maintain consistent fibre quality for the lowest possible cost (Hake et al., 1996). Fibre type and origin may vary within the laydown. Of the 10 cotton samples used in this experiment, three of the samples came from the USA, five were from Australia, and two were from China. These proportions (30:50:20) reflect the typical ratios of cotton from each growth environment used in this particular mill's laydowns. The US and Australian cottons were Upland varieties while the Chinese yarns were Pima cotton. As these samples were of mixed origin and variety it was hoped that a greater dyeability difference may be observed than was seen with varietal differences only. As the samples within the fabric were of different varieties and of mixed origins, it allowed examination of the effects of variety and growth location on dyeability, whereas the previous work only looked at varietal differences. Differential dye uptake between fabric samples with similar HVI™ properties could serve as an initial indication of other structural and chemical differences affecting dyeability.

5.2.1 Experimental Methodology

5.2.1.1 Sample Selection and Preparation

Cotton yarn samples were selected on the basis of similar HVI™ properties, particularly maturity and micronaire due to their proven influence on dyeability. Single knit jersey fabric was knitted on a Lawson Hemphill Fibre Analysis Knitter with a 28 gauge cylinder (Lawson-Hemphill, USA) using 12 tex yarns of the same 14 cotton varieties used in Section 5.1 (see Table 4.1 for cotton fibre properties, see Long et al. (2013 pp. 752–753) for details of yarn manufacture), along with an

additional 20 yarns (48 yarns in total). These samples were 12 tex combed ring-spun yarns prepared at CSIRO on industrial scale spinning equipment from 10 cotton varieties which originated from 3 different countries. The two yarn sets were both 50 count but had different twist factors (90 and 120). Of the 10 cotton samples, three came from US bales (Californian San Joaquin Valley Upland (USA SJV)), five were from Australia (Australian long staple Upland (AUS ALS)) and two were from Western China (Xinjiang extra-long staple (XJ ELS)). HVI™ testing (completed prior to this project at Auscott Classing Offices, Artarmon Sydney NSW following standardized ASTM and ITMF procedures) showed the 10 new varieties to range in micronaire from 3.99–4.59 (Table 5.2). Measurements of maturity, fineness, and micronaire were also obtained from the yarns with a twist factor of 90 using a Cottonscope (Table 5.3), measured as per the manufacturer's instructions, designed to stimulate polarised light microscopy (PLM) Standard Test Method (ASTM D1442, 2000) (Cottonscope Pty Ltd, 2016).

Table 5.2: HVI™ data of the fabric sample set.

Sample	Variety	Origin	Strength (gf/tex)	Micronaire	Maturity
15 & 25	SJV	USA	32.1	4.18	0.85
16 & 26	SJV	USA	34.8	3.99	0.84
17 & 27	SJV	USA	34.6	4.14	0.85
18 & 28	ALS	Australia	31.6	4.17	0.86
19 & 29	ALS	Australia	30.5	4.31	0.86
20 & 30	ALS	Australia	34.3	4.32	0.86
21 & 31	ALS	Australia	32.3	4.29	0.86
22 & 32	ALS	Australia	31.3	4.47	0.87
23 & 33	XJ ELS	China	47.2	4.59	0.88
24 & 34	XJ ELS	China	41.6	4.30	0.87

Table 5.3: Cottonscope data of the fabric sample set.

Sample	Variety	Origin	Micronaire	Maturity	Fineness
15	SJV	USA	4.86	0.88	186
16	SJV	USA	4.99	0.89	182
17	SJV	USA	5.09	0.90	188
18	ALS	Australia	4.66	0.87	193
19	ALS	Australia	4.75	0.87	194
20	ALS	Australia	4.98	0.89	194
21	ALS	Australia	4.8	0.88	189
22	ALS	Australia	4.97	0.89	193
23	XJ ELS	China	4.78	0.88	172
24	XJ ELS	China	4.83	0.88	173

The yarns had previously been tested on bobbins for tenacity, evenness, hairiness and imperfections (Table 5.4) (Yang and Gordon, 2016). The yarn characteristics highlight the differences in processing performance between Upland and Pima cotton varieties. Pima cotton such as the Chinese samples (23–24) is typically longer, stronger, and finer than Upland cotton, resulting in yarns that are more even, less hairy, and stronger. The fabric was knitted in a 10” diameter sock with 4.0 cm bands of each yarn. The fabric had a cover factor of 1.2. For each dyeing 12.0 cm x 4.0 cm pieces of fabric were cut, giving 3 cottons per sample piece, weighing on average 0.6 g.

Table 5.4: Properties of the yarns from various origins.

Sample	Count	Tenacity	Yarn irregularity	Hairiness	Thin places	Thick places	Neps
15	10.08	17.34	18.54	3.80	191	498	619
16	10.36	16.91	18.42	3.82	186	499	695
17	10.41	16.09	18.87	3.86	219	608	842
18	10.32	16.63	18.89	3.90	221	587	754
19	10.32	16.50	18.58	3.87	199	548	705
20	10.63	14.98	18.54	3.90	192	540	654
21	10.34	15.47	18.41	3.86	191	519	655
22	10.49	15.42	18.42	3.78	164	530	687
23	10.63	22.23	16.04	3.34	24	327	765
24	10.79	21.93	16.36	3.54	37	363	773

5.2.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. The dyes used were

Procion Orange H-2R, Procion Blue HE-RD, and Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). The pots of the dyeing machine were packed with one set of fabric pieces using the original cotton samples and one of the new sets with multiple growth origins, totalling around 7.6 g of fabric. The dyebath was prepared to an initial volume of 150 ml, giving approximately a 20:1 liquor ratio.

5.2.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3, however the small (10.0 mm x 7.5 mm) aperture was used. Samples were measured in both a single layer, and folded in half once. Colour was measured only after dyeing.

5.2.2 Results and Discussion

The cotton samples were scoured under alkaline conditions prior to dyeing. There was little to no difference visible with the naked eye within the samples both unscoured and scoured. An exception to this was the Australian Pima cotton varieties which showed an obvious difference in colour compared to the rest of the samples that became even more pronounced after scouring with the Pima variety developing orange tones. It is noteworthy that the same difference was not observed in the Chinese extra-long staple samples, which are also Pima cotton varieties. A possible explanation for this increase in redness is chemical reaction between the scouring solution and a component in the fibre surface chemistry of the Australian samples that is not present in the Chinese Pima samples. Differences in surface chemistry are often associated with environmental factors, such as soil nutrition and water availability during growth, rather than genotype. However the Australian Upland cottons grown in the same environment did not show the same colour difference, so in this case the difference may be due to variety. Alternatively, the removal of wax and other chemicals from the surface by scouring may have exposed chromophores or metal ions causing discolouration from further inside the fibre. Calcium and magnesium ions are thought to contribute to cotton yellowness (Millington et al., 2015). These ions have been associated with pectin, yet the majority of pectins are removed during scouring and studies have shown significant quantities of calcium

and magnesium ions remaining on the fibre (Gamble, 2009). These ions also have the potential to affect dye uptake as they can form insoluble complexes with sulfonate groups present in many dyes (Gamble, 2009). The addition of a sequesterant to the scouring solution may prevent the development of redness by binding to the metals ions responsible.

Dyeing was performed using Procion Orange H-2R, Procion Blue HE-RD, and Procion Yellow HE-6G. Each dye gave even coverage, however little to no shade variation could be seen visually within the cotton samples. An exception to this was again a noticeable difference between the Australian Pima varieties and the rest of the samples. Dye structure seemed to have little effect on dyeability.

The colour of the dyed fabric samples was measured as in the previous trials, however the readings were inaccurate and no conclusive information could be drawn from them. While there was almost no difference seen between the samples with the naked eye, the calculated ΔE values suggest obvious colour differences between many of the samples. As the fabric samples were cut in an overlapping manner duplicate measurements were taken for many samples, yielding vastly different results for the same cotton variety. An example of the typical results seen is shown in Table 5.5 for half of the samples, 14 of the original varieties and 10 of the additional yarns, dyed with the yellow dye. Although the instrumental error discussed in Section 4.3 could be a contributing factor, the problems seen in this trial were predominantly due to the small scale. Because of the small sample size reads were taken using the smaller aperture (10.0 mm x 7.5 mm), giving less accurate figures due to a smaller surface area being measured. The samples could also not be folded into four layers as the larger fabric samples were, blocking out less residual

background light. Colour was measured on the front side twice, on both the front and back sides of the fabric, and folded in half.

Table 5.5: ΔE values calculated from sample 1 for the banded fabric dyed with Procion Yellow HE-6G, measured by three different methods.

Sample	ΔE Front	ΔE Front and back	ΔE Folded
2	1.644	2.851	2.892
3a	3.058	3.168	0.878
3b	0.667	0.658	2.585
4	1.578	1.375	2.397
5a	4.653	4.149	0.401
5b	0.835	0.540	0.885
6	2.082	2.860	2.891
7a	0.834	1.851	0.337
7b	1.322	0.633	1.491
8	3.496	3.418	1.325
9a	5.210	0.964	1.890
9b	2.729	1.025	2.127
10	1.686	2.545	1.176
11a	1.378	1.029	2.067
11b	3.024	0.971	2.605
12	0.865	0.737	0.855
13a	3.741	3.692	5.121
13b	3.134	3.528	5.443

14	5.436	4.785	6.293
15a	1.360	1.554	0.588
15b	1.596	0.751	0.700
16	1.177	1.388	3.355
17a	0.740	1.030	0.602
17b	0.922	0.575	0.441
18	0.852	2.148	2.734
19a	1.937	1.856	1.368
19b	3.521	0.960	0.556
20	1.062	1.648	2.385
21a	2.588	2.277	1.753
21b	1.958	2.167	0.824
22	2.902	2.516	3.093
23a	1.822	2.126	1.923
23b	2.822	2.381	1.765
24	2.319	1.300	2.594

5.2.3 Conclusion

Dyeing of a fabric with knitted bands of cotton yarns from both a single growth environment and multiple growth locations for the most part showed no obvious shade variation between the samples. The exception to this was a notable colour difference between the Australian Pima cotton varieties and the rest of the samples, which was not seen in the Chinese Pima cotton varieties used. Three dyestuffs were used, representing a range of molecular structures, yet there was no notable differences in dyeability between them. Instrumental analysis of the fabric colour

was inconclusive as the small scale of the experiment caused inaccuracies in measurement.

5.3 Large Scale Banded Fabric Dyeing Trial

In the varietal study performed in Chapter 4 no significant colour difference between the samples could be observed visually, nor instrumentally as the colour difference was less than or equal to the level of instrumental error. This work was built on in Sections 5.1 and 5.2 with studies conducted to determine whether colour difference could be more readily identifiable by knitting wide bands of multiple cotton yarns into a single fabric, giving a direct visual comparison. On a laboratory scale this work was found to have many logistical issues and the results were inconclusive. A larger scale trial was designed, using an industrial dyeing machine. This trial was to focus on the set of 10 cotton yarns with different growth origins used in Section 5.2. As the cotton yarns were of different varieties and from a range of growth locations, examination of the effects of both genotype and environment on dyeability was possible. Additionally, three dyestuffs of various size were selected from those used previously in this work to determine if the molecular structure of the dye affects uptake. Differential dye uptake between cotton varieties with similar fibre properties could serve as an indication of structural and chemical differences causing dyeability variation.

5.3.1 Experimental Methodology

5.3.1.1 Sample Selection and Preparation

Cotton yarn samples were selected on the basis of similar HVI™ properties, particularly maturity and micronaire, and growth environment as it was hoped that a greater dyeability difference may be observed than was seen with varietal differences only. Single knit jersey fabric was knitted on a Lawson Hemphill Fibre Analysis

Knitter with a 28 gauge cylinder (Lawson-Hemphill, USA) using 10 of the 12 tex ring-spun yarn samples from various origins (Australian long staple Upland (AUS ALS), 5 samples), the USA (Californian San Joaquin Valley Upland (USA SJV), 3 samples), and China (Xinjiang extra-long staple (XJ ELS), 2 samples) used in the smaller scale study (samples 15–24, see Tables 5.1-5.3). The yarns were 50 count with a twist factor of 90. The fabric was knitted in a 10” diameter sock with 17.0–18.0 cm bands of each yarn. The fabric had a cover factor of 1.2. The different yarns were separated by bands of pink synthetic yarn. Although not directly touching, the larger size of the bands still allowed sufficient visual comparison and made colourimetry possible.

5.3.1.2 Scouring and Dyeing

Scouring and dyeing were done as a single continuous process using a 200 L capacity winch dyeing machine with a steam coil and Sedo ISO controller (JC Brown, Geelong). Scouring was performed in 30 L of a solution of 5.0 g/L NaOH (Sigma Aldrich, Australia), 0.5 g/L Albaflow FFW (Huntsman, Australia), 4.0 g/L Croscolor SDCF (Eurodye-CTC, Belgium) and 2.0 g/L Irgasol CO New (Huntsman, Australia). As in the previous work sodium hydroxide was used as the alkali. The detergent used was Croscolor SDCF. Albaflow FFW and Irgasol CO New were added as a wetting agent and sequesterant respectively. The samples were scoured for 30 mins at 100 °C, followed by a warm rinse.

Dyeing was carried out using 0.1% w/w reactive dyes (Procion Orange H-2R, Procion Blue HE-RD, Procion Yellow HE-6G), as detailed in Section 2.2. Due to the small fabric sample size for the industrial scale machine, dyeing was carried out at a 300:1 liquor ratio. The bath was held at 70 °C for 45 mins after the addition of soda

ash. The dyed samples were rinsed twice in cold water, dried, and conditioned for 24 hrs prior to colour measurement.

5.3.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. As the fabric was in a continuous sock it was only folded in half once. Colour was measured before scouring and after dyeing.

5.3.2 Results and discussion

Despite being a large increase in scale from the previous work, this experiment was very small in terms of an industrial scale so it was required that the samples be attached to a sock of fabric to allow proper dyebath rotation. This fabric was a synthetic so it would not take up any of the cellulose-specific reactive dye. Scouring and dyeing were performed as a continuous process to minimise damage to the fabric from attaching and reattaching the fabric, and to avoid lengthy drying times between steps.

Scouring was done under alkaline conditions, using a different scouring recipe from the previous small scale dyeing due to the greater quantities of alkalis and detergents required for the larger scale.

It was of interest to determine if dye structure may also influence dyeability, and if so whether dye uptake changes depending on fibre properties. Three dyes were chosen based on performance in previous dyeings and molecular structure, looking at features such as size, number of solubilising groups, and number of reactive sites. The dyes used were Procion Orange H-2R (small, 1 reactive site, 3 solubilising groups), Procion Blue HE-RD (larger, 2 reactive sites, 5 solubilising groups), and

Procion Yellow HE-6G (largest, 6 reactive sites, 6 solubilising groups), (see figure 4.1).

Due to a combination of low dye concentration and very high liquor ratio the resulting dyed fabrics were very pale. As dyeing at higher concentrations can mask subtle shade variations as seen in the previous experiments, the dyeing was performed at a 0.1% concentration. The fabric pieces were considerably smaller than the intended size for the industrial-scale dyeing machine, resulting in a very high 300:1 liquor ratio. Visual examination of the dyed fabrics showed subtle differences in dyed colour visible with the naked eye which were most obvious in the blue fabric.

Colour was measured on both the raw and dyed fabrics, however the colour of the scoured fabric could not be measured due to the continuous process of scouring and dyeing. Measurements were taken from the average of 3 reads for each sample. These values were used to calculate ΔE values, using sample 15 as the reference (Table 5.6). Average values of all three samples were used to calculate ΔE values for the raw samples. The greatest levels of variation were seen among the raw samples. Samples 15–17 were all from the USA, with ΔE values indicating some minor colour difference within the raw samples, but no visible differences in dyed appearance between them in all three colours. The Australian samples, 18–22, showed a greater colour difference from the American samples than the Chinese samples, 23–24, in the raw, blue and orange fabrics, but showed a similar level of difference in the yellow fabric. In all fabrics the ΔE values for the Australian samples indicated small to medium colour differences from the American samples, with the greatest difference seen in the blue fabric. Conversely, the ΔE values for the Chinese samples showed no visible difference from the American samples in the blue fabric.

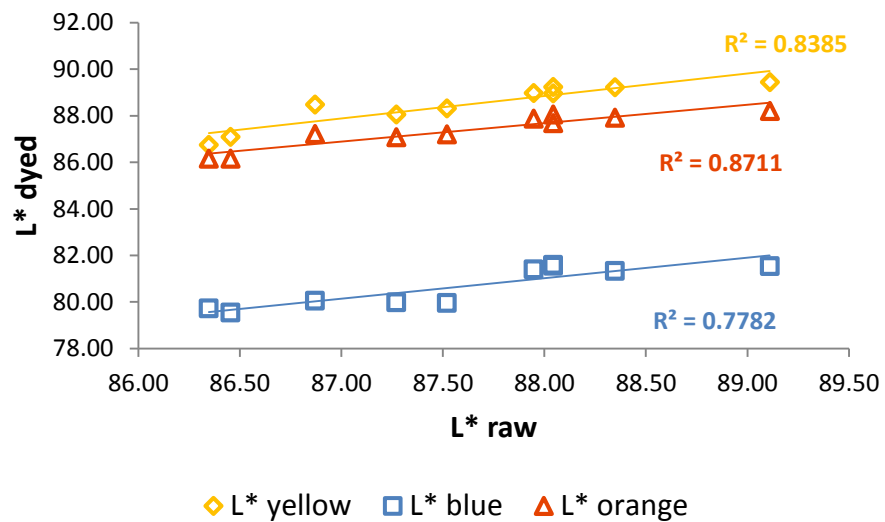
In the yellow and orange fabrics the ΔE values calculated for the Chinese samples indicated small differences only obvious to a trained eye. The fact there were colour differences in the dyed samples despite the samples being controlled for maturity emphasises that although this property is important, there are many other factors having an effect on dyeability. As the dyed colour followed the same colour difference trend as the raw fabric colour, it can be assumed that raw colour is the influencing colour.

Table 5.6: ΔE values calculated from sample 15 for each colour.

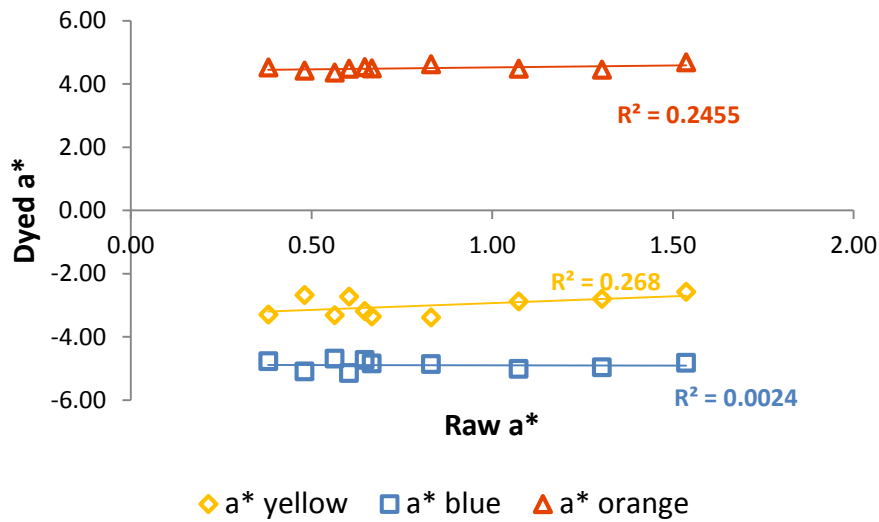
Sample	ΔE Raw	ΔE Blue	ΔE Yellow	ΔE Orange
16	1.293	0.693	0.643	0.369
17	0.862	0.639	0.781	0.466
18	3.368	2.329	1.378	1.757
19	3.445	2.359	1.375	1.826
20	3.791	1.961	1.420	2.059
21	3.895	2.203	1.494	1.729
22	3.532	1.956	1.595	1.428
23	1.744	0.599	1.476	1.082
24	2.351	0.437	1.788	1.103

The colour properties L^* , a^* and b^* for the raw fabric colours were plotted against the values measured for all three dyed colours to determine the strength of the relationship between raw colour and dyed appearance (Fig. 5.1). Linear correlations were seen for L^* and b^* , with no correlation seen between raw a^* and dyed a^* values. This suggests that reflectance and yellowness are more important in predicting the dyed colour of cotton fabrics than redness. Interactions between the

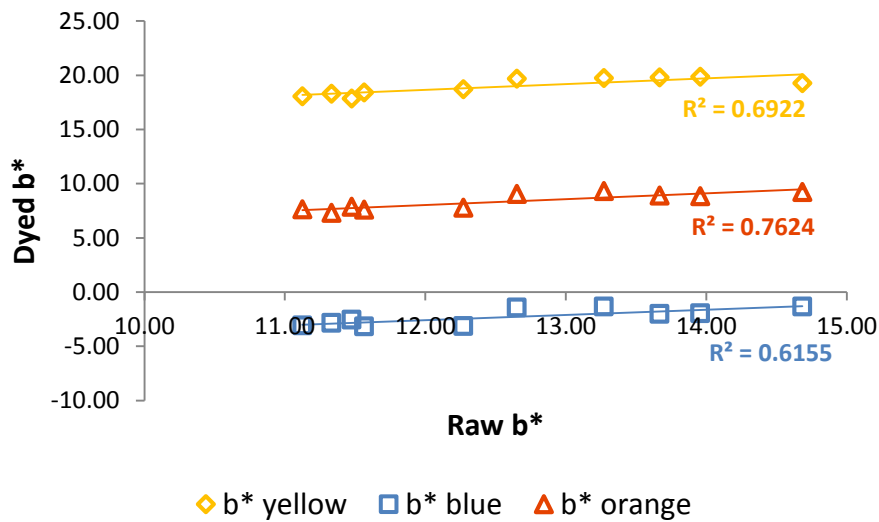
fabric base colour and the colour of the dye seem to have a greater influence on the dyed fabric colour than the chemical structure of the dyestuff itself. The orange and yellow dyes were the smallest and largest dye molecules respectively, yet performed more similarly to each other than the blue dye. The larger colour difference seen between the blue samples may result from interactions between the dye and the natural yellowness of the cotton. The raw colour of the Australian samples was less yellow than that of the US or Chinese samples, with these samples showing a smaller increase in greenness. As orange and yellow are both yellow-based colours it is possible the lower colour difference is due to change in lightness, which is harder to perceive as a colour change than a change in hue.



a. Raw L* values plotted against dyed values



b. Raw b^* values plotted against dyed values.



c. Raw b^* values plotted against dyed values.

Figure 5.1: Raw colour values for L^* , a^* and b^* plotted against dyed colour measurements.

As a difference in dyed appearance was seen despite the samples being controlled for maturity, further analysis was required to determine which other fibre or yarn properties might be having an effect. The colourimetric measurements taken gave evidence that base colour is a major contributor to dyed colour, however there

are many other fibre and yarn properties which could have an effect. A forward stepwise regression ($\alpha = 0.1$) was used to predict the variables most likely to be responsible for the difference in dyed appearance. Stepwise regressions are a particularly useful method for modelling large numbers of variables as they are added to the model individually in order of F ratio values. When the sample size is small but there are a large number of variables it is possible that the model will fit to randomness within the samples, rather than accurately modelling the samples. To prevent this problem the number of predictor variables given by the regression was limited to three. Regression analysis was run for each colour parameter (L^* , a^* and b^*) in all three dye colours.

Analysis was first run using only the HVITM fibre data (selected properties listed in Table 5.2), with the exclusion of moisture content (Table 5.7). A second regression was performed using the HVITM fibre data plus the yarn characteristics (selected properties listed in Table 5.4), excluding tenacity. Both regressions gave the same results suggesting that fibre properties have the greater effect on dyed appearance because yarn properties, such as evenness and hairiness, were not selected when in competition with fibre data. One of the main fibre properties selected by the analysis as causing colour difference was strength although this is not necessarily accurate. The HVITM fibre data shows the Chinese Pima samples to be almost 50% stronger than the Upland samples, which may have caused bias towards strength in the regression (Fig. 5.2). Other predictors selected were also related to the different traits of Upland and Pima cottons such as upper half mean length and short fibre index. Eliminating these properties from consideration left yellowness as the main predictor of dyeability difference. The Australian cotton samples typically displayed a lower yellowness and a higher reflectance compared to the other

samples, which could be due to increased scattering of light by the finer fibres as they have a higher collective surface area (Fig. 5.3). No predictors were shown for a* orange, even when α was increased to 0.25.

Table 5.7: Stepwise regression predictions from HVI™ fibre properties

Property	Predictors	R ²	Co-linearity
L* Orange	Strength	77.42	None
a* Orange	None	-	-
b* Orange	Yellowness, leaf area	46.53, 95.69	Some
L* Blue	Strength, yellowness, leaf area	53.17, 91.54, 96.43	Some
a* Blue	Strength, short fibre index, maturity	66.94, 82.00, 90.82	Some
b* Blue	Strength, yellowness, leaf area	45.88, 68.92, 89.85	None
L* Yellow	Strength	76.07	None
a* Yellow	Yellowness, leaf area	40.77, 87.71	None
b* Yellow	Yellowness, upper half mean length	57.61, 90.04	None

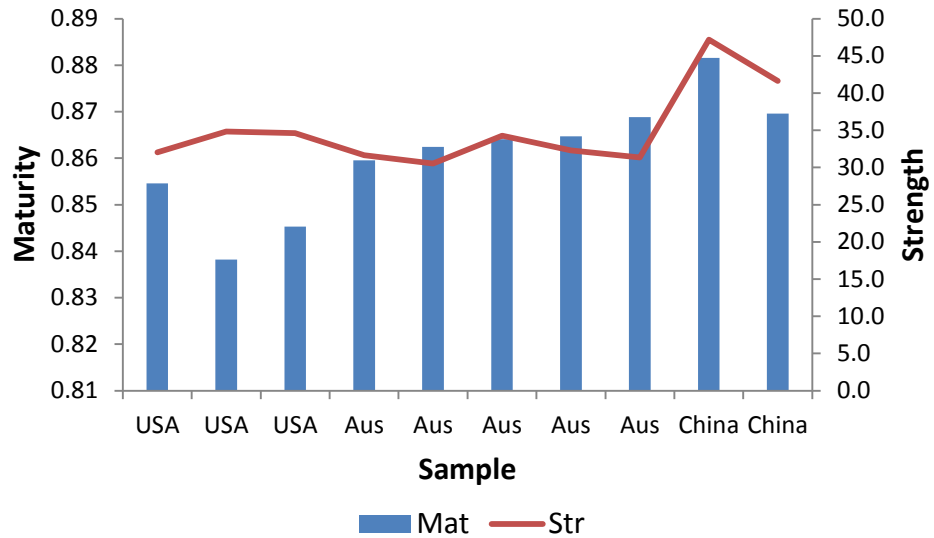


Figure 5.2: HVI™ maturity (Mat) and strength (Str) plotted against the samples.

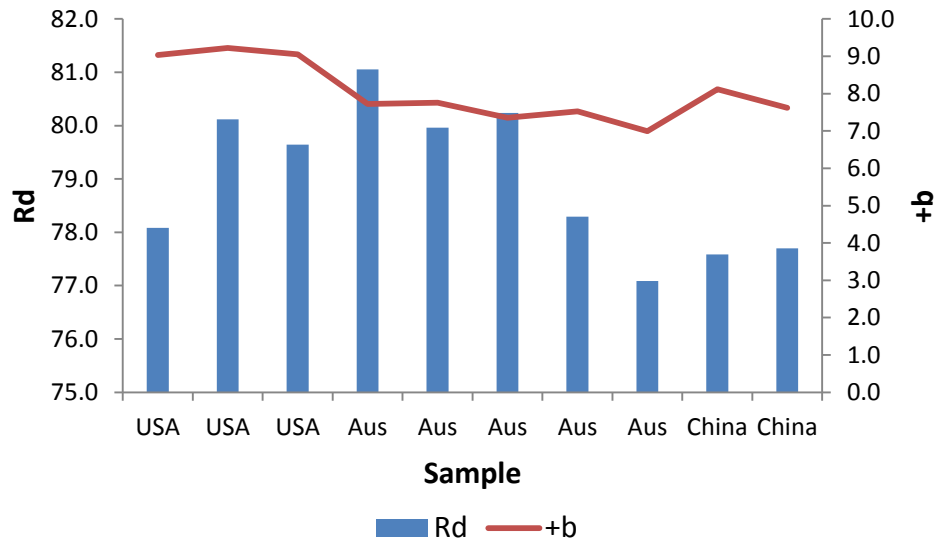


Figure 5.3: Reflectance (Rd) and yellowness (+b) plotted against the samples.

A third regression was run again using the HVI™ fibre data, but with the addition of the maturity and fineness values obtained using the Cottonscope (Table 5.8). The HVI™ system predominantly focuses on measurement of micronaire, length, and strength. Maturity values given by HVI™ testing are provided indirectly as a function of micronaire whereas the Cottonscope instrument is designed for direct measurement of maturity and fineness. Using this data fineness was selected as the

main predictor of dyed appearance. Reflectance and yellowness were also selected as predictors. The selection of reflectance reaffirms that fibre fineness, and therefore surface area, influences dyed appearance. Despite maturity being consistent within the set fineness varied considerably between the samples, with the Australian samples being coarser than the US and Chinese samples (Fig. 5.4). Whilst the maturity values show all samples to have similar ratios of cellulose to fibre size, the larger cross-section of the Australian samples may have an influence on dye uptake and colour appearance. Again no predictors were selected for a^* in the orange dyed samples.

Table 5.8: Stepwise regression predictions from Cottonscope fibre properties

Property	Predictors	R²	Co-linearity
L* Orange	Fineness	91.07	None
a* Orange	None	-	-
b* Orange	Fineness, yellowness, leaf area	95.92	Some
L* Blue	Fineness, maturity, yellowness	96.97	None
a* Blue	Fineness, reflectance	87.32	None
b* Blue	Fineness	67.39	None
L* Yellow	Fineness, maturity	94.62	None
a* Yellow	Fineness, upper half mean length	79.25	Some
b* Yellow	Micronaire, upper half mean length	94.21	Some

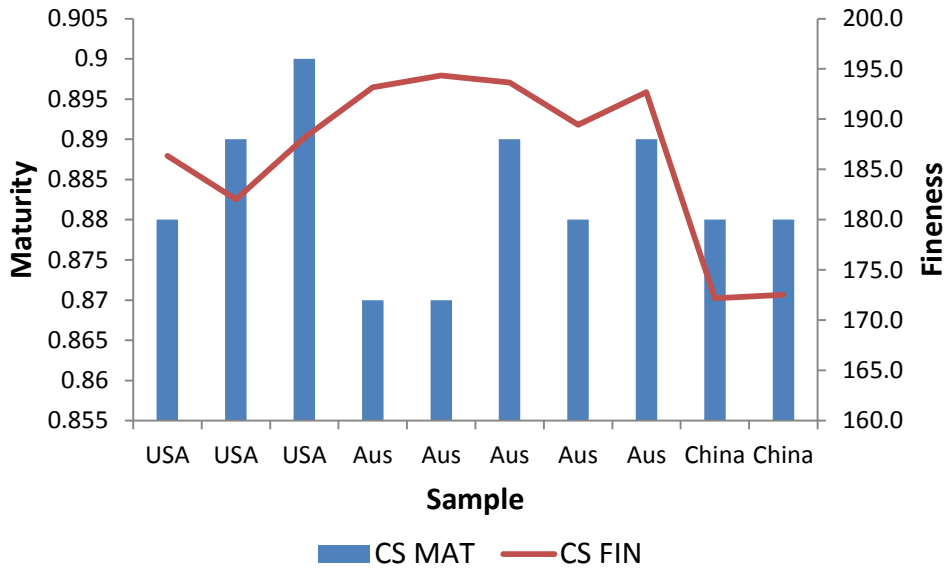


Figure 5.4: Cottonscope maturity (CS MAT) and fineness (CS FIN) plotted against the samples.

From these results it is apparent that any effects of growth location on dyeability are most likely due to environmental influences on fibre properties such as colour, fineness, and maturity.

5.3.3 Conclusion

Dyeing of fabrics knitted with small bands of different yarns showed little to no visible colour difference and instrumental analysis gave inconclusive results due to the small sample size. A larger scale experiment was designed, focusing on the samples of mixed growth origins. Cotton samples were dyed using three dyestuffs of varying molecular structures. The Australian samples appeared consistently brighter than the US or Chinese samples. Colour parameters L^* and b^* were shown to correlate between raw and dyed fabric colour, highlighting the importance of reflectance and yellowness properties in prediction of dyeability. The structure of the dyestuff was not seen to have a significant influence on dyeing behaviour compared to that of the fabric base colour and the colour of the dye. Regression analysis found

fineness, reflectance, and yellowness to be the most important fibre properties in prediction of dyed colour. The brightness of the Australian samples was attributed to higher reflectance values due to their greater fibre diameter and therefore lower degree of light scattering. Yarn properties were not found to significantly influence dyed colour, especially when fibre properties are also considered. These results suggest that although growth origin may influence fibre colour, maturity, and fineness, it does not have an impact on dyed appearance independent of fibre properties.

5.4 Overall Conclusion

A fabric with small bands of the yarns used in the varietal studies was knitted and dyed in an effort to more readily highlight both visual and instrumental differences in dyed appearance. Additionally, a second fabric containing these yarns plus a new set of yarns of mixed origins and fibre types was knitted and dyed to determine if dyeability differences could be seen between cotton samples from different growth environments. There was very little visible colour difference within the samples, with the most notable difference seen between the Australian Pima cotton varieties and the remaining samples. Instrumental analysis of the fabric colour was inconclusive as the small scale of the experiment caused inaccuracies in measurement.

A larger scale experiment was designed, focusing on the samples of mixed growth origins. Cotton samples were dyed using three dyestuffs of varying molecular structures however this was not seen to have a significant influence on dyeing behaviour. Colour parameters L^* and b^* were shown to correlate between raw and dyed fabric colour. Regression analysis also found reflectance and yellowness to be important fibre properties in prediction of dyed colour, along with fineness. Due to the relationships established between dyed colour and raw fabric colour no further

analysis of the structure or surface chemistry was performed. Yarn properties were not found to significantly influence dyed colour in comparison to fibre properties. These results suggest that although growth origin may influence fibre colour, maturity, and fineness, it does not have an impact on dyed appearance independent of fibre properties.

6. Storage Conditions

After being harvested cotton fibre may remain in a module for an extended period of time prior to ginning. The ginned cotton is then on sold to mills, where cotton bales may be stored long term before being processed into yarns and fabrics. In turn, yarns and fabrics may sit in dyehouses for a long time before being scoured and/or bleached and dyed. The majority of mills and dyehouses are located in Asia, a region with largely hot and humid climates. Microbes thrive in warm, moist conditions and potentially could be affecting dyeability by degrading cotton products.

At the time of picking the ideal moisture content of cotton is around 6.5–8%. Higher moisture levels can result in increased microbial growth, as well as processing performance issues. Storage of cotton with moisture contents above 9% has been shown to result in fibre brittleness and increased short fibre contents, which were attributed to bacterial degradation (Fleming and Thaysen, 1920). Cotton has been found to be more susceptible to bacterial degradation during different stages of fibre processing, with cotton waste having a bacterial content several magnitudes greater than a freshly picked boll and consequently showing visible fibre damage days sooner (Fleming and Thaysen, 1920). Work by Cooper and Taylor (1992) recommends that yarn deliveries be used in rotation as variation in dyeing behaviour between batches increases with time. Although the primary focus of this work was dyeability variation due to yarn source, microbial degradation of the cotton could also be a factor of variation in dye uptake over time.

While the literature acknowledges that microbial degradation affects fibre properties, much of what has been done is quite dated and there is little work from the perspective of dyeability. This chapter details the experimental methodology used in studies of the effects of storage in a moist environment on cotton dyeability over

various time frames. Section 6.1 details an initial experiment where samples were incubated in a single sealed bag. This is followed up in Section 6.2 where samples were incubated in individual bags. Section 6.3 outlines a third experiment in which the two methods were ran side by side. All treatments were performed on a single greige cotton of Chinese origin to minimise dyeability variation due to differential fibre properties.

6.1 Incubation of Cotton Fabric Samples in a Single Bag

This experiment aimed to determine if a difference in dyeability could be observed in cotton fabric samples which had been stored under humid conditions for various time frames. This was designed to simulate the environments seen in some mills where cotton bales may sit for prolonged periods of time prior to further processing. Moist, warm environments are ideal conditions for bacterial propagation and as cotton is nearly pure cellulose it provides a ready source of food. If dye uptake was found to vary within fabric over time this could serve as an indicator of intrinsic structural or chemical changes occurring in the cotton fibres by bacterial degradation, necessitating further investigation into fibre properties.

6.1.1 Experimental Methodology

6.1.1.1 Sample Selection and Preparation

This experiment was carried out using a commercial plain weave grieger cotton fabric of Chinese origins. As the same fabric was used for all samples variation due to fibre source and variety was controlled. The fabric weight was 136.4 g/m², as determined using Australian Standard 2001.2.13 (Standards Association of Australia, 1987).

From this fabric 2.0 g +/- 0.1 samples were cut.

The samples were immersed in water for 1 hour before being pad mangled to remove excess water. Samples were weighed before and after immersion, and the moisture content (C) calculated using the following formula:

$$C = \left(\frac{W}{W + D} \right) \times 100$$

Where the weight of water in the sample is expressed as W, and D represents the dry weight of the sample. The samples had an average moisture content of 43%. This is considerably higher than the moisture level typically observed in an average bale waiting for processing, accelerating the effects of prolonged storage under moist conditions.

The padded samples were placed in a single snap-lock plastic bag, and incubated at 35 °C in a Memmert BM 200 laboratory incubator (Memmert GmbH + Co. KG, Germany) (Figure 6.1). The bag was flipped daily to disperse the moisture throughout the samples. Every second day the top two samples were removed and dried in a 105 °C oven for 10 mins. A total of 20 samples were used. Separate to these samples were 2 “day 0” reference samples, which were wetted and dried immediately.

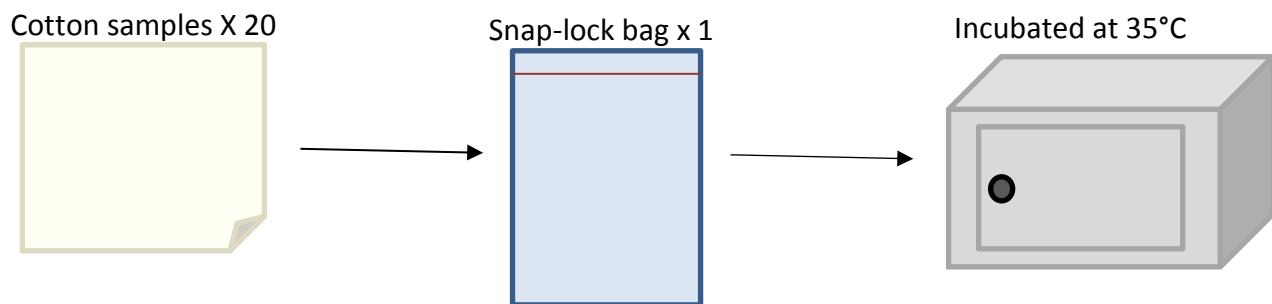


Figure 6.1: The experimental set up for the incubation.

6.1.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. Dyeing was performed using Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). Each pot of the dyeing machine was packed with 5 samples, totalling 10.0 g of fabric with a liquor volume of 150 ml, giving a 15:1 liquor ratio. The “day 0” sample was dyed alone, giving a 75:1 liquor ratio.

6.1.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before incubation, after incubation, after scouring, and after dyeing.

6.1.1.3 X-ray Diffraction

X-ray diffraction was performed as detailed in Section 2.4. The samples analysed had been incubated and scoured but not dyed.

6.1.1.4 Scanning Electron Microscopy

Scanning electron microscopy was performed as detailed in Section 2.5. The samples analysed had been incubated and scoured but not dyed.

6.1.2 Results and discussion

Throughout the incubation period the samples remained quite damp. Mould growth was evident from day 4, increasing throughout the remainder of the experiment.

Different colours of mould were observed, suggesting the presence of more than one type of mould.

At the completion of the incubation period the samples were then scoured and dyed. Scouring was performed under alkaline conditions to remove wax and surface contaminants prior to dyeing. The majority of mould was removed during scouring

however some traces remained, suggesting some types of mould are easier to remove than others. After scouring half of the samples were dyed, allowing one scoured sample for each time period to be kept for analysis.

Fabric colour was measured for each sample before incubation, after incubation, after scouring, and after dyeing. Average values for all raw samples were used to calculate ΔE from the incubated samples, using the average of the two samples. The “day 0” sample that had not been incubated was used as the reference in calculation of ΔE values for the scoured and dyed samples (Table 6.1).

Table 6.1: ΔE values for the samples after incubation, after scouring, and after dyeing.

Days Incubated	ΔE Incubated	ΔE Scoured	ΔE Yellow 6G
2	2.595	3.116	2.505
4	2.709	3.749	2.585
6	4.455	4.141	3.394
8	5.930	4.269	4.686
10	5.616	3.619	2.153
12	8.463	4.071	3.480
14	8.209	3.196	3.365
16	9.325	3.484	4.095
18	7.639	3.498	3.411
20	9.083	4.585	4.164

It is evident that mould growth on the incubated samples increasingly affected colour measurement as these samples showed the greatest level of

difference. A decrease in L^* was seen across the samples, with minor changes also seen in a^* and b^* values. The colour difference between the scoured and dyed samples and the reference as determined by ΔE values was quite high. As the “day 0” samples used as the reference were scoured and dyed separately to the incubated samples the scouring and dyeing solutions may not have had identical compositions. The “day 0” sample was also dyed at a much higher liquor ratio. When using the “day 2” incubated samples as the reference, the colour difference seen is much lower (Table 6.2).

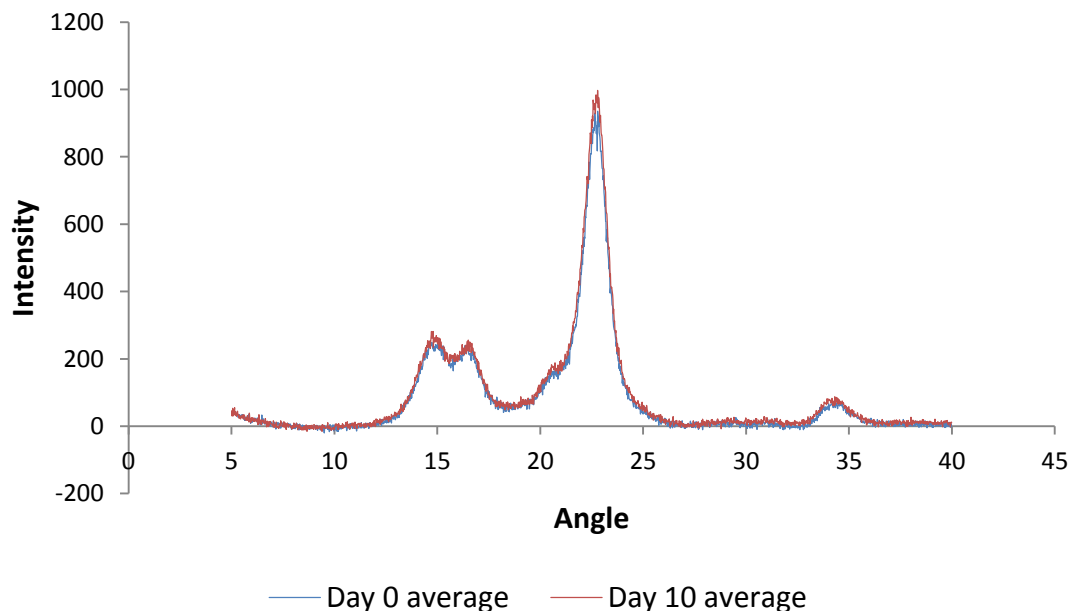
Table 6.2: ΔE values after scouring and dyeing calculated from day 2.

Days Incubated	ΔE Scoured	ΔE Yellow 6G
4	0.700	0.211
6	1.172	0.956
8	1.480	2.746
10	0.679	0.460
12	1.128	1.578
14	0.936	1.993
16	1.022	2.409
18	0.910	2.223
20	1.711	2.357

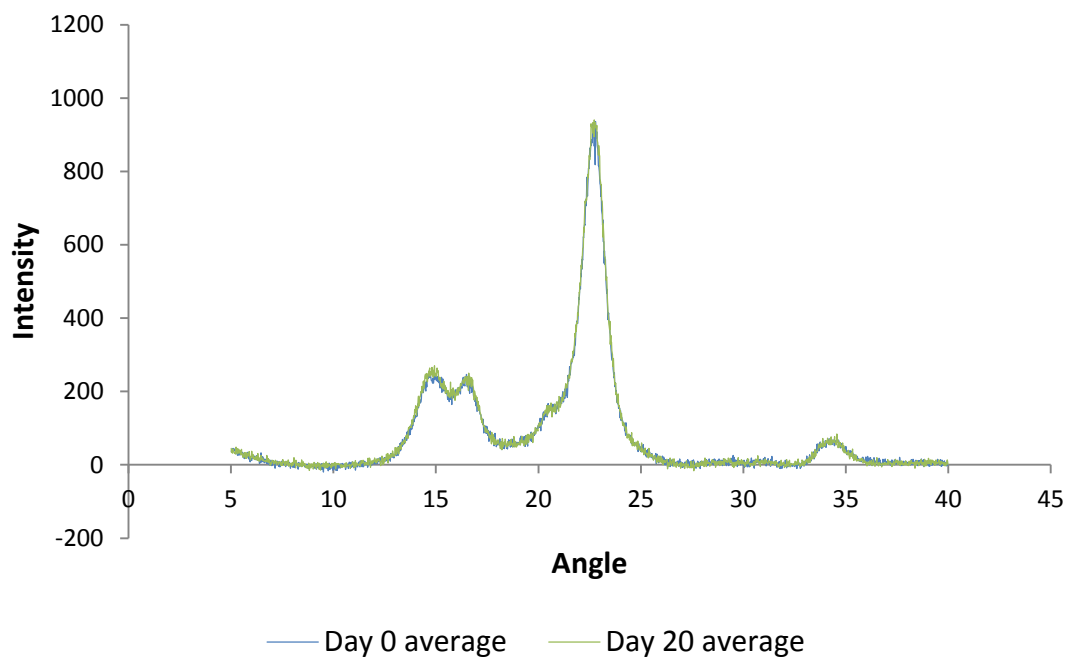
It is interesting to note that in the dyed samples there is an increase in the ΔE values with increasing incubation time, which is not seen in the scoured samples. This suggests that there are changes occurring in the fibre due to microbial action which affect dye uptake but not scouring. As scouring is predominantly a surface

treatment this suggests these changes may be structural. Further analysis of the samples was required to examine the extent of change in the fibres and how it affects dyeability.

Selected samples were analysed by x-ray diffraction (XRD) to determine if there were observable structural differences with increasing incubation time. This technique measures the scattering of x-rays by crystalline structures which varies depending on properties such as the crystallite size and shape. The diffraction pattern produced gives a characteristic fingerprint of the crystals within the sample. Use of XRD is a common method to qualitatively determine the crystallinity of cellulosic materials. Scoured but undyed samples from day 0, day 10, and day 20 were analysed. Three scans were taken for each sample and the values combined to give an average. Little difference could be seen between the diffraction patterns when plotted on the same axes (Figure 6.2). This suggests that there was no significant change in the crystalline structure of cotton fibre over the incubation period.



- a. Average of three scans of the day 10 sample plotted with the average of three scans of the day 0 sample.



b. Average of three scans of the day 20 sample plotted with the average of three scans of the day 0 sample.

Figure 6.2: Average XRD patterns for scoured samples incubated for 10 days (a.) and 20 days (b.) versus day zero samples. The beam angle is plotted against peak intensity.

The traces were analysed using OriginPro 2017 (OriginLab, USA) to determine the ratio of amorphous cellulose to crystalline cellulose for each sample. Gaussian deconvolution was used to better resolve the peaks and the area under each peak was determined. Figure 6.3 shows an example of a deconvoluted diffraction pattern. The ratio of amorphous cellulose to crystalline cellulose was then determined as a percentage of the total peak area (Table 6.3). The amorphous cellulose contents ranged from 32.0–33.2%. As this amount of variation is quite small and did not decrease with increasing incubation time it appears that incubation did not significantly affect the cellulosic structure of the cotton samples. Due to the results observed no other XRD measurements were taken during this project.

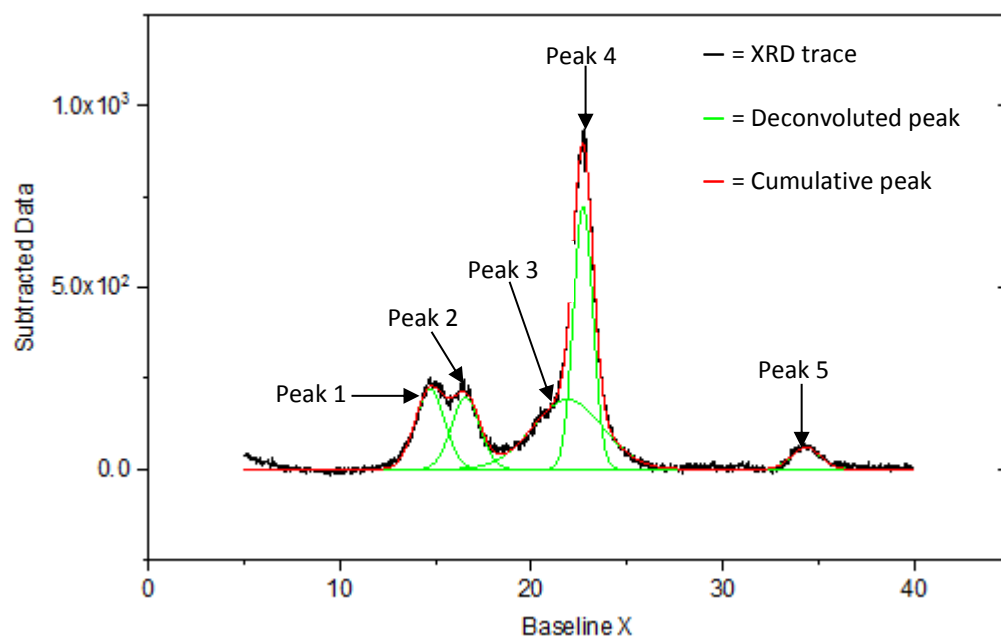


Figure 6.3: An example of Gaussian deconvolution of the x-ray diffraction patterns (day 0 sample shown).

Table 6.3: The area of each peak and the type of cellulose producing the signal for each sample, along with the calculated percentage of amorphous cellulose.

a. The peak areas and amorphous cellulose content for the day 0 sample.

Peak	Cellulose Type	Area
1	Crystalline	428.1
2	Crystalline	366.0
3	Amorphous	879.0
4	Crystalline	920.9
5	Crystalline	113.6
32.5% Amorphous		$R^2 = 0.995$
cellulose		

b. The peak areas and amorphous cellulose content for the day 10 sample.

Peak	Cellulose Type	Area
1	Crystalline	470.3
2	Crystalline	354.4
3	Amorphous	977.3
4	Crystalline	999.9
5	Crystalline	146.1
33.2% Amorphous cellulose		$R^2 = 0.995$

c. The peak areas and amorphous cellulose content for the day 20 sample.

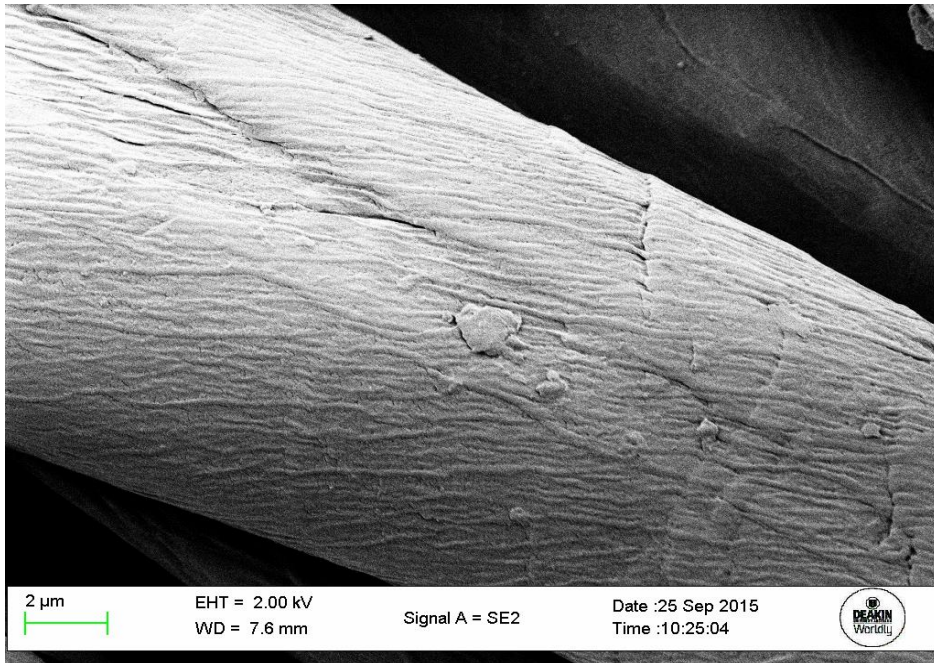
Peak	Cellulose Type	Area
1	Crystalline	555.7
2	Crystalline	253.0
3	Amorphous	886.0
4	Crystalline	966.5
5	Crystalline	108.8
32.0% Amorphous cellulose		$R^2 = 0.995$

Selected samples were imaged using scanning electron microscopy (SEM) to assess changes in the surface morphology of the samples following incubation.

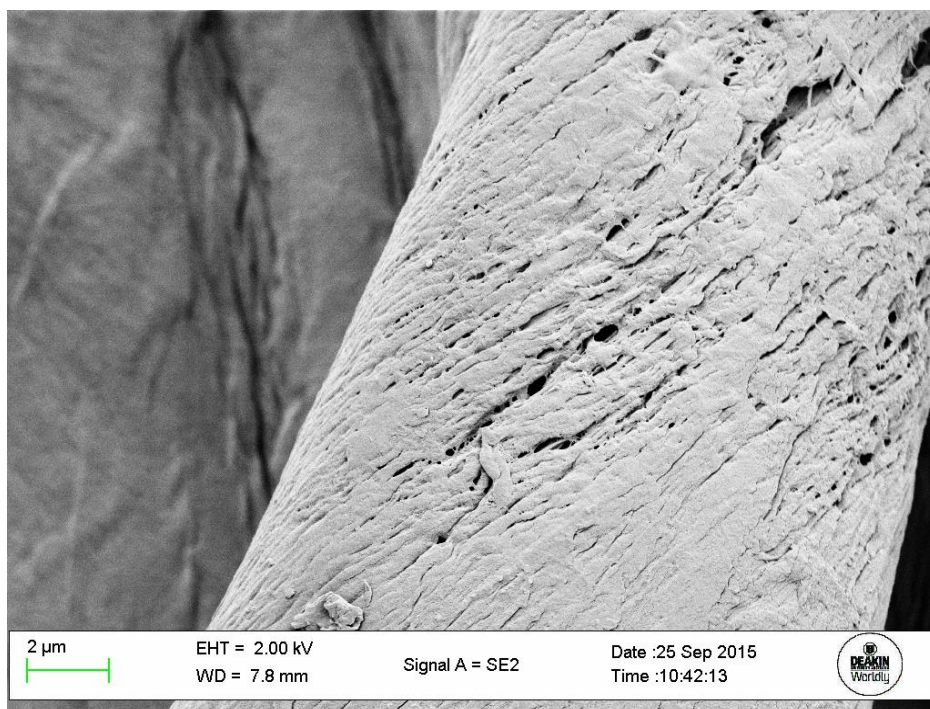
Various chemical treatments may cause a change in the surface chemistry of cotton fibre, which may influence cellulose accessibility and therefore dyeability. Samples

were coated with gold prior to imaging to enhance their conductivity by reducing electron build-up, known as charging, on the sample surface. Charging can cause contrast issues and image distortion. The samples were subject to a large amount of charging, requiring several layers of gold coating to reduce it. However this build-up of gold may have obscured features of the fabric surface.

Scoured but undyed samples from day 0, day 10 and day 20 from the first incubation were analysed, as well as an untreated raw fabric sample. Differences could be observed between the surface morphologies of the raw and day 0 samples (Figure 6.4a. and 6.4 b.). The day 0 sample shows holes in the cuticle layer not visible in the raw sample, however this is most likely due to scouring as this sample was not incubated long term. The fibre surface on the samples from day 10 and day 20 was noticeably smoother than the raw fibre, which is most likely due to removal of wax and other impurities by scouring (Figure 6.4c., 6.4d., and 6.4e.). In both the day 10 and day 20 samples there are visible tears in the outer layers, however these are most likely due to scouring as similar observations were made in other experiments (see Section 7.1). These images do not provide sufficient evidence to determine whether there is an increase in tearing with increasing incubation time.



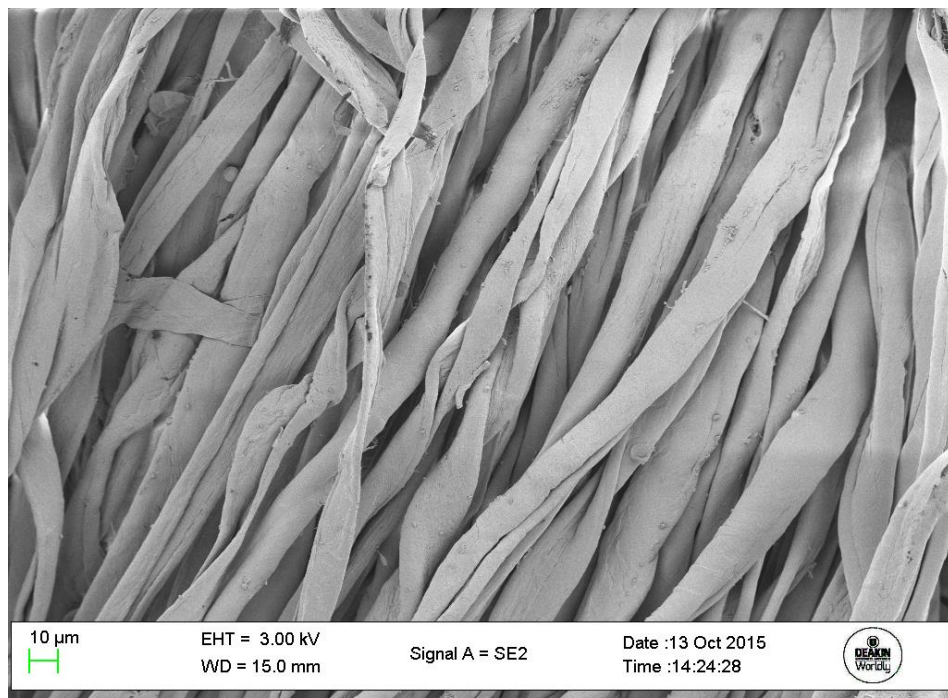
a. SEM image of the fibre surface from a raw cotton fabric sample.



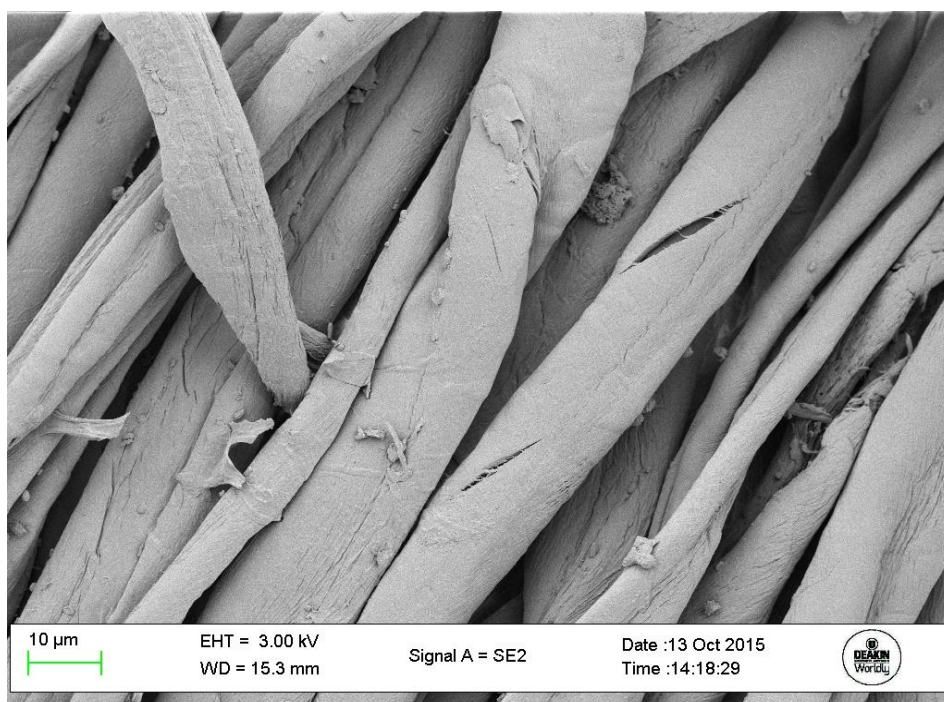
b. SEM image of the fibre surface from a scoured 'Day 0' fabric sample.



c. SEM image of raw cotton fabric.



d. SEM image of a scoured fabric sample from day 10.



e. SEM image of a scoured fabric sample from day 20.

Figure 6.4: SEM images of the fibre surface from raw cotton fabric (a.) and a scoured ‘Day 0’ sample (b.), and images of multiple fibres within raw fabric (c.), a scoured fabric sample from day 10 (d.), and a scoured fabric sample from day 20 (e.).

6.1.3 Conclusion

Cotton fabric samples were incubated in a sealed snap-lock bag for various periods of time. The treated samples were then scoured and dyed. A difference in dyed colour with increasing incubation time was observed, which was not seen to the same extent in scoured colour. This may indicate changes occurring in the fibre caused by mould damage that affect dyeing but not scouring, necessitating further investigation. Analysis of the samples by XRD indicated no change to the crystallinity of the fibre, suggesting any changes occurring are related to the surface chemistry rather than the structure. Some change to the surface morphology of the incubated samples compared to greige fabric was observed using SEM, but it is thought that this was mostly related to scouring treatment rather than incubation.

6.2 Incubation of Cotton Fabric Samples in Individual Bags

In the previous experiment incubation of cotton fabric samples under humid conditions in a single snap-lock bag showed a difference in dyed colour with increasing incubation time which was not seen in scoured colour. This experiment was designed to simulate the humid environments seen in some mills, where cotton bales may sit for an extended period of time before undergoing further processing. To see if these results could be replicated, a second experiment was designed this time with the samples incubated in individual snap-lock bags. Additionally a “day 0” reference sample was scoured and dyed alongside the incubated samples allowing more accurate colour comparison. Variation in dye uptake within the fabric samples over time could indicate intrinsic structural or chemical changes occurring in the cotton fibres by bacterial degradation, necessitating further investigation into fibre properties.

6.2.1 Experimental Methodology

6.2.1.1 Sample Selection and Preparation

Samples were cut and wetted as detailed in Section 6.1.1.1. The samples had an average moisture content of 40%. The padded samples were placed in individual snap-lock plastic bags, and incubated at 35 °C in a Memmert BM 200 laboratory incubator (Memmert GmbH + Co. KG, Germany) (Figure 6.5). As there was only one sample per bag there was no need to flip the bags as in the previous experiment. On 3 days per week two samples were removed and dried in a 105 °C oven for 10

mins. A total of 24 samples were used. Included in these samples were 2 “day 0” reference samples, which were wetted and dried immediately.

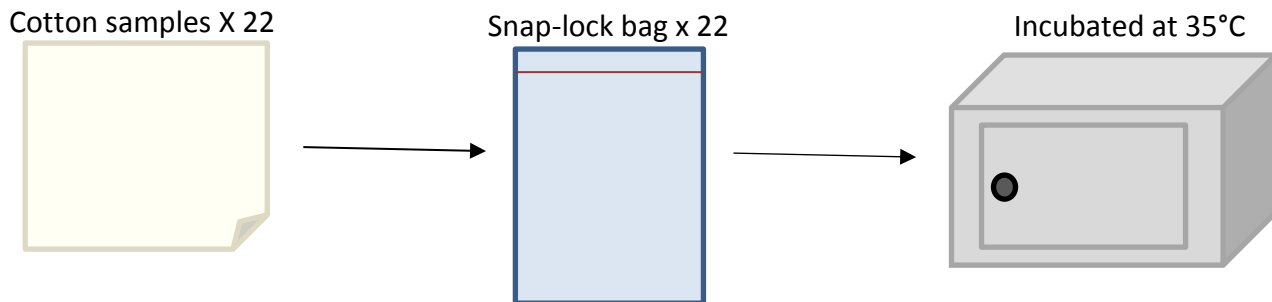


Figure 6.5: The experimental set up for the incubation.

6.2.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. Dyeing was performed using Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). Each pot of the dyeing machine was packed with 3 samples, totalling 6.0 g of fabric with a liquor volume of 150 ml, giving a 25:1 liquor ratio.

6.2.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before incubation, after incubation, after scouring, and after dyeing.

6.2.2 Results and discussion

Over the course of the experiment the samples began to dry out. Mould growth was evident from day 2, increasing throughout the remainder of the experiment. Different colours of mould were observed, suggesting the presence of more than one type of mould.

At the completion of the incubation period the samples were then scoured and dyed. Scouring was performed under alkaline conditions prior to dyeing. The majority of mould was removed during scouring however some traces remained. Only half of the samples were dyed, allowing one scoured sample for each time period to be kept for analysis.

Fabric colour was measured for each sample before incubation, after incubation, after scouring, and after dyeing. The “day 0” was used as the reference in calculation of ΔE values for the incubated, scoured and dyed samples (Table 6.4). The average of the two samples was used to calculate ΔE from the incubated samples.

Table 6.4: ΔE values for the samples after incubation, after scouring, and after dyeing.

Days Incubated	ΔE Incubated	ΔE Scoured	ΔE Yellow 6G
2	3.593	0.476	0.884
4	5.230	0.837	0.746
7	4.693	1.268	0.818
9	5.285	0.763	0.340
11	4.480	1.020	0.278
14	5.380	0.815	0.242
16	5.461	1.014	1.698
18	5.505	1.050	0.933
21	5.729	0.641	0.369
23	6.884	1.834	1.932
25	5.366	1.938	1.369

A slight increase in colour difference was seen across both the scoured and dyed samples. Additionally the colour differences observed across the incubated and dyed samples were not to the same extent as in the previous trial. As the colour difference was of similar magnitude across both the scoured and dyed samples, this may suggest that the scoured colour is affecting the dyed colour. This observation is similar to what has been seen in earlier chapters throughout this work, with raw fabric colour seeming to have a strong influence on dyed colour. As the two experiments used different methods these results don't necessarily disprove those seen in the initial incubation. It is possible that the two different methods result in different effects on the fabric. In the first experiment the samples were all in a single

snap-lock bag and remained quite moist during the incubation. The bag was flipped daily to redistribute the moisture between the samples, so they were in a constant cycle of being wetted and drying out. In this experiment the samples were in individual bags so were not flipped and the samples seemed to dry out more. A third experiment, in which both methods are ran in tandem, could help determine whether this is true.

6.2.3 Conclusion

The results of the previous experiment suggested changes in fibre surface chemistry may be occurring on incubation of samples under humid conditions, which seemed to affect dyed colour but not scoured colour. A second experiment with a slightly different design was performed, in which cotton fabric samples were incubated in individual sealed snap-lock bags for various periods of time. The treated samples were then scoured and dyed. A minor colour difference which increased very slightly with incubation time was seen across both the scoured and dyed samples. This is similar to what was seen in previous experiments within this work, with difference in dyed colour between samples being relative to that seen in the greige fabric colour. The observed colour difference was much smaller than that seen in the previous trial which suggests that the method of incubation also had an effect on colour, both before and after dyeing. As two different incubation methods were used in this and the previous experiment, both with different effects, the experiments cannot directly be compared and as such further investigation is required.

6.3 Tandem Incubation of Cotton Fabric Samples in a Single Bag and Individual Bags

This experiment is the third in a series designed to determine the effects on cotton dyeability of prolonged storage in humid conditions, as is seen in some mills. In an

initial experiment incubation of cotton fabric samples in a single snap-lock bag showed a difference in dyed colour with increasing incubation time which was not seen in scoured colour. A second incubation was performed with the samples incubated in individual snap-lock bags. A much smaller colour difference was seen across both the scoured and dyed samples. As the different methods used gave different results no solid conclusions could be drawn and accordingly another experiment was designed with both incubation methods run side by side. Variation in dye uptake within the fabric samples over time could indicate intrinsic structural or chemical changes occurring in the cotton fibres by bacterial degradation, necessitating further investigation into fibre properties.

6.3.1 Experimental Methodology

6.3.1.1 Sample Selection and Preparation

Samples were cut and wetted as detailed in Section 6.1.1.1. The samples had an average moisture content of 48%. Of the 44 padded samples, 22 were placed in a single snap-lock bag, and 20 samples were placed in individual snap-lock bags. These samples were then incubated at 35 °C in a Memmert BM 200 laboratory incubator (Memmert GmbH + Co. KG, Germany) (Figure 6.6). The samples in a single snap-lock bag were flipped daily to disperse the moisture and the top two samples removed every second day, as was done in Section 6.1. The samples in individual snap-lock bags, as in Section 6.2, did not need to be flipped and two samples were removed on 3 days per week. Upon removal from the incubator samples were dried in a 105 °C oven for 10 mins. The remaining 2 samples wetted samples were dried immediately to serve as a “day 0” reference.

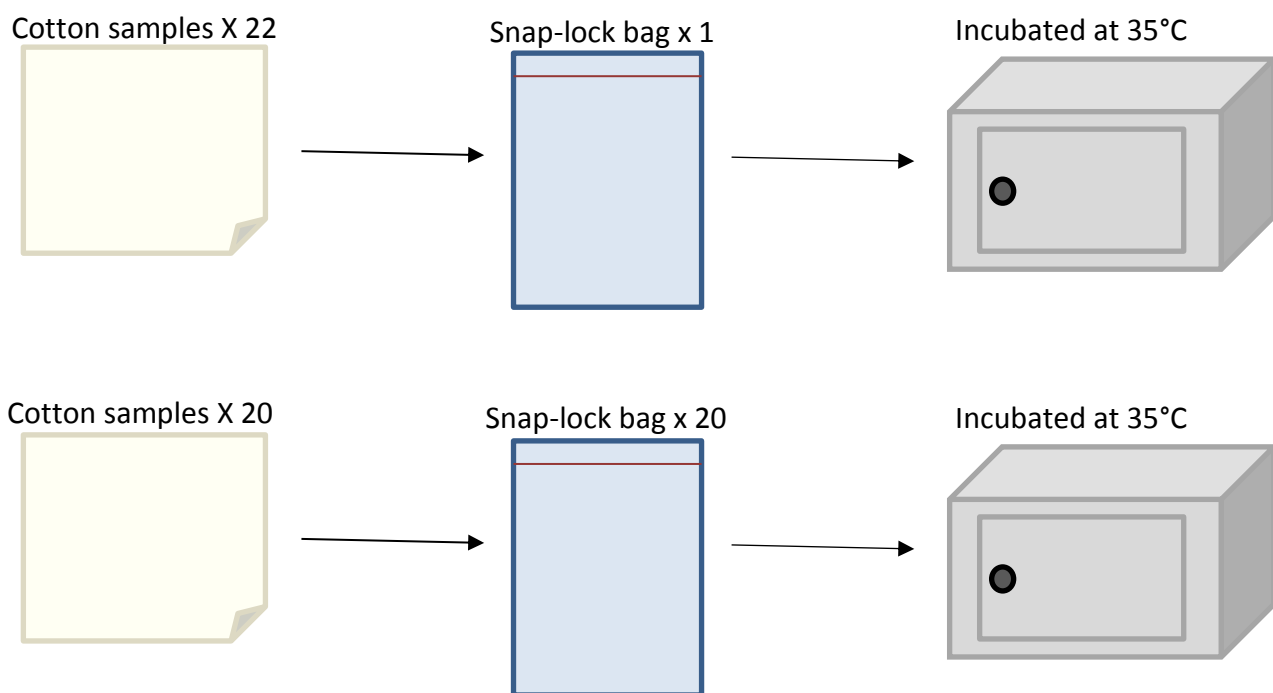


Figure 6.6: The experimental set up for the incubation.

6.3.1.2 Scouring and Dyeing

Scouring and dyeing were performed as detailed in Sections 2.1 and 2.2. Dyeing was performed using Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). Each pot of the dyeing machine was packed with 4 or 5 samples (totalling 8.0-10.0 g of fabric) with a liquor volume of 150 ml, giving a 19:1 or 15:1 liquor ratio respectively.

6.3.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before incubation, after incubation, after scouring, and after dyeing.

6.3.2 Results and discussion

Over the course of the experiment the samples in a single snap-lock bag remained quite wet, while the samples in individual snap-lock bags began to dry out. This

could partially be due to the fact that the samples in a single bag were flipped daily, allowing moisture to be redistributed throughout the samples, whereas the individual samples were not. In both methods, discolouration was observed from day 2, with the first signs of mould growth observed on day 4. Mould growth increased throughout the experiment, with significantly higher levels of mould growth observed in the sample set placed in a single snap-lock bag (Figure 6.7). In the samples placed in individual snap-lock bags mould growth seemed to reach a plateau. This difference in the extent of mould growth may be explained by the variation in moisture levels between the two incubation methods. These differences in mould growth levels were consistent throughout all three experiments.



a. Sample incubated for 4 days in an individual snap-lock bag.



b. Sample incubated for 4 days with other samples in a single snap-lock bag.



c. Sample incubated for 23 days in an individual snap-lock bag.



d. Sample incubated for 22 days with other samples in a single snap-lock bag.

Figure 6.7: Comparison between the sample incubation methods between samples incubated for 4 days individually (a.) and in a single bag (b.), and samples incubated for 23 days individually (c.) and for 22 days in a single bag (d.).

At the completion of the incubation period the samples were then scoured and dyed. Scouring was performed under alkaline conditions prior to dyeing. The majority of mould was removed during scouring however some traces remained. Only half of the samples were dyed, allowing one scoured sample for each time period to be kept for analysis.

Fabric colour was measured for each sample before incubation, after incubation, after scouring, and after dyeing. Average values for all raw samples were used to calculate ΔE from the incubated samples, using the average of the two samples. The “day 0” sample was used as the reference in calculation of ΔE values for the scoured and dyed samples (Table 6.5). It was again evident that mould growth on the incubated, unscoured samples increasingly affected colour measurement as these samples showed the greatest level of difference. A decrease in L^* was seen across the samples, with minor changes also seen in a^* and b^* values. The greater level of mould growth seen on the samples in a single snap-lock bag corresponded with a greater colour difference from raw fabric. The colour difference, as with mould growth, also seemed to reach a plateau which was particularly noticeable in the samples incubated in individual snap-lock bags.

Table 6.5: ΔE values for the samples after incubation, after scouring, and after dyeing.

a. ΔE values calculated for the samples incubated in a single snap-lock bag

Days Incubated	ΔE Incubated	ΔE Scoured	ΔE Yellow 6G
2	1.427	0.238	0.981
4	1.355	0.359	1.293
6	2.869	0.834	0.753
8	4.879	1.305	0.628
10	6.663	1.339	0.478
12	7.176	1.785	1.091
14	8.526	1.366	1.171
16	8.786	1.215	1.115
18	8.181	1.137	1.083
20	8.159	1.889	1.858
22	9.522	2.271	2.330

b. ΔE values calculated for the samples incubated in individual snap-lock bags

Days Incubated	ΔE Incubated	ΔE Scoured	ΔE Yellow 6G
2	1.790	0.389	0.677
4	2.458	0.516	0.476
7	3.638	0.612	0.334
9	3.642	0.591	0.182
11	4.486	0.390	0.229
14	3.684	0.296	0.682
16	3.509	0.480	0.226
18	3.587	0.544	0.360
21	4.443	1.004	0.552
23	3.737	0.602	0.722

In the first experiment an increase in the ΔE values with increasing incubation time was observed in the dyed samples but not to the same extent in the scoured samples, suggesting that structural changes occurred in the fibre due to microbial action which affect dye uptake but not scouring. However in the samples incubated in a single snap-lock bag in this experiment a much greater colour difference was observed within the scoured samples, which was of a similar magnitude to the colour difference in the dyed samples. This suggests that the colour difference seen in the first experiment was actually related to the base colour, and that extended exposure to moisture does not directly affect dyeability. The level of variation in scoured colour observed within the individually incubated samples was not as great, and was slightly lower but comparable to that seen in the second experiment.

In both this experiment and the first experiment an increase in dyed colour difference was observed with increasing incubation time when samples were incubated in a single snap-lock bag. The difference was of similar magnitude in both incubations. In this experiment and the second experiment a smaller level of dyed colour variation was seen in the individually incubated samples. Like the scoured colour, the level of variation in dyed colour was slightly lower but comparable to that seen in the second experiment. The differences in colour seen between the two methods may be explained by the different levels of moisture in the samples throughout the course of the experiment causing damage to differing extents, and therefore having different impacts on the fabric base colour.

As the differences in scoured and dyed colour were of similar magnitude throughout the experiment, this suggests that dyed colour is heavily influenced by the scoured colour. This observation is similar to what has been seen in the previous chapters, with dyed colour seeming to be relative to the grieger fabric colour.

6.3.3 Conclusion

The results of an initial incubation experiment, with samples incubated in a single snap-lock bag, suggested changes may have occurred in the fibre surface chemistry which affected dyed colour but not scoured colour. A follow up experiment, with samples incubated in individual snap-lock bags, showed a minor colour difference with increasing incubation time seen in both the scoured and dyed samples. As different experimental set ups were used for both of these experiments they could not be directly compared. Accordingly, a third experiment was designed running both methodologies side by side. Cotton fabric samples were incubated in either a single sealed snap-lock bag or in individual bags for various periods of time. The treated samples were then scoured and dyed. The samples in a single bag remained quite wet

throughout the incubation period. In both the scoured and dyed samples a colour difference was observed between the samples which increased with incubation time. The samples in individual bags dried out over the incubation time. Although a colour difference was observed in both the scoured and dyed samples, it was significantly smaller than that seen in the samples incubated in a single bag. In both methods the level of colour difference in the dyed colour was relative to that seen in the scoured colour, which is similar to what has been observed throughout this work. The colour difference was attributed to discolouration caused by prolonged exposure to moisture and microbes, with the variation between the two methods explained by the different moisture contents.

6.4 Overall Conclusion

A series of experiments were performed based on the hypothesis that storage of cotton under humid conditions, as are seen in some mills, may cause damage to the fibre which could in turn affect dyeability. To simulate prolonged exposure to water in a warm environment wet cotton fabric samples were incubated in snap-lock bags over a period of time.

In an initial experiment, dyeing of fabric samples incubated in a single sealed snap-lock bag for various timeframes showed a difference in dyed colour with increasing incubation time. This difference was not seen to the same extent in scoured colour. This potentially suggested surface chemistry or structural differences caused by mould damage that affect dyeing but not scouring. Analysis using XRD found no structural change to be occurring within the crystalline regions of the samples, indicating that the colour difference is more related to changes in the fibre surface chemistry. Although SEM images were obtained, it was thought that most of the observed changes in surface morphology were due to scouring. The data was not

sufficient to determine whether these changes increased with increasing incubation time.

A second experiment was performed, where fabrics were incubated individually in sealed snap-lock bags. Colour differences were observed in both scoured and dyed colour, however the differences were not to the same extent as in the first experiment. The level difference seen in the dyed colour was close to that seen in the scoured colour.

As these experiments were not directly comparable, a third incubation was performed where both methods were ran simultaneously. This experiment showed similar levels of colour difference within both sample sets for both scoured and dyed colour. This suggests that dyed colour is heavily influenced by the scoured colour. This is similar to what has been observed throughout this work, with the previous chapters showing dyed appearance to be related to greige fabric colour. The greater level of colour difference seen in the samples incubated in a single snap-lock bag compared to the individually incubated samples was attributed to a greater moisture content over the course of the experiment, leading to a greater extent of microbial damage. Microbial damage appears to mainly affect the surface of the fabric, particularly the fabric colour, rather than the internal fibre structure. The overall dyed colour differences seen with increasing incubation time were attributed to base colour differences due to microbial damage.

7. Pretreatment

Cotton may undergo a range of pretreatments prior to dyeing including singeing, desizing, scouring, bleaching, and mercerisation. The processes with the greatest impact on dyeability are scouring and bleaching.

The primary purpose of scouring is to remove the waxy cuticle layer from the outer surface of the fibre, which acts as a waterproof barrier that prevents dyes from penetrating the fibre. However other noncellulosic compounds potentially affecting dyeability such as pectin, proteins, ash, and hemicelluloses are also removed. Scouring traditionally involves boiling the cotton in a strong sodium hydroxide solution, though other alkalis such as sodium carbonate may also be used. The scouring solution may contain additional reagents such as detergents, wetting agents, and sequesterants to help facilitate the process.

Bleaching is done to remove pigmentation and other impurities causing discolouration or yellowness from cotton. The aim of bleaching is to improve dye evenness by creating a uniform white base, and is especially important for dyeing pale shades. The typical bleaching process is done using hydrogen peroxide at high temperatures under alkaline conditions. Cotton bleaching may also be performed using sodium hypochlorite, however it is a harsher treatment and has fallen out of favour in many countries due to environmental concerns. Scouring and bleaching may be performed in a single process, which minimises labor and water requirements.

Although a lot of research has been done on pretreatments of cotton prior to dyeing, much of this has been to reduce the severity of these treatments.

Conventional methods of scouring and bleaching can be quite harsh, potentially

causing fibre damage. Additionally there are environmental concerns due to the large amounts of water and energy required, and the potential release of harmful pollutants into the environment through textile wastewaters. One alternative that has been well researched is bioscouring, utilizing enzymes such as cellulases and pectinases, however these techniques are not presently suitably efficient or financially viable. If dyeability is considered, it is generally for the purpose of comparing the effectiveness of conventional and alternative treatments. There are few extensive studies on how variations on conventional treatments affect dyed colour.

This chapter details the experimental methodology used in dyeability studies of cotton fabrics prepared with a range of pretreatments. Section 7.1 looks at scouring treatments while Section 7.2 investigates bleaching. The experimental design used treatment matrices considering variables such as reagent concentrations, treatment time, and temperature. All treatments were performed on a single greige cotton of Chinese origin to minimise dyeability variation due to differential fibre properties.

7.1 Scoured Fabric Dyeing Trial

This experiment aimed to determine if a difference in dyeability could be observed between cotton fabric samples which had been treated under different scouring conditions. Different treatments may remove different levels of wax and other compounds affecting dyeability from the fibre surface, in turn influencing dyed appearance. Variables considered in the experimental design included temperature, time, detergent concentration, and alkali concentration (Table 7.1). As well as the sodium hydroxide used in scouring for previous dyeing experiments, treatments using sodium carbonate as the alkali were also carried out. These alkalis were chosen as they are the two most commonly used in the dyeing industry. An experimental

matrix was designed to minimise the amount of trials necessary but still get sufficient data. Samples were scoured with each alkali at 3 concentrations, 2 temperatures, and 2 detergent concentrations. A trial was also performed at an extended time period for each alkali and temperature used. If dye uptake was found to vary within fabric this could serve as an indicator of intrinsic structural or chemical changes occurring in the cotton fibres, necessitating further investigation into fibre properties.

Table 7.1: Factors taken into consideration for various scouring treatments using sodium hydroxide and sodium carbonate.

a. Variables to be considered in scouring using sodium hydroxide.

	Temp (C)	Time (min)	Detergent conc. (g/L)	Alkali conc. (g/L)
-	80	60	0.5	0
0	90	120	1.0	1.0
+	100	180	2.0	4.0

b. Variables to be considered in scouring using sodium carbonate.

	Temp (C)	Time (min)	Detergent conc. (g/L)	Alkali conc. (g/L)
-	80	60	0.5	1.0
0	90	120	1.0	2.0
+	100	180	2.0	4.0

7.1.1 Experimental Methodology

7.1.1.1 Sample Selection and Preparation

Samples (2.0 g +/- 0.1) were cut from a roll of a commercial plain weave grieger cotton fabric of Chinese origins. Fabric weight was determined using Australian Standard 2001.2.13 (Standards Association of Australia, 1987). As the same fabric was used for all samples variation due to fibre source and variety was controlled.

7.1.1.2 Scouring and Dyeing

Scouring and dyeing were both done using a SDM2-140 rotary dyeing machine (Fong, Hong Kong) or H24-C rotary dyeing machine (Rapid, Taiwan). Scouring was performed using 2 samples of cotton fabric per pot in the dyeing machine in 150 ml of a solution containing 0.5–2.0 g/L Hostapal FAZ (Achroma, Switzerland), and either sodium hydroxide or sodium carbonate. Samples were scoured under the conditions listed in Table 7.2. No wetting agents or sequesterants were used in this experiment. The scoured samples were rinsed warm, followed by a cold rinse. The samples were then spun to remove excess water in a MSE Basket 300 centrifuge (MSE, UK), and further dried in a 105 °C oven for 10 mins.

Dyeing was performed as detailed in Section 2.2, using Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). Each pot of the dyeing machine was packed with 4 samples, totalling 8.0 g of fabric with a liquor volume of 150 ml, giving a 19:1 liquor ratio.

Table 7.2: Conditions used for the scouring experiment.

Sample	Alkali	Alkali concentration (g/L)	Detergent concentration (g/L)	Temperature (°C)	Time (hr)
1, 2, 3	NaOH	0.0, 1.0, 4.0	0.5	80	1
4	NaOH	1.0	0.5	80	3
5, 6, 7	NaOH	0.0, 1.0, 4.0	0.5	100	1
8	NaOH	1.0	0.5	100	3
9, 10, 11	NaOH	0.0, 1.0, 4.0	2.0	80	1
12	NaOH	1.0	2.0	80	3
13, 14, 15	NaOH	0.0, 1.0, 4.0	2.0	100	1
16	NaOH	1.0	2.0	100	3
17, 18, 19	Na ₂ CO ₃	1.0, 2.0, 4.0	0.5	80	1
20	Na ₂ CO ₃	1.0	0.5	80	3
21, 22, 23	Na ₂ CO ₃	1.0, 2.0, 4.0	0.5	100	1
24	Na ₂ CO ₃	1.0	0.5	100	3
25, 26, 27	Na ₂ CO ₃	1.0, 2.0, 4.0	2.0	80	1
28	Na ₂ CO ₃	1.0	2.0	80	3
29, 30, 31	Na ₂ CO ₃	1.0, 2.0, 4.0	2.0	100	1
32	Na ₂ CO ₃	1.0	2.0	100	3

7.1.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before scouring, after scouring, and after dyeing.

7.1.1.3 Scanning Electron Microscopy

Scanning electron microscopy was performed as detailed in Section 2.5. The samples analysed had been scoured but not dyed.

7.1.2 Results and Discussion

Scouring was performed under the various conditions to remove wax and surface contaminants prior to dyeing. After scouring half of the samples were dyed, allowing one scoured sample for each time period to be kept for analysis.

Fabric colour was measured for each sample before scouring, after scouring, and after dyeing. Average values for all raw samples were used to calculate ΔE between the raw and unscoured samples. The ΔE values between the scoured and dyed samples were calculated for each alkali using the sample with the mildest treatment conditions as a reference (Table 7.3, see table 7.2 for treatment conditions). The ΔE values equate to visible differences between the reference and the majority of the scoured samples, corresponding to a slightly smaller level of difference in the dyed samples. These values correlate with what could be seen with the naked eye between the fabric samples. The difference seen in the sodium hydroxide treated samples was greater than in the sodium carbonate treated samples, which was expected as it is a stronger alkali and therefore a harsher scouring treatment.

Table 7.3: ΔE values for the samples after scouring and after dyeing.

a. ΔE values calculated for the sodium hydroxide treated samples

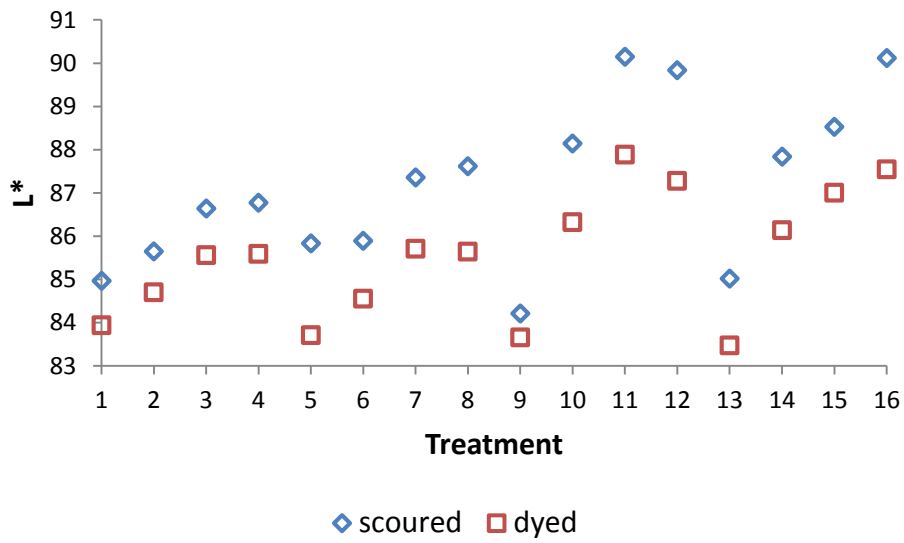
Sample	ΔE Raw to Scoured	ΔE Scoured (from sample 1)	ΔE Yellow 6G (from sample 1)
1	8.934	-	-
2	8.703	0.700	1.435
3	8.007	1.849	3.037
4	8.004	2.008	2.523
5	8.480	1.012	1.718
6	8.577	3.209	2.820
7	7.799	5.609	5.714
8	8.277	5.090	4.586
9	8.904	0.866	0.900
10	8.668	0.933	1.312
11	8.758	2.397	2.821
12	8.105	2.791	2.654
13	8.324	0.647	1.057
14	7.581	3.205	3.917
15	7.414	3.966	4.668
16	7.274	5.831	6.303

b. ΔE values calculated for the sodium carbonate treated samples

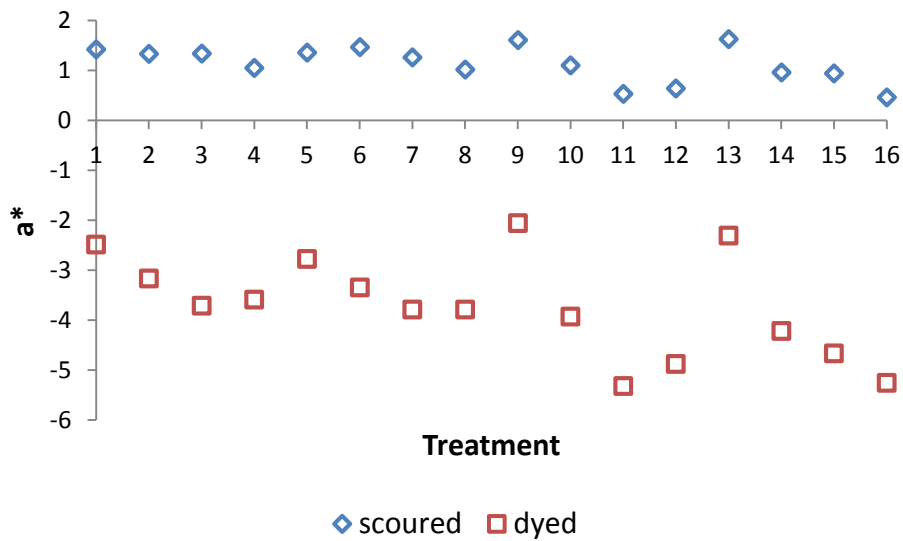
Sample	ΔE Raw to Scoured	ΔE Scoured (from sample 1)	ΔE Yellow 6G (from sample 1)
17	8.395	-	-
18	8.741	0.782	0.332
19	8.842	1.369	1.429
20	8.786	1.019	0.863
21	8.657	2.283	1.735
22	8.610	2.460	1.919
23	8.402	3.268	2.734
24	8.642	3.403	3.175
25	8.824	1.023	0.681
26	8.760	1.036	0.246
27	8.674	1.043	0.743
28	8.369	1.161	1.436
29	8.225	1.791	1.501
30	8.290	1.482	1.754
31	8.274	3.248	1.998
32	7.984	2.739	2.556

For each treatment, the L^* , a^* and b^* values were plotted against the treatments for the scoured and dyed samples (Figure 7.1). The colour differences in the dyed samples were attributed to the base colour variation caused by the different scouring treatments. Although the difference between scoured colour and dyed colour was more extreme in the sodium hydroxide treated samples, the trend was

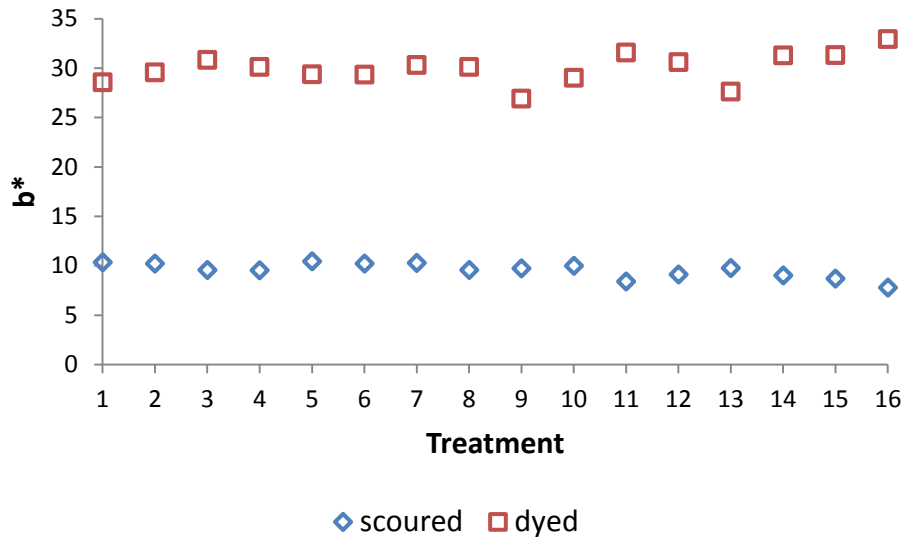
observed for both alkalis. This same trend has been observed throughout this work, with raw and scoured colour seen to have a large impact on dyed appearance.



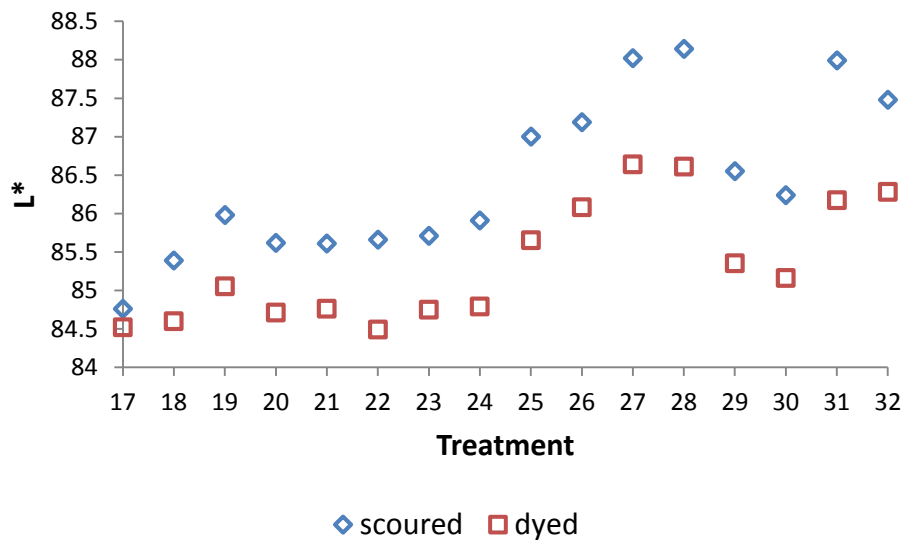
a. Plot of L* against the treatments with sodium hydroxide.



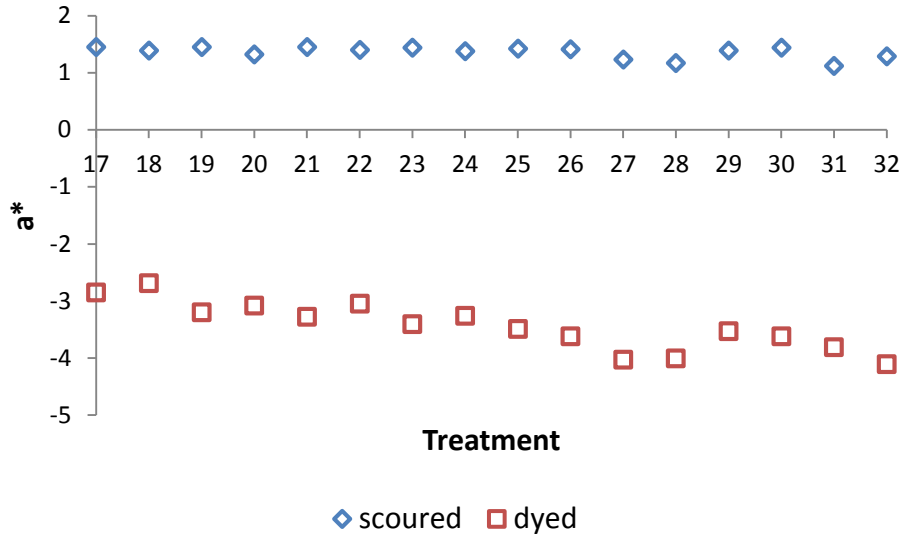
b. Plot of a* against the treatments with sodium hydroxide.



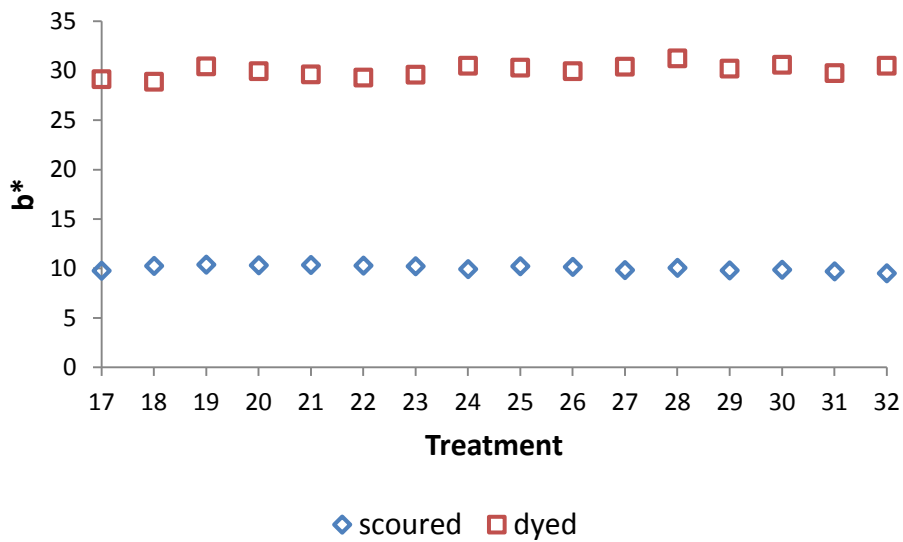
c. Plot of b^* against the treatments with sodium hydroxide.



d. Plot of L^* against the treatments with sodium carbonate.



e. Plot of a* against the treatments with sodium carbonate.



f. Plot of b* against the treatments with sodium carbonate.

Figure 7.1: Plots of L*, a*, b* against the treatments for the samples scoured with sodium hydroxide (a.–c.), and sodium carbonate (d.–f.).

The difference in lightness, ΔL^* , was calculated for each treatment between the scoured and dyed samples and the resulting figures graphed (Figure 7.2). The ΔL^* values mostly followed a linear progression according to chemical concentration, time, and temperature. As may be expected from the ΔE values, the

greatest differences in ΔL^* were seen in the fabrics subjected to prolonged scouring treatment with sodium hydroxide at 100 °C.

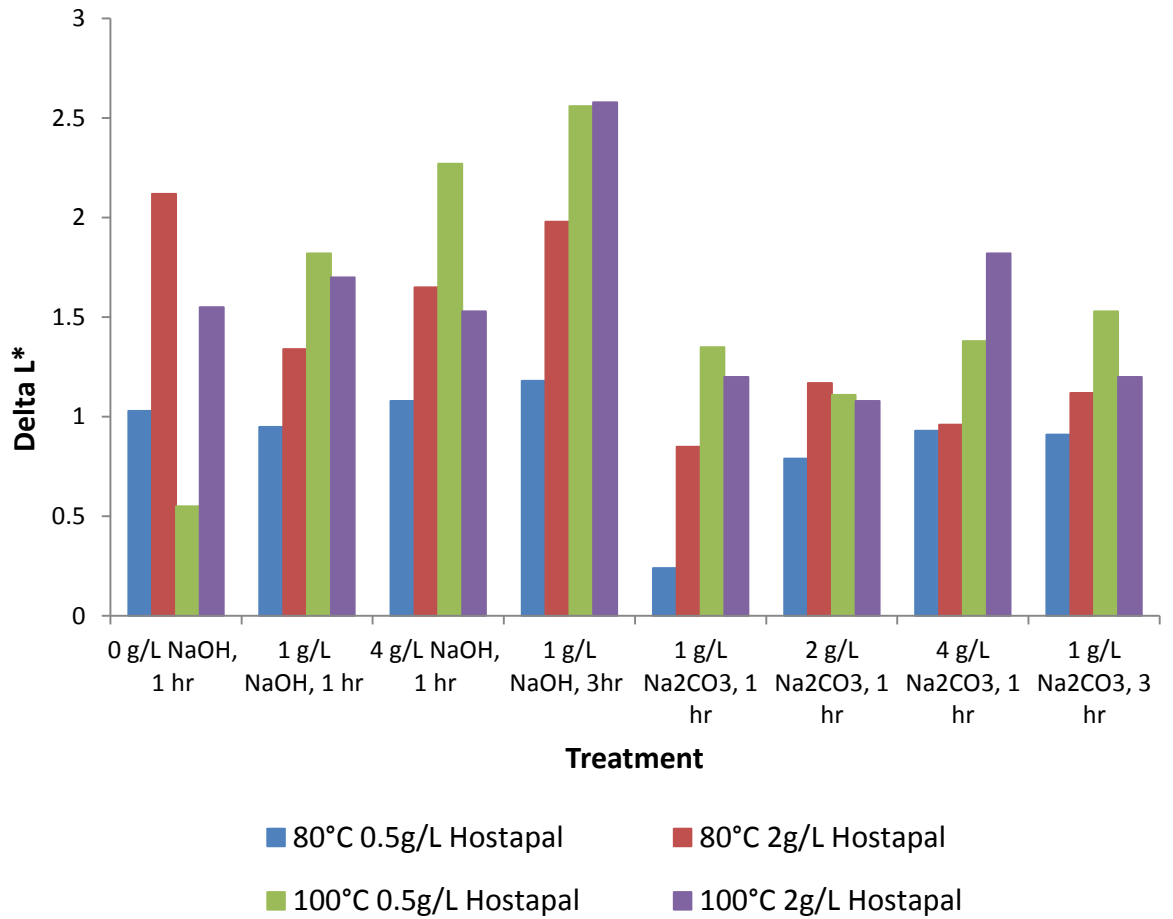
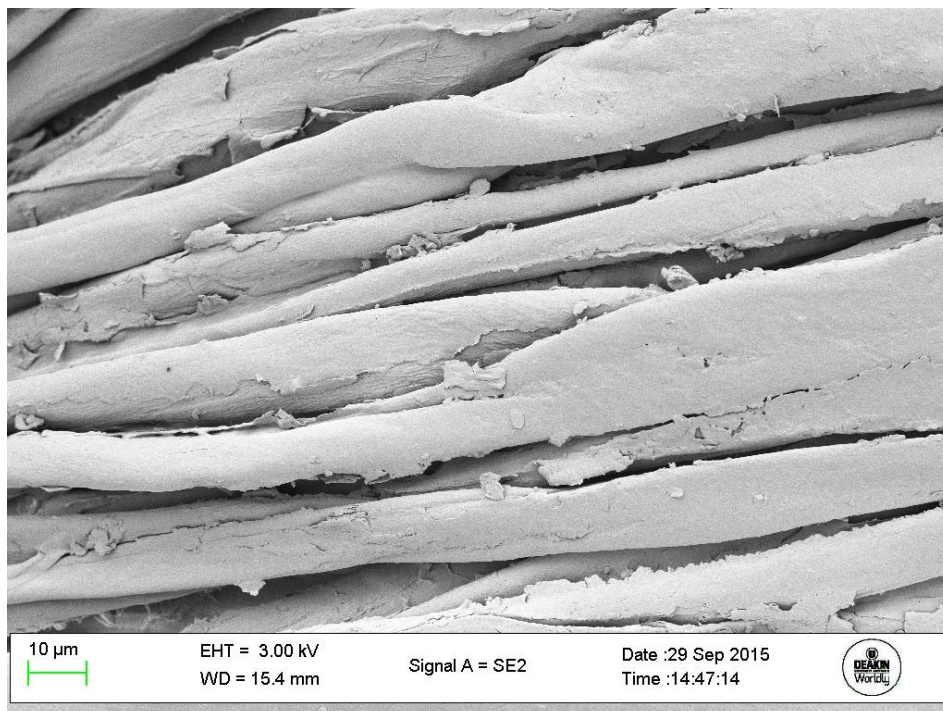


Figure 7.2: The difference in lightness (ΔL^*) between the scoured and dyed samples plotted against the treatment conditions.

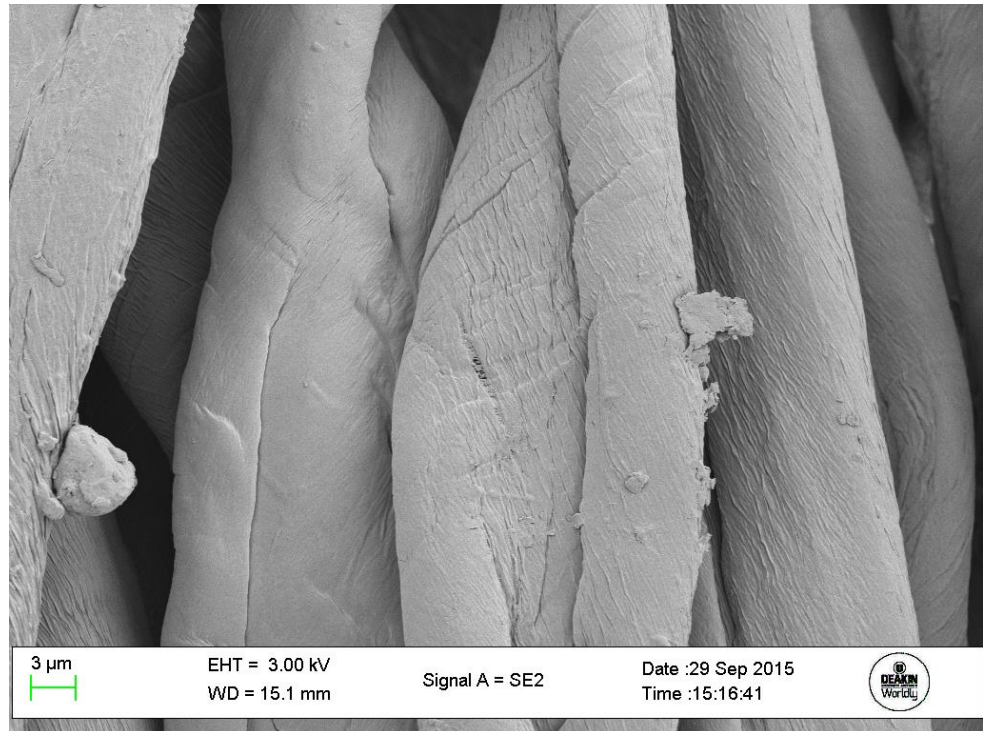
Selected samples were imaged using scanning electron microscopy (SEM) to assess changes in the surface morphology of the samples following scouring. Various chemical treatments may cause a change in the surface chemistry of cotton fibre, which may influence cellulose accessibility and therefore dyeability. Samples were coated with gold prior to imaging to enhance their conductivity, reducing electron build-up, known as charging, on the sample surface. Charging can cause contrast issues and image distortion. The samples were subject to a large amount of charging,

requiring several layers of gold coating to reduce it. However this build-up of gold may have obscured features of the fabric surface.

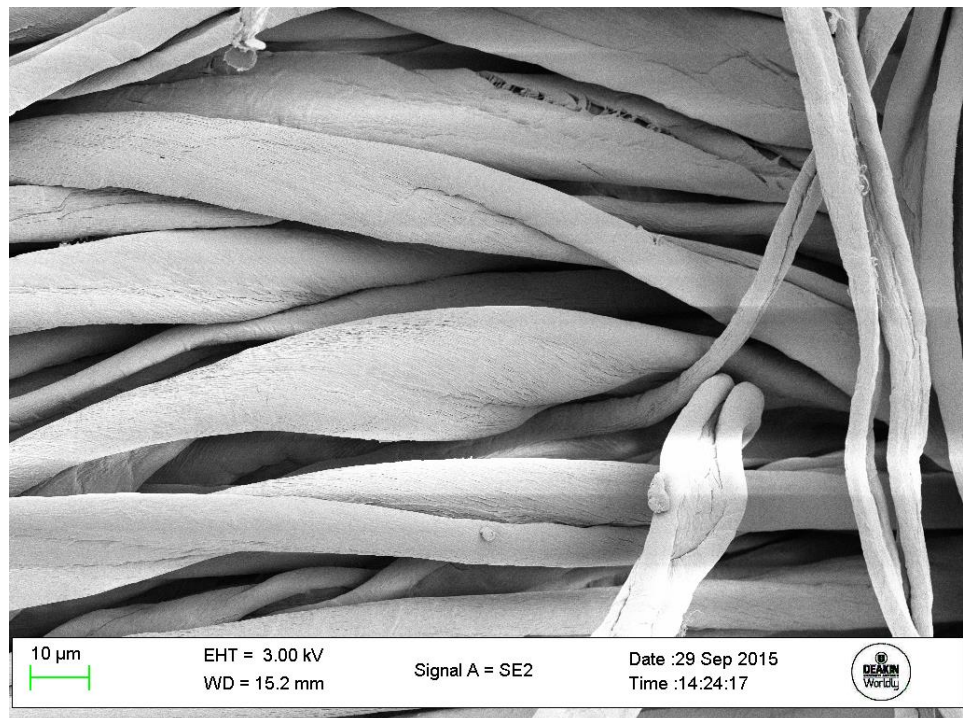
Undyed samples scoured with treatments 10, 14, and 15 were analysed, as well as an untreated raw fabric sample (Figure 7.3). These treatments were chosen as they represent a standard scour (14), a treatment at a lower temperature (10), and a treatment at a higher alkali concentration (15) (see Table 7.2 for treatment conditions). Differences could be observed between the surface morphologies of the raw and treated samples. The scoured samples have a much smoother surface, and show holes and tears in the cuticle layer not visible in the raw sample. The number and extent of the tears seems to increase with the severity of the scouring treatments. It would be logical that a harsher treatment creates more holes in the cuticle, therefore increasing dye access to the secondary cell wall cellulose resulting in a higher dye uptake. This theory correlates with the colour differences observed.



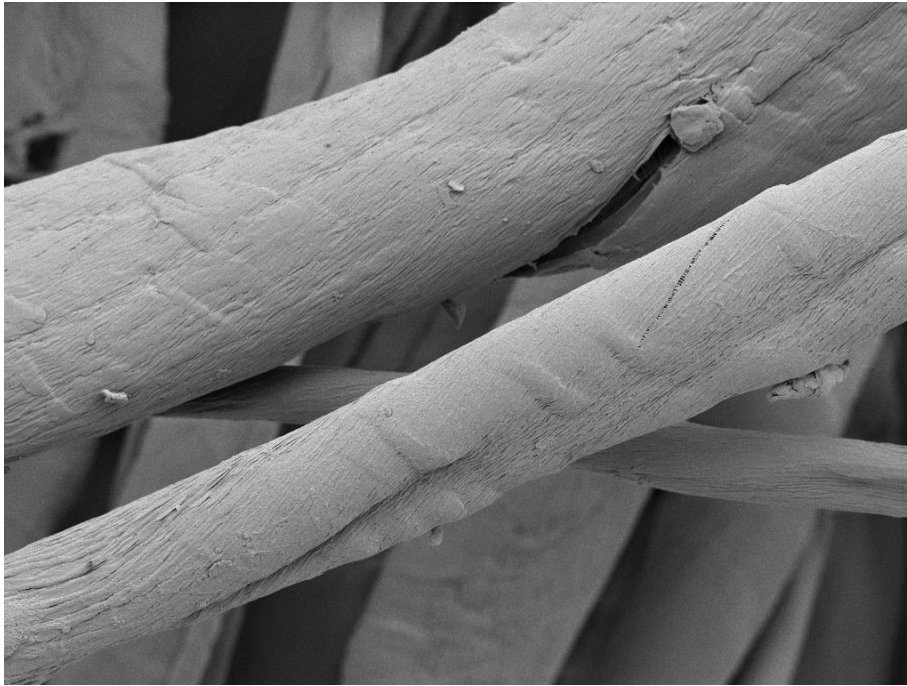
a. SEM image of raw cotton fabric.



b. SEM image of cotton fabric scoured with treatment 10.



f. SEM image of cotton fabric scoured with treatment 14.



g. SEM image of cotton fabric scoured with treatment 15.

Figure 7.3: SEM images of raw cotton fabric (a.) and fabrics scoured with treatments 10 (b.), 14 (c.), and 15 (d.).

7.1.3 Conclusion

Dyeing of fabric samples treated under different scouring conditions, using either sodium hydroxide or sodium carbonate, showed a difference in dyeability relative to the intensity of the scouring treatments. The difference in dyed appearance observed was attributed to the differential base colour of the fabrics post-scouring. This variation highlights the importance of consistent scouring conditions in dyehouses. The observations made in this experiment are similar to what has been seen throughout this work, with raw and scoured colour seeming to heavily influence dyed shade. Imaging of the samples using SEM showed an increase in surface changes with severity of the scouring treatments, suggesting that this is related to an increase in dye accessibility and uptake. This theory correlates with the observed colour differences.

7.2 Bleached Fabric Dyeing Trial

In the previous experiment a series of scouring treatments was performed to determine the effects of differential pretreatment on dye uptake. A similar experiment was designed to determine if a difference in dyeability could be observed in cotton fabric samples which had been bleached under different conditions prior to dyeing. Different treatments may remove different levels of wax, pigmentation, and other compounds affecting dyeability from the fibre surface, in turn influencing dyed appearance. Variables considered included temperature, time, peroxide concentration, and alkali concentration (Table 7.4). Hydrogen peroxide was selected as the bleaching agent as it is one of the most commonly used for cotton bleaching. Sodium hydroxide was used for the scouring as it is the most commonly used alkali for cotton scouring. An experimental matrix was designed to minimise the amount of trials necessary but still get sufficient data. Samples were treated at 2 peroxide concentrations, 2 alkali concentrations, and 2 temperatures. At each temperature trials were performed at two time periods, with the room temperature samples having a much greater treatment time than the hot bleached samples. If dye uptake was found to vary within fabric this could serve as an indicator of intrinsic structural or chemical changes occurring in the cotton fibres, necessitating further investigation into fibre properties.

Table 7.4: Factors taken into consideration for various bleaching treatments both heated and at room temperature.

a. Variables to be considered in hot bleaching.

	Temp (C)	Time (min)	Peroxide conc. (g/L)	Alkali conc. (g/L)
-	80	60	3.0	0.5
+	100	120	6.0	5.0

b. Variables to be considered in room temperature bleaching.

	Temp (C)	Time (min)	Peroxide conc. (g/L)	Alkali conc. (g/L)
-	RT	16	3.0	0.5
+	RT	24	6.0	5.0

7.2.1 Experimental Methodology

7.2.1.1 Sample Selection and Preparation

Samples (2.0 g +/- 0.1) were cut from a roll of a commercial plain weave grieger cotton fabric of Chinese origins. Fabric weight was determined using Australian Standard 2001.2.13 (Standards Association of Australia, 1987). As the same fabric was used for all samples variation due to fibre source and variety was controlled.

7.2.1.2 Scouring and Dyeing

Scouring and bleaching were performed in a single step under the conditions listed in Table 7.5. Room temperature bleaching was performed in snap-lock plastic bags, with each treatment done in duplicate. Samples were immersed in a solution

containing 1.0 g/L Hostapal FAZ (Achroma, Switzerland), 0.5 g/L Verolan NBO (Rudolf Atul Chemicals Ltd, India), and the required concentrations of 30% hydrogen peroxide (VWR, Australia) and sodium hydroxide (Sigma Aldrich, Australia). The excess solution was removed by pad mangle and the samples placed in snap-lock bags for the required period of time before being rinsed, spun to remove excess water in a MSE Basket 300 centrifuge (MSE, UK), and further dried in a 105 °C oven for 10 minutes.

Hot bleaching was done using a Datacolor AHIBA IR Pro (Datacolor, USA). Hot bleaching was performed with 2 samples of cotton fabric per pot in the dyeing machine in 150 ml of a solution containing 1 g/L Hostapal FAZ added as a detergent, 0.5 g/L Verolan NBO added as a sequesterant, and the required concentrations of 30% hydrogen peroxide and sodium hydroxide. The dyebath was heated to the required temperature and held for the required time before the samples were rinsed, spun to remove excess water in a MSE Basket 300 centrifuge (MSE, UK), and further dried in a 105 °C oven for 10 minutes.

Table 7.5: Conditions used for the bleaching experiment.

Sample	Hot/Cold	Alkali concentration (g/L)	Peroxide concentration (g/L)	Temperature (°C)	Time (hr)
1	Hot	5.0	6.0	80	1
2	Hot	5.0	6.0	80	2
3	Hot	5.0	6.0	100	1
4	Hot	5.0	6.0	100	2
5	Hot	0.5	3.0	100	1
6	Hot	0.5	6.0	100	1
7	Cold	5.0	6.0	RT	16
8	Cold	5.0	6.0	RT	24
9	Cold	0.5	3.0	RT	24
10	Cold	0.5	6.0	RT	24

Dyeing was performed using the hot bleached samples only, as detailed in Section 2.2, using Procion Yellow HE-6G (Kiri Industries Limited (KIL), India). The pot of the dyeing machine was packed with 6 samples, totalling 12.0 g of fabric with a liquor volume of 150 ml, giving a 12.5:1 liquor ratio.

7.2.1.3 Colourimetry

Colourimetry was performed as detailed for fabric samples in Section 2.3. Colour was measured before scouring, after scouring, and after dyeing.

7.2.2 Results and discussion

Scouring and bleaching were performed in a single step process to remove wax, pigmentation, and other surface contaminants prior to dyeing. The hot bleached samples showed a large increase in whiteness after treatment, with a visible difference in the level of whiteness seen between different treatments. The cold bleached samples also appeared lighter in colour after treatment but to a much lesser extent. As the treatment was significantly less effective than the hot bleaching no further work was carried out with these samples. After treatment half of the hot bleached samples were dyed, allowing one scoured sample for each time period to be kept for analysis.

Fabric colour was measured for each sample before bleaching, after bleaching, and after dyeing. Average values for all raw samples were used to calculate ΔE between the raw and unbleached samples. The ΔE values between the bleached samples were calculated for each treatment condition, using sample 1 as the reference for the hot bleached samples and sample 7 as the reference for the cold bleached samples (Table 7.6, see table 7.5 for treatment conditions). The ΔE values between the dyed hot bleached samples were calculated for each treatment condition using sample 1 as the reference (Table 7.6a).

Table 7.6: ΔE values for the samples after bleaching and after dyeing.

a. ΔE values calculated for the hot bleached samples

Sample	ΔE Raw to Bleached	ΔE Bleached (from sample 1)	ΔE Yellow 6G (from sample 1)
1	12.177	-	-
2	12.711	0.577	0.562
3	13.339	1.214	0.662
4	13.439	1.409	1.925
5	9.819	2.460	1.722
6	11.088	1.243	1.107

b. ΔE values calculated for the room temperature treated samples

Sample	ΔE Raw to Bleached	ΔE Bleached (from sample 7)
7	4.769	-
8	5.224	0.477
9	2.524	2.736
10	3.328	1.660

In the hot bleached samples the calculated ΔE values equate to minor colour differences which may not be obvious between the reference and the majority of the scoured samples, with the exception of sample 5 which showed a medium level of difference. The ΔE values for the dyed samples all indicate minor colour differences. Overall, the colour difference between the undyed samples was greater than that

between the dyed samples. In the cold bleached samples the calculated ΔE values represent minor to medium colour differences, with the biggest difference seen in sample 9. These values correlate with what could be seen with the naked eye between the fabric samples. Both sample 5 and 9 were treated with lower concentrations of hydrogen peroxide and sodium hydroxide. Samples 6 and 10 were treated with a lower concentration of alkali but with a higher hydrogen peroxide concentration. The colour difference from the raw samples was closer to that of the samples treated with higher concentrations of alkali and peroxide, suggesting that hydrogen peroxide concentration is more important in removal of discolouration than alkali concentration. A considerably large colour difference was seen between the hot bleached samples and the cold bleached samples, indicating that the hot bleaching treatments were much more effective. Additionally they were much faster with each treatment taking 1–2 hours, whereas the cold bleaching treatments took 16–24 hours.

The difference in lightness, ΔL^* , was calculated for each treatment between the raw and bleached samples and the resulting figures graphed (Figure 7.4). The ΔL^* values mostly followed a linear progression according to chemical concentration, time, and temperature. However, the increase in lightness seems to plateau with little difference seen between 1 hr and 2 hr treatment times with the higher concentrations of hydrogen peroxide and sodium hydroxide at 100°C. The largest ΔL^* values were seen in the fabrics subjected to hot bleaching treatments with a 30% hydrogen peroxide concentration of 6 g/L. The smallest ΔL^* values were seen in the cold bleached samples with sample 9 showing the smallest difference, being treated with lower concentrations of hydrogen peroxide and sodium hydroxide.

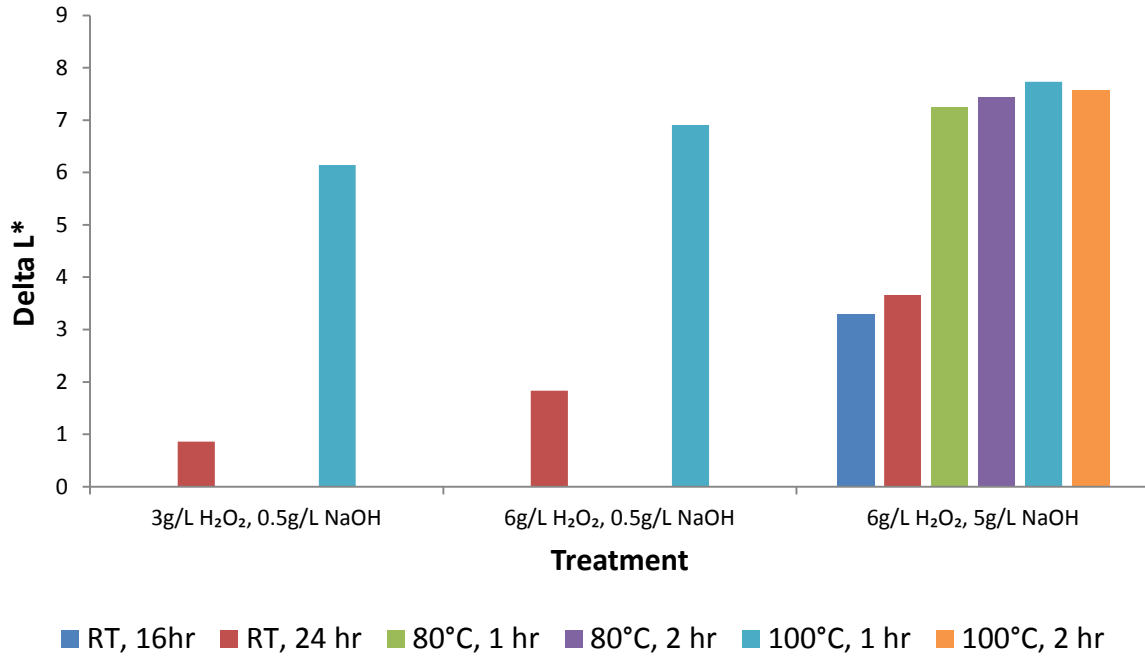
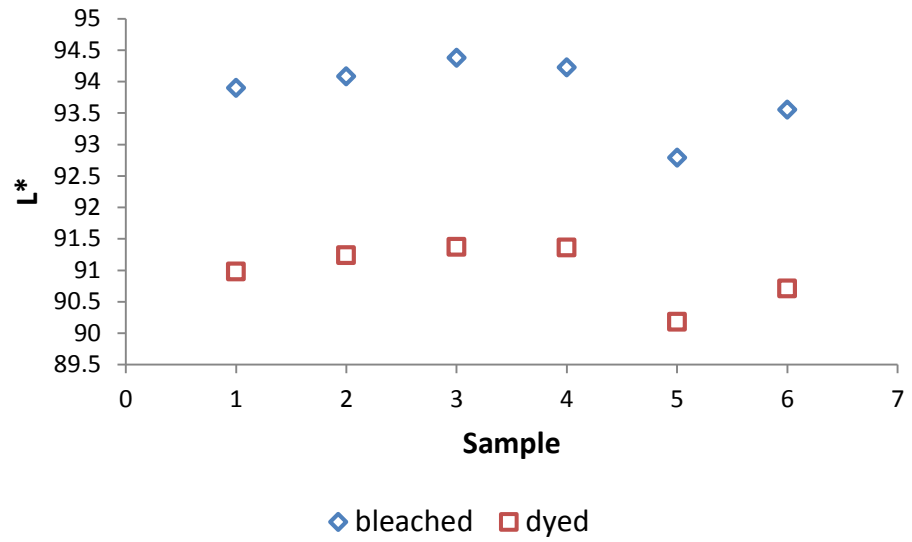
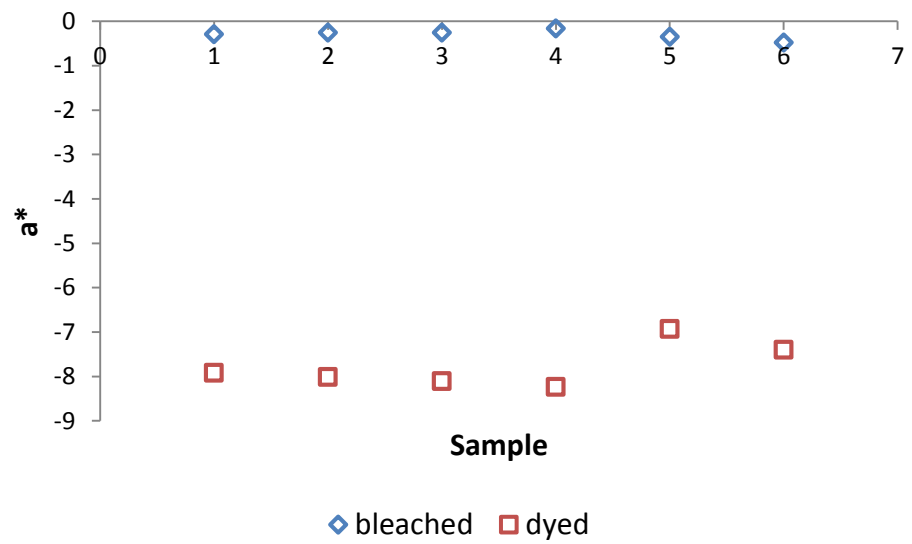


Figure 7.4: The difference in lightness (ΔL^*) between the raw and bleached samples plotted against the treatment conditions.

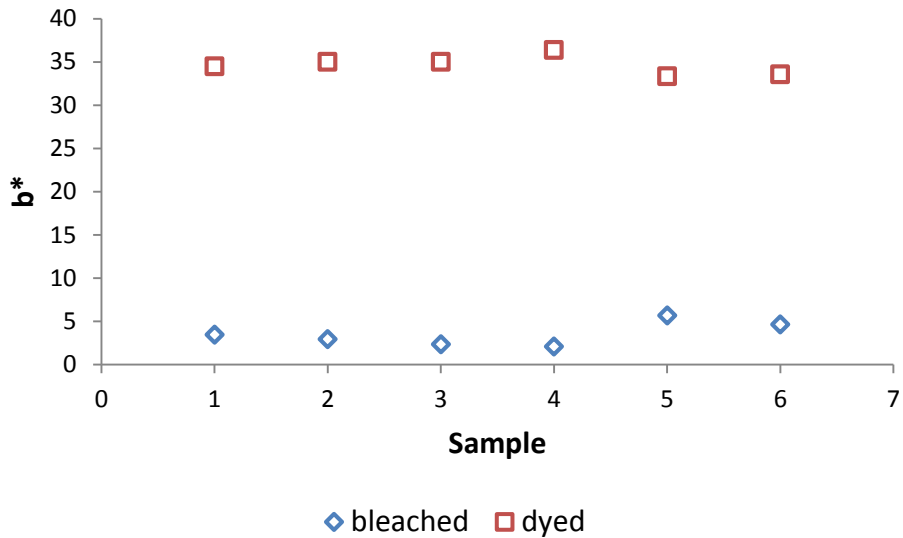
The colour parameters L^* , a^* , and b^* for the hot bleached samples after treatment and after dyeing were plotted on the same axes against the treatments (Figure 7.5). The bleached and scoured fabrics follow the same trend in lightness, suggesting that the colour difference seen between dyed samples is due to the different treatments removing varying levels of discolouration. The samples treated with lower concentrations of sodium hydroxide appeared to have a higher level yellow pigmentation prior to dyeing, and a higher level of red pigmentation after dyeing. The colour differences in the dyed samples were attributed to the base colour variation caused by the different bleaching treatments. This is a trend which has been seen throughout this work, with the shade of dyed samples being strongly linked to the raw or scoured colour.



a. Plot of L^* against the hot bleached samples before and after dyeing.



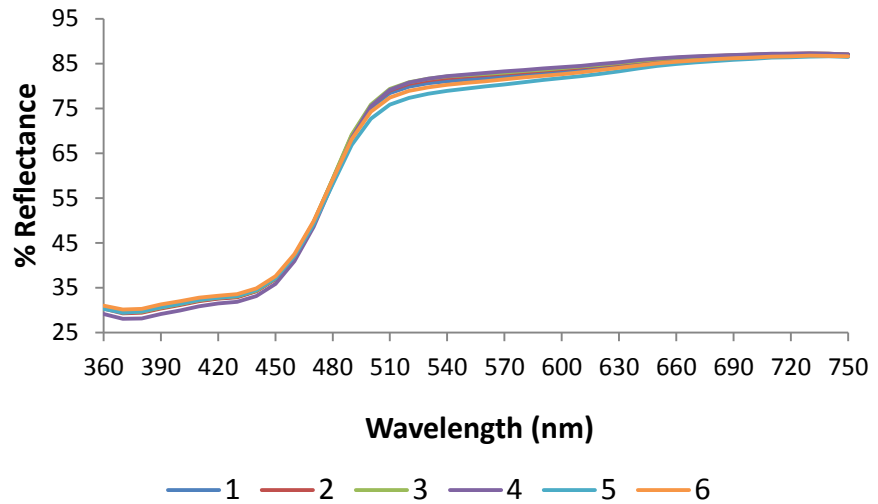
b. Plot of a^* against the hot bleached samples before and after dyeing.



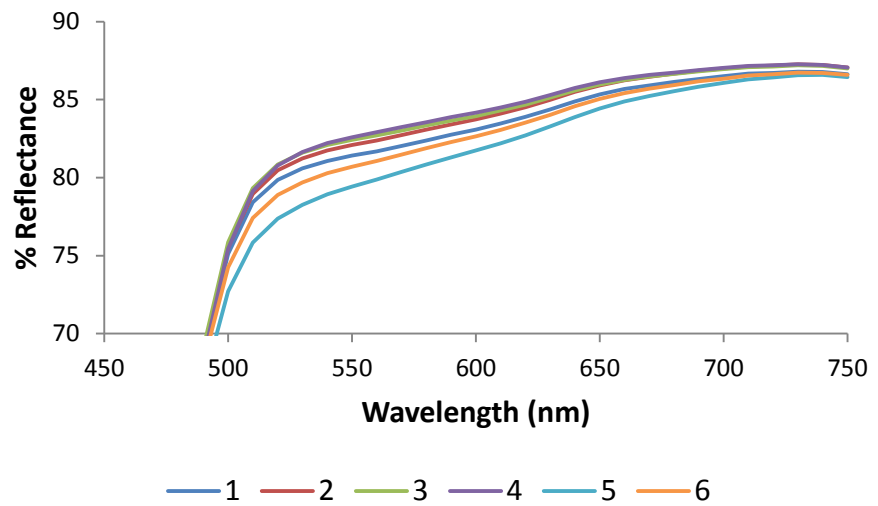
c. Plot of b^* against the hot bleached samples before and after dyeing.

Figure 7.5: Plot of the colour space parameters L^* (a.), a^* (b.), and b^* (c.) against the hot bleached samples before and after dyeing.

A plot was also made of the reflectance values (%) measured for each dyed sample at a range of wavelengths, predominantly lying within the visible region (Figure 7.6). These values are recorded by the colorimeter during measurement of L^* , a^* and b^* . A plateau in dyed colour intensity is evident with almost no difference in reflectance seen between samples 3 and 4, and sample 2 sitting close behind (Figure 7.6b.).



a. The reflectance values of the samples plotted at each measured wavelength.



b. The reflectance values enlarged from 450–750 nm.

Figure 7.6: The reflectance values of the dyed samples plotted against each measured wavelength.

7.2.3 Conclusion

Fabric samples were scoured and bleached using hydrogen peroxide in a single step. Both hot and cold treatments were performed with the hot bleaching treatments being

much more effective. For all treatments the lightness of the samples increased with treatment intensity, with hydrogen peroxide concentration having the greatest effect. The hot bleached samples were dyed, with a difference in dyeability observed relative to the intensity of the bleaching treatments. This difference in dyed appearance was attributed to the differential base colour of the fabrics post-bleaching. This is similar to what was seen in the scouring experiment, and to what has been seen throughout this work with dyed colour being relative to raw or scoured colour.

7.3 Overall Conclusion

A scouring treatment matrix resulted in differences in dyed fabric appearance relative to the intensity of the treatments. Imaging of the samples using SEM showed surface changes to increase with the severity of the scouring treatments, which suggests harsher scouring treatments increase dye accessibility and uptake.

A similar experimental matrix was designed to look at the effects of different bleaching treatments on dyed colour. The hot bleaching treatments were magnitudes more effective and required a much shorter treatment time than the cold bleaching treatments. The lightness of the samples increased with increasing treatment intensity however a plateau was reached. Dyeing of the hot bleached samples showed a difference in dyeability relative to the intensity of the bleaching treatments, with hydrogen peroxide concentration having the greatest effect.

These results suggest that for both scouring and bleaching the difference in dyed appearance observed was due to the differential base colour of the fabrics after treatment. This is in accord with what has been observed throughout this work, with the shade of dyed fabrics being tied to the raw and/or scoured colour.

8. Conclusions and Recommendations for Future Work

This section summarises the conclusions made from the experimental work undertaken in this project, along with recommendations for future work in cotton dyeability.

8.1 Overall Conclusions

This project posed three primary research questions in an effort to further understanding of cotton fibre properties and surface chemistry and how they influence dyeing behaviour:

1. Why do cotton fibres that are nominally the same in terms of fibre properties differ in dyed appearance?
2. What are the key factors related to fibre properties and processing of cotton textiles that affect dyeability?
3. Is there an effective method to directly assess the dyeability of cotton fibre?

These questions were addressed by examination of fibre properties, variety, growing conditions, and fibre handling.

Micronaire and maturity are regarded by many as the fibre properties most significantly effecting dyeability. Micronaire is one of the HVI™ properties considered by mills in purchase and blending of fibres. Small variations in both micronaire and maturity can have a large impact on dyeing behaviour. Accordingly, as seen in the literature review, there is already a significant amount of work studying these properties. As the objective of this project was to determine what other fibre properties may influence dyeability, the effects of maturity and micronaire were only briefly studied in this work. The dyeing study presented in

Chapter 3 was in accord with the current knowledge of dyeability tolerance levels for variation in maturity and micronaire. However, evidence of differential dyeing kinetics were seen when the low and high micronaire sets were dyed competitively.

Fibre properties are influenced by both varietal and environmental factors. Variety had been shown to result in colour difference between species, however there have been few studies of dyeability differences within varieties. The effects of cotton variety on dyeability was the focus of Chapter 4, with samples controlled for maturity and growth environment. Variation in scouring and dyeing behaviour was seen between the Upland and Pima cotton samples, but there was no difference observed within the Upland varieties. This work was extended in Chapter 5 to also consider the effects of growth location. Samples from three cotton producing countries were studied, with maturity values again controlled. Growth environment was found to primarily effect dyeability by influencing fibre properties such as fineness, reflectance, and yellowness. This experiment also looked at the interactions of the samples with three different dyes. It was found that the molecular structure of the dyestuff was less important to the final dyed colour than fabric base colour and colour of the dye itself.

Storage conditions and chemical pretreatments were also considered as potential sources of dyeability variation. The work in Chapter 6 showed increased discolouration to fibres with prolonged exposure to excessive levels of moisture. Additionally, the colour difference prevailed after scouring and therefore translated to differential dyed appearance. Similar results were seen in Chapter 7 in the studies of chemical pretreatments including scouring and bleaching. Different treatment levels were found to remove varying quantities of waxes, pigmentation, and other

impurities, which in turn resulted in base colour differences that affected dyed colour.

From the above work it is clear the overarching conclusion reached in this project is that the raw fibre base colour is the property of cotton primarily effecting the colour that can be achieved by dyeing. The key fibre traits that influence base colour were found to be fineness, reflectance, and yellowness. Chemical pretreatments prior to dyeing can also contribute to dyeability differences by affecting fibre surface chemistry and colour.

8.2 Recommendations to Industry

The above conclusions lead to the following recommendations of how the knowledge gained in this project could best be applied to the cotton industry.

The main recommendation would be that tolerance levels of variation in properties for fibres being processed and dyed together be revised. As well as properties already considered such as maturity and micronaire, other measurements such as fineness, reflectance, and yellowness should also be included.

One implication of this recommendation would be the need for more extensive colour measurement of raw fibre in mills and dyehouses. This may require a review of the effectiveness of HVI™ measurements of reflectance and yellowness to see if they fully correlate with values obtained by other methods such as colourimetry. It would also be interesting to see how dyeability varies across cotton colour classing grades.

It is also recommended that consistent storage and pretreatment conditions be strictly adhered to. It would be advisable for cotton colour to be measured

periodically during storage to ensure it hasn't changed in a way that would affect dyeability. This would be particularly important for bales with higher moisture contents, and those stored in humid environments. Dyehouses should do all they can to ensure all routine pretreatments are consistent, and develop protocols to best integrate fibres with similar mechanical properties but differing base colours.

8.3 Recommendations for Future Work

There still remains a broad scope for future work in cotton dyeability based on the results of this project and other work in the field.

This work stemmed from the concept that some fibres dyed a different colour to others, causing barré effect in industrial dyeing. It was of interest to identify if there were any fibre structural or chemical properties that could enhance dye uptake. It was thought that if colour differences were caused by raw fibre structural or chemical differences, these could then be targeted in the growing of fibre to improve dye uptake and exhaustion for cotton reactive dyes. This work initially set out to identify fibres that dyed differently and then analyse their structure and chemistry to determine what was causing the difference, which would then enable targeting of fibres with these properties. By selecting samples with consistent maturity values, the work aimed to eliminate structural differences caused by this property as maturity is well established to cause difference in dye uptake. A large number of cotton samples were investigated and although dyeing colour differences were found these were all attributed to base colour differences, as opposed to structural or chemical differences. Although fibres with a range of properties and treatments were investigated, the possibilities were not exhausted and future work could continue to analyse fibre dyeability to identify fibres with structural or chemical properties that may offer enhanced dye uptake.

This project had a focus on Australian cotton due to the work that brought about its inception, much of which was research into the properties and global perception of Australian grown cotton, and the relative importance of cotton to the Australian economy. Although touched on in this work, it would be of interest to do further comparison of how the dyeability of Australian cotton compares to internationally grown fibre. Ideally this would include samples from other major cotton producers not studied in the present work such as India and Brazil. This serves the purposes of determining whether dyeability issues are a global problem, investigating the market competitiveness of Australian cotton, and testing the repeatability of the results seen within a different sample set. It is hoped that the presented conclusions regarding base colour and fineness and dyeability can be observed in other cotton samples to further solidify that these are key properties affecting dyeability.

As most of the results presented relate dyed colour back to the cotton base colour it would be interesting to see how dyeability changes over cotton colour classing grades. It would also be of interest to analyse the noncellulosic components on the fibre surface, particularly for the studies involving different pretreatments to determine what is being removed and what remains. Analysis of noncellulosic compounds on the fibre surface may also give an explanation as to why the Australian Pima cotton turned red on scouring, creating dramatic colour differences, whereas the Chinese Pima varieties studied did not. Further study of the yellow discolouration that accumulated on storage in moist conditions would also be of note, particularly to determine if it is removable by bleaching.

There is large scope to further explore dyeing behaviour of pretreated cotton samples particularly in terms of dyeing kinetics. The structural and chemical changes

induced by treatments such as scouring and bleaching may affect exhaustion rates as differential fibre structures may allow faster or greater rates of dye uptake from the bath. This could be examined by periodic sampling of dyebath liquor followed by analysis using UV-Visible spectroscopy. There may also be changes in kinetics due to fibre properties not previously studied in this work such as fineness, yellowness, and variety.

A wide range of further chemical treatments that were not studied in this project may also affect dyeability, such as partial degradation and swelling. Partial degradation of the fibre may potentially affect dye uptake by causing variation in the cellulose structure, making the secondary wall cellulose more accessible. Treatments may include acid hydrolysis or selective removal of chemical components of cotton fibres using enzymes which affect different parts of the fibre structure such as cellulose (cellulases), pectin (pectinases) and xyloglucan (xyloglucanases). For example, pectin acts as a glue holding together the outer layers of the fibre. The use of pectinase enzymes may facilitate removal of only these layers of the fibre whereas a cellulase enzyme would target the inner cellulosic layers of the fibre, possibly degrading much of the bulk of the fibre. Cotton fibres may have differing levels of these components which may have an influence on the chemical and physical interactions between dyes and fibres. The quantity and composition of the various noncellulosic components of cotton fibre can be determined by chemical extraction and analysis. Also of interest in relation to the structure of cotton fibre is the effect of swelling on dye uptake. Cotton fibres naturally swell in water but may also be chemical swollen by treatments such as alkaline mercerization. Mercerization opens up the fibre structure, which may alter the accessibility of the fibre to dyes and other reagents, and could also affect other fibre properties. These areas have been well

studied in terms of scouring and fibre properties but not so much in the context of dyeability.

For all of the above treatments further analysis of the surface morphology would be required. This would ideally be done by a combination of SEM and AFM, with the two techniques giving complementary information to gain a better insight of the fibre surface. Using SEM a 2D image of a sample is constructed based on electron scattering signals, whereas AFM provides a 3D image by physically probing the surface.

For both the work already done and the suggested future work it would be of interest to analyse the chemistry of dyed fibres using FT-IR or Raman. There is a possibility this type of spectroscopy could demonstrate the extent of bonding, or in this case dye uptake, by the intensity of the peaks in the spectra, with a more intense peak indicating a greater concentration of dye in the fibre.

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