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Processing of Dyed Cotton-based Waste Garments for Re-use Through the Lyocell Processing Technology

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Abstract

The world's population growth together with the change in lifestyle and fashion culture has led to an increased demand for textile fibres. Fuelling this growth is the increasing number of short fashion seasons in the clothing retail markets, which has led to the overall decreased lifespans of clothing in developed countries such as the United Kingdom, which in turn has resulted in a significant increase in waste textile. The current disposal routes for the generated waste textile is through reuse or recycling, with up to 30% of the waste being landfilled or incinerated. Both landfill and incineration of waste textile are associated with environmental pollution, while reuse of waste garment as second-hand clothing is associated with the decline of the textile industries in developing countries due to the lower cost of the imported second-hand garments undercutting the local products. Moreover the common mechanical recycling of the waste textile back to the component fibre is also compromised by the presence of colour and mixed fibre blends which in turn results in low value non-woven products.

This study investigated the potential methods to chemically recycle waste cotton garments and reuse the recycled materials as feedstock for producing regenerated cellulosic fibres through the Lyocell process. Methods to chemically 'strip' colorants and finishing agents from waste cotton garments were first established and their efficiency evaluated. Acid and alkali hydrolysis, dithionite reduction and oxidative bleaching were evaluated as potential methods for delivering cheap, efficient and environmental-friendly colour removal from cotton substrates. It was established that, the sequential acid/dithionite/peroxide treatment could strip a wide range of colorants from cotton fabrics, while the sequential acid/alkali/peroxide treatment could only strip relatively few colorants from the cotton substrates.

The recycled waste cotton garments were successfully used to generate Lyocell fibres from both 100% recycled cotton pulp and a blend of recycled cotton pulp (20%) and wood pulp (80%). Both the fibre's mechanical and structural properties were assessed using tensile parameters, X-ray diffraction spectroscopy (XRD), Fourier Transform Infrared (FTIR) and scanning electron microscopy (SEM) and were compared to the conventional Lyocell fibres from wood pulp. The overall findings of this study demonstrated the potential of reusing waste cotton garments through the Lyocell process and producing fibres with properties similar to conventional Lyocell fibres.

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Chapter One: Introduction

1.1 BACKGROUND OF THE STUDY

World population growth together with the ongoing improvement in consumer living standards' has resulted in a steady increase in global fibre consumption over the past few decades [1]. Similarly the increasing number of fashion seasons per year in the clothing retail markets has led to decreased lifespans of textile garments in developed countries such as the United Kingdom and the United States of America. Availability of cheap clothing from retailers such as Primark, Zara and H & M has also made fashion more affordable to millions of consumers [2]. Accordingly the impact on the amount of waste generated has increased, making the textile industry one of the most significant waste-generating sectors in the world [3-5]. For instance, about 1.14 million tons of waste textiles (including clothing, carpets and footwear) were generated in the UK in the year 2012, accounting for about 4.3% of the total waste from households [6]. More than half of the generated waste textiles were clothing [7].

As with all solid waste, the current methods for handling waste clothing are reuse, recycling and disposal through landfill or incineration [1, 8]. A report by the Waste and Resource Action Programme (WRAP) indicated that, of all end-of-life clothing generated annually in the UK, 48% is reused in their original form while 14% are recycled into other products such as filling materials and wiping cloths for industrial use. The remaining 38% are discarded into domestic waste streams through incineration or landfill due to being unfavourable for both reuse and recycling [9] or because they were probably not separated from other waste. Figure 1.1.1 shows the destination for end-of-life clothing, where the largest volume of these materials is reused as second-hand clothing, primarily in developing countries.

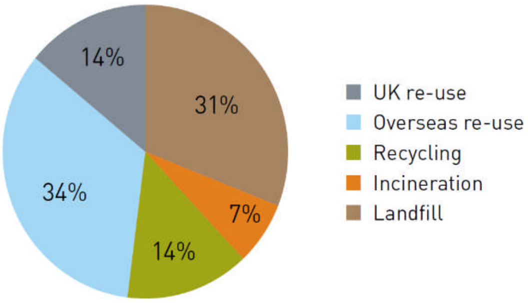


Figure 1.1.1 Destinations of end-of-life clothing [9]

Reuse of waste clothing refers to using an existing product within the same production chain [10], with or without any modification. Developed countries dispose most of the first generation clothing by channelling them to developing countries, especially African countries, where they are reused as second-hand clothing [5, 11]. However the quality of the collected waste clothing is decreasing annually due to the nature of fast fashion which produces products with short lifespans and low quality standards [12]. For instance, in 2005, about 55% reusable clothes and shoes were collected, however, only 43% of these materials were collected in the year 2008 [13]. In addition, second-hand clothing is associated with the decline of the local textile manufacturing industries in these developing countries [14, 15], the reason being unfair competition between cheap second-hand clothing and local clothing manufacturers [15]. Some African countries such as Nigeria, Ethiopia and South Africa have already banned the importation of second-hand clothing while other countries like Ghana, Tanzania, Rwanda and Uganda are currently debating the introduction of restrictions on their importation [14] for the purpose of reviving their local textile industries [16]. This could potentially lead to a big fall in a large market for second-hand clothing in the near future. Moreover the importation of new, low-cost Chinese clothing into African countries also suggests declining of the second-hand clothing market in Africa [5, 12, 14].

Garments that are unsuitable for reuse can be recycled into new products usually through mechanical shredding or pulling of garments into small fractions and into subsequently individual fibres [1, 5]. Products of the mechanically recycled waste garments are fibrous materials used for producing yarns, high quality papers and non-woven products for insulation, furniture filling and automotive materials [1]. However the diversity of the end-of-life clothing in terms of colour and fibre content usually results in yarns of poor colour consistency, while mechanical processing of waste garments results in fibre shortening and poor strength in the resultant yarns [1, 17, 18]. Chemical recycling in which waste materials are depolymerised or dissolved in a selected solvent before being spun into new fibres is another waste recycling option. The process is well established for synthetic polymeric materials such as polyester (PET) and PET bottles [19-21] where it is reported to produce fibres of superior quality in terms of colour uniformity and yarn strength in comparison to the mechanically recycled materials [18]. However the process is not fully exploited for the clothing grade waste where the presence of impurities such as dyes and finishing agents remain as processing challenge. Additionally little research is also reported on chemical recycling of waste cotton garments [5, 17, 22] which suggests the need to explore further the possibility of chemically recycling these materials.

End-of-life clothing that are not suitable for reuse or recycling are disposed of through incineration or landfill. However the current landfill and incineration waste disposal routes present a mounting problem as the population continues to grow and we seek to maintain and improve our environment. Too much waste in landfill can lead to environmental pollution due to overloading of the biodegradation processes, resulting in rapid filling up of landfill. Additionally the process can lead to the production of large amounts of greenhouse gases, such as methane, a significant contributor to global warming. Waste clothing in landfill can also decompose producing leachate which has the potential to cause contamination of both surface and ground water sources [11, 23]. Despite the constant need to create new landfill spaces, the increasing landfill costs and strictly enforced environmental regulations are also challenges to this waste disposal route [22] suggesting the need to explore alternative waste disposal methods and by-product recycling. Although the incineration of waste for energy recovery is said to be a better alternative to landfill, the amount of energy and resources (water, land, fertilizers and pesticides) initially put into the production of fibres and the energy used for subsequent garment production does not equate effectively to the small proportion of energy (about 4% of the energy consumed in garment production) recovered from the incineration process [24]. Similarly the process generates harmful end-products in the form of ash and noxious gases, and still requires landfill to dispose the post-combustion ash materials [8, 25].

Apart from increased waste generation, the increased world population has also led to a significant growing demand for natural fibres, such as cotton and man-made cellulosic fibres [1, 26]. The overall global fibre consumption reached 72.5 million tons in 2010 and is projected to grow with an average growth rate of 3.1% p.a. to about 133.5 million tons in 2030 [27]. However the current trend of cotton fibre production is being influenced by pressure on land usage due to the population growth which indeed requires more arable land and water for food crop production than for non-food crops [26, 28, 29]. The enormous demand for fertilizers, pesticides and irrigation used for cotton production has also been linked with various impacts to the environment, including the disappearance of the Aral Sea in Central Asia – formerly the world’s fourth largest freshwater sea [30].

The above issues limit the possibility of increasing production of cotton fibres despite its huge demand, suggesting the need to explore other ways to fill the resource gap resulting from reduced cotton fibre production.

The combination of waste impact to the environment and resource restructuring makes recycling of waste cotton into new cellulosic fibres an attractive option. A number of researchers have reported the possibility of using waste cotton materials as the pulp for manufacturing of regenerated cellulosic fibres; where cellulosic materials are recovered, dissolved and spun back into yarns [31, 32]. However the process is not yet commercially available. Moreover the reported work only looked at clean-undyed cotton materials, crease resist finished cotton garments and denim waste. None of the work reported to have successfully chemically processed waste cotton garments that contained dyes or pigment prints. In 2014, Renew:cell in Sweden reported to have created a dress out of recycled cotton using the rayon (viscose) process, but reported the presence of dyes as a limitation to their chemical recycling technology [33]. This suggests the need for further investigations into the possibilities of purifying waste cotton garments that can be used as feedstock for manufacturing regenerated cellulosic fibres. The most common sources of cellulose pulp are wood pulps and cotton linters [26], but it’s clear that a significant amount of cellulose could be obtained from recycled waste cotton garments.

In this study we investigated the possibility of using a chemical recycling technique to process waste cotton garments that contained dyes and pigments and used the recycled materials to generate ‘new’ fibres through the Lyocell process as a potential solution to the mounting waste textiles and the problem of resource scarcity. The benefits of recycling waste cotton garments into Lyocell fibres include less environmental issues associated with the fibre manufacturing process due to the solvent used being less problematic, non-toxic and over 99.5% recyclable [26, 34, 35]. The chemical recycling technique was selected due to its potential to offer a closed-loop recycling system as the waste materials can be re-spun and made into new yarns, fabrics and new garments.

1.2 OBJECTIVES OF THE WORK

The main objective of this research was to develop an environmentally-friendly method for recycling waste cotton garments with the aim of minimizing the impact of waste textiles on the environment. The research investigated ways of reducing the total amount of waste garments that is landfilled or incinerated annually, while offering an economically viable source of regenerated cellulosic fibres. In the context of this study, waste cotton garments are referred to as dyed or printed waste cotton garments. In order to accomplish the stated main objective of the study, the following specific objectives were established:

I. Develop methods that could chemically remove colorants, crosslinks and impurities from waste cotton garments

A large proportion of waste cotton garments usually contain cellulosic dyes/prints such as direct, vats, sulphurs, reactive dyes and pigments. However, the presence of dye molecules and other finishing agents cross-linked to cellulose present challenges to further processing of the recycled cellulose into a spinning solution through regeneration systems due to the reduced cotton solubility in the selected solvents. Furthermore, the presence of impurities such as heavy metals present safety issues with the NMMO solvent and has the potential to decrease the solvent recycling rate by contaminating the solvent. The colour components of the waste cotton garments can also affect the quality (such as the brightness and re-dyeability) of the new fibre. Therefore to reuse the waste cotton garments as feedstock for fibre regeneration, purification of the waste material is vital in order to establish a cost-effective regeneration process and allow further processability of the regenerated fibres.

In this study methods to chemically remove colorants, finishing agents and other impurities from waste cotton garments were developed and were optimised in order to purify the waste cotton materials and facilitate cost effective fibre regeneration process. Two methods, based on a combination of acid, alkaline and peroxide solutions as well as a combination of acid, dithionite and peroxide solutions were analysed. Optimal treatment conditions such as concentrations, time and temperature were also established. The effect of the established methods in removing colorants was assessed in terms of changes in colour strength, CIELAB colour difference and ISO brightness. Unlike the combination of acid, alkali and peroxide treatment; the combination of acid, dithionite and peroxide treatment removed a wide range of colorants from waste cotton garments.

The efficiency of the established methods in terms of removal of applied colourless chemicals was also extended to removing performance finishes such as crease resist finishes, cationic fixing agent and fluorescence brightening agents where Fourier Transform Infrared (FTIR) spectroscopy was used to assess the effectiveness of the stripping methods in removing the specific finishing agent.

II. Production of a fibrous cotton pulp from the recycled cotton material

The stripped waste cotton garments were broken down into fibrous materials to form a pulp thereby allowing the subsequent dissolution of the pulp in a specific solvent. The suitability of the resultant pulp was analysed in terms of fibre length analysis and its solubility through dissolution in a cupriethylenediamine hydroxide (CED) solution. The level of polymer degradation caused by chemical treatment of the waste cotton garments was also analysed through changes in limiting viscosity and the degree of polymerization (DP) of the pulp reclaimed from the waste cotton garment.

III. Production of fibres through the Lyocell processing technology

The resultant cotton pulp was dissolved as per the Lyocell processing technology, and the obtained solution (spinning dope) was extruded through a spinneret and into the fibre regeneration bath. Five types of Lyocell fibres, namely: Lyocell-1, Lyocell-2, Lyocell-3, Lyocell-4 and Lyocell-5 were produced as detailed in Table 1.2.1. The properties of the resultant fibres were analysed and compared to the conventional Lyocell fibres from 100% wood pulp (Lyocell-0), where surface, supermolecular and mechanical properties of the spun fibres were established.

Table 1.2.1 Description of the Lyocell fibres regenerated from recycled cotton pulp

Fibre name	Description
Lyocell-0	Regenerated from 100% conventional undyed wood pulp pretreated by reductiom and oxidation processes [36].
Lyocell-1	Regenerated from 100% recycled cotton pulp obtained from unmercerised cotton fabrics previously dyed with C. I. Reactive Black 5 then stripped in the sequential acid/dithionite/peroxide method.
Lyocell-2	Regenerated from 100% recycled cotton pulp obtained from unmercerised cotton fabrics previously dyed with C. I. Reactive Blue 19 then stripped in the acid/dithionite/peroxide method.
Lyocell-3	Regenerated from 100% recycled cotton pulp obtained from post-consumer denim jeans, stripped in the sequential acid/dithionite/peroxide treatment.
Lyocell-4	Regenerated from 20% recycled cotton pulp used in Lyocell-1 and 80% wood pulp used in Lyocell-0.
Lyocell-5	Regenerated from 20% recycled denim pulp used in Lyocell-3 and 80% wood pulp used in Lyocell-0

Figure 1.2-1 shows the suggested life cycle for the waste cotton garments and for the cellulosic fibres regenerated from recycled waste cotton garments.

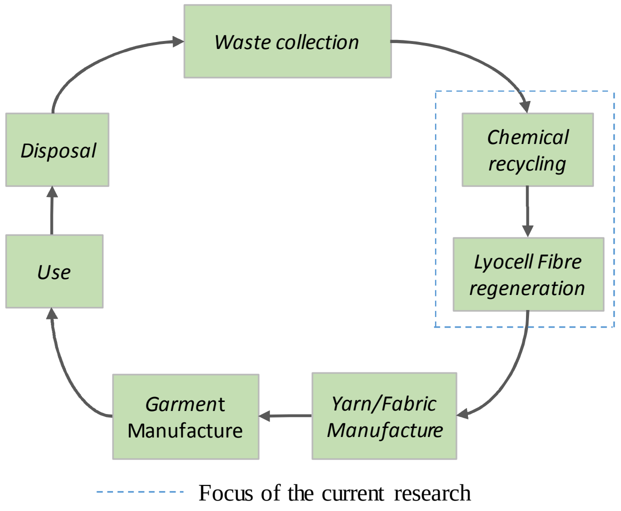


Figure 1.2.1 Suggested life cycle of the waste cotton garments

Chapter Two: Literature Review

In this chapter the overview of the current global recycling process, together with the background ideas related to cellulosic fibres, their coloration, finishes and solubilising solvents used for cellulosic fibres are reviewed. The chapter also reviews the existing methods used to remove colorants and finishing agents from cotton substrates. Lastly, the chapter also summarises a study previously done by Dr. L. Haule on the recycling of cotton garments for reuse as raw materials for the generation of Lyocell fibres.

2.1 OVERVIEW OF THE GLOBAL CLOTHING RECYCLING PROCESS

2.1.1 Introduction

World fibre and textile consumption has been increasing annually due to the increased population growth and the overall increase in textiles consumption by consumers. The world population has increased from 6.1 billion to 7.3 billion in the period of 2000 to 2015 [37]. Accordingly, the annual fibre consumption has increased from 47.3 million tons to 95.6 million tons [38, 39] within the same timeframe.

The increase in people’s consumption habits has led to the increased buying of fibres and textile products in general. Most of these textile products (especially clothing) have a short to medium service life, lasting up to a few years in their ‘first life’ [1]. The short life cycle of these products is driven by the fast fashion sector, which is characterised by lower costs and clothing with short lifespans. At the end of their ‘first life’, these materials are discarded as waste. This behaviour has resulted in a significant amounts of waste clothing being generated annually. For the purpose of this study, ‘first life’ clothing refers to garments that have only been worn by one consumer.

The UK consumes about 2.7 million tonnes of textiles per annum [40]. Approximately half of this consumption (about 1.4 million tonnes) is clothing with the fast fashion sector making up one-fifth of the UK market [7]. Subsequently, about 1.13 million tons of end-of-life clothing is generated annually [9] and are either reused, recycled, incinerated or go to landfill. Figure 2.1.1 presents the ideal hierarchy for managing waste textiles. The waste management hierarchy favours the reuse option which is reported to account for about 80% of the sorted volume of post-consumer textiles [40]. Recycling of waste garments is also favoured by this hierarchy, however, the actual amount of waste garments that are being recycled into other products are significantly lower than that presented in the model [9]. Similarly large amounts of waste garments (between 350,000 and 700,000 tonnes) are disposed of through landfill and incineration, despite the materials having commercial value either as reused clothing or when recycled into wiping cloths, insulation materials and other non-clothing uses [9].

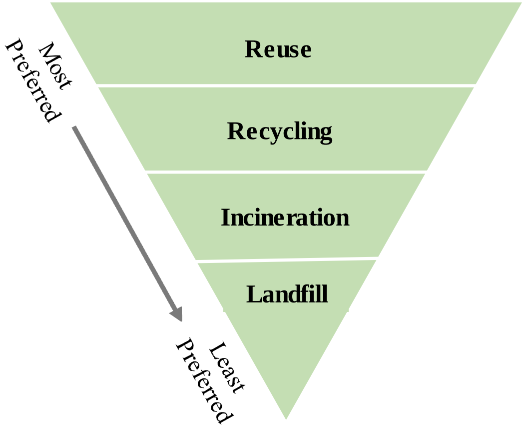


Figure 2.1.1 The hierarchy for waste management routes [adapted from DEFRA [41]]

Despite the increasing demand for fibres, the current preference for cotton fibre production is being influenced by pressure on land usage due to population growth, which indeed requires more arable land and water for food crop production [26, 28, 29]. The amount of available arable land is however decreasing. It is reported that the available arable land decreased by 1.2% in 2015, and is expected to decrease by almost 5% by the year 2030 [27]. This implies that more arable land that is currently used to grow non-food crops, particularly cotton, will be needed to secure food crop production. Additionally the environmental impact associated with the cotton production is significant. The fibre requires enormous amounts of irrigation water (varying from $2m^3$/kg to $29m^3$/kg of fibre depending on the geographical area), fertilizers and pesticides which in one way or another affect the environment [18]. For instance the irrigation needed for cotton growth has been linked to the disappearance of the Aral Sea in Central Asia – formerly the world’s fourth largest freshwater sea [30]. The above issues limit the possibility of increasing production of cotton fibres despite its huge demand.

The combination of resource restructuring and the overall waste clothing impact to the environment suggest the need to explore other ways to fill the resource gap resulting from reduced cotton fibre production while reducing the amount of waste textiles that are annually disposed of through landfill or incineration. It’s therefore the aim of this study to explore potential methods for recycling waste cotton garments and reuse the recycled materials as feedstock for generating Lyocell fibres. This will potentially provide an economic and environmental valuable use of waste cotton garments (that would otherwise be sent to landfill) whilst producing raw materials for cellulosic fibres.

2.1.2 The secondary flow of waste clothing in the UK

There are a number of pathways through which consumers can dispose of clothing that are no longer needed. These include: direct reselling or exchanging between individuals for reuse; discarding the clothes through domestic disposal and donation for reuse through collection services provided by charities, local authorities, retailers and other organisations [40]. Clothes that are directly resold are being reused by new owners, while those discarded through domestic disposal end up in landfill or incineration. The donated clothing are collected, and they are sorted according to their end-markets, namely: reuse of clothing that can be worn again, recycling of clothing that can no longer be worn and disposal of the remaining waste through incineration or landfill. The overview of the secondary stages of clothing after their first life use is presented in Figure 2.1.2. Reuse, recycling and disposal of collected end-of-life clothing are further discussed in the following sections.

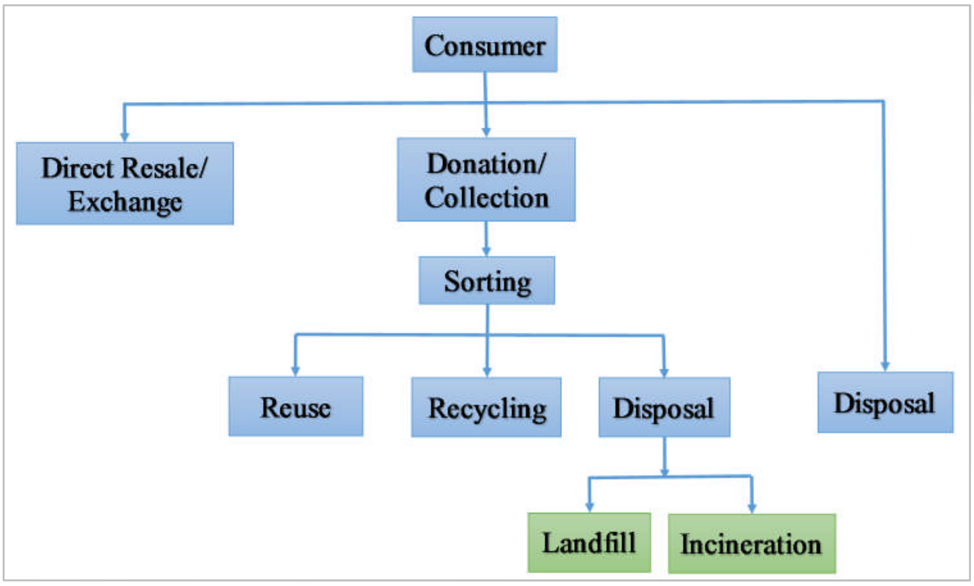


Figure 2.1.2 Overview of clothing end-of-life management routes [18]

2.1.2.1 Reuse of end-of-life clothing

Reuse of the post-consumer clothing accounts for about 48% of the total volume of the collected materials [9]. A small quantity of the material (14%) is resold through charity shops and vintage clothing markets within the UK, however, the largest output for these garments (34%) is through exportation to developing countries such as Bangladesh, some African countries, and some East European countries that buy the garments at low costs and reuse them as second-hand clothing. The United Kingdom is reported to be the second largest exporter of second-hand clothing in the world with about 319,998 tonnes of clothing exported in 2010, second only to the United States of America who exports over 500,000 tonnes yearly [42].

The main advantage of the reuse route is its ability to offset new purchases while reducing the amount of first life waste clothing sent to landfill [1, 10]. As a result of these offsets, the need for resource and energy use, the cost of production and its associated environmental impacts that would otherwise be created as a result of producing new items are also avoided [5, 10]. However the reuse route is currently under pressure due to the decline in the quality of the clothing which is associated with the nature of the fast fashion which produces products with short lifespans and low quality standards [5]. For instance the composition of the textile waste collected in 2008 had 43% by volume of reusable quality clothes and shoes compared to 55% collected in the year 2005 [13]. The low quality materials cannot be reused and therefore require other disposal possibilities, including recycling, landfill or incineration. In addition the reuse route is limited to clean and proper clothing; stained or torn clothing cannot be accommodated by the route [24], requiring other disposal options.

A further impact of the reuse of second-hand clothing is believed to be the decline of the local textile manufacturing industries in developing countries [14, 15], with unfair competition between cheap second-hand clothing and local clothing manufacturers being cited as the major issue [15]. Some developing countries such as Ghana, Tanzania, Rwanda and Uganda have imposed strict importation rules for second-hand clothing [14, 16, 43] which could have a significant negative impact on the market for second-hand clothing in the near future. Moreover the importation of new, low-cost clothing from the Far East into African countries may also suggest a decline of the second-hand clothing market in Africa [5]. It is also worth noting that, exporting of used garments to developing countries for reuse does not completely solve the problem of landfill, as once they are no longer serviceable in their new location they could ultimately end up in landfill. However the route is still beneficial as it temporarily diverts waste clothing from landfill by extending their life cycle while eliminating the need for new purchases.

2.1.2.2 Recycling of waste clothing

Clothing that can no longer be worn is resold to recycling and reclamation industries where they are used to make other products such as industrial wipes, non-woven materials or yarns [11, 29]. Recycling can be defined as a process of breaking down products that are at the end of their useful life and transform them into new products of the same function or to a secondary function [10]. The process can be categorised into two groups: closed and open loop recycling. In closed loop recycling, end of life products are recycled into the same or similar products, for instance, recycling of waste clothing into new fibres or yarns that can be used to make new clothing [17] as indicated in Figure 2.1.3.

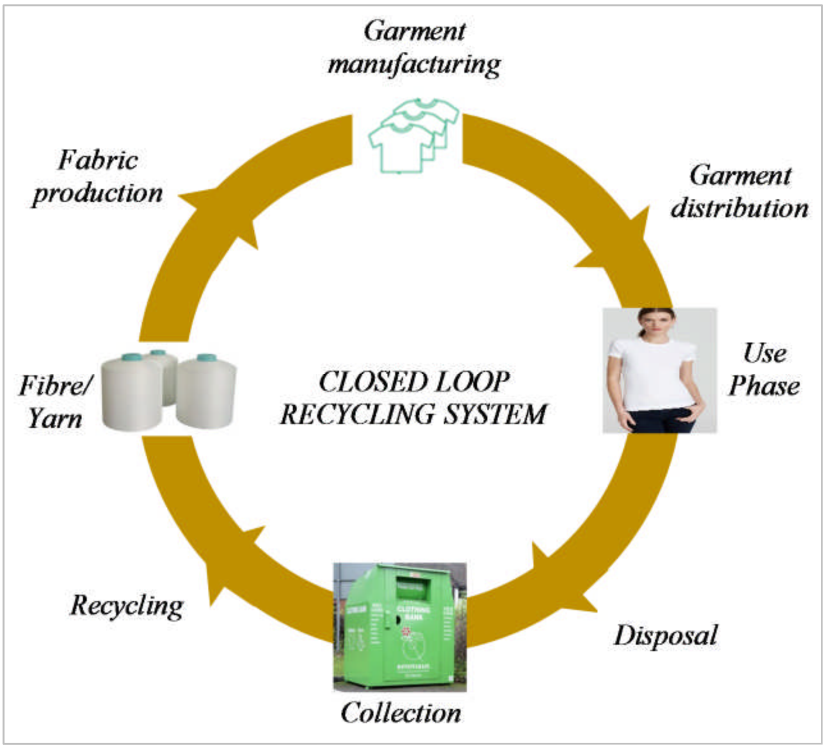


Figure 2.1.3 Closed loop recycling technique adapted from ECO-CIRCLE [19]

In contrast in an open loop recycling, the process input parameter is different from the output parameter. The recycling process results in products of lower grade, lower purity and lower value than the original material [10]. After its use, the formed products will ultimately be disposed of in landfill or by incineration as it cannot be recycled repeatedly. Therefore open loop recycling only temporarily diverts waste from landfill or incineration. Figure 2.1.4 show the open loop recycling process for post-consumer waste textiles, where garments are recycled into non-garment products.

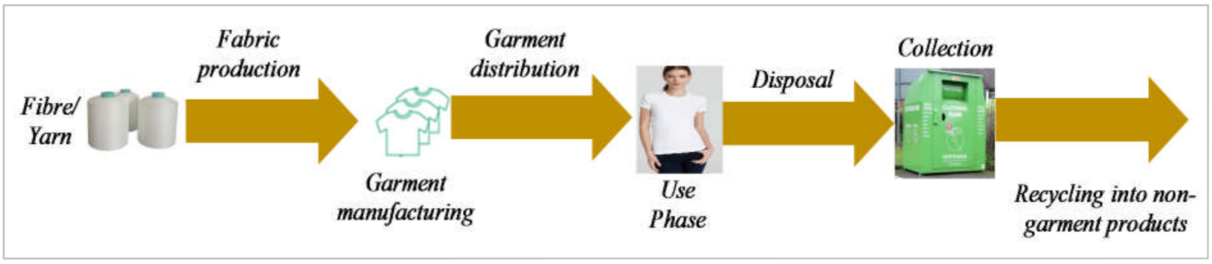


Figure 2.1.4 Open loop recycling technique [19]

Textile recycling includes both pre-consumer (industrial) waste such as yarns and off-cut fabrics as well as post-consumer waste. Industrial waste can be obtained from centralized locations and is potentially easily recycled by recycling industries in large quantities because it's not yet sewn into complicated garments [11, 20]. On the other hand, recycling of post-consumer waste is only performed on a small-scale due to the labour intensive sorting process required before recycling. In addition the post-consumer waste usually contains a mixture of fibres, dyes, finishes and other additives [25] which complicate the recycling process.

Waste clothing can be recycled through mechanical processes where materials are physically broken down into fibrous materials without changing the chemical structure of the material or through chemical processes where materials are depolymerised or chemically dissolved to their precursor chemicals which are then made into new fibres through spinning (Figure 2.1.5).

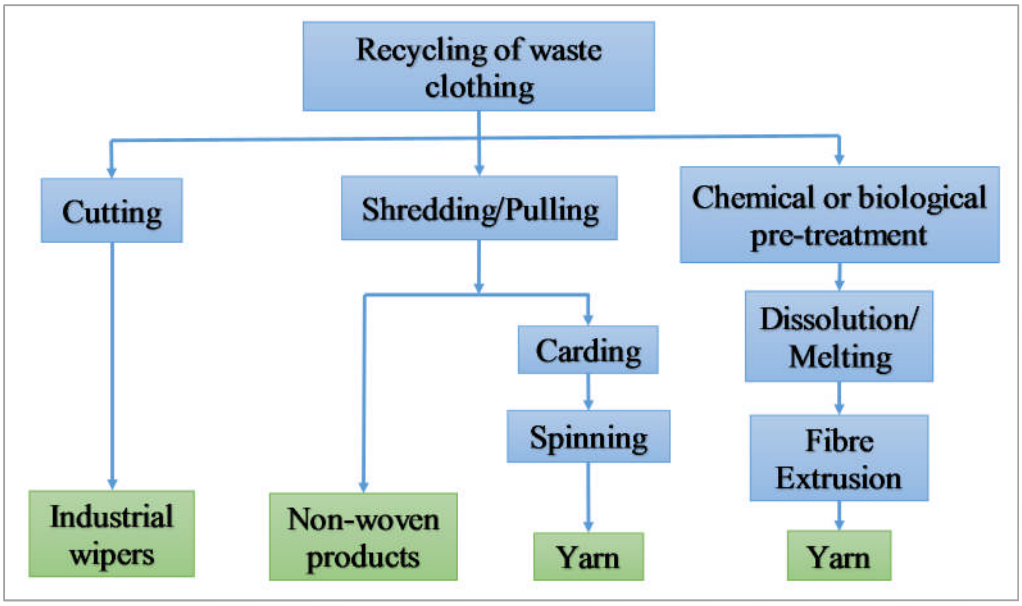


Figure 2.1.5 General recycling process for waste clothing [18]

Cutting of waste into industrial wipes is another category for recycling of waste clothing through mechanical recycling however, it is out of the scope of the current study. Mechanical and chemical recycling processes are hereunder described in detail.

2.1.2.2.1 Mechanical recycling of waste clothing

Conventional methods for mechanical recycling of textile articles are well known [1]. A typical recycling process of post-consumer waste clothing involves re-sorting the materials from a collection centre in terms of colours and fibre content and disintegration of the textile articles into smaller sizes by a mechanical action called shredding or grinding usually by the rotary blades before further separating fabric pieces into individual fibres using spiked surfaced drums to clean and mix the fibres [1, 11, 25]. Non-fibrous materials such as zippers, threads, buttons, metals and labels are removed prior to the carding process. The obtained fibrous materials can be used for producing non-woven materials or can be used as pulp for paper production. In addition, some recycled materials can be re-spun into yarns for fabric production such as low-end blankets and carpets [11].

The main advantage of mechanical recycling is its ability to accept a wide range of inputs without being affected by the material contents. However the actual processing of recovered waste clothing into new fibres/yarns is limited by the overall poor quality of the materials resulting from colour inconsistency and poor yarn strength. For instance, the diversity of colours in waste clothing result in fibres and yarns of poor colour consistency or of duller colours [1, 10]. Additionally mechanical recycling involves continuously chopping down of fibres into shorter lengths, resulting into fibres of reduced strengths unless blended with virgin fibres. Moreover the presence of short fibres in the recycled materials presents difficulties in the subsequent yarn spinning. For these reasons, the actual processing of the mechanically recovered waste clothing into new fibres/yarns is still relatively minor [5].

The poor quality of the mechanically recycled materials makes them unsuitable for high-end uses such as high quality apparel [13] unless they are mixed with high quantities (more than 70%) of virgin fibres [18]. A major proportion of mechanically recycled fibres are, therefore, limited to the production of lower value products such as non-woven materials for producing mattresses, carpet underlay and in automotive applications. In Germany for instance, about 95% of the recycled fibres are used for non-woven production including, carpet underlay, thermal and acoustic insulation materials for the automotive industry, geotextiles and agro-textiles [1].

2.1.2.2.2 Chemical recycling of waste clothing

Chemical recycling involves processes that either maintain the chemical structure of the materials through melting or dissolution and re-extrusion of the dissolved materials to generate new fibres or breakdown the fibre to a polymer (depolymerisation) followed by re-polymerisation and re-extrusion of the materials through a spinneret to generate new fibres [18]. Hydrolysis and enzymatic based recycling processes are also categorised as chemical recycling processes, however, they were out of the scope of this study. In this study the solvent based recycling technique, where materials are dissolved in a specific solvent to generate a spinning solution was of relevance and importance. The process was selected due to its ability to generate fibres with physical properties nearer to those of virgin fibres without degrading the original polymer.

A typical solvent based chemical recycling process involves disintegration of the textile articles into smaller sizes, dissolution of the material in a chemical solvent, passing the solution through a spinneret to generate new fibres which are then spun into yarns ready to be used for fabric weaving or knitting [10].

The main advantage of the chemical recycling process is the possibility of removing colours and other impurities (such as metals and finishing agents) and its capability to produce fibres with properties that are similar or superior to those of the virgin fibres [20]. In addition, the process allows the waste materials to be re-spun and made into new yarns, fabrics and garments; thereby offering value-added recycling. The disadvantage of chemical recycling is however its limitations on what can go into the recycler. The presence of coatings and fibre blends may contaminate the chemical process and inhibit the separation of the precursor chemicals [18, 20]. Therefore careful sorting of the inputs is critical for successful chemical recycling.

The most established chemical recycling process is via depolymerisation and re-polymerisation of synthetic fibres, particularly polyester. An example of the process is the Patagonia-Teijin (ECO-CIRCLE) process in which polyester materials are chemically dissolved to their precursor chemicals (dimethyl-terephthalate and ethylene glycol) prior to re-polymerisation and re-spinning into new fibres [8, 17, 20]. However there seems to have been little progress in this area mainly due to high investment and operational costs [40]. Additionally the process is not fully exploited for recycling post-consumer clothing except for the Patagonia range of garments. This could be due to the complexity of most post-consumer clothing, presence of contaminants and fibre blends which could contaminate the chemicals if used. Furthermore the technology has limited input materials; it can only process polyester rich (at least 80%) garments which exclude many polyester blends [13, 18].

Little knowledge is currently available on the application of chemical recycling process on natural fibres, specifically cotton based waste clothing. As already stated, the presence of colorants, finishes, impurities and fibre blends in most waste clothing not only contaminate the solvent but also limit their dissolution in most solvents [31]. The introduction of a pre-treatment stage such as clean up techniques to extract and remove contaminants such as dyes and other finishing agents from the waste materials could help alleviate the problem. Technological investigations to chemically recycle waste cotton textiles are currently underway in countries such as the United Kingdom (Worn again), Austria (Lenzing), Sweden (Renewcell), USA (Loopool), Netherlands (Saxion) and Tempere University in Finland [18].

2.1.2.3 Disposing of waste clothing

Clothing that is unsuitable for both reuse and recycling is discarded either through landfill or incineration. Landfill is by far the most dominant municipal waste disposal route in the UK, where between 350,000 and 700,000 tonnes of waste textiles are landfilled annually [9, 13]. Today, a number of landfill sites are closed while many others are reaching their full capacity. The costs of dumping waste in landfill are also increasing dramatically, for instance, in the UK, the prices increased from £48/tonne in 2010 to £82.6/tonne in the year 2015 [44]. Similarly the decomposition of the waste textiles in landfill contributes to the formation of leachates which can potentially contaminate underground water [1, 11, 23]. Furthermore waste textiles in landfill can decompose and generate landfill gases such as methane and carbon dioxide which contribute to global warming. These effects signify the need for a closer examination of other waste disposal alternatives such as the recycling described above.

An alternative to landfill waste disposal is incineration or incineration for energy recovery. Incineration for energy recovery is well practiced in some European countries such as Denmark, Sweden and German [8]. The process aims at reducing the bulk of waste needing ultimate disposal in landfill to an inert inorganic ash residue that has virtually no capacity to produce organic leachates or methane when disposed of in landfill [24], whilst generating energy (heat or electricity). However incineration is less practiced in the UK with only 7% by volume of the collected waste clothing being incinerated annually [9]. Nevertheless the process not only requires modern incinerators to recover energy released by the combustion process, but also the price of incineration is relatively high. In addition the portion of reclaimable energy is relatively low (about 4%) compared to the embedded energy of textile products [24]. Moreover the burning process generates carbon dioxide and other volatile pollutants and still requires land to dispose of the post-combustion ash residues through landfill [8, 25].

In 2014, Zero Waste Europe suggested banning both landfill and incineration by the year 2030 [45] as a step towards a Circular Economy which, among others aims at reducing waste generation as well as reducing the environmental impacts associated with production and consumption in both the UK and abroad [46-48]. The Circular Economy requires that resource efficiency is maximised and that waste materials become valuable inputs to other processes instead of being thrown away [48]. However the current process is predominantly linear, involving resource extraction, product manufacture, use and disposal [47, 48]. This suggests the need to find a solution to have a Circular Economy. The current research aims at establishing viable techniques to chemically recycle waste cotton garments and reuse the recycled materials as feedstock for regenerated cellulosic fibres or other value-added products with higher quality in terms of strength and colour. This could potentially reduce the amount of waste that is landfilled annually, while offering raw materials for fibre regeneration.

2.2 CELLULOSIC FIBRES

2.2.1 Introduction

Cellulose is a naturally occurring organic polymer, consisting of long chains of anhydroglucose units [49]. The anhydroglucose pyranose ring structures (Figure 2.2.1) are connected together by β-1, 4-glucosidic oxygen linkages. Each glucose unit contains three alcoholic hydroxyl groups (–OH), one primary located at C-6 and two secondary located at the C-2 and C-3 positions [50-52]. The –OH attached to C-1 forms a part of a reducing group while that at C-4 is a free secondary alcohol group.

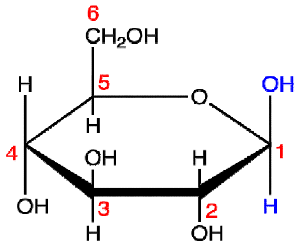


Figure 2.2.1 Structure of the pyranose ring showing positions of hydroxyl groups [53]

The number of anhydroglucose units (AGU) represents the length of the polymer chain known as the Degree of Polymerisation (DP), expressed as an average number of anhydroglucose units per chain molecule (n). The DP usually varies with the treatment on cellulose, for instance undamaged cellulose can have a DP as high as 14,000 which can be reduced to about 2,500 for purified cellulose [53].

Figure 2.2.2 shows the Howarth projection structure of a cellulose polymer. It can be seen from the figure that the cellulose chain is made up of three different kinds of anhydroglucose units, namely: the intermediate unit (I) joined at C-1 and C-4; non-reducing end group (II) with a free hydroxyl group at C-4; and the reducing end group (III) with free aldehyde groups at C-1 [54, 55]. Each of the intermediate groups contains one primary alcohol group and two secondary alcohol groups, while the non-reducing group contains an extra secondary alcohol group at C-4. The reducing end group is a cyclic hemiacetal [56], characterised with both alcohol and aldehyde.

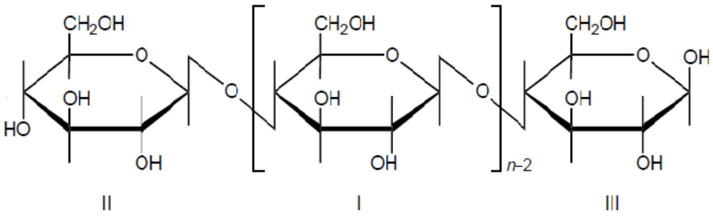


Figure 2.2.2 The Howarth Projection structure of Cellulose [53]

Cellulose exists in about five different forms [53], however for textile processing, cellulose I (obtained from nature) and cellulose II (obtained when cellulose is regenerated from solution or when cotton is mercerised) are of importance. The main sources of native cellulose are plants such as cotton, wood and bast fibres including flax (linen), hemp, jute, kenaf and ramie. Cotton is however the most significant and common source of cellulose, containing more than 90% cellulose [49, 52].

The cellulose polymer and its derivatives find use in the manufacturing of papers and paper products; regenerated cellulosic fibres such as viscose rayon, Lyocell, acetate and triacetate; and in the production of films and membranes such as cellophanes [57]. The focus of the present study was on cotton and regenerated cellulosic (viscose and Lyocell) fibres which are further described.

2.2.2 Cotton fibre

Cotton fibres are obtained as hairy cellulosic fibres attached to the seeds of the cotton plants called Gossypium. When the plant grows, the fibres develop inside a boll (seedpod) around the seed. On maturity, the boll bursts open and the cotton fibre appears as soft, fluffy wads. Many cotton species are grown commercially, but they are conveniently divided into three categories, according to their average fibre lengths. Type 1, such as cotton from Egyptian seed type, is known as long staple fibre with lengths of 25 – 60 mm and a high degree of fineness. Type 2, such as the American upland variety is coarser with shorter staple lengths of 13–33 mm. Type 3, include that from Asian countries are of even shorter staple lengths between 9–25 mm [52]. Cotton can grow in many countries with warm climates, however the major cotton producers in the world are the USA, China, India, Pakistan and the Central Asian republics; other countries producing small but not insignificant quantities include Mexico, Turkey, Brazil, Egypt and Sudan [56].

2.2.2.1 Structure and morphology of cotton fibres

The physical appearance of mature cotton fibre is that of a highly convoluted flat ribbon characterised by a bean shaped cross section, sometimes described as a bilateral structure (Figure 2.2.3), indicating that the cellulose chain density is not uniformly packed across the fibre. This results in variable reagent accessibility of the chain segment across the fibre [58, 59], with accessibility increasing in the A-B-C-D sequence. The two highly curved ends of the bean-shaped cross section (area A-A) have the highest molecular packing density and lowest accessibility to reagents while the convex-shaped structures (area C and D) are less dense and easily accessed by chemical attack [52, 56].

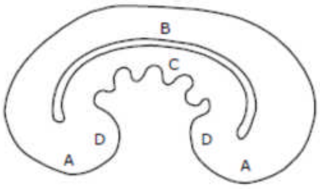


Figure 2.2.3 Bilateral cross-section shape of cotton fibres showing different molecular packing density of a cotton structure [56]

Cotton fibre contains about 96% cellulose while the rest of the remaining material is made up of natural waxes and proteins [49]. The fibre has a fibrillar structure containing three essential parts: primary wall, secondary wall and lumen, as shown in Figure 2.2.4. The primary wall consists of cellulose micro-fibrils in a randomly interlaced network and is protected by an outer layer of pectin, known as a cuticle, containing other non-cellulosic materials like protein, mineral matter and wax [49, 56]. The presence of non-cellulosic materials (mainly waxes and pectin) affects a number of properties of cotton fibres, in particular, absorbency and wettability, and has an important influence on processing and the end-use properties of the fibre [52]. Scouring and bleaching removes non-cellulosic materials which increases absorbency and wettability properties [58].

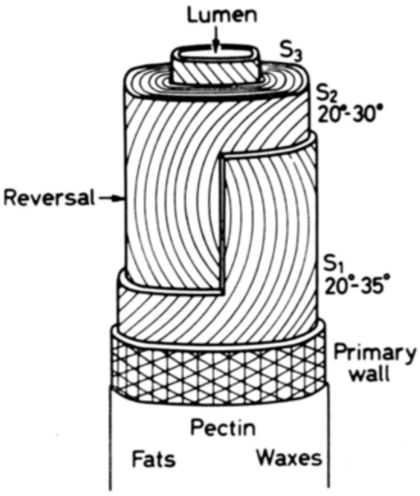


Figure 2.2.4 Morphology of a cotton fibre [56]

The secondary wall (S_1, S_2 and S_3) is located beneath the primary wall and is composed of pure cellulose which constitutes the bulk of the fibre. In this wall, closed packed bundles of cellulose fibrils are arranged spirally around the fibre axis with the direction of the spirals periodically reversing along a single fibril. The cellulose fibre in this wall is highly crystalline, however its fibrillar surface is easily accessible to most chemical reagents through a system of voids and channels [49].

The lumen is the innermost part of the fibres consisting of fibrils running continuously in the centre of the fibre. It is said to be the remnants of the protoplasm after the fluids [26] responsible for fibre layer formation have dried out. The lumen may contain non-cellulosic materials which are removed during scouring or bleaching processes [49, 52].

2.2.3 Regenerated cellulosic fibres

The demand for textile fibres is expected to increase from 69.7 million tons in 2010 to 118 million tons in 2025 [27, 38], with cellulosic fibres (both natural and man-made) accounting for about 33% - 37% of the total fibre demand [27] due to their attractive physiological (hydrophilicity, absorbency and breathability) properties which are ideal for moisture management. With limited cotton supply, increasing production capabilities for man-made cellulosic fibres will help to fulfil the demand available for cellulosic fibres. Regenerated or man-made cellulosic fibres were therefore developed for two main reasons [26]; firstly, the desire for a natural like product with controllable properties such as mechanical and chemical performance; secondly, the limited supply of cotton fibres which is mainly attributed to agricultural limitation for production.

Most regenerated fibres were originated from the paper industry after the Industrial Revolution in the late 19th century [57]. To date, the consumption of man-made cellulosic fibres continues to grow. Its consumption increased from 3.9% in 2010 to 6.8% in 2014 of the total world's fibre market [38, 60] due to continuous improvements in their production processes and development of new products. Wood pulp remains the main raw material for regenerated cellulosic fibres due to its high degree of polymerisation, although cotton linters are sometimes used for speciality applications which demand high purity [61].

To convert wood pulp into textile fibres the pulp is dissolved in a suitable solvent, from which filaments can be extruded through a spinneret and regenerated as cellulosic fibres through a coagulation bath [62]. The viscose process is one of the first techniques developed for producing regenerated cellulosic fibres. Other processes are also available and are used to produce cuprammonium rayon, cellulose acetate, cellulose triacetate and Lyocell fibres. This study focused on the viscose and Lyocell processes because viscose is the most common form of regenerated cellulosic fibre while Lyocell is a relatively new process which has very important environmental benefits.

2.2.3.1 Viscose fibres

The viscose process was first discovered in 1891 when three British chemists (Edward Bevan, Clayton Beadle and Charles Cross) dissolved cellulose in alkali and carbon disulphide to form cellulose xanthate [57]. The discovery led to the development of the viscose production process, where cellulose is treated to create sodium cellulose (soda cellulose) which then undergoes 'ageing', a process where the solubility of cellulose is increased while decreasing its viscosity. The aged soda cellulose is then mixed with carbon disulphide (CS_2) to form cellulose xanthate which is then dissolved in dilute sodium hydroxide to form a spinning solution. The spinning solution is left to ripen before being spun into a coagulation bath containing sulphuric acid and mineral salt to regenerate the cellulose into viscose rayon [63]. The schematic diagram for the Viscose production process is shown in Figure 2.2.5. The most common cellulose source for viscose fibre is wood, particularly, eucalyptus and acacia species [57].

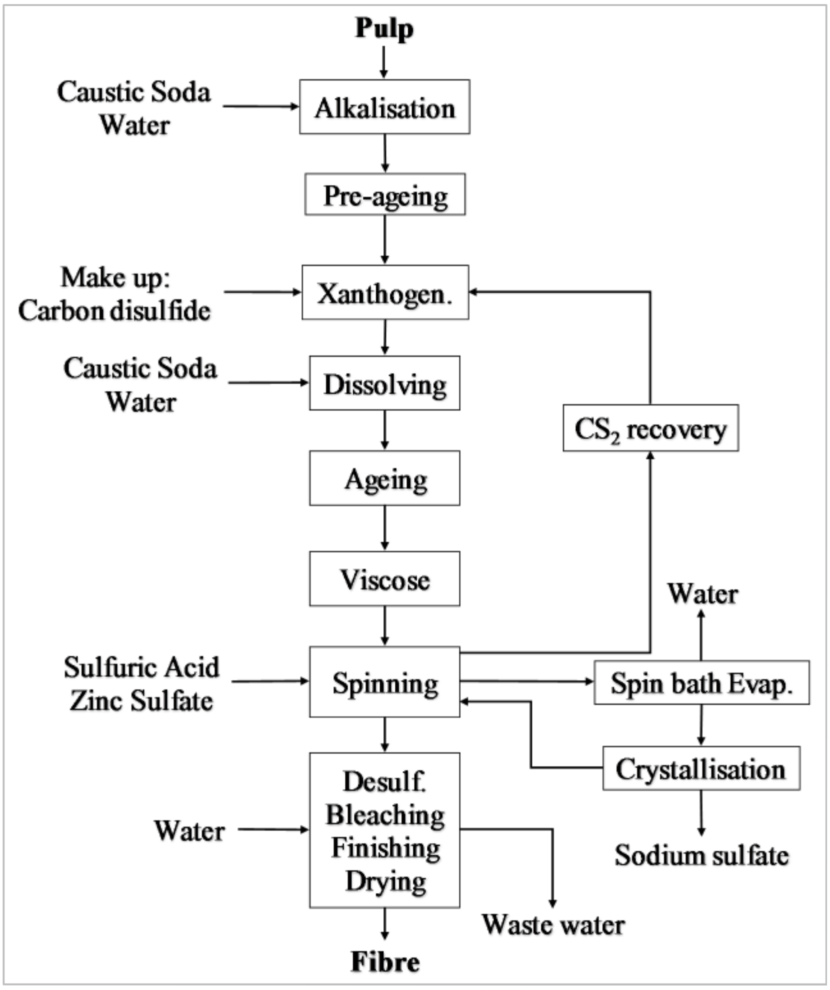


Figure 2.2.5 Schematic diagram of the viscose fibres production process [61]

In the mid 1950s, the acceptability of the viscose manufacturing process was increasingly questioned due to its significant impact to the environment, mainly associated with its liberation of carbon disulphide as by-products and the overall costs of treating its process effluents [57]. Producers were therefore forced to either reduce the production or improve the production methodologies to comply with the environmental policies put in place [61]. Such pressures led the industry to develop lower impact processes, and of particular importance, the Lyocell process was developed. The Lyocell process has less environmental issues due to the non-toxic and recoverable chemicals used for the cellulose dissolution stage of the process [35, 61].

2.2.3.2 Lyocell fibres

Research into lower impact fibre regeneration processing led to the use of cyclic mono (N-methylamine-N-oxide) compounds such as the N-methylmorpholine-N-oxide (NMMO), illustrated in Figure 2.2.6, which could directly dissolve cellulose without forming cellulose derivatives or by-products [35, 57]. The technology was adopted for the commercial manufacturing of man-made cellulosic fibres, obtained by an organic solvent spinning process called the Lyocell process. Since its development in the mid 1970's, Lyocell has been the focus of much interest in the textile industry due to its manufacturing technology which is simple, does not involve cellulose derivation and the NMMO solvent used is non-toxic, less polluting to the environment, easy to recover and recycle and biodegradable in the waste water treatment [26, 64].

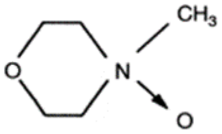


Figure 2.2.6 Structure of N-methylmorpholine-N-oxide (NMMO)

In the Lyocell process (Figure 2.2.7), the wood pulp, usually from eucalyptus, is directly dissolved in an aqueous NMMO-water solution to form a dope (homogeneous concentrated solution of cellulose). The highly viscous solution is then filtered and extruded through an air gap into a precipitation bath for coagulation of the cellulose fibre, a process called dry jet-wet spinning. The fibre is then washed, dried and post-treated. The NMMO solvent is recovered from both precipitation and washing baths, purified and recycled [35, 57, 61]. In general, the Lyocell process avoids the use of the toxic carbon disulphide while reducing the number of processes and the overall chemical consumption.

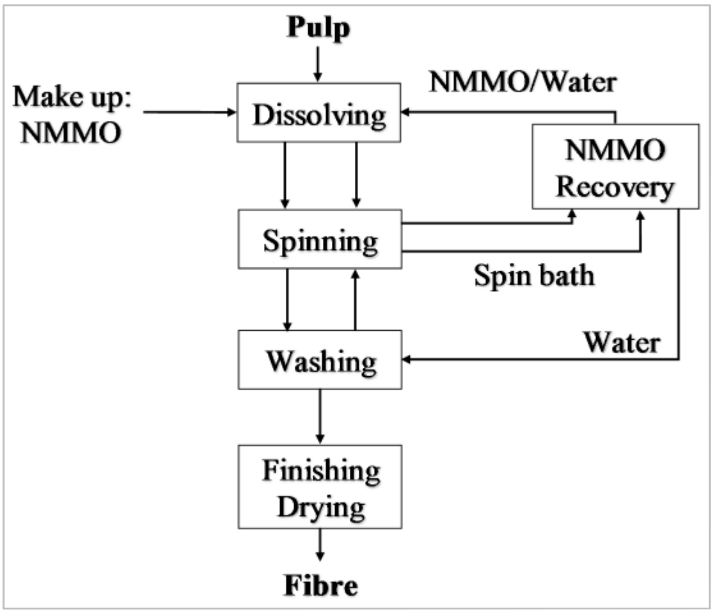


Figure 2.2.7 Schematic diagram of the Lyocell fibres production process [61]

Lyocell fibres offer high mechanical properties with tenacity of 34-42 cN/tex compared to tenacity of 10-26 cN/tex offered by viscose fibres and that of 24-40 cN/tex on cotton fibres [26]. They also have the comfort of natural fibres coupled with excellent aesthetic properties, and like any other cellulosic fibres, they are biodegradable and their raw materials are renewable [57, 65]. Similarly the Lyocell processing technology requires less water (about 260 litres per kg, for pulp and fibre production) compared to viscose process which is characterised by high water consumption (about 445 L/kg fibre) and generation of by-products [61, 66] which have a significant environmental impact. The positive environmental credentials of the Lyocell technology and the advantageous mechanical and chemical properties of the fibres produced are the reasons why the process has been selected as the means to convert cotton waste into fibres.

2.2.4 Stability of cellulosic fibres in chemical reactions

Cellulose is susceptible to a number of chemical agents, mainly acids, alkalis and oxidising agents [49, 54]. The chemical attack on cellulose depends on the supermolecular structure and the activity of hydroxyl groups and usually starts from the readily accessible amorphous region and the surfaces of the crystalline region [52]. The stability of cellulosic fibres is impaired when glucosidic links are attacked by hydrolysis and other degradation reactions, when hydroxyl groups are oxidised or substituted and when the C-O bond or other low-energy bond is broken [54]. Cellulose exposure to these agents can also lead to modification of the cellulose polymer by disrupting the inter and intra-molecular hydrogen bonds and converting the crystalline lattice of native cellulose into cellulose II and III which have lower crystallinity [67].

A relatively small chemical attack on the cellulosic material can result in a significant loss in strength or tendering [53, 63], however other properties such as reducing power (measured by copper number), acidity (methylene blue absorption), stability towards hot dilute alkali solutions, the fluidity in cuprammonium hydroxide solution and the solubility in cold concentrated sodium hydroxide solution can also be affected by cellulose degradation [50]. Complete cellulose degradation results in the formation of carbon dioxide and water, while any intermediate stage is regarded as partial degradation [49]. In this research the acid and alkali hydrolysis reactions together with oxidative bleaching were used to prepare waste cotton materials for recycling into Lyocell fibres. It was therefore necessary to understand how cellulose is affected by these chemical modification reactions. The effects of reducing agents on cellulose were also included in the scope of the study.

2.2.4.1 Acidic hydrolysis of cellulose

Acidic conditions can easily affect both chemical and physical properties of cellulosic materials. The acidic chemical hydrolyses the glycosidic linkage of cellulose resulting in fission of long molecular chains into shorter chains of varying lengths, with less glucose residues than the parent cellulose molecule [63]. The extent of acid-catalysed hydrolytic attack depends on the nature of the acid, its concentration, treatment time and temperature [55]. For instance, shorter hydrolysis periods only weaken the fibre but retain the fibrous properties; however extended hydrolysis yields a powdery material (known as microcrystalline cellulose) with lost fibrous structure. Similarly lower acid concentrations require more extreme conditions such as higher temperature and longer time for hydrolysis to occur [68].

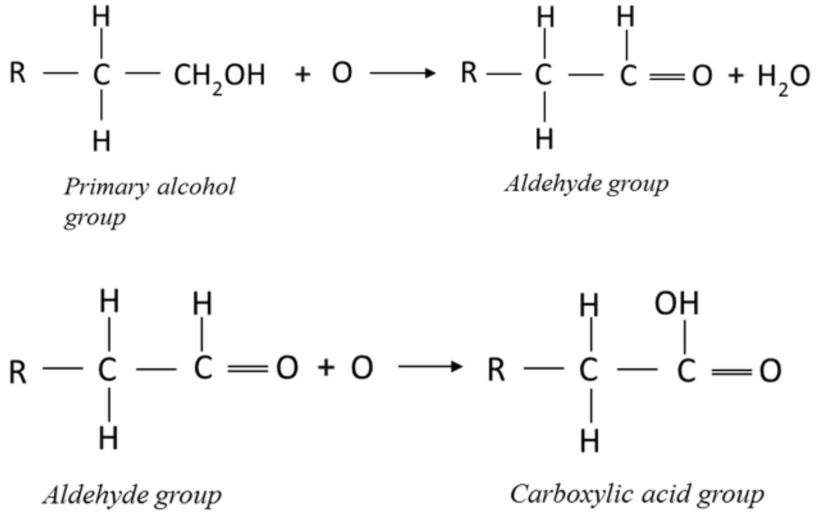
With acid treatment, linkages or crystalline structures of cellulose are destroyed due to cellulose dissolution or swelling in acid. For each broken linkage, an aldehydic reducing group (-CHO) and a new hydroxyl group is formed at the end of the molecular chain. The product of partial hydrolysis of cellulose is hydrocellulose, an important substance in cotton processing due to their increased solubility in both alkali and water [50, 63].

The main effect of acidic hydrolysis of cellulose is loss in strength due to shortening of molecules confirmed by an increase in the fluidity of cuprammonium solution of cellulose. Increased reducing power (due to aldehyde groups) measured by its capacity to reduce the copper number is another effect of hydrolysis. A copper number close to zero indicates complete cellulose degradation [63, 68]. Similar changes are observed when cellulose is attacked by oxidising agents as will be detailed hereunder.

2.2.4.2 Oxidative hydrolysis of cellulose

Although the mechanism of oxidising agents attack on the cellulosic chain molecules is mostly unknown [50], the presence of three hydroxyl groups in each cellulosic glucose molecule suggests the likelihood of oxidation taking place. The reaction between cellulose and oxidising agents such as hypochlorites, peroxides, dichromates, permanganates and periodate salts results in cellulose oxidation [54] although the degree of oxidation varies with pH [53, 68].

For the major part of the cellulosic fibre, the glucosidic linkages is not readily accessible by most oxidising agents [53], however the adjacent primary alcohol group (-CH_2OH) attached at the C_5 of the molecule is oxidised to carbonyl or aldehyde groups (-CHO) resulting in the formation of a reducing oxycellulose. Further oxidation results in the formation of carboxyl groups (COOH) called acidic oxycellulose. Secondary alcohol groups are also oxidised in a similar manner. The presence of aldehyde groups in oxidised cellulose is determined by increased copper number or reducing power while that of carboxylic group is determined by the increase in methylene blue absorption [63]. Scheme 2.2.1 summarises the oxidation process of cellulose.



Scheme 2.2.1 Progressive oxidation of cellulose. R is the cellulose residue [63]

The formation of both reducing and acidic oxycelluloses cause weakening or scission of the glucosidic linkages, thereby reducing tensile strength and the degree of polymerisation while increasing the fluidity or solubility of the material [50, 63]. Apart from carbonyl and aldehyde groups, ketone groups may also be formed. The introduction of these functional groups may cause changes in the forces between adjacent chain molecules, thus changing the relation between tensile strength and the degree of polymerisation [53].

In this study oxidation of cellulose was investigated through the use of hydrogen peroxide, due to peroxide bleaching being the main oxidative treatment used in the processing of cotton materials. This agent was chosen as it has fewer environmental issues associated with it in comparison to other oxidative agents such as chlorine based bleaching agents [69]. If used properly hydrogen peroxide will not damage the cellulose, however, it can cause serious degradation when using unfavourable conditions. The oxidation process is done in the presence of alkali, usually in aqueous sodium hydroxide. This alkaline peroxide oxidation process involves peroxide radicals resulting in a chain-scission and materials containing carboxyl groups and a small number of reducing groups [53, 70]. The main reducing groups formed by peroxide are usually ketone groups thus forming ketocelluloses. Carboxylic and aldehyde groups are also being produced, but generally in smaller quantities [71].

2.2.4.3 Alkali hydrolysis of cellulose

Cellulose is reported to be more resistant to alkalis; for instance, dilute alkali has no effect on cellulose when used at temperatures below 170°C [53]. Therefore cellulosic fibres can be treated in alkali solution below the said temperature to improve their mechanical and chemical properties such as tensile strength, dimensional stability, dyeability, fibrillation tendency as well as fabric lustre and smoothness [55, 63, 72].

The most obvious effect of alkali on cellulose is the swelling property which increases as the treatment temperature is decreased. This swelling of cellulose on alkali treatment is said to be the basis of cotton mercerisation in which the action of strong alkaline solutions increases the amorphous fraction and chemical reactivity of cotton [55]. However the process does not significantly affect the fluidity, copper number, methylene blue absorption and weight loss of the material. The reaction between alkali and cellulose leads to the formation of alkali celluloses (sodium cellulosates), however on prolonged washing with water, the product decomposes and alkali is completely removed leaving cellulose to regenerate [63].

Unmodified cotton cannot be fully dissolved in alkaline solutions due to the length of their molecular chains [50]. However cellulosic materials that have been pre-treated with acids or oxidising agents can be easily dissolved in alkali, particularly sodium hydroxide. The degree of solubility of a modified cellulose in alkaline solution increases with decreasing temperature [50]. Alkali treatment of oxidised cellulose (even in weak alkali and at room temperature) can also result in greater cellulose strength loss. This is due to the aldehyde groups formed as a result of oxidation causing the nearby glucosidic linkage, otherwise stable to alkaline conditions, to become susceptible to alkali hydrolysis [68]. The decrease in strength can be analysed by observing the change in viscosity of the oxidised cellulose before and after alkali treatment.

Extreme alkali treatment conditions dissolve and eventually degrade the cellulose, even if that same cellulose is usually stable under high concentrated alkalis [63]. A random scission of glucosidic chain is obtained when cellulosic material is treated in dilute sodium hydroxide at temperature above 170°C. New reducing end groups with shorter molecular chains are formed and they undergo rapid degradation in the same way as at lower temperatures. This rapid degradation causes greater weight loss than those occurring at lower temperatures. Temperatures of 250 – 300°C can dissolve and degrade cellulose by breaking it to lower molecular weight compounds, usually acids such as formic, acetic, glycolic and lactic acids [53, 63].

2.2.4.4 Effect of reducing agents on cellulose

Reducing agents such as sodium dithionite are unable to chemically modify native cellulose such as that of cotton. However direct reduction by the action of hydrogen gas can be achieved at high temperature and pressure [63]. At this point cellulose is considered degraded, and products such as liquids and gases can be produced. The presence of metals such as nickel accelerates the cellulose degradation process.

2.3 COLORATION OF CELLULOSIC FIBRES

Among the objectives of this study was to develop a method to chemically strip colorants from waste cotton garments as a way of preparing and purifying the cotton pulp for generating Lyocell fibres. It was therefore important to understand the basis of cellulosic coloration before establishing an effective method for colorant stripping. In this section the basic concepts of cellulosic colorants including dyes, pigments and fluorescent whitening agents are reviewed.

2.3.1 Introduction

Textile colorants can be defined as chemical substances that appear coloured due to their ability to absorb light in the visible region of the electromagnetic spectrum (400 to 700 nm). Coloration of textile substrates can be done by using dyes (water soluble compounds) or pigments (water-insoluble compounds) which are usually applied to textile materials so as to impart different colour and shades [56, 73].

Dyes can be introduced into various forms of material such as fibres, yarns, fabrics and garments as a result of adsorption, diffusion and migration of the dye over/into the fibre. The commonly used dyes for cellulosic fibres are direct dyes, vat dyes, sulphur dyes and reactive dyes [74]. Direct dyes impart shades with lower wet fastness while vat and sulphur dyes produce better wet fastness properties; however their application process is more complicated as it involves converting the insoluble dye compounds to water soluble dye compounds and then back into relatively insoluble compounds once in the fibre. Reactive dyes offer better wet fastness properties under commercial application conditions [54, 56]. Figure 2.3.1 shows the world’s consumptions of cellulosic dyes with reactive dyes being the most important dye class for cellulosic materials.

Other classes such as azoic dyes can also be used for cellulosic dyeing, however, they are not currently used to any great extent [75] and so were not discussed in this research. Pigments are also used in the coloration of cellulosic materials and were included in the scope of the study due to their common use in textiles.

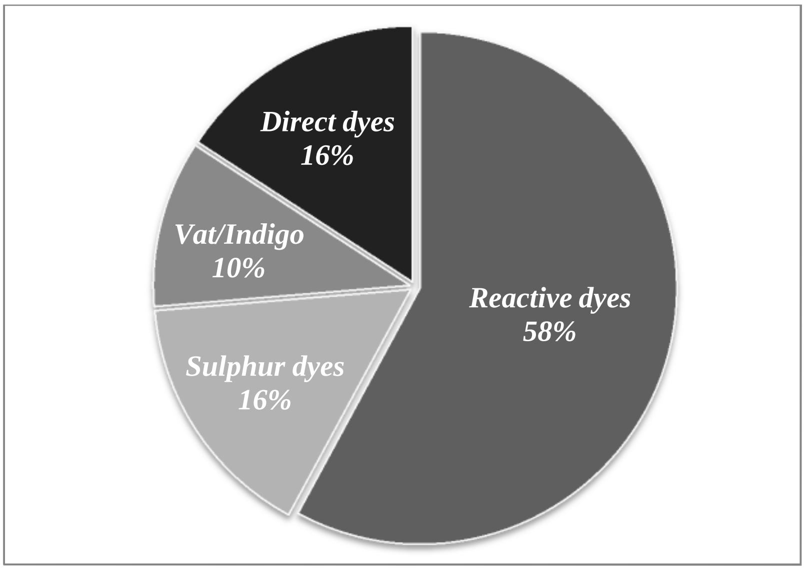


Figure 2.3.1 World consumption of cellulosic dyes by volume in 2010 [76]

2.3.2 Direct dyes

Direct dyes are water-soluble anionic dyes with high substantivity for cellulosic fibres [56] which allow them to be absorbed directly by cellulosic substrates. They were the first dyes to be applied directly to cotton substrates without the need for mordanting agent, hence the name *direct cotton dyes* [51]. Once on substrates direct dyes are linked to the fibre through hydrogen bonding, van der Waal forces and other interaction forces between the dye and the fibre molecules. The water-soluble behaviour of direct dyes is due to the presence of one or more solubilising groups (e.g. -SO_3Na) in the dye molecule while the substantivity of direct dyes is derived from the planar, conjugated, double bond system which usually involves polyazo systems such as disazo structure [77]. A typical example of direct dyes is presented in Figure 2.3.2.

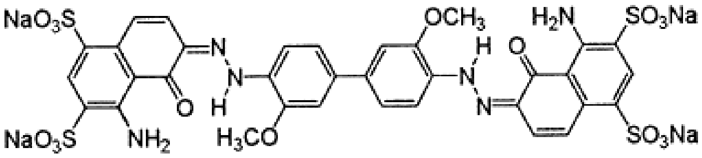


Figure 2.3.2 Structure of C. I. Direct Blue 1 dye [56]

2.3.2.1 Classification of Direct dyes

Direct dyes can be categorised according to their chemical structures which shows the nature of the chromophore responsible for colour [78]. The structures of the direct dyes are therefore based on azo, stilbene, oxazine and phthalocyanine [56, 79]. The most common structures of direct dyes are azo, usually disazo (about 50%) or polyazo (about 33%) compounds with two or more sulphonic acid groups [73, 74], the former dominating in bright yellow to blue range and the latter in duller greens, browns, greys and blacks. Typical examples of azo direct dyes are C. I. Direct Red 81 (disazo) and C. I. Direct Black 22 (polyazo). Stilbene direct dyes offer important yellow, orange and browns hues, such as C. I. Direct Yellow 12 (Figure 2.3.3) while phthalocyanine direct dyes give brilliant turquoise blue colours of high light fastness but poor wet fastness unless resin finished [56]. Direct dyes are also classified according to their dyeing methods and their fastness properties. An extensive discussion of these classes is given in the literature [78, 80].

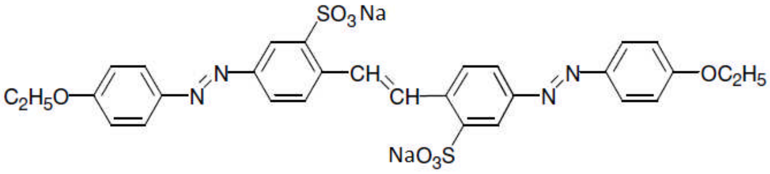


Figure 2.3.3 Structure of C. I. Direct Yellow 12 dye [56]

2.3.2.2 Procedure for direct dyeing

Direct dyeing of cellulosic fibres is considered to be simple and low cost compared to other cellulosic dyes such as vat dyes [73]. They are usually applied to cotton at or near boil temperature, although in some cases lower temperatures or temperatures above boil may be used, such as in a jig or in package dyeing. Direct dyeing is also performed in the presence of electrolytes such as sodium chloride to achieve reasonable exhaustion by preventing electrostatic repulsion between the anionic dye molecules and the negatively charged wet cotton surface, thereby promoting dye aggregation, dye-fibre bonding and other reactions due to attractive forces between the dye molecules and cellulosic hydroxyl groups [74, 75].

The main drawback of direct dyes is their poor fastness to washing and wet treatments, thereby requiring pretreatment of the substrate to improve cellulosic site dye acceptance or aftertreatment of the direct dyed substrate, usually by crease resist treatment or cationic fixing agents to improve the fastness of the direct dyeing [56, 81]. Of the two methods, aftertreatment of the direct dyed substrate with cationic fixing agents is the most popular [82].

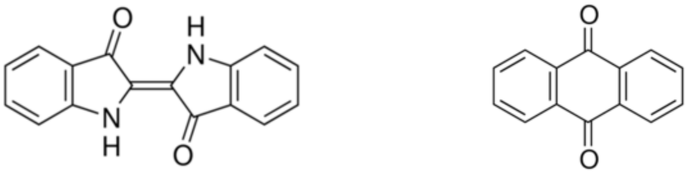
The most important cationic fixing agents for textile materials are typically quaternary ammonium salts [56, 83]. When in water, the agents ionise into long cations and small anions, similarly, on dissolution in water direct dyes ionise into long coloured anions and small cations (sodium ions). Therefore when the cationic fixing agent is applied to direct dyed substrate attraction forces between cations of the agent and anions of the dye combine together forming a complex with high molecular weight and reduced solubility on the fibre. It is the insolubility of the formed cation-anion complex that renders the direct dyed substrate wet fast [81, 84, 85]. However the aftertreatment process usually results in changes in hues or reduction in colour strength which is suggested to be due to colour wash-off as a result of the hot, aqueous after-treatment process [81]. Moreover the process requires multiple processes which is unattractive to most dyers and printers and thus the after-treated direct dyeing is often replaced by using reactive dyeing [85].

2.3.3 Vat dyes

Vat dyes can be defined as water insoluble colorants containing two or more keto groups [74]. They are among the oldest colorants used for cellulosic dyeing and are reported to give the best overall fastness properties including light, wash and chlorine fastness which is uncommon in other dye classes. Their insolubility in water prevents these dyes from being applied directly to textiles substrates. Therefore dyeing with vat dyes is based on the principle of converting the water insoluble vat dye to its water soluble form (called leuco dye), absorption of the solubilised leuco form by cellulosic substrates and re-oxidising of the dye back to its insoluble form [73]. Subsequent wash-off is also necessary to remove dye residues, excess alkali and reducing agents.

2.3.3.1 Classification of Vat dyes

The most common chemical structures of vat dyes are based on anthraquinones (approximately 80%) and indigoids [74] with the former having excellent fastness properties as compared to the latter. Indigoid vat dyes include indigo, thioindigo and their derivatives while anthraquinonoids include anthraquinones derivatives and other heterocyclic quinones [80]. The structures of indigo and anthraquinone are illustrated in Figure 2.3.4.



Indigoid structure *Anthraquinone structure*

Figure 2.3.4 Chemical structures of indigo and anthraquinone vat dyes [74]

Some examples of the commonly used anthraquinone vat dyes are the indanthrones (e.g. C. I. Vat Blue 4), carbazoles (e.g. C. I. Vat Black 27), flavanthrones (e.g. C. I. Vat Yellow 1), isodibenzanthrones (e.g. C. I. Vat Violets 1) and pyranthrones (e.g. C. I. Vat Oranges 9) [56]. However the most commonly used indigo dye is C. I. Vat Blue 1 which is used for denim materials [79].

Vat dyes are also classified according to the substantivity of the leuco compounds and their dyeing conditions such as temperature, time and concentration of the auxiliaries needed. Three classes, namely: Class I or IN, Class II or IW and Class III or IK exist in this category. Detailed explanations of their nature are found in the literature [56, 78].

2.3.3.2 Procedure for vat dyeing

The molecule of the vat dye is usually large and planar with multiple ring systems to provide the leuco form with affinity for cellulosic fibres due to the van der Waals and dipolar forces [73, 75]. The overall vat dyeing process involves three main processes, namely: vatting, absorption and oxidation:

a. *Vatting (or reduction)*: where the water-insoluble keto form of the dye is reduced to its water-soluble sodium enolate form (leuco dye) by using a reducing agent usually sodium dithionite and in the presence of an alkaline agent usually sodium hydroxide;

b. *Absorption:* where the leuco form of the dye is absorbed by the textile substrate during dyeing via hydrogen bonding and van der Waals forces, until a state of equilibrium is reached. When the substantivity of the dye for the fibre is high, the dye will be highly concentrated in the fibre and less concentrated in the dye liquor;

c. *Oxidation*: where the insoluble vat dye is regenerated inside the dyed material with the aid of an oxidising agent such as hydrogen peroxide. Exposure to air is sometimes used for oxidation purposes, although it can take longer. Soaping at boil is then performed to remove any dye residuals leading to aggregation of the dyes into pigments inside the fibre and developing the true colour with high fastness properties [78]. Figure 2.3.5 shows the reduction and oxidation structures of indigo vat dye.

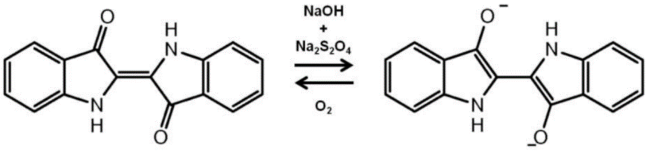


Figure 2.3.5 Reduction and Oxidation of Indigo dye [86]

A number of vat dyes are also marketed as solubilised vat dyes eliminating the need for vatting before dyeing. They are sodium salts of sulphuric acid esters of leuco dyes, such as C. I. Solubilised Vat Blue 1 illustrated in Figure 2.3.6. Once on the fibre, the ester is decomposed by a suitable treatment and the leuco compound is oxidised to a water-insoluble form [56].

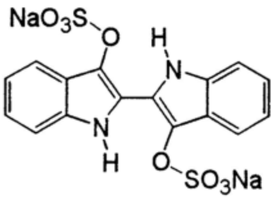


Figure 2.3.6 Structure of C. I. Solubilised Vat Blue 1 dye [56]

2.3.4 Sulphur dyes

Sulphur dyes are complex polymeric aromatic molecules, with heterocyclic S-containing rings, representing more than 15% of the global dye production. They are synthesised by sulfurization (thionation) of one or more organic compounds and they are characterised by sulphide bridges incorporated into their aromatic rings. Sulphur dyes offer important hues such as blacks, navy, brown, olives and greens in medium to heavy depths and they are relatively inexpensive [74]. C. I. Sulphur Black 1 is the most commercially used type of sulphur dye, representing a substantial portion (20 - 25%) of the dyestuff market for cotton and it offers an exceptional black shade and depth on cellulose [78, 87].

The chemistry of sulphur dyes is said to be very complex [73]. The simplest possible form and probably the most commonly used structure of sulphur dyes is presented as;

$$\text{Dye} - \text{S} - \text{S} - \text{Dye}$$

The structure shows two chromophores linked together by two sulphur atoms called a disulphide linkage. These bonds are usually present in water-insoluble form, but; they can be reduced to individual heteroaromatic units with thiol groups which are soluble in the alkaline solution in the form of thiolate ions with substantivity for cellulose [78].

2.3.4.1 Classification of sulphur dyes

There are four classifications for sulphur dyes [78] based on their chemical and physical form; sulphur, leuco sulphur, solubilised sulphur and condensed sulphur. Of all the categories only sulphur dyes and leuco sulphur dyes are important to textile dyers and are hereunder described.

a. *C. I. Sulphur dyes* – contain sulphur both as an integral part of the chromophore and in the attached polysulphide chains. They are insoluble in water hence have limited substantivity for cellulose. They are converted into their leuco soluble form by reducing agents before being applied onto a fabric and subsequently oxidised back to their insoluble form on the fibre.

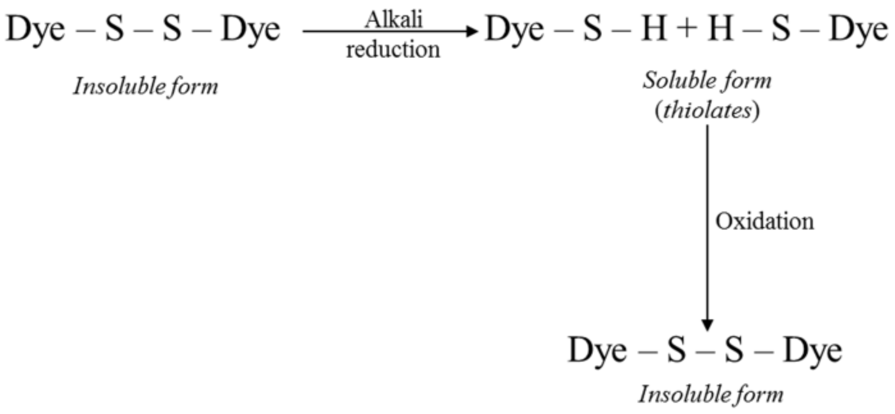
b. *C. I. Leuco Sulphur dyes* – they are available in powder or liquid formulations as the soluble leuco form of the parent dye. Dilution in water is done before applying to fabric, although a small amount of reducing agent can be added to the dyeing liquor.

c. *C. I. Solubilised Sulphur dyes* also known as ‘Bunte salts’ are highly water-soluble thiosulphonic acid derivatives of leuco sulphur dyes. They are non-substantive to fibres, but they can be converted to their substantive thiol form by using reducing agents. They are commonly used in paper dyeing where they are precipitated as insoluble salts by the fillers used in the paper making.

d. *C. I. Condensed Sulphur dyes* – are sodium *S*-alkyl or *S*-aryl thiosulphates. Although they contain sulphur, their constitution, manufacturing and dyeing methods differ from those of the traditional sulphur dyes.

2.3.4.2 Procedure for sulphur dyeing

As with vat dyeing, the sulphur dyeing also involves a reduction of the insoluble compounds into its soluble leuco form, absorption of the dye onto the fibre and re-oxidation of the thiolate ions back to their insoluble form once on the fibre with the disulphide bonds linking the aromatic units. The leuco form of sulphur dyes behaves similar to direct dyes in the sense that they can be exhausted into cotton substrate in the presence of salt [78]. On re-oxidation of the leuco form to its water-insoluble form, a dyeing of good wet fastness is obtained. Scheme 2.3.1 illustrates the reduction and oxidation processes occurring during sulphur dyeing.



Scheme 2.3.1 Reduction and Oxidation of sulphur dyes

Unlike vat dyes, reduction of sulphur dyes involves breaking apart the disulphide bonds, whilst, the molecule of vat dyes is usually left intact [78]. In addition re-oxidation of sulphur dyes is difficult, requiring stronger oxidative agents as compared to re-oxidation of vat dyes [73].

2.3.5 Reactive dyes

Reactive dyes are the most important dye class for cellulosic dyeing [73], accounting for over 50% of all dyes used on cotton [76]. They can be defined as anionic coloured compounds containing functional groups capable of forming covalent bonds, usually under alkaline conditions, with fibre functionalities such as the hydroxyl groups of cellulosic fibres [88]. They can also form covalent bonds with amines (–NH), thiols (–SH) and carboxylic (COOH) groups in wool, silk and other polyamide fibres such as nylon in the presence of weak acidic conditions [89, 90]. Alongside their relatively easy application method, this class of dyes offer a wide range of bright shades with better wet fastness on cotton materials than other dye classes and are the only dye class that form covalent bonds with textile fibres [56].

The first commercially available reactive dye was the dichlorotriazinyl Procion M class (e.g. C. I. Reactive Orange 1 presented in Figure 2.3.7) produced by Imperial Chemical Industry (ICI) in 1956 after their development in 1954 by Rattee and Stephen [91]. They were later followed by the Cibacron series (Ciba-Geigy) in 1957, the Remazol series by Hoechst and BASF and the Drimarenes by Sandoz now Archroma [92]. The common feature in all of these dyes was the presence of a group in the molecule that covalently bonds with hydroxyl groups present in cellulose molecule.

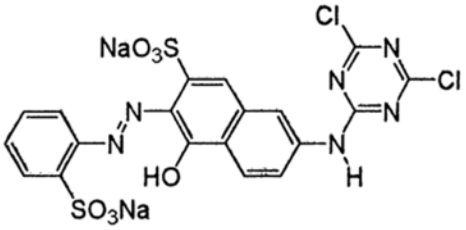
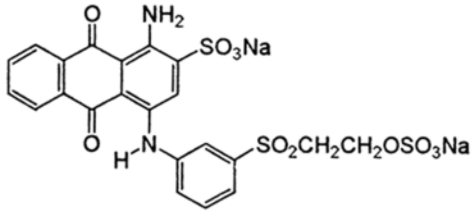


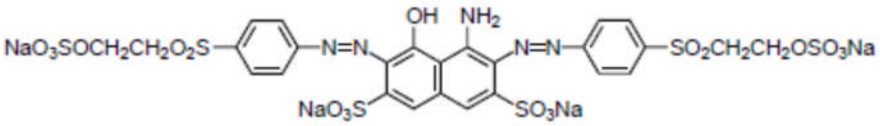
Figure 2.3.7 Structure of Procion Orange MX-G (C. I. Reactive Orange 1)[93]

Despite the continuous growth of their use, reactive dyes do have some limitations [56]. The most profound limitation being the need for a thorough wash-off of the unfixed/hydrolysed dye and the need for subsequent treatment of the effluent created. Researchers and dye manufacturers are actively working on ways to eliminate hydrolysis associated with reactive dyeing, where dyes with more than one reactive groups have been introduced aiming at increasing dye fixation rate. Bi-functional reactive dyes with similar or different reactive groups (e.g. C. I. Reactive Black 5) and poly-functional reactive dyes consisting of three or more reactive groups in their systems (e.g. C. I. Reactive Red 228) have been developed [90-92]. Figure 2.3.8 shows examples of the commercially available reactive dyes with variable number of reactive groups.



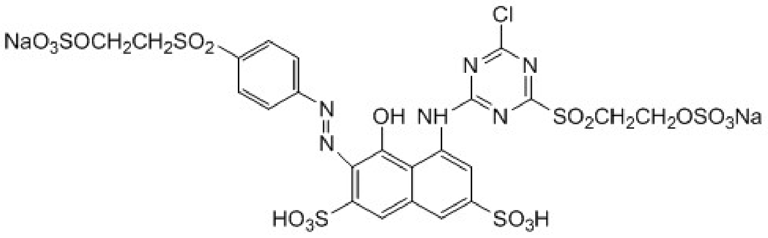
C. I. Reactive Blue 19

(Mono-functional i.e. has one reactive group)



C. I. Reactive Black 5

(Bi-functional i.e. has two similar reactive groups)



C. I. Reactive Red 228

(Poly-functional i.e. has three reactive groups)

Figure 2.3.8 Examples of reactive dyes with varied number of reactive groups [93]

2.3.5.1 Structure of Reactive dyes

A typical reactive dye contains four characteristic features [56]. These features are; the chromophore which is responsible for colour and in great part for dye substantivity to the cellulosic material; the reactive groups, enabling the dye to react with functional groups of fibres; solubilising group and the bridging group which links the reactive part of the molecule to the chromophore. Examples of dye chromophores are azo (most commonly available), anthraquinone, phthalocyanine and metal-complex compounds, whilst the main reactive groups for cellulosic materials are dichlorotriazinyl and vinylsulphone [94], although other systems like aminofluorotriazine and trichloropyrimidine are also present. Imino groups (-NH-), substituted imino and amide linkages present the most common bridging groups while solubilising groups are usually sodium sulphonate substituent that dissociates to give coloured sulphonate anions and sodium cations when in contact with water. The sulphonate anions formed are responsible for the dye solubility [78, 89].

2.3.5.2 Application principles of reactive dyes

Reactive dyeing of cotton fibre is normally started under neutral conditions [73] as in direct dyeing. However the aqueous solution renders the surface of the fibres negatively charged due to the presence of carboxylate groups in some cotton fibres resulting from oxidation of end-chain aldehydes, which also increases the negative charges on the fibre [95]. Since reactive dyes are also negatively charged, electrolytes e.g. common salt is usually added to promote the exhaustion of the dye onto the fibre by preventing electrostatic repulsion between the dye molecules and the fibre surface. At this stage dye molecules are free to move from fibre to fibre, but the addition of alkali increases the dyebath pH, initiating the dye-fibre bonding while limiting further dye movement. The added alkali dissociates the weakly acidic hydroxyl groups of cellulose (Cell-OH) to form cellulosate ions (Cell-O^-) as the nucleophilic reagent (Equation 2.3.1), which reacts with dye reactive groups (Equation 2.3.2) to form covalent bonds [73].

$$\mathrm{Cell-OH+OH^-} \leftrightarrow \mathrm{Cell-O^-+\ H_2O}$$ **(Equation 2.3.1)**

$$\mathrm{Cell-O^-+Dye-X} \rightarrow \mathrm{Cell-O-Dye+\ X^-}$$ **(Equation 2.3.2)**

Some of the dye reacts with the hydroxyl ions present in water and is hydrolysed (Equation 2.3.3). The hydrolysed dye is unable to covalently bond with the fibre and has to be washed-off during the rinsing stage [56, 78]. During this stage electrolyte and alkali residues are also removed.

$$\mathrm{OH^- + Dye - X \rightarrow Dye - OH + X^-} \qquad \textbf{(Equation 2.3.3)}$$

2.3.6 Printing of cellulosic fibres

In addition to dyeing, printing is another coloration technique that is used to produce multi-coloured effects and designs on textile fabrics [52, 96]. The process involves applying colour on a localised area of a fabric using a thickened paste containing pigments or dyes [73]. When dyes are used the printed area will need to be dried, washed and steamed, however pigments only requires curing usually on dry heating. Subsequent washing is usually not necessary.

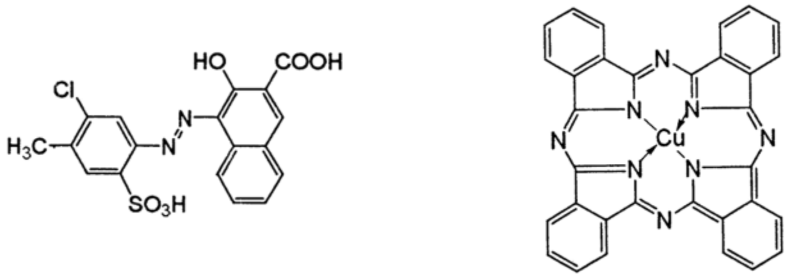
Despite the introduction of tailor-made printing dyes, pigment printing remains to be more popular than dye printing with over 80% of printed goods based on pigment printing [97]. This is due to its simple application process, low cost and minimal equipment needed for finishing [96, 97]. The main difference between pigments and dyes is the fact that pigments have no solubilising groups making them insoluble in water and with no affinity for fibres. They are held on a substrate by mechanical means, usually by polymeric binders. In addition, pigments can be applied to all textile fibres including glass fibres which has no coloration alternative [96]. In this study pigment printing was therefore of importance.

2.3.6.1 Pigment printing of cotton fabrics

Pigment printing involves applying a thickened print paste on a restricted part of a fabric and curing the dried printed areas by heating [73]. The permanency of the pigment print is due to the polymeric binders which are added into the print paste during printing. These binders are capable of attaching the pigments to the fabrics through strong adhesion forces [97], without affecting the softness, light and wash fastness of the printed fabric. In general, a successful pigment print depends on the pigment dispersion, binders and crosslinking systems as well as thickening agents [96].

2.3.6.2.1 Pigments

Pigments are coloured materials usually organic compounds synthesized by dye manufacturers [73]. They belong to normal chemical classes as those of soluble dyestuff (azo, naphthalene, anthraquinone and halogenated copper phthalocyanine derivatives) but they have no ionic groups. Inorganic pigments such as Carbon black also present a special class of pigments [74]. Figure 2.3.9 show examples of commercially available azo (C. I. Pigment Red 48) and phthalocyanine (C. I. Pigment Blue 15) pigment classes.



C. I. Pigment Red 48
(Monoazo)

C. I. Pigment Blue 15
(copper phthalocyanine)

Figure 2.3.9 Structures of commercially available pigments [74]

2.3.6.2.2 Binder system for pigment printing

A binder is a film-forming substance made up of long macromolecule chains which on curing by heat, produce a three dimensional network on the textile substrate. Since pigments have no affinity for fibres, polymeric binders play an important role in linking the pigment and the fabric, thereby influencing the fastness properties. This is achieved through curing which involves dry air heating and pH change that cause the dispersed binder to coagulate and coalesce into a coherent film through the self-crosslinking mechanism of the binder polymer or a reaction with other groups also present in the polymer [96, 98]. The film encloses the pigment particles adhering them onto the fabric.

The reaction between the binder and the fibres (Scheme 2.3.2) occurs under acidic conditions such as in the presence of salts of ammonia [98]. With the removal of reaction by-products (i.e. water or methyl alcohol), through curing in air at high temperature, the binder is fixed onto the fibre substrate.

$$\mathrm{Binder} - \mathrm{CH_2} - \mathrm{OR} + \mathrm{HO} - \mathrm{Cell} \leftrightarrow \mathrm{Binder} - \mathrm{CH_2} - \mathrm{O} - \mathrm{Cell} + \mathrm{ROH}$$

Scheme 2.3.2 Binder and cellulosic fibre reaction (R = CH_3 or H) [99]

Initially, natural occurring binders, such as gelatine and cellulose derivatives were used for pigment printing, but their drawbacks led to the development of synthetic binders. These synthetic binders are usually made by the polymerisation of different monomers and are usually based on styrene-butadiene, styrene-acrylate and vinyl acetate-acrylate copolymers [96].

2.3.6.2.3 Thickening system of the pigment printing

A thickener is a colourless, viscous paste containing one or more thickening agent. They are usually added to a print paste to provide the required viscosity and pseudoplastic flow, a flow in which the viscosity decreases with the increased shear rate [73]. Pseudoplastic flow is important in pigment printing as it allows the paste to be transferred easily onto the substrate but with limited penetration. This means that, under shear stress induced by a squeegee, the paste viscosity is temporarily reduced to allow its flow through the screen onto the fabric, however once the shear stress is removed, the paste viscosity increases to prevent its penetration into the fabric [73, 96]. Thickening agents are also responsible for holding or adhering the pigment particles in the desired place of the fabric until the fixation of the particles to the fabric is completed [96].

Natural thickening agents, including those from colloidal polysaccharides such as starch, cellulose ethers, alginates or locust bean gum can be used for textile printing. However these water-soluble agents are often unsuitable for modern pigment printing, since they remain soluble once enclosed in a binder film even after curing, thereby affecting the wet fastness of the print. In addition these agents are macromolecular substances with a high content of polar groups and since such products always form a hard film, it is logical that their use will result in a firmer handle for the printed substrate [100]. Emulsion thickeners of white spirit/water (o/w type) have been very popular for pigment printing. They contain about 70% hydrocarbons, 0.5-1% non-ionic emulsifier and 29% water in their continuous phase [96]. Their main advantage is the ability of all components of the thickener, except the emulsifying agents, to evaporate on curing leaving a soft substrate handle with no residues. However the process releases organic substances which do not meet the environmental emission laws in many countries. Additionally recovery of white spirit from the exhaust gases of drying chambers is also complicated and too expensive; as a result these types of thickeners are being phased out [96]. Synthetic thickeners such as Printofix CA (Archroma) and Lutexol HP (BASF) are commercially available. They are basically polyanionic compounds derived from monomers such as acrylic acid and maleic anhydride. Synthetic-polymer thickening agents have rheology similar to that of emulsion thickening agents, however they contain extremely low solid compounds resulting in higher levels of fixation [96].

2.3.7 Fluorescent Whitening Agents

Fluorescent whitening agents (FWAs) also known as fluorescent brightening agents (FBAs) or optical brighteners, are organic compounds which exhibit fluorescence and usually contain a system of conjugated double bonds in their molecules. They are colourless to weakly coloured organic compounds that, in solution or when applied to a substrate, can absorb light in the ultraviolet region (340 - 370 nm) of the electromagnetic spectrum and reemit most of the absorbed light in the blue-violet region (420 - 470 nm) of the spectrum [83]. Apart from having a system of conjugated double bonds, the FWAs molecules have a planar structure and contain electron-donating groups such as hydroxyl (OH) and amino (NH_2) and are free from electron accepting groups such as nitrogen dioxide (NO_2) [101].

Textile fibres tend to absorb visible light in the 400 – 500 nm range of the electromagnetic spectrum. This results in a pronounced brownish-yellowish appearance, a phenomenon that is observed in both natural and synthetic materials, cotton being among them [102]. Oxidative chemical bleaching can be used to eliminate the yellow-brown effect, however excessive bleaching can significantly degrade the material. Fluorescent brighteners, strongly reflect but do not absorb in the visible range, and are therefore, applied to textile fibres for the purpose of reducing the yellowness. As a result of FWA application the amount of blue light reflected by the substrate is increased, thus improving the whiteness of the substrate. The brightened fabric is usually characterised as being 'whiter than white' i.e. has a reflectance of over 100% [103].

Brighteners can be introduced to textile materials during manufacturing process, although most of the agents are also incorporated into laundry detergents [104] to replace the whitening agents removed during domestic washing. Fluorescent brighteners for cotton fibres are applied by methods similar to that used in direct dyes [83], as part of the bleaching process or as an after-treatment either by exhaust or by padding methods. Further application methods have been described in the literature [101, 105].

2.3.7.1 Classification of FWAs

FWAs are categorised into three major classes, namely: stilbene, coumarin, and 1,3-diphenylpyrazoline structures, with about 80% of all FWAs containing one or two stilbene groups [102]. Stilbene, particularly the derivatives of 4:4'-diaminostilbene-2:2'-disulphonic acid, also called DAS (Figure 2.3.10) are the most common FWAs for cellulose [103]. They are also marketed as DAST brighteners and are usually synthesised from 4-nitrotoluene-2-sulphonic acid. These brighteners are characterised by being unstable towards chlorine containing bleaches and they also have limited stability towards peracids [83].

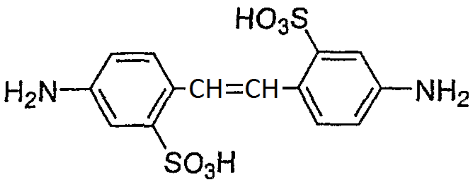


Figure 2.3.10 Structure of Diaminostilbene disulphonic acid [103]

An important class of stilbene fluorescent brightener for cotton are the triazinylaminostilbene. The stilbene structure of these fluorescent brighteners also called 4:4'-*bis*-triazinylaminostilbene-2:2'-disulphonic acid are derivatives of DAS and attach to a triazine nucleus, giving an affinity for cellulose. The substituent groups in the triazine nuclei can be varied to change the fluorescent properties such as solubility, affinity, hue and fastness to chlorine and light [103, 106]. Similarly by increasing the number of substituent triazine nuclei, the substantivity for fibres is also increased. An example of triazinylaminostilbene fluorescent whitening agent is C. I. Fluorescent Brightener 85, illustrated in Figure 2.3.11, where its diaminostilbene structure is attached to two triazine nuclei, suggesting higher substantivity for fibres.

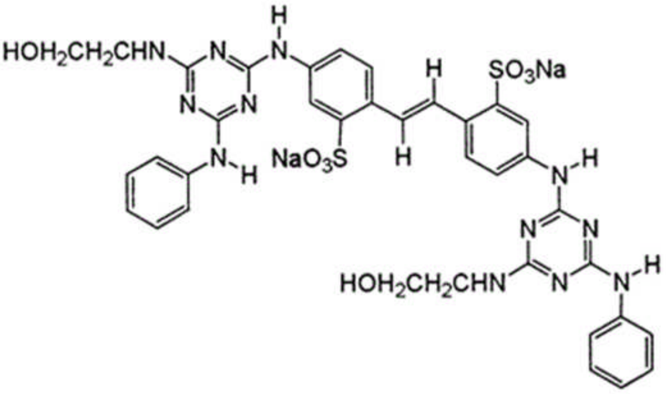


Figure 2.3.11 Chemical structure of C. I. Fluorescent Brightener 85 [107]

Distyryldiphenyl (DSBP) type are another important class of FWAs used for brightening cotton during laundering, although they can also be applied during fabrics manufacturing by exhaustion method [83]. An example of a distyryldiphenyl is C. I. Fluorescent Brightener 351, commercially known as Tinopal CBS (Figure 2.3.12).

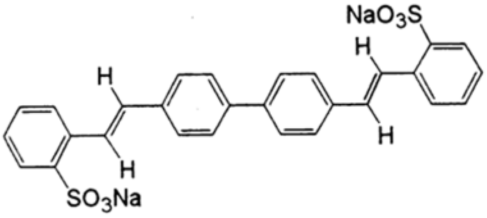


Figure 2.3.12 Chemical structure of C. I. Fluorescent Brightener 351 [83]

Distyryldiphenyl fluorescent brighteners are characterised by being effective in enhancing the brightness properties of detergents and offer high stability towards peracids and hypochlorite bleaching. However when in fibres, the brighteners are reported to have limited fastness to washing in soft water [83]. A special advantage of the sulphonated distyrylarene brighteners is their environmental–friendliness. This is due to the fact that their end-products cannot accumulate in the environment, with the ether bonds of the brightener readily oxidising during effluent treatment, forming soluble acids of low relative molecular mass [83].

2.4 CREASE RESIST FINISHING OF COTTON FABRICS

2.4.1 Introduction

Finishing of textile fabrics is performed to impart desired functional properties to the fabrics. “Resin” finishes, for example, are applied to textile materials to improve wash and wear, durable press, permanent press and easy care features of the material [108]. Both mechanical and chemical finishing techniques can influence the easy care processing of cotton, however only cross-linking chemical finishes applied to cotton fabrics to impart dimensional stability such as crease resistance properties were of importance to this study. This is because the finishes crosslink with the hydroxyl reactive groups of cellulosic materials forming covalent bonds. At the end-of-life of the textile material it is probable that the crosslinks will still be present, which will in turn limit the processability of the material during recycling. In this section a survey of literature together with the basic concepts of crosslinking agents will be presented.

2.4.2 Mechanism of Crosslinking agents

Any movement of the cellulosic chains with respect to the neighbouring chains is capable of changing the dimensions of fibre and forming creases within the fibre. For instance, during laundering the fibres swell as they absorb water molecules causing stresses on the fibres. This results in the readjustment of the internal polymer chains in the less ordered cellulosic region (amorphous regions) to relieve the stresses. On drying new hydrogen bonding forms between the polymer chains in their new configuration resulting in fabric creasing until an additional process such as ironing is introduced. Accordingly crease resist finishes are applied to cotton fabrics to reduce the swelling and limit movement of polymer chains, thereby reducing the likelihood of creasing [109]. The crosslinking agents introduce intra-fibre crosslinks between hydroxyl groups of adjacent cellulosic molecules which impart "memory" to the fibres so that when the fabric is creased, the cross-linker pulls the fibres back to their original crease-free state. The precise nature of the formed crosslinks depends on the specific finishing agents and may involve not only covalent bonding but also hydrogen bonding and van der Waals forces. The chemistry of the crease-resist finishes has been extensively reviewed elsewhere [110, 111].

For many years polymeric resins based on urea and formaldehyde formulations have been used as crosslinking agents for cellulosic fibres. However these chemicals have major disadvantages such as sensitivity to chlorine based bleaching, poor durability as well as the release of formaldehyde, a toxic and carcinogenic substance [108]. Research has been focussed on developing crosslinking agents which reduce the amount of formaldehyde such as those based on N-hydroxymethyl derivatives [112]. To date the most commonly used crosslinking agent has been *N,N'*-dimethylol-4,5-dihydroxyethylene urea (DMDHEU), Figure 2.4.1, synthesized from urea, glyoxal and formaldehyde [108, 109]. The compound is not completely formaldehyde free but it contains low levels of the agent. An important property of the DMDHEU is its ability to remain chemically unchanged at relatively low temperature, ~130°C [110]. It can therefore be applied to a textile material and it will not hydrolyse or crosslink unless higher temperatures are applied.

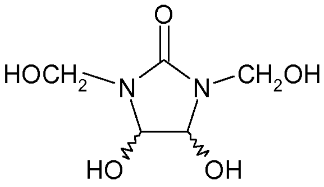


Figure 2.4.1 Structure of Dimethylol dihydroxyethylene urea (DMDHEU)

Other crosslinking agents such as polycarboxylic acids and *N,N'*-Dimethyl-4,5-dihydroxyethylene urea (DMeDHEU) that can crosslink with cellulose without releasing formaldehyde have been developed [112-114]. But the toxicity, moderate mechanical performance and their high cost of manufacturing (up to four times the cost of DMDHEU) limit their commercial success as cross-linkers [115].

2.4.3 Application of Crease resist finishes

The most common application procedure for crease resist finishes is the pad-dry-cure method. In this method the finishing agents, a catalyst and other components are padded on the fabric prior to the crosslinking reaction which occurs during curing. DMDHEU and other *N*-methylol based crosslinking agents are applied to cellulosic fabrics in a presence of an acidic catalyst such as magnesium chloride. Sulphuric acid, hydrochloric acid and the salts of sulphate and ammonia have also been reported as excellent catalysts, but they lead to fibre degradation and unstable finish baths [23, 111]. Since DMDHEU is non-reactive at temperatures below 130°C, curing is usually performed at 150-170°C for 0.5 to 3 minutes to activate the crosslinking mechanism. On curing the agent crosslinks with cellulose, thereby imparting the crease recovery properties on the treated fabric.

2.5 REVIEW OF SOLVENTS FOR DISSOLVING CELLULOSIC MATERIALS

2.5.1 Introduction

Dissolution of cellulose is highly important in cellulose applications such as the generation of man-made fibres and in the formation of films, membranes and other cellulosic products. The process is also important in the characterisation of cellulosic materials such as the determination of molecular mass and the degree of polymerisation [53]. Complete cellulose dissolution is however very difficult due to the strong inter and intra-molecular hydrogen bonding within the cellulose, which creates networks of close compact structures with both highly ordered (crystalline) regions and regions of low order (amorphous), as illustrated in Figure 2.5.1. These regions, especially the crystalline regions, are responsible for the limited solubility of cellulose in most common solvents. Dissolving cellulose of higher molecular weight, such as native cellulose present an even bigger solubilisation challenge due to its long range order crystalline regions which do not allow the solvents to access the core of the cellulose polymer [55].

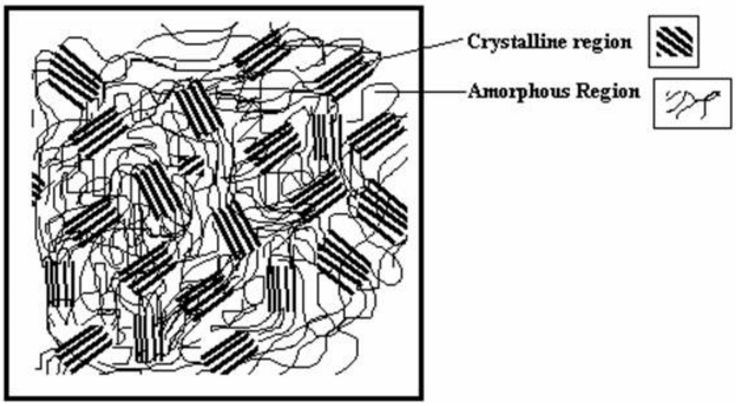


Figure 2.5.1 Amorphous and Crystalline regions in a polymer structure [116]

Cellulose dissolution occurs as a result of disrupting the inter- and intra-molecular hydrogen bonds, thereby destroying the long range ordered crystal regions to allow the formation of a polymer solution [55]. Pre-treatment of the cellulose either mechanically, chemically or by enzymatic reaction is sometimes necessary to increase the level of cellulose dissolution as these processes can increase the swelling of the cellulose by opening their crystalline structures [117]. Mechanical treatments such as milling, disrupt the interfibrillar bonds located mainly on the primary cell wall, thereby increasing the reactive surface area of the cellulose fibre while improving its accessibility to solvents [55]. Chemical treatments such as alkali treatment are also used prior to dissolution to increase the swelling of fibres causing breakage of some hydrogen bonds as a result of stresses caused by swelling. The disruption of the bonding structure results in a less ordered cellulose structure, which in turn increases the active surface area and increased number of accessible hydroxyl groups [64].

Many solvent systems for cellulose have been reported to either dissolve the cellulose indirectly with prior derivation/activation or directly without derivative formation [64, 118-120]. The most common indirect cellulose solvent is the carbon disulphide/sodium hydroxide system for viscose processing, while the most common ‘direct’ cellulose solvent is *N*-methylmorpholine-*N*-oxide (NMMO), although the cupriethylenediamine hydroxide system (CED), *N*, *N*-dimethylacetamide (DMA)/lithium chloride (LiCl), Ionic Liquids (ILs) and the NaOH/urea solvent system are also used for ‘direct’ dissolution of cellulose.

In this study the non-derivative CED and NMMO solvent systems were of importance. The CED was chosen due to its simplicity in the characterisation of chemical properties of cellulose such as the viscosity and the degree of polymerisation (DP). Similarly NMMO was chosen due to its promising environmental preserving behaviour and the overall excellent properties of the resultant fibres produced from extruding the NMMO-cellulose solution.

2.5.2 Dissolution of Cellulose in the CED solution

The aqueous solutions of metal-amine complexes such as the cupriethylenediamine hydroxide system referred in the literature as Cuen or CED are reported to be good solvents for cellulose [55]. The Cuen system is the main alkaline metal (Copper-II-ethylenediamine) complex based solvent that is used for the determination of viscosity and the DP of cellulosic materials due to the stability of the compound as well as its simplicity in the application and low level of degrading the cellulose [53, 121]. On dissolution the cellulose forms a coordinated complex with copper (II) ions of the solvent. The C_2 and C_3 glycol groups of a glucose unit chelates to occupy the two of the coordination sites of copper (II) ions by displacing one molecule of diethylenediamine [53], as shown in Figure 2.5.2.

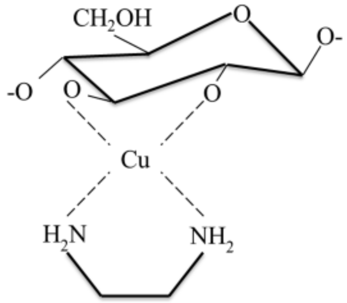


Figure 2.5.2 Cuen/CED complex with cellulose glycol group [53]

The dissolution mechanism depends on the alkalinity nature of the solvent. Both hydroxide and ethylenediamine are good swelling agents for cellulose. This swelling disrupts the intermolecular hydrogen bonding, facilitating molecular chain separation and allowing the solvent to penetrate the cellulose structure and enhance complex formation with cellulose glycol groups. The complex formed is highly stable, thereby preventing the re-aggregation of molecular chains and precipitation [53]. The major drawback of Cuen is the high alkalinity of the solution, which may induce degradation reactions at oxidized functionalities. Care should therefore be taken to ensure no oxygen is in contact with the cellulose-solvent complex.

In this study the CED solvent was used to determine the limiting viscosity of the cellulose which is an important parameter during the regeneration of fibres through the Lyocell process in order to minimize the processing difficulties of the dope materials into fibres [35, 122]. The viscosity was then used to estimate the extent of cellulose degradation caused by chemical treatment of the cotton fabrics.

2.5.3 Dissolution of Cellulose in the NMMO solution

To date, the most promising non-derivative solvent for cellulose is the *N*-methylmorpholine–*N*-oxide (NMMO), an oxidation product of ternary amine N-methylmorpholine with hydrogen peroxide [35, 64] as shown in Figure 2.5.3.

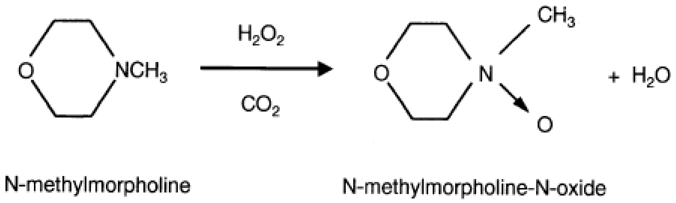


Figure 2.5.3 Formation of *N*-methylmorpholine-*N*-oxide (NMMO) [35]

The NMMO solvent was developed as an alternative to the carbon disulphide/sodium hydroxide system used for the manufacturing of viscose fibres. The solvent can directly dissolve highly concentrated cellulose without changing the chemical properties of the cellulosic chain. NMMO is therefore used to produce Lyocell fibres using the technology which produces less harmful by-products compared to the conventional viscose process. Additionally over 99% of the solvent can be recovered [57, 64] which reduces the need for effluent treatment.

2.5.3.1 Mechanism of the NMMO dissolution of cellulose

The exact nature of the dissolution process and cellulose interactions with NMMO is still unclear [123]. However the ability of the solvent to physically dissolve cellulose is said to be due to its strong N-O dipole, which can disrupt the hydrogen bond network of the cellulose and form solvent complexes by establishing new hydrogen bonds between the macromolecules and the oxygen of the N-O bond in NMMO [123]. It is the hydrogen bonding between the cellulose and NMMO (Figure 2.5.4) that causes dissolution of cellulose. It is also reported that cellulose can be dissolved if the intermolecular attractive forces between the cellulose, NMMO solvent and water are greater than the attraction forces within each single species. A detailed literature on the structure formation of cellulose regenerated materials made from NMMO solutions is available [35].

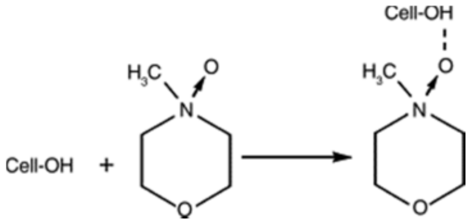


Figure 2.5.4 The mechanism of cellulose dissolution by NMMO [124]

A typical NMMO-Cellulose spinning solution contains about 14% cellulose, 10% water and 76% NMMO and is usually dissolved at temperatures above 100°C to obtain a homogeneous solution [35, 123]. The dissolution process is highly dependent on the cellulose concentration and its degree of polymerisation [123], where both high cellulose concentration and high DP decreases the cellulose dissolution efficiency.

During dissolution cellulose is first dispersed in NMMO and water to make a slurry. The water is then removed from the suspension under vacuum and high temperature until the NMMO monohydrate, with a water content of 13.3% by weight and a melting point of 74°C is made. The NMMO monohydrate produced is reported to dissolve cellulose better than pure NMMO [35]. After dissolution, the cellulose/NMMO/water solution is extruded from a nozzle over an air gap and into an aqueous coagulation bath where the cellulose is precipitated and regenerated. The solvent is then recovered, cleaned and reused in the system. Figure 2.5.5 shows the solubility of cellulose in the binary NMMO/Water system.

The phase diagram shows a relatively small region where cellulose is completely dissolved in highly concentrated NMMO and less water [35].

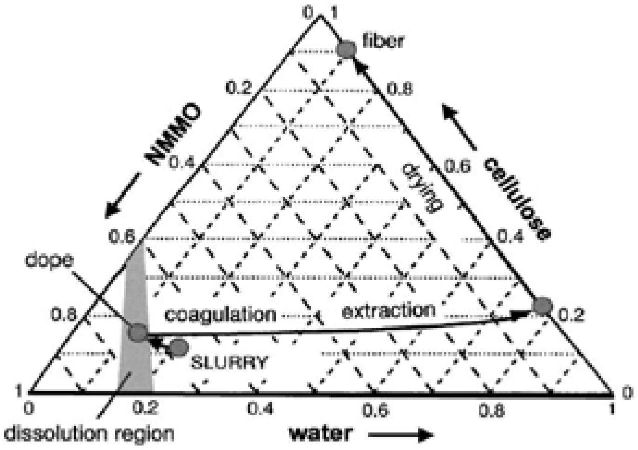


Figure 2.5.5 Phase diagram of the ternary Cellulose/NMMO/Water system expressed in percentage weight [35]

2.6 TECHNIQUES FOR STRIPPING DYES FROM COTTON FABRICS

Dyes and pigments are usually applied to textile materials in order to improve the aesthetic properties of the materials. These colorants are designed to be fast and resist removal or chemical attack and therefore their stripping is usually difficult. However the presence of dyes and finishes crosslinked in the cellulosic fibres of the recycled cotton pulp prevent dissolution and subsequent extrusion of the materials for fibre regeneration. Therefore dyes and pigments have to be removed from the textile materials prior to their being reprocessed for fibre regeneration. In this section existing methods for ‘stripping’ dyes from cotton substrates are reviewed in order to establish an understanding of the stripping of colorants from cotton fabrics with a view to reusing the stripped materials for fibre regeneration.

2.6.1 Introduction

In the textile coloration industry, colorants are sometimes removed from dyed materials to correct uneven dyeing or off shade coloration [125]. This process of removing dyes and pigments from a material is usually referred to as ‘stripping’ [126, 127]. A complete dye removal is however difficult to achieve as the dye molecules are not only bound to the surface of the fibre but also held in the amorphous regions of the fibre matrix by ionic forces, covalent bonds, van der Waals forces as well as hydrogen bonds [128].

Direct dyes do not form covalent bonds with fibres, but they interact with fibres through van der Waals forces and hydrogen bonding. However, when a direct dyed substrate is after-treated with fixing agents such as cationic fixing agents, the attractive forces between the agent and the dye combine them together to form a complex with a higher molecular weight and reduced solubility. This complex is responsible for the improved wet fastness of the dyed substrate [81, 84], although it can dissociate in detergent solutions at temperatures above 60°C [56]. Similarly reactive dyes form covalent bond with fibres making the dye-fibre bond resistant to most chemical attacks [77].

Besides the nature of the dye-fibre bonding system, the dye structure can also affect the stability of the dyes present on the textile fibre. For instance, the fused aromatic ring structures of the anthraquinone based dyes (usually reactive or vat dyes) make them highly resistant to degradation [129]. Sulphur dyes are reported to be relatively easily destroyed by bleaching agents such as hypochlorites and peroxides, however, vat dyes are more resistant to bleaching agents [78].

To completely strip dyes from a textile material it is therefore necessary to break the dye-fibre covalent bond formed on the reactive dyed substrate [78, 126], to solubilise the insoluble pigment mechanically entrapped in the fibre as a result of vat or sulphur dyeing [79] as well as to break any other dye-fibre intermolecular forces such as hydrogen bonding, ionic and van der Waals forces that operate within a dyed fibre. To strip the after-treated direct dyeing, it is also necessary to solubilise the dye-cationic fixing agent complex [56, 99], thereby freeing the dye molecules from the agent for stripping. Similarly, to strip pigment prints, the linkage formed between the binder, the pigment and the fabric must be disrupted. In addition some finishes such as crosslinking agents for durable press and crease resistance provide a degree of protection to dyeing against oxidation or reduction processes thus increasing the difficulty of dye removal. These finishes will need to be stripped off before dyes can be removed from the fibres.

Both chemical and biological methods have been reported to successfully strip colorants from dyed fabrics [126], usually partial stripping for the purpose of correcting faults and re-dyeing of the materials. In this section the dye stripping methods have been reviewed in order to establish an understanding of the stripping colorants from cotton fabrics for the purpose of reusing the stripped materials for fibre regeneration.

2.6.2 Chemical stripping methods

With chemical stripping, complete decolouration can be achieved by using stripping agents that react with the chromophore responsible for the dye colour. The chromophores are usually conjugated systems of single and double bonds, therefore for decolouration to occur, the stripping agents need to saturate the conjugated double bonds. Once the bonds are modified, the modified chromophore is unable to absorb and reflect electromagnetic radiation in the visible region of the spectrum thereby appear as a colourless compound [70, 80]. Additionally the stripping agent needs to detach the dye from the fibre by breaking the dye-fibre bonds, such as the covalent bonds formed during reactive dyeing.

Various chemicals are available to correct faults and uneven dyeing of the material usually by using different oxidising or reducing agents in acidic or alkaline conditions and at varying temperature ranges. A combination of either reduction followed by oxidation process or oxidation followed by reduction process has been reported to offer a more efficient colour removal [78, 130]. Although most dyes for cotton including a wide range of direct and azo dyes can be easily decolourised by reducing agents [130], oxidation is also important in permanently colour removal, thereby giving a more permanent white [131]. In contrast reactive dyes are reported to resist various stripping agents as they are covalently bound onto cotton fibres. Efficient removal of these dyes requires disrupting the bond between reactive groups of the dye and hydroxyl groups of the cotton fibres [126].

2.6.1.1 Reduction bleaching method

In the reduction method, reducing agents work by either chemically reducing coloured compounds (chromophores) into colourless compounds (leuco-chromophores) or by promoting their solubility in different media. However through the reduction process, there is the risk of the colour reversing back to its original colour as well as yellowing of the reduced material due to oxidation once exposed to air or sunlight [23, 80]. Incorporating oxidative bleaching after the reductive bleaching process can help to alleviate the reversion.

Various reducing systems such as alkaline sodium dithionite, thiourea dioxide, a combined bisulphite/borohydride system and sodium hydroxymethane sulphinate have been reported to successfully strip dyes from textile substrates and are discussed further.

2.6.1.1.1 Alkaline Sodium Dithionite (Sodium Hydrosulphite) Stripping

Alkaline sodium dithionite has been used successfully in stripping colorants from textile materials. The reductive property of sodium dithionite is reported to be due to the evolution of hydrogen when the agent reacts with water or sodium hydroxide [132]. At low temperatures or low pH, their aqueous solutions are unstable forming sodium bisulphite as shown in Equation 2.6.1. The presence of atmospheric oxygen in the alkaline dithionite solution results in the formation of sulphate and sulphite (Equation 2.6.2) which reduces the reduction efficiency of the solution. Therefore an excess of alkali and dithionite are required to prevent the formation of sulphates and sulphites [83].

$$2Na_2S_2O_4 + H_2O \rightarrow 2NaHSO_3 + Na_2S_2O_3 \qquad \textbf{(Equation 2.6.1)}$$

$$Na_2S_2O_4 + 2NaOH + O_2 \rightarrow Na_2SO_3 + Na_2SO_4 + H_2O \qquad \textbf{(Equation 2.6.2)}$$

The addition of non-ionic surfactants in the bleaching liquor may also assist in improving the stripping efficiency of the alkaline dithionite solution. Similarly incorporating some quaternary ammonium compounds and some polymers such as poly(vinylpyrrolidone) presented in Figure 2.6.1 promote stripping of vat and sulphur dyes by complexing with the leuco anions in dithionite solution, thereby increasing the stripping efficiency [83].

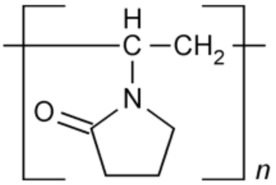


Figure 2.6.1 Structure of Poly(vinylpyrrolidone) [83]

Alkaline sodium dithionite is reported to have the capability of cleaving azo reactive dyes into amines [73] which are then easily removed during further processing such as in sodium hypochlorite bleaching as suggested in the literature [79, 131]. However stripping of pre-metallized dyes requires first removing of the metals through boiling in ethylenediamine tetraacetate (EDTA) solution, followed by reduction stripping in a solution of alkaline dithionite before treating the material in sodium hypochlorite then thorough washing-of the fabric to remove any chemical residues [78]. However hypochlorite bleaching involves generating chemicals such as trichloromethane (chloroform) and other chlorinated by-products containing large amounts of adsorbable organic halogens (AOX) that are above specified safety limits [133, 134]. These by-products affect the environment unless the effluent is treated with expensive anti-chlorine treatments to remove excess sodium hypochlorite [133]. The use of hypochlorites is therefore completely banned in Germany [135], while in other European countries its application has been reduced to specific processing [136].

Alkaline reduction solutions of sodium dithionite and sodium hydroxide have also been reported to successfully remove C. I. Reactive Black 5 from Lyocell fibres at the boil without incorporating an oxidative bleaching [137]. However effective dyestuff removal was only obtained after two consecutive reduction processes. The effectiveness of stripping process was confirmed by the small amount of nitrogen content values (approximately 0.09% Nitrogen atomic composition) that remained in the stripped fabric, equivalent to the amount of nitrogen in the undyed fabric.

A method that uses the reductive power of combined sodium dithionite and sodium hydroxide while incorporating quaternary ammonium compounds as stripping assistants in removing organic dyes has been patented [138]. The method is said to remove reactive dyes and pigments like phthalocyanine, vat and azo that are normally applied in the presence of binding agents. The stripping assistants are obtained from primary aliphatic amines or diamines which have been ethoxylated with ethylene oxide and then quaternized with benzyl chloride. When applied to a greenish–blue reactive dyed cotton fabric the method removed large amounts of dye, leaving slightly greenish residues which were removed by using a mild sodium hypochlorite bleaching. The method has also been used to strip phthalocyanine pigments from printed textile materials [139].

In summary, alkaline sodium dithionite can remove large amounts of colorants from textile materials, however, the agent does not usually give complete colorant removal usually leaving some residues unless oxidative bleaching is incorporated.

2.6.1.1.2 Thiourea-dioxide stripping

Thiourea dioxide, also known as formamidine sulphinic acid or FAS has been previously suggested as an alternative to sodium dithionite stripping of reactive dyes from cotton fabrics [126]. The active reductive bleaching species in thiourea dioxide are sulphinic acids [23, 99], Equation 2.6.3; and the stripping process follows the same principle as that of sodium dithionite, where stripping is done in alkaline condition, usually in the presence of sodium hydroxide.

$$\mathrm{(NH_2)_2C = SO_2 + H_2O \rightarrow (NH_2)_2C = O + H_2SO_2} \qquad \textbf{(Equation 2.6.3)}$$

Thiourea dioxide *Sulphinic acid*

This method resulted in a clearer fabric under varied working parameters such as incorporating levelling agents which increased the homogeneity of the stripping effect [126]. However the agent is relatively expensive (three times more expensive than sodium dithionite) and it is not easily removed from wastewater as it resists hydrolysis. In addition the agent undergoes photochemical oxidation by hydroxyl radicals present in the atmosphere [83, 99]. Although there are no reports on levels of carcinogenicity with human exposure to thiourea, a number of studies have reported carcinogenic effects with animals as it reacts with their DNA [140].

2.6.1.1.3 Bisulphite/Borohydride reaction in stripping of dyes

A method for stripping dyes in an aqueous bath produced by the reaction between bisulphite and borohydride in the presence of an alkali has been patented [128]. The agents are mixed together at a pH of about 6.6 before being added to an aqueous bath containing the textile material. The invention uses an aqueous alkaline solution containing 12% sodium borohydride and 40% sodium hydroxide due to its high stability and its availability under the trade name BOROL. During stripping, the agents produce active sodium hydrosulphite (Equation 2.6.4) which aids in the reduction process.

$$\mathrm{BH_4^-} + 8\mathrm{HSO_3} + \mathrm{H^+} \xrightarrow{\mathrm{pH}\ 5-8} 4\mathrm{S_2O_4^{-2}} + \mathrm{B(OH)_3} + 5\mathrm{H_2O} \qquad \textbf{(Equation 2.6.4)}$$

The stripping process is performed at higher temperatures (82-110°C) while maintaining the pH of the stripping liquor at 10.2 - 12, due to the cotton fibre requiring higher pH to initiate swelling and allowing entry of chemicals into the fibre matrix. Ionic or non-ionic surfactants can also be added to the stripping bath to aid levelling by lowering the surface tension of the bath water and increasing the wettability of fibres. After stripping the materials are rinsed in a bath, preferably an aqueous acetic acid bath for neutralization of the material. The method is reported to successfully strip varied types of dyes including, direct dyes, sulphur dyes, vat dyes, and reactive dyes.

The advantage of using this method is that fewer chemicals are necessary as it does not require other agents like chelating/sequestering agents and fire retardants as well as odour scavengers as in some sodium dithionite stripping methods. The reclaimed textile material is also reported to have high receptivity for new dyes [128]. However the cost of sodium borohydride and the associated effluent problems are barriers to their commercial exploitation [99]. Sodium borohydride solutions can also release flammable hydrogen gas upon contact with acids, oxidizing agents, and transition metals, or if diluted with large amounts of water.

2.6.1.1.4 Sodium hydroxymethane sulphinate dye stripping

A method that involves stripping dyes in a heated aqueous solution containing sodium hydroxymethane sulphinate, an ammonium cation and a sulphite anion at pH 5 - 9 has also been patented [141]. The method involves dissolving ammonium sulphate and sodium sulphate in water before heating the solution to about 60 - 80^{o}C and adding the sodium hydroxymethane sulphinate. A wetting agent (usually a long chain phosphate alcohol) is also added and stripping is performed for 30 – 60 minutes. After stripping the fabric is rinsed in hot water containing detergent such as phosphate or alcohol sulphonate to remove dye residues and excess stripping chemicals. The invented method can be used to strip reactive dyes, direct dyes and vat dyes from cotton materials, but can also strip other dye classes from other textile materials.

The advantages of this method include the use of moderately alkaline conditions (i.e. below pH 9) which reduces the possibility of the alkali harming the fibre which could result in difficulties in the re-dyeing process. A small amount of reducing agent (almost half that used in traditional methods) is used, thereby reducing the amount of agent in the effluent. This decreases the chemical oxygen demand (COD) of wastewater, making it less harmful to the environment [141]. However the method could not completely strip colorants from the fabrics leaving up to 40% dye residues on the stripped fabrics.

2.6.1.2 Oxidative bleaching methods

The oxidative process involves breaking down the large dye molecules into smaller, usually colourless molecules [142]. The main oxidative bleaching systems used for textile materials are hypochlorite, sodium chlorite and hydrogen peroxide bleaching processes. However hypochlorite and sodium chlorite bleaching processes are currently less used due to high concentrations of salts and chlorine in their effluent process water which is unacceptable in terms of ecological impact [99, 133]. This only leaves hydrogen peroxide which has an oxidation potential (E_o) of 1.78V [129], as the main oxidative bleaching system despite it being relatively more expensive (about six times higher) than hypochlorite solutions. The agent only contributes to about 0.92 mg/L AOX compared to 27 mg/L contributed by sodium hypochlorite and in the subsequent effluent treatment, it decomposes into water and oxygen which does not create effluent problems [83].

Although there is no absolute certainty on the nature of hydrogen peroxide bleaching action, it is however believed that the main bleaching effect is due to active perhydroxyl ion (HO_2^-) species obtained when hydrogen peroxide is decomposed in alkaline conditions (Equation 2.6.5) usually at pH 10.5-12 and at temperatures close to the boil. The perhydroxyl is highly unstable and in the presence of oxidisable materials (such as coloured matters in cotton) it decomposes into hydroxyl radicals ($HO\cdot$) (Equation 2.6.6) and thus bleaching occurs [70, 143]. The perhydroxyl anion acts as a nucleophilic bleaching agent, thereby destroying the carbon-carbon double bonds present in chromophores [70]. Increasing the amount of perhydroxyl anions is also necessary to achieve a high bleaching effect, although the process can also accelerate the rate of side reactions (Equation 2.6.7).

$$\mathrm{H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O} \qquad \textbf{(Equation 2.6.5)}$$

$$\mathrm{H_2O_2 + HO_2^- \rightarrow HO^{\cdot} + H_2O + \cdot O_2^-} \qquad \textbf{(Equation 2.6.6)}$$

$$\mathrm{2H_2O_2 \rightarrow H_2O + O_2} \qquad \textbf{(Equation 2.6.7)}$$

Other species such as singlet oxygen ($^{\cdot}O_2$), and perhydroxyl radical anion ($^{\cdot}O_2^-$) are also reported to be possible active bleaching species [144]. However hydroxyl radicals are specifically reported to play an important role in the oxidative splitting of azo groups.

Stilbene groups are however more sensitive to oxidation than the azo linkages in spite the protection offered by the two *o*-sulphonate groups [74].

Bleaching with hydrogen peroxide usually requires activation for bleaching to occur and alkali is the most common activator [80]. The process is more rapid in alkaline condition than in acid solutions which is reported to be due to hydroxyl ions present in alkaline liquor neutralizing the hydrogen ions of hydrogen peroxide, thereby promoting the liberation of perhydroxyl ions [131]. Other agents such as anionic nonanoyloxybenzene sulphonate (NOBS) and tetraacetylethylene diamine (TAED) can also be used as peroxide bleach activators by generating peracid, thus allowing bleaching to take place at lower temperatures and reduced time [145]. UV (Photo-catalytic oxidation), Iron (Fenton reagent), and ozone have also been studied on the decolouration of wastewater from textile dyeing [146], however these agents are out of scope for the current study.

The main challenge when using hydrogen peroxide is its tendency to decompose into oxygen and water (Equation 2.6.7) when in alkaline conditions, at higher temperatures and in the presence of transition metals such as iron and copper. The oxygen generated has no bleaching effect and can result in the increased tendering of cellulose by oxidation and subsequent formation of oxycellulose. Stabilisers like sodium silicate are therefore necessary to keep the pH within the limits and also control the decomposition of hydrogen peroxide in bleaching solutions [70, 80, 131]. Metal chelating agents such as ethylenediamine tetraacetic acid (EDTA) can also be added to the bleaching liquors to bind free metal ions and significantly reduce the catalytic rate of decomposition and subsequent mechanical and oxidative deterioration of the material.

2.6.3 Biological stripping of dyes

Biological or enzymatic stripping has been commonly studied for the decolouration of industrial wastewater containing dyes [147, 148], although only fewer enzymes such as xylanases, cellulases, and proteases exert some bleaching effect on the textile substrates [149]. There have also been some reports of using bacterial degradation as well as enzymatic reactions such as fungi, especially white rot fungi in stripping dyes from fabrics [150, 151]. The enzymatic degradation process is environmentally friendly due to the biodegradability and naturally occurring enzyme products [83]. The process is also non-harmful to the stripped fabrics. However enzymes are quite expensive and the stripping process takes time; an incubation time of up to 15 days may be required for maximum stripping to occur [151]. By using higher enzyme concentrations the reaction speed can be increased, but at additional costs. The process is also reported not to satisfactorily decolourise materials unless it is combined with other chemicals such as hydrogen peroxide, where they are used to catalyse the oxidation process [152].

2.6.4 Summary

Various existing methods for partial or fully stripping colorants from cotton fabrics have been reported. However these methods only aim at stripping dyes for the purpose of fault corrections or re-dyeing of the materials. Nevertheless these methods usually do not attain full decolourisation instead colorants are only partially removed to a substantially less coloured form. Moreover none of the methods can successfully strip all the dye classes, but different stripping solutions have to be designed for each dye class. No work has been done to develop and implement methods that can completely strip all dyes from cotton fabrics for the purpose of recycling and reprocessing of the stripped materials for reuse through fibre regeneration. All in all, the literature has indicated that currently there is no one reducing agent that can replace sodium dithionite despite its instability in water and oxygen. It was therefore the purpose of this study to investigate and develop methods that could completely strip colorants from cotton fabrics for the purpose of reusing the material through the fibre regeneration technology.

2.7 SUMMARY OF THE PREVIOUS WORK ON COTTON WASTE IN LYOCELL REGENERATION

In an effort to develop the reuse of waste cotton garments through the Lyocell processing technology, the previous work by Dr. Liberato Haule exploring the possibility of removing easy-care finishes from waste cotton and preparing a purified cellulosic source for pulp and subsequent fibre regeneration is reviewed. It was necessary to remove all finishes from the materials since they inhibit the deconstruction of the fabrics into their fibrous form and its subsequent dissolution required prior to extrusion and fibre regeneration. Therefore the wash durabilities of the formaldehyde based crosslinking agent, dimethylol dihydroxyethylene urea (DMDHEU) and the formaldehyde-free 1, 2, 3, 4-butane tetracarboxylic acid (BTCA) crosslinking agents were first established by washing the crosslinked samples under ISO C06/C09 conditions and through extended domestic laundering. It was established that the easy-care finishes were durable to laundering hence the need to include the removal of the easy care finishes from waste cotton garments as a preparation stage before processing the materials for fibre regeneration. Sequential acid/alkali stripping method was therefore proposed as the robust method to ‘strip off’ all types of easy care finishes applied to cotton due to its high efficiency in removing these agents while offering minimum degradation to the cellulose polymer.

The work also explored wet and dry fabrics deconstruction methods by using a Valley beater and an Intimus grinder, respectively, as possible ways to deconstruct fabric materials into their fibrous form. After a thorough investigation, the Valley beater wet deconstruction method was identified as the best deconstruction method due to overall relatively little fibre modification by the method. The fibre breakage resulting from this method generated pulp with mechanical properties and a degree of polymerisation appropriate for producing pulp of ‘paper making quality’. A much clearer advantage of selecting the Valley beater deconstruction technology was the fact that the technology is readily available in both pulp and paper industries.

The dissolving of cotton fabrics that had been previously cross-linked with easy-care finishes was not possible in both CED and NMMO solvents. However after treating the materials in the established sequential acid/alkali method, the materials could be successfully dissolved in these solvents. The materials that could be dissolved in CED solvent were used in the fibre regeneration as per the Lyocell process. The new regenerated fibres had higher molecular properties than the conventional Lyocell fibres from wood pulp, with the fibres exhibiting the cellulose II structure which is similar to the conventional Lyocell fibre. In addition the new fibres had higher Total Crystallinity Index (TCI) and Lateral Order Index (LOI) compared to the conventional Lyocell fibre which was reported to be due to higher crystallinity and higher molecular weight of the precursor cotton material feedstock compared to the standard wood pulp.

The removal of non-cellulosic material is important in order to ensure complete solubility of the cellulose in a solvent and smooth the spinning process. Therefore the previous work also investigated the possibility of obtaining viscose from viscose/polyester blended fibres, through the wet cyclone separation technology. It was primarily discovered that fibre separation could be achieved by using gravity separation, although it was later established that a combination of both gravity settling and wet cyclones could be a potential method for fibre separation. The method was however challenged by agglomeration of fibre into tufts, which toughened the separation process and therefore required further investigation to optimise the separation parameters.

However the previous work did not investigate the possibility of processing dyed-cotton waste garments as feedstock for fibre regeneration. It was therefore the objective of this current work to explore the possibility of processing the dyed-cotton waste garments for the purpose of reusing the materials for fibre regeneration through the Lyocell process.

Chapter Three: Experimental and Analytical techniques

3.1 INTRODUCTION

In this chapter the materials, experimental processes and analytical techniques applied to investigate the potential for recycling waste cotton garments through the Lyocell processing technique are reported. The experimental processes included stripping of colorants and finishing agents from cotton substrates, disintegration of the stripped fabrics into fibrous pulp materials, dissolution and extrusion of the materials for fibre regeneration. The analytical work involved assessment of the colour parameters of the stripped samples as well as morphological and structural change of the materials as analysed by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) and X-ray Diffraction Spectroscopy (XRD) techniques.

Most of the research work was conducted at the School of Design chemistry laboratory at the University of Leeds. However fibre spinning and testing of their physical properties was conducted at the Lenzing fibre manufacturing facility in Austria. In addition some of the chemical composition testing such as ICP-OES and XRD were also performed at external analytical facilities.

3.2 MATERIALS

The textile materials used for this study are presented in Table 3.2.1. Mercerised cotton fabric was used in Chapter 4 and 5 of this thesis due to its ability to accept chemical reactants such as dyes and its ability to provide reproducible data in experiments as a result of the mercerisation process modifying the chemical properties of the fibre [55, 63]. However Chapter 6 of this study used unmercerised cotton fabric to imitate the common type of substrate used in modern apparel.

Table 3.2.1 Textile materials used for the study

Material	Source
Plain weave 100% cotton fabric (135g/m^2) - Scoured and Bleached (unmercerised) - Scoured, Bleached and Mercerised (mercerised)	Phoenix Calico ltd, Cheshire, UK
Dyed cotton fabrics (4% on weight of the material) - Sulphur dyed fabrics - Vat dyed fabrics - Direct dyed fabrics	Mr. Phil Cohen, University of Manchester
Post-consumer garments - Blue shirt - Black T-shirt - Denim jeans	Oxfam charity shop, Leeds

3.3 DYEING OF COTTON MATERIALS

In this study reactive dyeing was done by the researcher at the School of Design chemistry laboratory at the University of Leeds using a procedure described in Section 4.2 while sulphur dyeing (Section 5.2), vat dyeing (Section 5.3) and direct dyeing (Section 5.4) was done by Mr. Phil Cohen of the University of Manchester using exhaust dyeing technique. C. I. Vat Blue 1 was also applied to cotton fabrics by the researcher using the padding method described in Section 5.3 to imitate the ring dyeing of denim materials.

3.4 STRIPPING OF DYES FROM COTTON SUBSTRATES

3.4.1 Introduction

In textile processing, dyes and pigments are usually incorporated into materials to impart the desired aesthetic appearance, usually as per customer specifications. Finishing agents such as crease-resist agents and flame retardant finishes are also applied to textile materials for the purpose of enhancing the technical properties of the product. However in chemical recycling of the textile materials, the presence of dye-fibre bonds and crosslinks such as those from finishing agents may impair the recyclability of the materials, especially during the dissolution and subsequent spinning of the recycled materials [66] as they limit accessibility of the hydroxyl groups of cellulose to the chemical solvents. In addition these colorants and crosslinks may also impart deleterious properties to the new formed products including preventing future coloration of the material. It was therefore necessary to investigate and establish methods that could strip colorants and any other crosslinks prior to reuse of the recycled waste cotton garments.

Reduction by sodium dithionite; hydrolysis by acid and alkali; and oxidative bleaching by hydrogen peroxide were investigated as potential methods to strip both colorants and finishing agents from waste cotton garments. The stripping treatments were applied to cotton fabrics dyed with reactive, direct, sulphur and vat dyes and also printed fabrics. A three step treatment (sequential acid/alkali/peroxide – Method A or sequential acid/dithionite/peroxide – Method B) was used in the removal of colorants from cotton fibres due to the different and distinct chemistries of each treatment. The efficiency of the established colour stripping methods was also assessed for post-consumer cotton garments obtained from local second-hand shops.

3.4.2 Chemicals

Sodium dithionite and hydrogen peroxide were obtained from Sigma Aldrich, while polyvinylpyrrolidone (PVP) and Chromabond S-100 dye inhibitors were kindly supplied by Ashland Specialties UK Ltd. An aqueous non-ionic washing detergent (Hostpan N/N) was obtained from Clariant, UK while all chelating agents were obtained from Sigma Aldrich. All other reagents including sodium chloride (NaCl), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sulphuric acid (H_2SO_4) and acetic acid were of general purpose grade obtained from various chemical companies.

3.4.3 Equipment

In this research unless stated, all exhaust dyeing and stripping were performed using a *Pyrotec Infra-red* laboratory scale dyeing machine and 275 mL dyeing pots or 1000 mL pots for larger sample sizes. The machine uses a water cooling system for its operation.

3.4.4 Method A: Sequential Acid/Alkali/Peroxide stripping

Both acid and hot alkali treatment have been reported to initiate cotton swelling [153] thus allowing enough penetration of the agent to remove crosslinks including those from dye-fibre bonds. However some dye molecules and some crosslinking agents are resistant to alkali hydrolysis while others are susceptible to acid hydrolysis. In this study stripping of colorant and other finishing agents was therefore performed in a two-step treatment (acid, then alkali hydrolysis) adopting a previously reported procedure for removing easy care finishes from cotton fabrics [66, 153].

Subsequent oxidative bleaching by hydrogen peroxide was also performed on the acid/alkali treated materials in order to remove any remaining dye chromophores and dye/fibre bonds, thereby enhancing the whiteness level of the material. Hydrogen peroxide was chosen for the bleaching stage due to its environmental acceptance compared to other bleaching agents such as sodium hypochlorite and other chlorine based agents [83, 99, 133]. Table 3.4.1 describes the conditions used in the acid/alkali/peroxide treatment.

Table 3.4.1 Acid/Alkali/Peroxide treatment conditions

Treatment No.	Treatment conditions		Treatment type
1	Sulphuric acid Non-ionic detergent *Temperature* *Time*	10 mL/L 2 mL/L 60˚C 60 minutes	Acid hydrolysis
2	Sodium Hydroxide *Temperature* *Time*	23% w/v 100°C 10 minutes	Alkali hydrolysis
3	Hydrogen Peroxide (35%) Sodium Hydroxide Sodium Carbonate Sodium silicate *Temperature* *Time*	1 M 1.2 g/L 1.8 g/L 7 g/L 85°C 60 minutes	Oxidative peroxide bleaching

3.4.4.1 Treatment 1 - Stripping by acid hydrolysis

Dyed cotton samples were stripped in 30:1 liquor to goods stripping bath containing 10 mL/L sulphuric acid and 2 mL/L non-ionic washing detergent to ensure complete wetting of the samples and to aid the washing process. Stripping was performed at 60°C for 60 minutes and then the samples were rinsed in warm, then cold water, then neutralised in a solution containing 2 mL/L of sodium hydroxide and finally further washed in running tap water. The stripped sample was then air dried (*Acid treated*) or was further stripped in a subsequent alkaline treatment.

3.4.4.2 Treatment 2 - Stripping by alkali hydrolysis

The acid stripped samples were further stripped in 50:1 liquor to goods bath containing 23% w/v sodium hydroxide for 10 minutes at 100^{o}C temperature. The higher liquor to goods ratio of 50:1 was selected as it removed more colorants as compared to lower liquor ratios. After stripping, fabrics were washed in warm water for about 10 minutes, followed by cold water rinsing. Samples were then neutralised in a solution containing 2 mL/L acetic acid, then further washed in running water tap. The treated sample was then air dried (*Acid/Alkali treated*) or was further treated in an oxidative peroxide bleaching bath.

3.4.4.3 Treatment 3 - Hydrogen Peroxide stripping

Hydrogen peroxide stripping of the dyed cotton was performed in a 30:1 liquor to goods bath containing 1M hydrogen peroxide (selected after parameter optimisation – Appendix B), 1.2 g/L sodium hydroxide, 1.8 g/L sodium carbonate and 7 g/L sodium silicate. The machine was run for 1 hour at 85^{o}C temperature, then samples were thoroughly rinsed in warm, then cold water followed by air drying (*Acid/Alkali/Peroxide treated*).

3.4.5 Method B: Sequential Acid/Dithionite/Peroxide stripping

In this study a three step treatment, involving hydrolysis, reduction and oxidative bleaching was applied to ensure complete colorant removal. The process was chosen because a combination of both reductive and oxidative treatments has been reported to be more effective in attaining high colorant removal from textile substrates [23]. The acid treatment was used to hydrolyse any crosslinks available in the fibre samples and to aid the removal of other impurities while alkaline dithionite was used to remove colorants from samples by using its reduction mechanism. Oxidative hydrogen peroxide bleaching was used to remove any residual colorant.

Table 3.4.2 describes the conditions used in the acid/dithionite/peroxide stripping process. Treatments 1 and 3 were performed as per section 3.4.4.1 and 3.4.4.3, respectively, while treatment 2 was performed as per section 3.4.5.1.

Sodium dithionite was chosen as the reducing agent because it is commonly available and it is widely used in both laboratory and industrial scale for reduction and decolouration purposes. The agent has high reduction potential of about -850mV at 50°C compared to that of -650mV for sodium sulphide [83]. In the absence of air the solution is highly stable compared to other reducing agents such as thiourea dioxide [79]. Higher concentrations of sodium dithionite are needed to prevent premature decomposition of the agent, thereby maximising its efficiency in dye desorption from the fibres.

Table 3.4.2 Acid/Dithionite/Peroxide treatment conditions

Treatment No.	Treatment conditions		Treatment type
1	Sulphuric acid Non-ionic detergent *Temperature* *Time*	10 mL/L 2 mL/L 60°C 60 minutes	Acid hydrolysis
2	Sodium Dithionite Sodium Hydroxide PVP Non-ionic detergent ***<u>Stage 1</u>*** *Temperature* *Time* ***<u>Stage 2</u>*** *Temperature* *Time*	30 g/L 40 g/L 2.5 g/L 2 mL/L 80°C, 30 minutes 100°C, 60 minutes	Reduction bleaching
3	Hydrogen Peroxide (35%) Sodium Hydroxide Sodium Carbonate Sodium silicate Non-ionic detergent *Temperature* *Time*	1M 1.2 g/L 1.8 g/L 7 g/L 2 mL/L 85°C 60 minutes	Oxidative peroxide bleaching

3.4.5.1 Treatment 2 - Sodium Dithionite stripping

In this study the sodium dithionite treatment was performed as part of the sequential acid/dithionite/peroxide stripping method as detailed in Table 3.4.2 and in Figure 3.4.1, where the acid treated samples were introduced into the alkaline dithionite stripping liquor (30:1 liquor to good ratio) before raising the temperature to 80°C. The samples were treated at this temperature for 30 minutes, then the temperature was raised to 100°C and the stripping process continued for 1 hour. The treatment bath was then cooled down to 50°C and the stripped samples were then rinsed in warm water for 5 minutes followed by distilled water rinses and air drying.

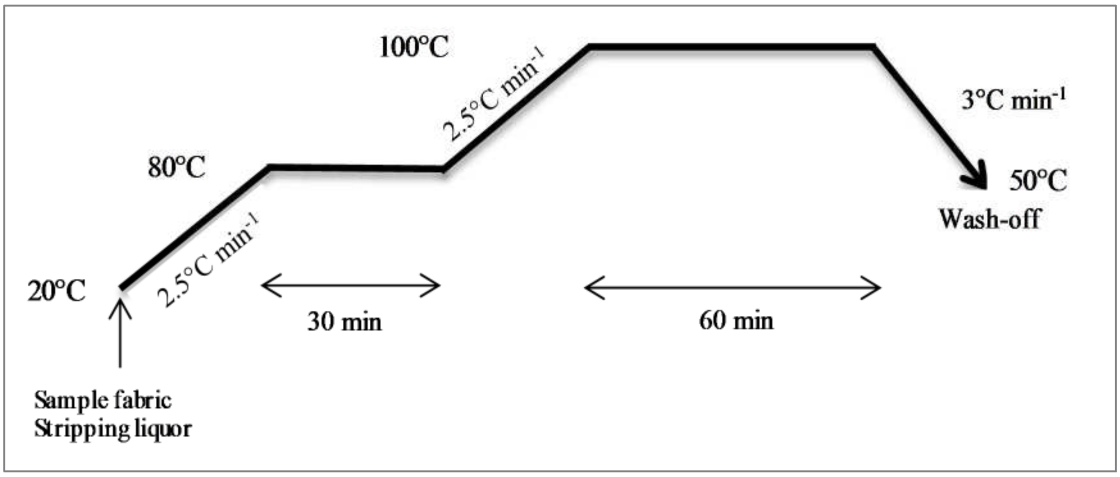


Figure 3.4.1 Stripping profile for the alkaline dithionite process

Prior to arriving at this method, parameters such as concentrations of dithionite, alkali, and PVP; treatment times and temperatures, were optimized (Appendix A) and those with the highest level of colour removal were selected for the study.

Stripping assistants such as polyvinylpyrrolidone (PVP) are sometimes added into the alkaline dithionite stripping liquor to prevent redeposition and reformation of the dyes on the fabrics [125]. The mechanism of PVP interaction with dyes has been extensively reviewed elsewhere [23, 154-158]. In this study a PVP polymer with a molecular weight of 40,000 was incorporated into the alkaline dithionite stripping liquor to aid the colour removal. Prior to selecting this polymer other polymer including Chromabond (S-100) were analysed, with the best results obtained when using PVP.

3.5 ANALYSIS OF THE COLORIMETRIC PARAMETERS

3.5.1 Introduction

In this study colorimetric parameters were analysed in order to determine the change in shades of dyed samples treated under different ISO 105 washing conditions. The effectiveness of the standardised colorant stripping methods was also assessed by colour measurement and benchmarked the final whiteness of the stripped “white” fabric. CIELAB colour difference (ΔE), colour strength (K/S) and ISO brightness were determined. For the fluorescently brightened cottons, whiteness index (WI) values were also determined. In all cases the dyed unstripped cotton fabric was used as a standard; however the final stripped fabric was also compared to the original undyed cotton.

A Datacolor Spectra Flash 600 spectrophotometer was used to measure the colorimetric parameters of the samples by recording the K/S values at sixteen equally spaced wavelengths between 400 and 700 nm. The corresponding CIELAB values (L^*, a^* and b^*) were also measured at the appropriate λ_{max} of each dye and were used to compute the total colour difference on each stripped substrate in relation to the dyed unstripped substrate. Fabric samples were folded four times and an average of four measurements was taken. The instrumental measurement conditions were: a medium 20 mm aperture, illuminant D65, UV component included, specular component excluded, reflectance mode and a 1964 (10^o) CIE standard observer.

3.5.2 Determination of CIELAB colour difference, ΔE

CIELAB 1976 colour space was used to calculate the colour parameters of the untreated and treated samples. The space defining colour in three dimensions (Figure 3.5.1), is based directly on CIE XYZ and aims at achieving uniformity in the perceptibility of colour differences. The space coordinates L^* (lightness/darkness), a^* (red/green), and b^* (yellow/blue) imitate the logarithmic response of the eye in describing and determining specific colour location [159].

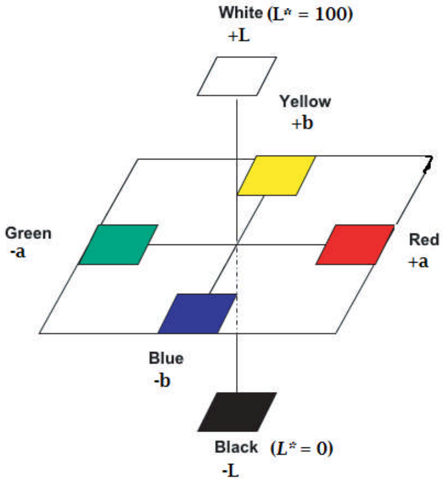


Figure 3.5.1 CIE-L^* a^* b^* colour space [160]

Once a sample is measured by the spectrophotometer, L^*, a^* and b^* coordinates are then calculated from tristimulus values (X, Y and Z) using the CIE 1976 equation. CIE L^*, a^*, b^* coordinates can also be presented in a cylindrical form defined as L^*, C^* and h, where C^* is chroma or brightness and h is hue angle computed from a^* and b^* coordinates [159, 161]. The cumulative colour difference between two colours in the CIE space is usually presented as ΔE and is computed based on the difference of the L^*, a^* and b^* colour coordinates as per Equation 3.5.1 below:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad \textbf{(Equation 3.5.1)}$$

where,

ΔL^* = liqhtness difference

Δa^* = red/green difference

Δb^* = yellow/blue difference

3.5.3 Determination of Colour strength, *K/S*

Colour strength is the numerical value representing the relative strength of a colour. In this study the Kebulka-Munk equation (Equation 3.5.2) was used to describe the relationship between the dye concentration and the reflectance of the dyed sample by relating reflectance to the absorption and scattering of the light, the *K/S* value being the direct measure of the colour yield. *K* and *S* are defined as the absorbance and scattering coefficients of the dyed material at a specific wavelength and R is the percentage reflectance value of the dyed sample at λ_{max} [134, 159].

$$\frac{K}{S} = \frac{(I-R)^2}{2R} \qquad \textbf{(Equation 3.5.2)}$$

3.5.4 Determination of ISO Brightness

ISO brightness is the colorimetric parameter used to characterise the whiteness of a pulp on a scale from 0% (absolute black) to 100% (relative to MgO standard, which has an absolute brightness of 96%) [36]. It can be defined as an intrinsic reflectance factor measured at a specified wavelength of 457 nm and a half bandwidth of 44 nm. The measuring instrument, usually a reflectometer has to be adjusted in such a way that the UV content of the irradiation incident upon the sample corresponds to that of the CIE illuminant C [162]. The ISO brightness values are usually expressed as a percentage.

In this study the ISO brightness values of the stripped and unstripped samples were determined by measuring the reflectance values at 460 nm wavelength using a normal Datacolor SF600 spectrophotometer measuring wavelength at 10 nm intervals.

3.5.5 Determination of CIE whiteness index (*WI*)

Whiteness is an important attribute in industries, such as paper making, textiles, laundering and paint manufacture. Reflectance spectra of an object with whiteness deviate strongly from those showing just a white colour as they have high reflectance at all wavelengths in the visible region of the spectrum [73]. In a textile material a level of whiteness can be imparted as a result of fluorescent whitening agents (FWAs). These agents are capable of compensating for the yellowness present in a substrate by adding a blue light from the fluorescence process [101, 163]. The level of whiteness can be assessed visually, or instrumentally by using a spectrophotometer.

In this study the degree of whiteness obtained as a result of fluorescent whitening agents was determined using the CIE method as per EN ISO 105-J01:2000 and EN ISO 105-

J02:2000 standards [164, 165]. The tristimulus values of the studied sample (X, Y and Z) were calculated from reflectance factors measured by the spectrophotometer using the D65 CIE standard illuminant and a 10° observer. The obtained values were then used to calculate the chromaticity coordinates (x, y) and the subsequent values of *WI* by applying the CIE 1982 whiteness formula shown in Equation 3.5.3;

$$W_{CIE} = Y + 800(x_n - x) + 1700\ (y_n - y) \qquad \textbf{(Equation 3.5.3)}$$

where x_n and y_n are the chromaticity coordinates of the perfect reflecting diffuser, for which the whiteness index is 100. Values for x_n and y_n were 0.3138 and 0.3310, respectively.

3.5.6 Determination of stripping efficiency

The percentage of dye stripped from fabrics was calculated by relating *K/S* values of stripped fabrics and that of unstripped dyed fabrics using Equation 3.5.4.

$$\%\,Stripping = \frac{K/S_{\text{unstripped fabric}} - K/S_{\text{stripped fabric}}}{K/S_{\text{unstripped fabric}}} \text{ x } 100 \qquad \textbf{(Equation 3.5.4)}$$

3.6 FABRICS AND GARMENTS DISINTEGRATION

The main objective of fabric disintegration is to convert the fabrics and garments into a fibrous pulp material in order to improve the accessibility of the materials to the solubilising solvent and facilitate better cellulosic dissolution and subsequent formation of a spinning solution (dope). In this study disintegration of the stripped fabrics was done by first cutting the samples into small pieces of approximately 10x10 mm using scissors. The cut pieces were then soaked in water for about 10 minutes and were then agitated in a 500W Breville blender (with stainless steel blades, using medium speed setting) until the complete disintegration of the fabric pieces was achieved. It was important to cut the fabric samples into smaller pieces so as to ease the disintegration process. About 10 g of the specimen was fed into the blender and distilled water was added so as to get a consistency of 1.56%. After disintegration the pulps were washed in distilled water, air dried and were then stored in re-sealable plastic bags.

3.7 DISSOLUTION OF THE COTTON PULP

3.7.1 Introduction

In this study dissolution of the cotton pulp was done using two solvents namely: cupriethylenediamine hydroxide (CED) and N-methylmorpholine-*N*-oxide (NMMO) solvents. CED was used for characterisation purposes due to its simplicity in cellulose characterisation in terms of viscosity and subsequent degree of polymerisation determination while NMMO was used for Lyocell fibre production due to its recognised environmentally friendly credentials as detailed in Chapter 2.

3.7.2 Dissolution of cellulose in CED solution

Dissolution in CED was important in order to assess the solubility of the materials as well as to determine the extent of cellulose polymer degradation as a result of the colorant stripping process. The recycled cotton pulp was dissolved in 0.5M CED solution as per British standard BS ISO 5351:2010 [166] with some modification on the cellulose contact time with water (1 hour instead of 30 minutes) so as to maximize the swelling properties of the cellulose polymer and facilitate its dissolution in the solvent.

The recycled cotton pulp was introduced into 60 mL polyethylene bottles and 25 mL of distilled water was added using a pipette. About 8 pieces of copper wires were added to the bottle and the bottle was closed and was shaken for 1 hour in a mechanical shaker at 250 rpm and 25°C temperature to ensure proper mixing of the test mixture. After proper mixing, 25 mL of 1M CED solution was added to the bottle to make 0.5M CED solution and the bottle was then squeezed to remove any air remaining. The bottle was reclosed and shaking was continued for another 30 minutes for complete dissolution.

3.7.2.1 Analysis of the cotton pulp solubility in CED solution

Before analysing the limiting viscosity and the degree of polymerisation it was necessary to assess the extent of solubility of the material in the CED solvent. Only samples which completely dissolved in 0.5M CED solution were advanced to the determination of the limiting viscosity and the degree of polymerisation. This was necessary in order to avoid blockage of the capillary viscometers used for the analysis as a result of undissolved cellulose particles present in the CED-cellulose solution.

In this study solubility was evaluated both microscopically and by ‘filtration and oven-drying’ method using a Whatman Glass microfiber-GF/C. For microscopic analysis, a drop of cellulose-CED solution was put on a glass slide and was viewed using Olympus BH-2 optical microscope while in the filtration method, the solution was filtered onto a pre-weighed glass filter which was then oven dried for 4 hours before being cooled for 2 hours in a desiccator containing phosphorus pentoxide. The cooled glass filter was then weighed and the percentage of cellulose dissolved in CED solution was calculated as per Equation 3.7.1 below:

$$\%\,Solubility = \frac{X-(F_a - F_b)}{X} \times 100 \qquad \textbf{(Equation 3.7.1)}$$

where X is the oven dry (OD) weight of the sample before dissolution in grams, and F_a and F_b are the OD weights in grams of the glass filter after and before filtration, respectively.

3.7.2.2 Analysis of limiting viscosity and the degree of polymerisation

Viscosity is an important parameter of the Lyocell fibre spinning dope that needs to be controlled in order to minimize the spinning difficulties of the dope [35, 122]. For instance the increase in viscosity as a result of either increased degree of polymerisation (DP) or cellulose concentration increases the elasticity of the NMMO-cellulose solution. The increase in these parameters increases the aggregation of cellulose in the solution which in turn decreases the interaction between the cellulose and the solvent [35, 167]. High elasticity of the spinning solution is also reported to affect the stability of the jet outflow during spinning [167, 168].

In this study the dissolved cellulose was analysed for its limiting viscosity as per standard BS ISO 5351:2010 [166], where cellulose was dissolved in the CED solution and its efflux times measured through a capillary tube viscometer at 25°C. Table 3.7.1 shows the calibration parameters obtained for various calibration liquids.

Table 3.7.1 Viscometric calibration parameters

Viscometer type	Efflux times (s) for:		
	Distilled water (t_w)	65% w/w glycerol solution	0.5 mol/L CED solution (t_s)
Calibration viscometer	60.1	779.0	76.2
Test viscometer	-	124.3	-

The calibration parameters were then used to calculate the viscometer factor, $\boldsymbol{f}$ and viscometer constant, $\boldsymbol{h}$ using Equations 3.7.2 and 3.7.3 [166]:

$$f = \frac{t_c}{t_v} \qquad \textbf{(Equation 3.7.2)}$$

$$h = \frac{f}{t_s} \qquad \textbf{(Equation 3.7.3)}$$

where $\boldsymbol{h}$ is expressed in cycles per seconds (s^{-1});

$\boldsymbol{t_c}$ is the efflux time, in seconds, of the glycerol solution in the calibration viscometer;

$\boldsymbol{t_v}$ is the efflux time, in seconds, of the glycerol solution in test viscometer;

$\boldsymbol{t_s}$ is the efflux time, in seconds, of 0.5 mol/L CED solution in the calibration viscometer.

The viscosity ratio, η_{ratio} was then calculated as per Equation 3.7.4 below:

$$\eta_{ratio} = \frac{\eta}{\eta_o} = h \times t \qquad \textbf{(Equation 3.7.4)}$$

where $\boldsymbol{t}$ is the efflux time, in seconds, of the test solution.

3.7.2.2.1 Limiting viscosity number

The limiting viscosity number $[\eta]$, also called intrinsic viscosity can be expressed as per Equation 3.7.5 below:

$$[\eta] = \frac{[\eta]\rho}{\rho}$$ **(Equation 3.7.5)**

Where $[\eta]\rho$ is a value read from the British standard [166] using the corresponding value of the calculated viscosity ratio, η_{ratio}, and

$\boldsymbol{\rho}$ is the concentration of cellulose in solution in g/ml, calculated from the test portion mass and the dry matter content using Equation 3.7.6 below:

$$\rho = \frac{W_m}{50} D_m$$ **(Equation 3.7.6)**

where W_m and D_m are the weight of the sample in grams and percentage dry matter respectively. 50 is the amount of solution used in dissolution.

3.7.2.2.2 Degree of Polymerisation (DP)

The Degree of Polymerisation was analysed to assess the extent of the fibre damage caused by various chemical treatments of the fabrics. The analysis was also done in order to establish the suitability of the stripped materials in the regeneration of fibres. In this research the DP was calculated from the previously obtained limiting viscosity using the relation reported by Marx-Figini [121] for samples with;

$$DP = \frac{[\eta]}{0.42}$$ for DP<1000 **(Equation 3.7.7)**

and

$$DP = \sqrt[0.76]{0.44[\eta]}$$ for DP>1000 **(Equation 3.7.8)**

3.7.3 Dissolution of cellulose in NMMO solvent and fibre spinning

Dissolution of the recycled cotton pulp in NMMO solution was necessary in order to prepare a homogeneous concentrated solution (dope) of the material for the purpose of fibre spinning and subsequent cellulose regeneration in a water bath.

To prepare the Lyocell spinning solution, also known as the spinning dope, pulp from recycled cotton was first dissolved in NMMO solvent, where the spinning dope was prepared by mixing 49.6%v/v NMMO hydrate solution with pulp and propyl 3,4,5-

trihydroxybenzoate (propyl gallate ester) in a suitable ratio (confidential) using a Lenzing knitter mixer. The dissolution process followed impregnation, dissolution and cooling phases and was made possible by mixing the pulp and NMMO solution at increasing temperature and pressure starting from room temperature and 250 mbar to 110°C and 400 mbar, respectively. Through this process excess water which originated from the highly hydrate NMMO solvent was removed allowing dissolution to occur. The final spinning dope had 9% cellulose concentration, 78% NMMO and only 13% water as determined by Lenzing. Each solution was filtered to remove impurities such as undissolved fibres which would otherwise block the spinneret in the subsequent spinning process. The spinning dope was then checked for solubility using a light microscope.

Fibres were spun in a laboratory scale spinning machine at Lenzing AG, Austria, where a spinneret with a single hole of 100µm in size was used. The dope throughput was 0.03 g/min and the air gap conditions were set at 20 mm, with temperature and relative humidity adjusted to fit the required fibre output. The winding speed was 26 m/min and water was used to precipitate the fibres and regenerate cellulose. Other spinning parameters including the draw ratio, spinning speeds, relative humidity and temperature could not be reported due to confidentiality. The spun fibres were then oven-dried overnight at 60°C temperature.

Lyocell fibres spun from chemically recycled cotton pulp were then characterised to determine their structural, mechanical and surface properties. These properties were then compared to properties of conventional Lyocell fibres from wood pulp.

The fibre linear density (L, in dtex) was calculated from the relation between the winding speed (Ws, in m/min), percent cellulose in the spinning dope (cell) and the rate of extrusion of the dope (Ds, in g/min) as per Equation 3.7.9 below:

$$L = 121 \times \frac{D_S}{W_S} \times cell \qquad \textbf{(Equation 3.7.9)}$$

3.8 OTHER ANALYTICAL METHODS USED

In this section analytical methods other than colorimetric measurements that were used to investigate the morphology and structural change on cotton materials that were exposed to different dye stripping treatments are described. These methods included; Fourier Transform Infrared Spectroscopy, analysis of the crease recovery angle, Optical Emission Spectroscopy, Light and Scanning Electron Microscopy and X-ray Diffraction Spectroscopy. The methods were also used to establish the structure of the Lyocell fibres generated from recycled cotton pulp.

3.8.1 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR – FTIR)

Infrared (IR) spectroscopy is a technique used in the identification and characterisation of materials [169]. It measures the frequency of IR radiation required to excite vibrations of an atom in molecular bonds. An infrared absorption spectrum is obtained by passing infrared radiation through a sample and the amount of incident radiation absorbed at a specific energy is determined. Each energy peak in the absorption spectrum corresponds to specific frequencies of vibrations of a molecule. Molecules of different structures have different infrared spectra [170] which allow qualitative identification of the chemical bonds/functional groups within a material. Similarly determining the size of the absorption peak provides quantitative information about the material such as the concentration of the molecule in a sample [169, 171].

ATR is a type of FTIR analysis used for qualitative and quantitative analysis of samples without needing sample preparation. The technique measures changes occurring in a total internal reflected IR beam when the beam passes through a crystal which is in contact with the sample. In the analysis the IR beam is directed onto the ATR crystal of relative higher refractive index (usually diamond) where it reflects at the internal surface of the crystal and creates an evanescent wave which projects orthogonally into the sample placed in direct contact with the crystal. Some of the evanescent wave energy is absorbed by the sample while the reflected radiation is returned to the detector for generation of the IR spectrum [172, 173]. Figure 3.8.1 shows the graphical representation of the phenomenon.

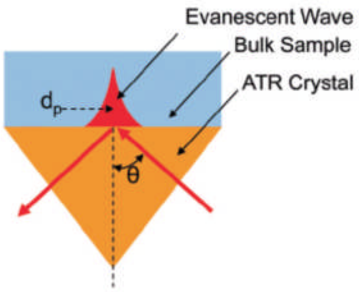


Figure 3.8.1 Graphical Representation of a Single Reflection ATR, where θ is the incidence angle and d_p is the depth of penetration [172]

The ATR-FTIR technique has previously been used to characterise the amount of impurities remaining on the surface of cotton fabric after the scouring process [174]. The study examined the C–H stretching vibrational region to estimate the quantities of waxes left, while the presence of pectin and/or waxes was established by observing the carbonyl peak induced by the HCl vapour treatment on the fabric. The technique has also been used successfully to measure the crystallinity of cellulose [175] and compare the crystallinity and accessibility of Lyocell, modal and viscose fibres that had been mercerised with varied concentrations of sodium hydroxide [176]. It was established that the crystallinity of the viscose fibres increased at low alkali concentrations, while that for Lyocell fibres decreased in crystallinity. Additionally the transformation of the cellulose from cellulose II to amorphous cellulose was partial for Lyocell fibres while both modal and viscose showed a complete transformation. FTIR has also been used to assess the effect of different crease-resist finishes [177] and their durability on cotton fabrics [31].

In this research the ATR-FTIR technique was used to assess the effectiveness of the stripping methods in removing crosslinking agents from the cotton substrates, where the untreated cotton fabric was compared to the DMDHEU crosslinked and stripped cotton samples. The IR spectra were obtained using a Perkin Elmer Spectrometer BX FT-IR which recorded at a frequency range of 400 to 4000 cm^{-1}, 16.0 cm^{-1} resolution and the data presented were the average of 32 scans. The obtained data were processed using the OriginPro 9.0 software.

The crystallinity of the fibres regenerated from recycled cotton pulp were also analysed using the ATR-FTIR method proposed by Nelson and O’Connor [178], who defined the Total Crystallinity Index (TCI) and the Lateral Order Index (LOI) as the ratios of the

FTIR 1372/2900cm^{-1} and 1420/893cm^{-1} absorptivity peak intensities, respectively. Results were compared to those of conventional Lyocell fibres made from wood pulp.

3.8.2 Analysis of the Fabric Crease Recovery Angle

Easy care finishes are applied to cotton fabrics and garments in order to improve their wrinkle recovery performance. These finishes are usually applied to fabrics through a pad-dry-cure method with the padding liquor containing the finishing agent and an acidic catalyst usually magnesium chloride [111]. On curing, usually through high temperatures, the crosslinking is achieved. To assess the efficiency of the applied easy care finishes, analysis of the crease recovery angle (CRA) of the crosslinked fabrics is used [111, 177].

In this study Crease Recovery Angle (CRA) was measured in order to assess the effectiveness of removing the crease resist finishes from cotton fabrics. The CRA were measured as per BS EN 22313:1992 standard [179] using a Shirley crease recovery tester in order to determine the crease resistance performance of the fabrics as they were being treated from one chemical to another. A 40 mm by 15 mm rectangular specimen was folded and maintained in a folded state for 5 minutes under load of 10N. The load was then removed and the specimen was allowed to recover for 5 minutes before recording the recovery angle immediately at the end of recovery time. For each sample at least ten replicates were performed for warp and weft directions and the mean CRA (W+F)° were reported. Prior to the analysis samples were conditioned for 24 hours at 20°C temperature and 65% relative humidity.

3.8.3 Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

Optical Emission Spectroscopy (OES) also known as Atomic Emission Spectrometry (AES) uses the argon-supported inductively coupled plasma (ICP) as its source of excitation hence the name ICP-OES or ICP-AES [180]. The instrument characterises the emitted spectrum of the sample where it is excited in the ICP to its higher energy levels before decaying back to its lower energy level by emitting light [181] as shown in Figure 3.8.2. The emitted light is then analysed through the OES. Analysis of the received spectrum provides the possibility of identifying the composition of the sample while determining the components of the composition [182].

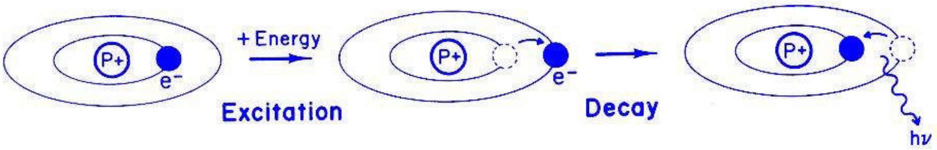


Figure 3.8.2 Excitation and decay of an atom in an ICP [183]. Energy absorption excites the atom to a higher energy level, which on decaying back to its original state emits a photon, hν, of a characteristic wavelength depending on the element present

During analysis the sample is pumped into the instrument where it is converted into an aerosol by a nebulizer. The aerosol is then transported by the carrier gas into the plasma where it is desolvated, vaporised, atomised, excited and ionised. The excited atoms and ions emit their characteristic visible radiation, which is then measured at a specific wavelength, allowing determination of the type and concentrations of elements present [184]. In general the type of element present is related to the wavelength at which electromagnetic radiation is emitted or absorbed while their concentration is related to the intensity of the radiation. A schematic representation of a typical ICP-OES instrument is shown in Figure 3.8.3.

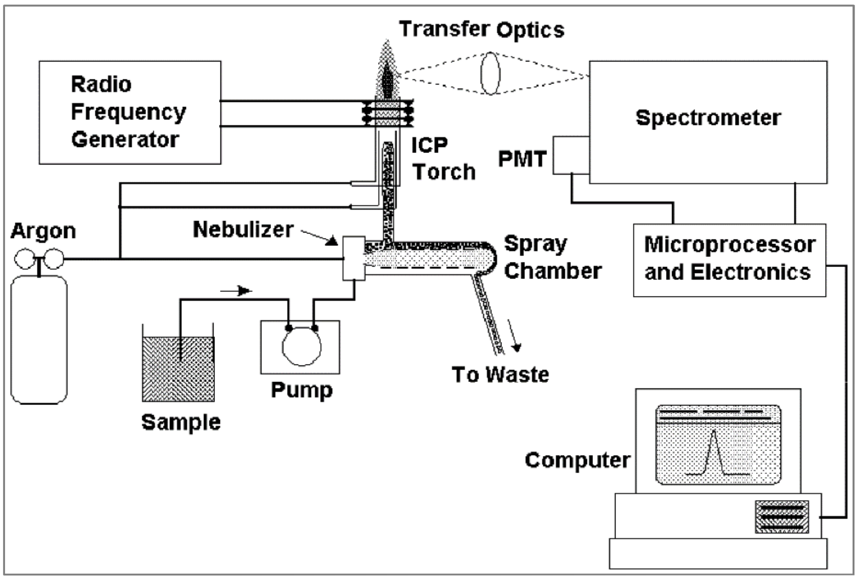


Figure 3.8.3 Schematic representation of ICP-OES instrument [183]

In this study ICP-OES analysis was used to assess the level of metal content in the cotton samples where the untreated cotton sample, reactive dyed cotton samples and stripped cotton samples were analysed. The technique was chosen due to its recognised precision and accuracy for most trace elemental analyses as well as its ability to determine a large number of elements over a wide range of concentrations using the same analytical run.

All preparations and analyses were performed at the Trace Elemental Analysis Laboratory of Hull University, United Kingdom. Prior to the analysis the digestion of the samples was performed in sulphuric acid, nitric acid and hydrogen peroxide. About 0.05 g sample was digested in 5 mL of H_2SO_4, 10 mL of HNO_3 and 1 mL H_2O_2 and diluted to 50 mL with distilled water. This was conducted at a higher temperature in XP1500Plus digestion vessels using a CEM MARS 5 microwave digestion system. A blank digestion was carried out in the same way. The analysis of the digests was conducted on the Perkin Elmer Optima 5300DV ICP Optical Emission Spectrometer.

3.8.4 Light Microscopy

Light or optical microscopy uses a series of glass lenses to refract light waves and create magnified images which can be viewed through an eyepiece (ocular) or an imaging device. During analysis visible light with a common propagation direction but different vibrational directions is directed onto the sample and the sample is rendered visible based on the principles of absorption, refraction and reflection of the incident light [185]. A similar mechanism is used when a polarised light microscope is used, however the vibrational direction is restricted to a single plane, thereby providing information about the orientation of the long chain molecules of the fibres [186]. Figure 3.8.4 shows a schematic presentation of a specimen magnified by a light microscope. A detailed description of the light microscopic techniques can be found in the literature [185-187].

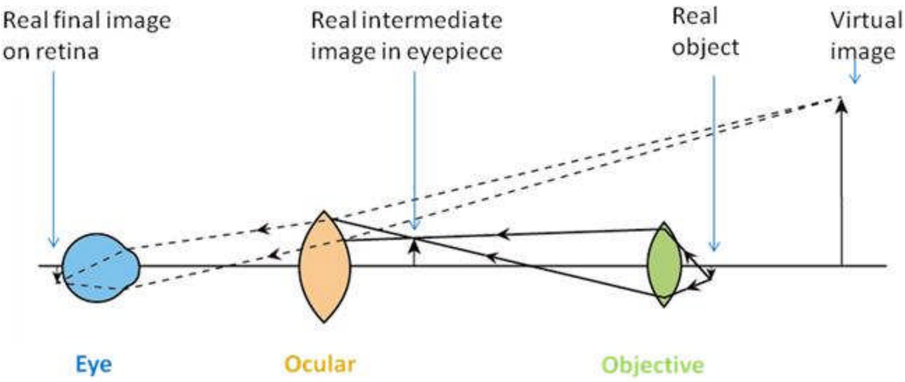


Figure 3.8.4 Schematic representation of a magnified virtual image of a specimen in the microscope [187]

In this research light microscopy was used to analyse fibre length and to assess the level of solubility of the stripped cotton materials. Two microscopes, namely: the Nikon Eclipse E200 and Olympus BH-2 microscope were used for measuring the fibre length and solubility of cellulose, respectively. Solubility of the samples was assessed by placing a sample on a microscope slide and onto a microscope stage and were viewed through an eyepiece at 100x magnification. However fibre length was obtained using a Leica M205C microscope equipped with a Leica DFC295 digital camera and LAS V 4.1 software. The microscope resolution was 0.78mm and the fibre images were captured by the camera connected to a computer. The fibre length measurements were then analysed using the Image-Pro Plus 7.0 software. For each sample a total of 50 fibres were measured and their mean result was recorded.

3.8.5 Scanning Electron Microscopy (SEM)

SEM is used to create magnified images by using an electron beam instead of the light waves that are used in a light microscope. The technique offers higher magnification than a light microscope and allows a larger amount of sample to be in focus at once [55, 188]. The combination of higher magnification, large depth of focus, greater resolution and ease of sample observation makes SEM one of the most commonly used techniques in textiles.

Before scanning samples are sputter coated with a thin layer of gold (10 - 20 nm thickness) to ensure electrical conductivity and so prevent electrostatic charging of the samples when exposed to an electron probe [188]. The coated samples are then placed in a microscope vacuum column through an airtight door and a beam of high-energy electrons is focused on a sample to generate a variety signals at the surface. The signals derived from the electron-sample interaction are measured by a detector, where sample information such as external morphology, chemical composition, crystalline structure and orientation of the materials within the sample [189] are detailed. The image of the sample structure is also created based on the number of secondary electrons emitted from each point of the sample. By monitoring the x-rays produced by the electron-sample interaction, elemental composition analysis of the sample surface as well as characterisation of fine particulate matter in terms of size, shape and distribution can also be investigated using a microanalysis technique called energy dispersive x-ray analysis (EDAX) [190]. A schematic representation of SEM set-up is presented in Figure 3.8.5.

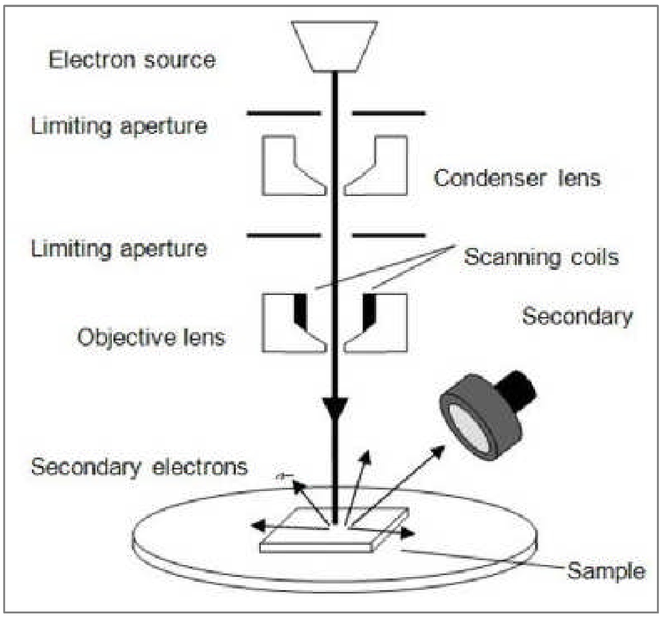


Figure 3.8.5 Schematic diagram of a Scanning Electron Microscopy [191]

SEM analysis has been previously used to establish the morphological changes in cotton fabrics treated with acrylamide to improve its acceptance of reactive dyes [192] where no significant surface change was observed. The technique has also been used to assess the changes on a sulphur dyed cotton fabric subjected to various washing conditions [87].

SEM has also been used to assess possible changes in the surface roughness and morphology of cellulose fabrics after plasma treatment [193]. Similarly no important change in surface morphology was observed.

In this study a Hitachi S-2600N SEM was used to assess the surface of the fibres regenerated from recycled cotton pulp and compared with the standard Lyocell fibres from wood pulp. Microscopic images were taken at either 1000 or 2000x magnifications, using 4kV or 5kV accelerating voltage and an average working distance of 5.3 mm.

3.8.6 Wide angle X-ray diffraction (WAXD)

X-ray diffraction is a powerful, non-destructive tool used to analyse the crystal structures of materials [185]. The interaction between the x-ray beam and a crystalline substance produces a diffraction pattern characterised by the direction and intensity of the diffracted beam [194]. This diffraction pattern provides information on the material, including the crystal structure, crystalline quality, orientation and the internal stress of a crystalline region.

In a diffraction experiment a crystal material is incident by an x-ray beam where its atomic planes which have different orientations and spacing, diffract the beam just like a grating diffracts an ordinary light. The wavelength of the incident x-ray beam, λ, the distance between atomic layers in a crystal, d, and the incident angle θ, called the Bragg angle are related by the Bragg's Law of diffraction as per Equation 3.8.1:

$$n\lambda = 2d\sin\theta$$ **Equation 3.8.1**

where n is an integer representing the order of diffraction. Figure 3.8.6 shows the geometry for wave interference needed to derive Bragg's law.

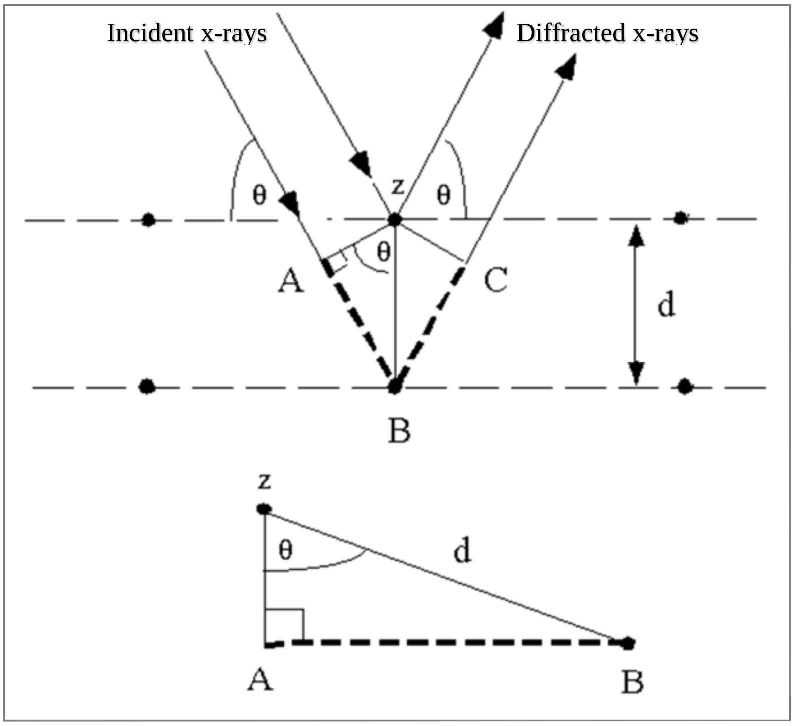


Figure 3.8.6 Geometry for interference of a wave scattered from two planes separated by a spacing, *d*. AB = BC = *d*sinθ

X-ray diffraction occurs only when Bragg's Law is satisfied, usually when the angle *θ* changes with the change in *d* spacing [185]. At this point the reflected beams are in phase and interfere constructively. Each unit cell can be mathematically related to the interplanar *d* spacing, allowing the determination of the size and shape of the repeat unit of the crystal structure without knowing the exact position of the atoms in the structure. By measuring the *d* spacing in semi-crystalline polymers which form the fibres, the fibre repeat distance can also be determined.

The diffraction angle relative to the incident beam is 2θ. This is the angle that is practically measured and is called diffraction or scattering angle. By altering the settings of the diffraction angles X-ray diffraction can be categorised as either small angle X-ray diffraction (SAXD) or wide angle X-ray scattering (WAXD). In SAXD, scanning proceeds by setting the X-ray detector at a diffraction angle of 2θ less than 5° whereas, in WAXD, patterns are collected when 2θ is greater than 5 degrees.

In textiles X-ray diffraction has been applied to a variety of analyses, a common use being the determination of crystalline structures of fibres [175, 178]. Based on the XRD data, various methods have been developed to determine the crystallinity of cellulose. These have been reviewed in the literature [195-197].

In this study the WAXD technique was used to develop diffraction patterns which were then used to determine the crystalline/amorphous regions and the crystallite sizes of Lyocell fibres regenerated from recycled cotton pulp. For comparison purposes Lyocell fibres produced from wood pulp were also analysed. The diffraction patterns were obtained using a Bruker D8 diffractometer with Nickel-filtered copper radiation of 1.5406 Å X-ray wavelength. The generator was set at 40 kV and 40 mA and scans were recorded from 2 and 86 degrees 2θ in 0.02 degrees steps for 2 seconds per step.

Crystalline properties were determined by first obtaining the diffractogram height at the position of the 002 (I_{002}) peak with $2\theta = 21.7°$ and at suitable locations for the amorphous background (I_{am}) with $2\theta = 16.0°$ [178]. The crystalline index, (*CrI*), defined as the relative amount of crystalline material in cellulose was then calculated from the height ratio between the crystalline peak ($I_{002} - I_{am}$) and the total intensity (I_{am}) according to Equation 3.8.2.

$$\% CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad \textbf{(Equation 3.8.2)}$$

The crystallite size was calculated from the half breadths of equatorial diffraction (002) as per Scherrer Equation 3.8.3.

$$Crystalline\ size = \frac{K\lambda}{BCos\theta} \qquad \textbf{(Equation 3.8.3)}$$

where K is the dimensionless Scherrer's constant, normally taken as 0.9 and *B* is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size expressed in radians [198, 199].

Chapter Four: Stripping of reactive dyes from cotton

4.1 INTRODUCTION

Chemical recycling of waste garments is limited for a number of reasons (as discussed previously) with the presence of colorants and crosslinks resulting from the modification of the cellulose by finishing agents being one of these limitations. The presence of these colorants and crosslinking across the hydroxyl groups of the cellulose may impair not only the processability (dissolution and subsequent spinning) of the recycled materials but also the final properties of the new regenerated cellulosic fibres [66]. Because of these crosslinks, the future coloration of the new formed product may also be compromised. Removal of both colorants and crosslinks prior to chemical recycling of the waste cotton garments for new fibre regeneration is therefore essential.

In this chapter both sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments were investigated as potential methods to strip reactive dyes (being the most commonly used dye class for cellulosic fibres [132]) from cotton fabrics for the purpose of preparing the cotton materials for chemical recycling. Prior to the stripping of the reactive dyes, their stability on BS ISO 105 washing conditions were first established in order to simulate the amount of colorants remaining on the garments after they complete their ‘first’ life cycle. Both ISO 105 C06 and the bleach activated ISO 105 C09 washing standards were evaluated in order to determine the effect of washing reagent formulations on the reactive dyes and to establish if the dyes will be present once the garments have reached their end of ‘first life’.

The stability of reactive dyes in ISO 105 and in dye stripping methods was examined by monitoring changes in colorimetric parameters where colour strength, *K/S*, CIELAB colour difference, ΔE and ISO brightness of the treated samples were evaluated. The efficiencies of each dye stripping method were also determined with a view to the maximum colour removal which was characterised by decreased colour strength, but increased in both colour difference and ISO brightness.

4.2 EXPERIMENTAL

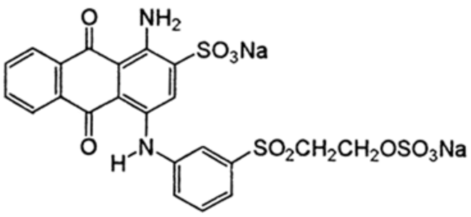
4.2.1 Materials and chemicals

Bleached and mercerised, plain woven cotton fabrics were obtained from Phoenix Calico limited (Section 3.2.1). Three Reactive dyes were selected based on azo and anthraquinone dye chromophores and according to the number of reactive groups incorporated into the molecule that is, mono-functional, bi-functional or tri-functional. Table 4.2.1 shows generic names, commercial names, reactive groups and chromophoric groups for the dyes used in this study while Figure 4.2.1 shows their chemical structures.

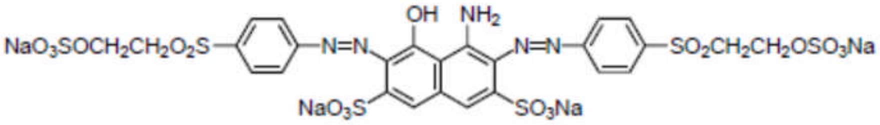
ECE phosphate and non-phosphate based detergents, tetraacetylethylenediamine (TAED), and perborate tetrahydrate were obtained from the Society of Dyers and Colourists (SDC), Bradford, UK. All other chemicals used were of laboratory grade obtained from various chemical suppliers.

Table 4.2.1 Reactive dyes used for coloration of cotton fabrics

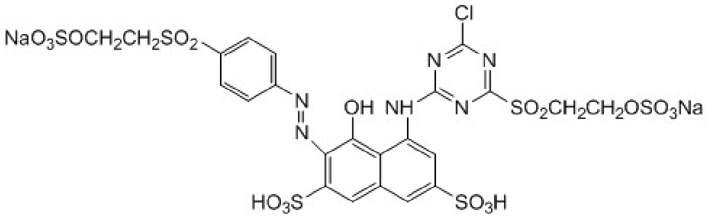
Sample Code	Generic Name; Commercial Name	Reactive System; Chromphore group	Supplier
RBL19	C. I. Reactive Blue 19; Remazol Brilliant Blue R	Vinylsulphone; Anthraquinone	Dystar, Germany
RB5	C. I. Reactive Black 5; Remazol Black B 133%	Bis (vinylsulphone); Azo	Dystar, Germany
RR228	C. I. Reactive Red 228; Cibacron Red C2G	Chloro-s-triazine and 2-vinylsuphone; Azo	Huntsman, UK



C. I. Reactive Blue 19 (Mono-functional)



C. I. Reactive Black 5 (Bi-functional)



C. I. Reactive Red 228 (Tri-functional)

Figure 4.2.1 Structure of Reactive dyes used in this study [93]

4.2.2 Reactive dyeing of cotton fabrics

Reactive dyeing of cotton fabric was performed at the School of Design of the University of Leeds using an exhaustion method following conditions recommended by dye manufacturers. Dyes were applied at 4% (o.w.f.) depths of shades and 15:1 liquor to goods ratio was used. Before dyeing fabrics were first wetted-out with distilled water, then squeezed to remove any entrapped water. Fabrics were dyed once and in a large quantity (bulk) to maintain consistency and reproducibility of the dyeing strength.

For RB5 and RBL19 dyeing, cotton fabrics were immersed in the dye liquor containing the dye and dyeing was carried out using the dyeing method shown in Figure 4.2.2. Sodium chloride (50 g/L), sodium carbonate (5 g/L) and of sodium hydroxide (2 g/L) were also added to the dye-liquor as required. Dyed samples were then washed in warm, then cold water to remove any residual dyes.

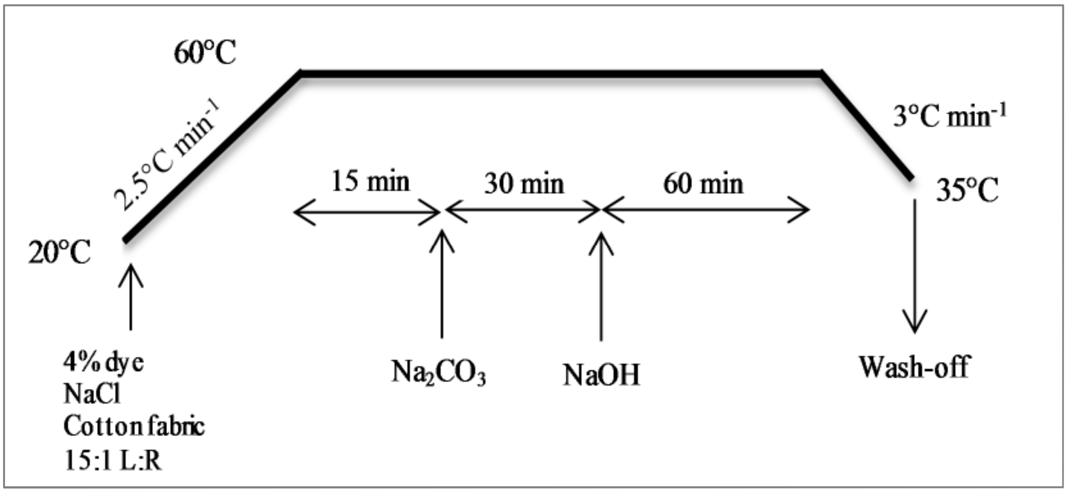


Figure 4.2.2 Dyeing process for C. I. Reactive Blue 19 and C. I. Reactive Black 5 dyes

For RR228 dyeing, fabrics were dyed in a solution containing the dye, 50 g/L sodium chloride and 18 g/L sodium carbonate using the dyeing method shown in Figure 4.2.3. Dyed samples were washed in warm and cold water to remove any residual dyes.

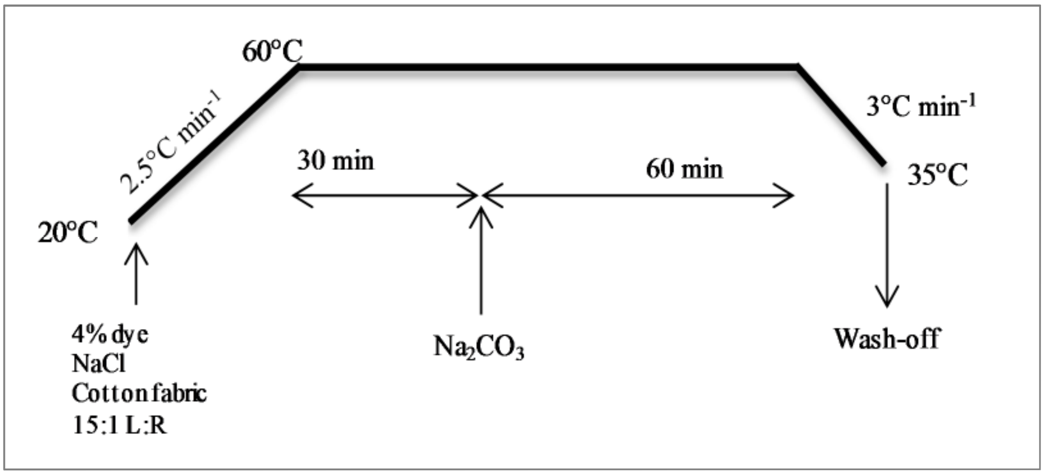


Figure 4.2.3 Dyeing process for C. I. Reactive Red 228 dye

4.2.3 Washing-off of the reactive dyed cotton fabrics

All dyed fabrics were then soaped for 10 minutes at 60°C in a solution containing 2 mL/L of aqueous non-ionic detergent to remove any unfixed and hydrolysed dyes. Washed fabrics were rinsed in warm then cold water prior to air drying.

4.2.4 ISO 105/C06 Washing

The stability of the reactive dyed cotton fabrics to ISO 105 C06 washing were assessed as per British Standard [200] while varying the quantity of perborate used and maintaining the quantity of the ECE phosphate based detergent (Table 4.2.2). In the C06 washing system sodium perborate is responsible for bleaching action [201], therefore varying its concentration in the washing liquor was necessary in order to assess its effect on reactive dyes. In this study multi-fibre fabrics were not used as the aim was only to assess the loss of dyes from the fabrics and not staining properties of the dyes. Each sample of 100 x 40 mm was added in stainless steel pots containing 50 mL of the prepared wash liquor and 25 steel balls. Washing was then performed for 30 minutes at 60^{o}C in sealed pots housed in a *Roaches Washtec P* machine, followed by rinsing in warm water and air drying.

Table 4.2.2 Detergent and auxiliaries used for ISO 105 C06 washing test

Washing reagent	Procedure 1 (no perborate)	Procedure 2 (standard wash)	Procedure 3 (2 x perborate)
ECE phosphate detergent	4 g/L	4 g/L	4 g/L
Perborate	-	1 g/L	2 g/L

4.2.5 ISO 105/C09 Washing

The stability of reactive dyed materials to ISO 105 C09 washing were assessed as per British Standard [202] while varying the concentrations of the bleaching system (perborate/TAED), as shown in Table 4.2.3, in order to establish its effect on reactive dyes. Fabrics of 100 x 50 mm dimension were immersed in stainless steel washing pots containing the prepared washing liquor so as to maintain 100:1 liquor to goods ratio. The pots were then placed in a *Roaches Washtec P* mechanical washing machine and temperature of water bath was raised at a rate of 2.5^{o}C/minute to the required 60^{o}C and washing was continued for further 30 minutes. At the end of the wash cycle, samples were rinsed in cold running tap water then in distilled water before being air-dried.

Table 4.2.3 Detergent and auxiliaries used for ISO 105 C09 washing test

Washing reagent	**Procedure 1 (no perborate)**	**Procedure 2 (standard wash)**	**Procedure 3 (2 x perborate)**	**Procedure 4 (2 x perborate, 2 x TAED)**
ECE non-phosphate detergent	10 g	10 g	10 g	10 g
Perborate	-	12 g	24 g	24 g
TAED	-	1.8 g	1.8 g	3.6 g

4.2.6 Stripping of reactive dyes

The stripping of reactive dyes from cotton fabrics was performed using both sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods as described in Section 3.4.

4.3 RESULTS AND DISCUSSION

4.3.1 The stability of Reactive Dyes to ISO 105 Washing Conditions

In this study the stability of reactive dyes on cotton fabrics was assessed as per ISO 105 C06 and ISO 105 C09 washing conditions in order to simulate the amount of colorants remaining on the garments after they complete their ‘first’ lifecycle. The amount of reactive dyes lost on washing was determined by monitoring variations in colour strength and CIELAB colour difference and results are discussed below.

4.3.1.1 Effect of ISO 105 C06 wash conditions on Reactive dyed cotton fabrics

The effects of varying the C06 wash conditions on the reactive dyed fabrics are presented in Table 4.3.1 and in Figure 4.3.1. Varying the C06 wash conditions resulted in minor changes to both colour strength, *K/S* and colour difference, Δ*E* for RB5 fabrics even after doubling the amount of perborate. This minor change can be attributed to the physical action resulting from the friction between the fabric, steel balls and container walls as well as mechanical agitation of the washing machine [201].

Table 4.3.1 Colour strength of the 4% (o.w.f.) reactive dyed cotton fabrics treated in different C06 wash conditions

Sample	**Treatment conditions**	***K/S***
RB5	Untreated dyed fabric	29.7
	ECE detergent (no perborate)	28.7
	Normal/standard conditions	28.4
	Double Perborate	28.4
RBL19	Untreated dyed fabric	22.9
	ECE detergent (no perborate)	22.3
	Normal/standard conditions	22.8
	Double Perborate	22.7
RR228	Untreated dyed fabric	26.0
	ECE detergent (no perborate)	24.6
	Normal/standard conditions	23.3
	Double Perborate	23.0

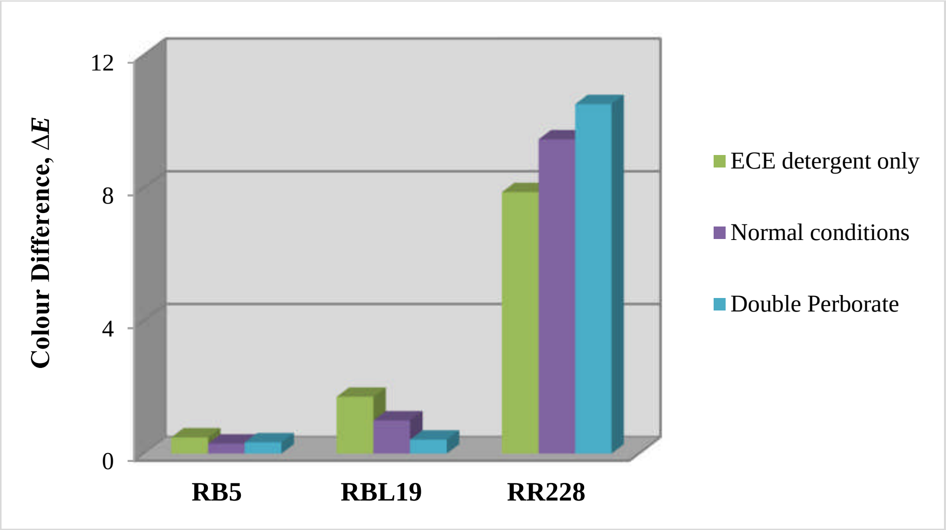


Figure 4.3.1 CIELAB colour difference for the reactive dyed fabrics treated under different C06 wash conditions.

The high stability of the anthraquinone-based C. I. Reactive Blue 19 dye structure also resulted in minor changes on both *K/S* and Δ*E* of the RBL19 samples washed in the varied C06 wash conditions. The largest colour difference of 1.7 was observed on treating the fabrics with ECE perborate-free detergent. The difference is again associated with the wet abrasion between the fabric, steel balls and container walls together with the mechanical agitation of the washing machine [201].

Treating the RR228 dyed fabrics under different C06 wash conditions resulted in a greater decrease in colour strength, where a *K/S* value as low as 23.0 was observed when the amount of perborate was doubled compared to *K/S* of 26.0 of the unwashed materials. The standard washing conditions also decreased the *K/S* of the RR228 sample to 23.3, while, a perborate free washing also decreased the *K/S* to 24.6. The results for colour difference (Figure 4.3.1) also exhibited the same behaviour, with a higher ΔE value of 10.5 observed on doubling the perborate concentrations.

The monochlorotriazinyl reactive group present in the C. I. Reactive Red 228 dye has one labile chlorine atom which is replaced by the cellulose hydroxyl during dyeing to form the dye-fibre bond. This bond is reported to be weaker in alkaline conditions due to the cellulose being less strongly electron-releasing than the amino group which is also present in the dye molecule [203]. As a result the dye-fibre bond is more susceptible to hydroxyl ion (OH^-) attack. This together with the friction action between the fabrics, steel balls and the container walls may have contributed to a greater colour change on RR228 fabric than on the RB5 and RBL19 dyed fabrics.

4.3.1.2 Effect of ISO 105 C09 wash conditions on Reactive dyed cotton fabrics

About 70% of modern domestic detergents available commercially contain an activated oxygen bleaching agent capable of chemically destroying the dye chromophore [201]. In this study the stability of reactive dyes to this oxidative bleaching process was performed as per ISO 105 C09 standard and results are presented in Table 4.3.2 and in Figure 4.3.2. It can be seen from the table that washing the RB5 fabric in varied amounts of perborate and TAED slightly decreased the colour strength of the material with the lowest *K/S* of 27.6 obtained on the standard wash conditions compared to that of 29.7 for the untreated sample. The decrease was also slightly higher when both perborate and TAED were doubled, resulting to a *K/S* of 27.9. The phenomenon was also confirmed by the colour difference results (Figure 4.3.2) where a ΔE of 2.3 was obtained on standard washing conditions while a ΔE of 1.6 was attained on doubling the amounts of perborate and

TAED. Similarly increasing the amount of perborate without increasing the amount of TAED had no apparent effects on the treated fabrics.

Table 4.3.2 Colour strength of the 4% (o.w.f.) reactive dyed cotton fabrics treated in different C09 wash conditions

Sample	C09 treatment conditions	*K/S*
RB5	Untreated dyed fabric	29.7
	ECE detergent (no perborate)	28.1
	Normal/standard conditions	27.6
	Double Perborate/single TAED	29.0
	Double Perborate/double TAED	27.9
RBL19	Untreated dyed fabric	22.9
	ECE detergent (no perborate)	22.0
	Normal/standard conditions	22.5
	Double Perborate/single TAED	22.8
	Double Perborate/double TAED	21.5
RR228	Untreated dyed fabric	26.0
	ECE detergent (no perborate)	24.7
	Normal/standard conditions	17.5
	Double Perborate/single TAED	18.7
	Double Perborate/double TAED	16.1

The varied C09 washing conditions had no obvious effect on the *K/S* of the anthraquinone-based RBL19 fabric (Table 4.3.2), although doubling the concentrations of both perborate and TAED slightly decreased the *K/S* of the material to 21.5 compared to *K/S* of 22.8 for the untreated sample. A higher ΔE of 1.5 (Figure 4.3.2) was also observed when both perborate and TAED were doubled. This indicates that higher concentrations of both perborate and TAED could impair the stability of the highly resistant anthraquinone structure of the C. I. Reactive Blue 19 dye.

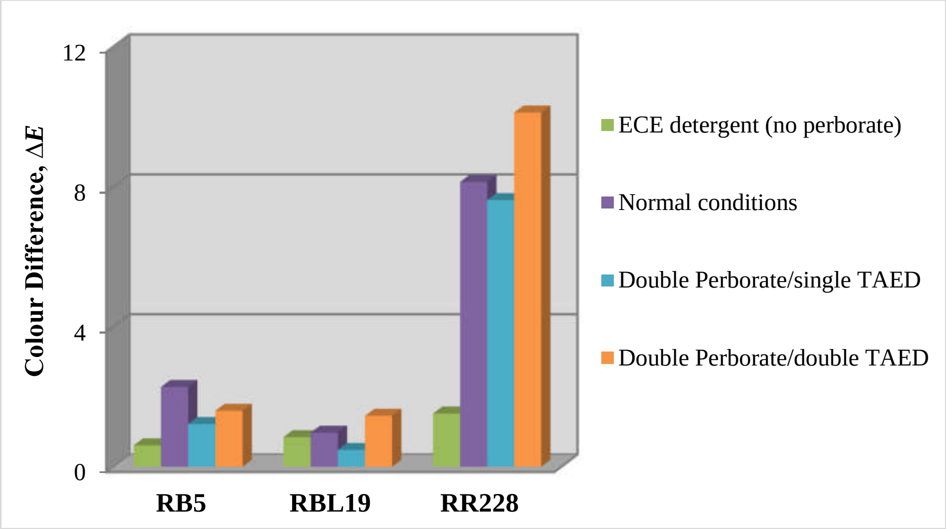


Figure 4.3.2 CIELAB colour difference for the reactive dyed fabrics treated under different C09 wash conditions.

Varying the amount of perborate and TAED significantly decreased the colour strength of RR228 samples (Table 4.3.2). Larger decreases were achieved on the doubling of the concentrations of both perborate and TAED resulting in a *K/S* of 16.1 compared to *K/S* of 26.0 for the untreated samples. A perborate free treatment of the RR228 samples also resulted in a slight decrease in colour strength of the sample where a *K/S* of only 24.7 was attained. Analysis of the colour difference (Figure 4.3.2) also showed a similar trend with greater Δ*E* achieved on doubling the quantities of both perborate and TAED.

Both C. I. Reactive Blue 5 and C. I. Reactive Red 228 dyes have been previously reported to be sensitive to oxidative bleaching which is due to lacking of electron-withdrawing sulphonate groups in the diazo component, *ortho* to the azo/hydrazo linkage [201]. It's therefore logical to conclude that the colour change on the C09 treated dyed samples resulted from the cleavage of the highly sensitive azo chromophore on oxidative-bleach attack caused by the increased quantities of perborate/TAED. It is also worth noting the colour change observed on all samples on perborate-free washing which is again thought to be due to physical action resulting from the friction between the fabric and container walls as well as mechanical agitation of the washing machine as suggested by Phillips and colleagues [201].

4.3.2 The stability of Reactive Dyes to Stripping Methods

In this study the reactive dyed cotton fabrics were treated in both sequential acid/alkali/peroxide and acid/dithionite/peroxide methods described in Section 3.4 of this study in order to strip dyes and any crosslinking established by dyes from the fabrics. The reason to strip dyes and other crosslinking from cotton fabrics was to purify and prepare the cotton materials for reprocessing into new fibres using the Lyocell process. To determine the success of the stripping methods colorimetric parameters were monitored by observing changes in colour strength, *K/S*, CIELAB colour difference, Δ*E* and ISO brightness determined by measuring the reflectance values at 460 nm wavelength.

4.3.2.1 The effect of the sequential Acid/Alkali/Peroxide on reactive dyed cotton fabrics

In the acid/alkali/peroxide method the reactive dyed fabrics were stripped by the hydrolytic actions of sequential acid and alkali treatment prior to the oxidative bleaching reaction of hydrogen peroxide. Colorimetric parameters of the treated and untreated samples are discussed below.

4.3.2.1.1 Colour strength (K/S) of the reactive dyed fabrics stripped in the sequential acid/alkali/peroxide method

The colour strength of the reactive dyed cotton fabrics decreased dramatically as the fabrics were sequentially treated with one chemical agent followed by another (Figure 4.3.3). Acid treatment had the least effect on the RB5 sample as the *K/S* did not change significantly, indicating the stability of the dye chromophore present in the C. I. Reactive Black 5 dye, and the covalent linkage to the cellulose to acidic hydrolysis. However subsequent alkali treatment had a significant effect on the RB5 sample resulting in a *K/S* of 0.3 compared to the original *K/S* of 29.7, which highlights the instability of the dye in hot alkaline conditions. Further hydrogen peroxide treatment stripped more dye from the sample resulting in a *K/S* of 0.04, similar to that of the undyed cotton fabric.

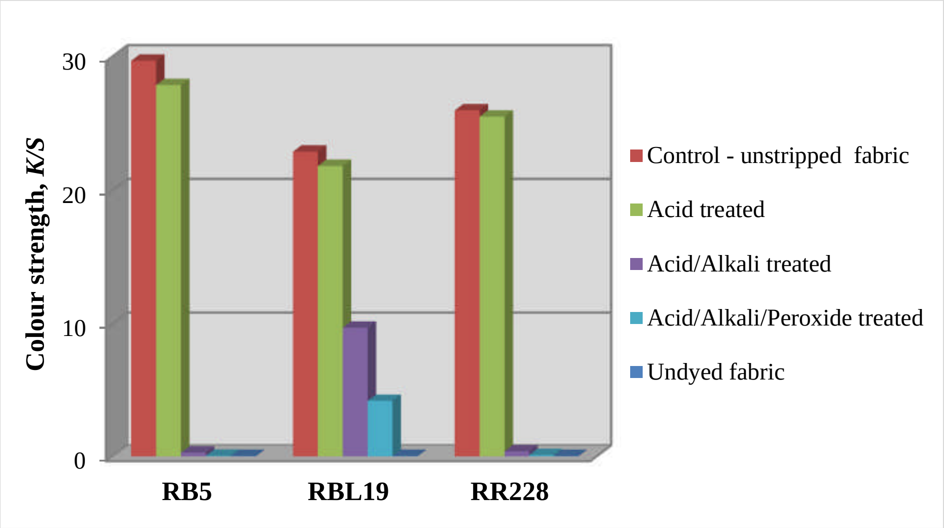


Figure 4.3.3 Comparison of the colour strength for undyed, reactive dyed and acid/alkali/peroxide treated cotton fabric

As with the RB5 treated fabrics, the RR228 fabric was also resistant to acidic hydrolysis, resulting in little dye being stripped by the treatment. However the subsequent alkali treatment stripped significantly larger amounts of dye from the fabric giving a *K/S* of 0.4 compared to the original *K/S* of 26.0. Further hydrogen peroxide treatment stripped more dye from the material resulting in a *K/S* of 0.1 which shows the instability of the C. I. Reactive Red 228 dye in both alkali hydrolysis and oxidative bleaching, despite the dye having three reactive groups which are supposed to offer better dye-fibre bonding.

The anthraquinone chromophore of the C. I. Reactive Blue 19 dye has been reported to enhance the stability of the dye to acidic hydrolysis [204, 205]. This was proved by the minimal decrease in colour strength observed on their acid treated RBL19 fabric. However subsequent alkali treatment of the fabrics substantially decreased the *K/S* to 9.7 compared to the original *K/S* of 22.9. Further decreases in colour strength were achieved when fabrics were further treated in the oxidative peroxide bleaching bath resulting in a *K/S* of 4.2. The relatively small decrease in colour strength observed on RBL19 fabric indicated the higher stability of the anthraquinone chromophore to both hydrolysis and oxidative bleaching.

4.3.2.1.2 CIELAB colour difference, ΔE, of the reactive dyed fabrics stripped in the sequential acid/alkali/peroxide method

The CIELAB colour difference between the untreated reactive dyed cotton samples and those treated with the sequential acid/alkali/peroxide stripping method are presented in Figure 4.3.4. The acid treatment had the least effect on all samples resulting in Δ*E*s of 3.1, 0.8 and 3.8 on RB5, RBL19 and RR228 samples, respectively. Further treatment of the samples in alkali and subsequent peroxide oxidative bleaching significantly increased the Δ*E* values of RB5 fabric to 66.1 and 77.9, respectively. A similar trend was also observed on the RR228 fabric where Δ*E*s of 70.3 and 76.5 were obtained for the acid/alkali and acid/alkali/peroxide treated samples, respectively. Conversely, alkali and subsequent peroxide oxidative bleaching of the acid treated RBL19 sample did not cause much increase in Δ*E* of the material resulting in Δ*E*s of only 19.2 and 27.4 for the acid/alkali and acid/alkali/peroxide treated samples, respectively. Again the greater chemical stability of the anthraquinone chromophoric structure of the C. I. Reactive Blue 19 dye is thought to be the reason for the lower colour difference obtained.

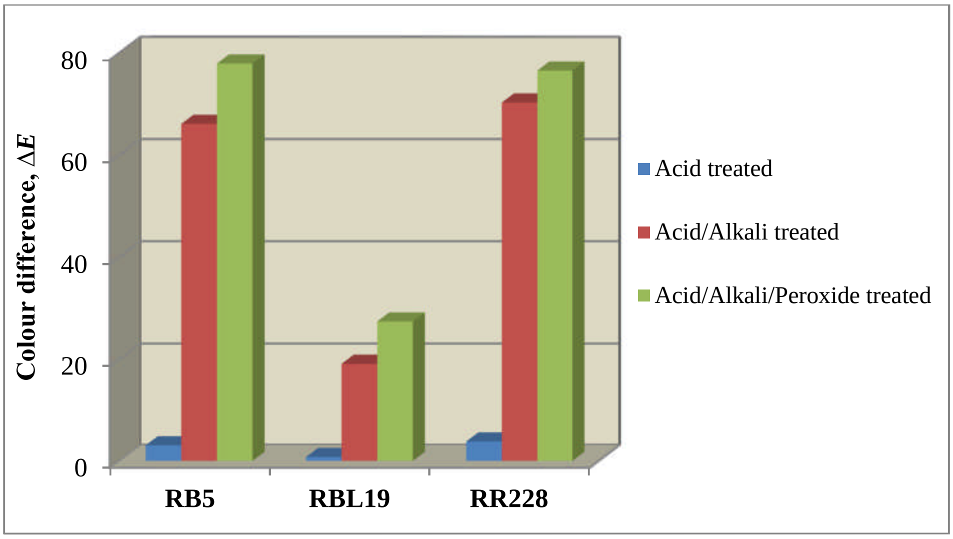


Figure 4.3.4 CIELAB colour difference for the reactive dyed cotton samples stripped in the sequential acid/alkali/peroxide method.

4.3.2.1.3 ISO brightness of the reactive dyed fabrics stripped in the sequential acid/alkali/peroxide method

The ISO brightness of the acid/alkali/peroxide stripped reactive dyed cotton fabrics are presented in Figure 4.3.5. The acid treatment of the reactive dyed samples slightly increased the ISO brightness to 3.6%, 23.4% and 4.6% on RB5, RBL19 and RR228 fabrics, respectively, compared to the original brightness of 3.5%, 23.3% and 4.4%, respectively. Further alkali treatment of the fabrics significantly increased the ISO brightness of both RB5 and RR228 samples to 54.2% and 45.9%, respectively. However the treatment only increased the brightness of RBL19 fabric to only 24.0%. Subsequent hydrogen peroxide treatment further increased the brightness of RB5 and RR228 fabrics to 78.7% and 65.0%, respectively, approaching a brightness of 82.4% for the undyed cotton fabric. As anticipated, the peroxide treatment did not cause any obvious difference to the ISO brightness of the RBL19 fabric which is due to the chemical stability of the anthraquinone chromophore of the C. I. Reactive Blue 19 dye.

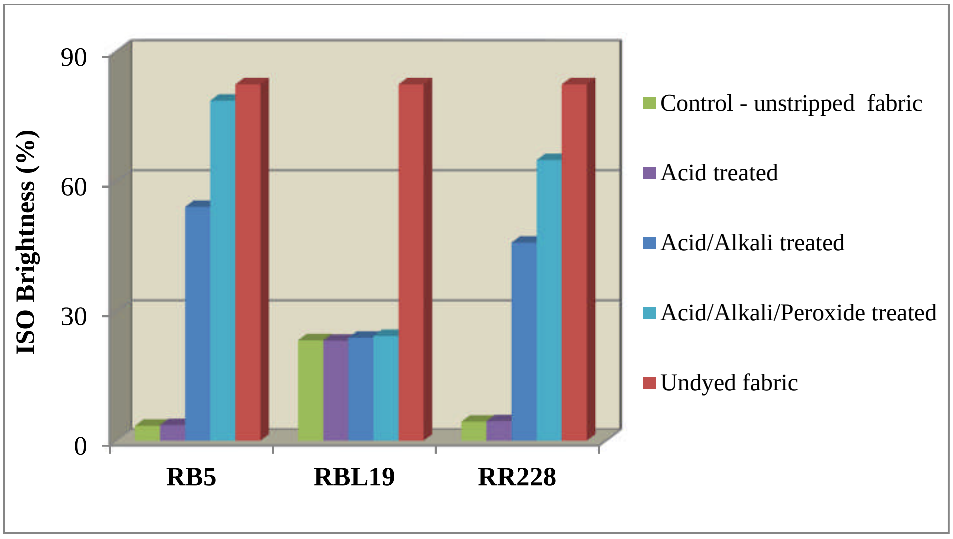


Figure 4.3.5 Comparison of the ISO brightness of the undyed, reactive dyed and acid/alkali/peroxide treated cotton fabric.

4.3.2.1.4 Visual comparison of the reactive dyed fabrics stripped in the sequential acid/alkali/peroxide method

Visual analysis of the reactive dyed cotton samples treated in the sequential acid/alkali/peroxide stripping method is presented in Figure 4.3.6. The acid treatment showed no apparent change on any of the reactive dyed fabrics, however subsequent alkali and peroxide treatment resulted in an extensive colour loss on all samples, although the effect was more severe on the azo-based RB5 and RR228 fabrics as compared to the chemically resistant anthraquinone-based RBL19 material.

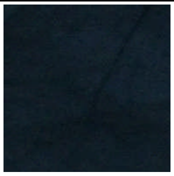
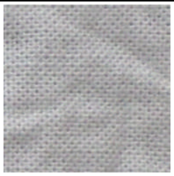
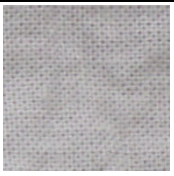
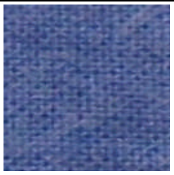
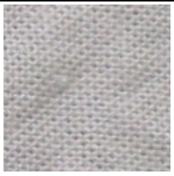
Colorant	**Dyed fabric**	**Acid treated**	**Acid/Alkali treated**	**Acid/Alkali/ Peroxide**	**Undyed fabric**
RB5					
RBL19					
RR228					

Figure 4.3.6 Visual appearance of reactive dyed cotton fabrics following stripping in the sequential acid/alkali/peroxide treatments.

4.3.2.2 The effect of the sequential Acid/Dithionite/Peroxide treatment on reactive dyed cotton fabrics

In this study reactive dyed fabrics were also stripped using the combined effects of acid hydrolysis, alkaline dithionite reduction and peroxide oxidative bleaching of the acid/dithionite/peroxide treatment. Colorimetric parameters of the stripped and unstripped fabrics are discussed below.

4.3.2.2.1 *Colour strength (K/S) of the reactive dyed fabrics stripped in the sequential acid/dithionite/peroxide method*

The colour strength of the reactive dyed fabrics treated in the sequential acid/dithionite/peroxide stripping method are compared in Figure 4.3.7. As previously explained the acid treatment of the reactive dyed fabrics resulted in a minimal decrease in colour strength of all the treated materials. However subsequent alkaline dithionite treatment resulted in an obvious decrease in colour strength of all samples. A *K/S* of 0.1 was obtained on both RB5 and RBL19 fabrics, while a *K/S* of 0.6 was obtained on the RR228 fabric compared to the original *K/S* values of 29.7, 22.9 and 26.0, for RB5, RBL19 and RR228 fabrics, respectively. The high reducing potential of the alkaline sodium dithionite [-850mV at 50°C] [83] together with the dye binding capacity of the polyvinylpyrrolidone (PVP) polymer [154, 157, 158] added to the dithionite stripping liquor are thought to have caused the high level of dye removal. The PVP polymer has the ability to combine with the stripped dye, thereby forming a dye-polymer complex, which can be washed out during subsequent washing.

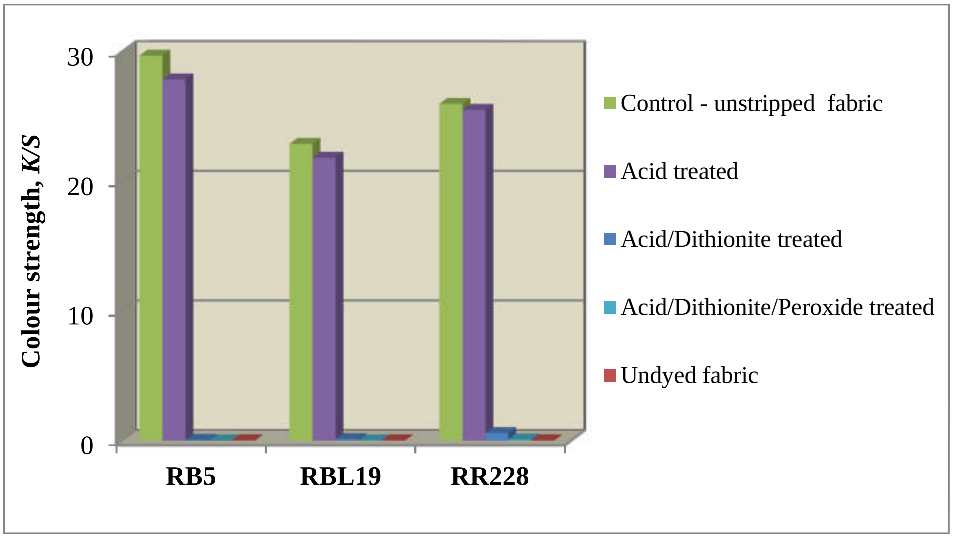


Figure 4.3.7 Changes in colour strength for the undyed, reactive dyed and acid/dithionite/peroxide treated cotton fabrics.

Further peroxide oxidative bleaching of the samples resulted in an additional decrease in the *K/S* values to 0.02 and 0.03 on RB5 and RBL19 fabrics, respectively, compared to a *K/S* of 0.04 for the original undyed cotton fabric. However the treatment was slightly less effective on the RR228 dyed cotton resulting in a *K/S* of only 0.1 which is thought to be due to the multiple crosslinking nature of the C. I. Reactive Red 228 dye. The dye has three functional groups (two vinylsulphones and one monochlorotriazine) [90] thereby forming three possible bonds with the hydroxyl groups of the cellulose. It is therefore possible that the treatment could only destroy one or two of the dye-fibre bonds, leaving the other bonds slightly attached to the cellulose fibre [204].

4.3.2.2.2 *CIELAB colour difference, ΔE, of the reactive dyed fabrics stripped in the sequential acid/dithionite/peroxide method*

The CIELAB colour difference between the untreated reactive dyed fabrics and the reactive dyed fabrics treated in the sequential acid/dithionite/peroxide baths are compared in Figure 4.3.8. As already shown in the previous sections, the acid treatment had minimal effect on all reactive dyed materials. However it’s clear that further dithionite treatment removed a significant amount of dye resulting in Δ*E*s of 76.3, 71.2 and 70.1 on RB5, RBL19 and RR228 fabrics, respectively. Subsequent peroxide oxidative bleaching resulted in a greater Δ*E* of approximately 78.5 observed in all treated fabrics.

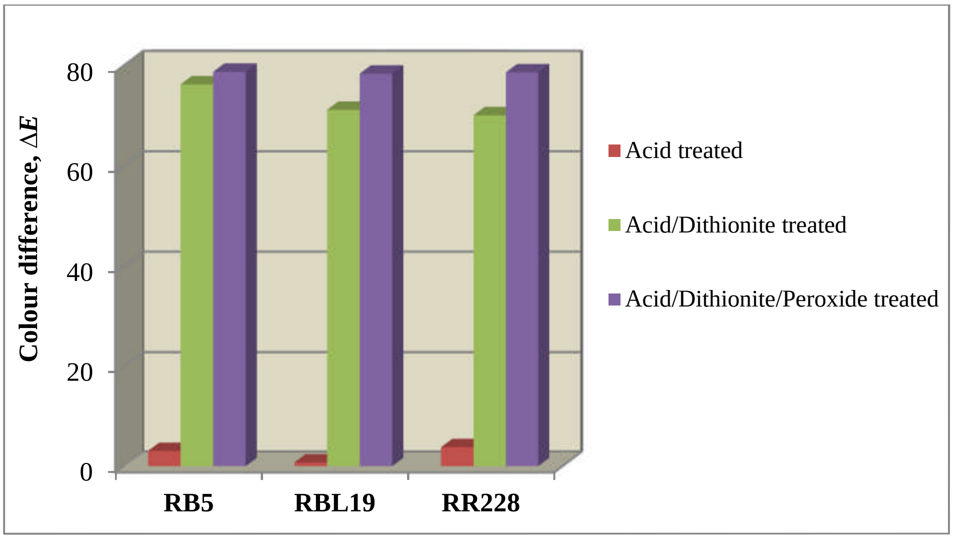


Figure 4.3.8 CIELAB colour difference of the reactive dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatments.

4.3.2.2.3 ISO brightness of the reactive dyed fabrics stripped in the sequential acid/dithionite/peroxide method

The ISO brightness of the acid/dithionite/peroxide stripped samples are presented in Figure 4.3.9. As expected the acid treatment had little effect on the ISO brightness, however further treatment of the fabrics in the alkaline dithionite solution significantly increased the ISO brightness values to 76.1%, 61.2% and 38.5% on the RB5, RBL19 and RR228 fabrics, respectively. Further peroxide oxidative bleaching also resulted in a greater increase in ISO brightness of the fabrics to 83.2%, 82.7% and 66.1% on the RB5, RBL19 and RR228 dyed materials, respectively, compared to a brightness of 82.4% of the original white undyed cotton fabric.

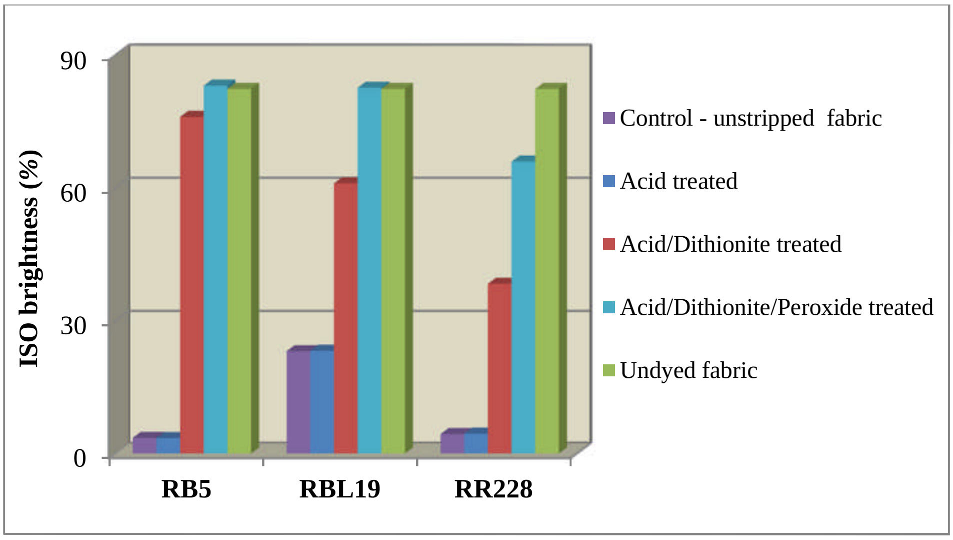


Figure 4.3.9 Comparison of the ISO brightness for the undyed, reactive dyed and acid/dithionite/peroxide treated cotton fabrics.

4.3.2.2.4 Visual comparison of the reactive dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide method

Visual assessment of the reactive dyed fabrics stripped in the sequential acid/dithionite/peroxide method are presented in Figure 4.3.10. It is clear that the acid treatment resulted in a minimal effect on the reactive dyed fabrics, however, subsequent dithionite and peroxide treatments resulted in a significant colour loss on all fabrics. The effect was especially severe on RB5 and RBL19 dyed cotton that appeared similar to that of the undyed cotton fabric. Conversely, the treatment was slightly less effective on the RR228 dyed fabric leaving some residual colorant on the treated material.

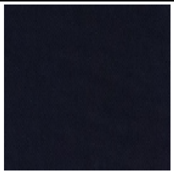
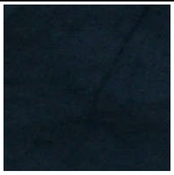
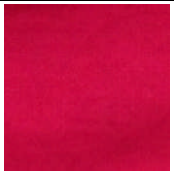
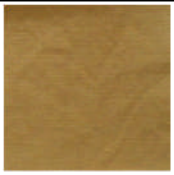
Colorant	**Dyed fabric**	**Acid treated**	**Acid/Dithionite treated**	**Acid/Dithionite/ Peroxide**	**Undyed fabric**
RB5					
RBL19					
RR228					

Figure 4.3.10 Visual appearance of reactive dyed cotton fabrics that have been stripped with the sequential acid/dithionite/peroxide treatments.

4.3.2.3 Comparison of the dye stripping methods on reactive dyed cotton fabrics

The efficiencies of the sequential acid/alkali/peroxide and the sequential acid/dithionite/peroxide methods on stripping reactive dyes from cotton fabrics were determined as per Equation 3.7.4 and results are presented in Figure 4.3.11. It is obvious that the two methods had similar effects on the azo-based RB5 and RR228 dyed fabrics stripping up to 99.9% of the dyes. However the effect of the acid/alkali/peroxide method was lower on the chemically resistant RBL19 dyed fabric resulting in a stripping efficiency of only 81.6%. In contrast the acid/dithionite/peroxide method stripped up to 99.9% of the dyes from all the fabrics, including the highly chemical resistant anthraquinone-based C. I. Reactive Blue 19 dye.

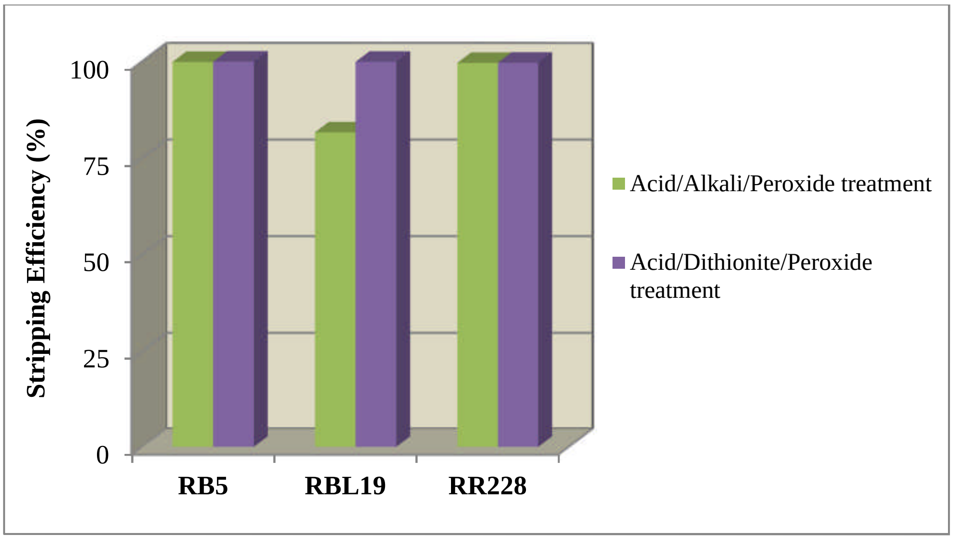


Figure 4.3.11 Stripping efficiencies of the sequential acid/alkali/peroxide and the alternative acid/dithionite/peroxide treatments on reactive dyed cottons.

4.4 CONCLUSIONS

In this chapter the stability of reactive dyes on ISO 105 washing conditions were investigated in order to determine the effect of washing detergent formulations on the reactive dyes and to establish if dyes will be present on the garments once they complete their ‘first’ life. The results obtained have demonstrated that most reactive dyes are stable to chemicals used in washing detergents and that complete removal of the colorants throughout their lifetime is impossible. Although some of the dyes are possibly being removed during the usage period, most dyes will remain linked to the fibres at the end of the garment’s usage. This suggests that colorants need to be stripped from waste garments prior to reprocessing of the materials for new fibre regeneration.

Two methods based on the sequential acid/alkali/peroxide and the sequential acid/dithionite/peroxide methods were therefore established and their efficacies in stripping reactive dyes from cotton fabrics were analysed. It was found that the anthraquinone based C. I. Reactive Blue 19 was highly resistant to the acid/alkali/peroxide method compared to the azo based C. I. Reactive Black 5 and C. I. Reactive Red 228 which were easily stripped by the sequence. This was thought to be due to the anthraquinone structure of the C. I. Reactive Blue 19 dye which is not easily hydrolysed by chemicals compared to the azo chromophoric structure. However the sequential acid/dithionite/peroxide treatment was highly effective in stripping the three reactive dyes. This was thought to be due to the high reduction potential of the alkaline sodium dithionite which could reduce both azo and anthraquinone dye chromophores. Furthermore the inclusion of the PVP polymer in the dithionite stripping liquor was also thought to have increased the stripping efficiency as the polymer is capable of complexing with the stripped dye preventing it from being redeposited on the fibre.

Chapter Five: Investigation into the removal of other colorants and crosslinks from cotton

5.1 INTRODUCTION

As already stated the presence of crosslinks between the cellulosic chains resulting from treatments with colorants and other finishing agents affects the processability (solubility and subsequent extrusion of the spinning solution for fibre regeneration) of the recycled cotton pulps. In this chapter the sequential acid/alkali/peroxide and the alternative sequential acid/dithionite/peroxide dye stripping methods were investigated as potential methods for stripping other cellulosic dyes (including sulphur dyes, vat dyes and direct dyes); pigments and finishing agents from cotton fabrics. The efficiencies of the two treatments were also extended to post-consumer cotton garments where a T-shirt, a shirt and denim obtained from a local charity shop were used. The effect of fluorescent whitening agents and transition metals were also included in the scope of the study. Colorimetric parameters were monitored by evaluating changes occurring in colour strength, *K/S*, CIELAB colour difference, ΔE and ISO brightness of the treated fabrics.

5.2 STRIPPING OF SULPHUR DYES FROM COTTON FABRICS

Sulphur dyes are an important class of cellulosic dyes as they offer a wide range of important hues such as blacks, navy, brown, olives and greens in medium to heavy depths and at relatively low costs as detailed in Section 2.3. It was therefore necessary to assess the efficiencies of the established methods in stripping sulphur dyes from cotton fabrics.

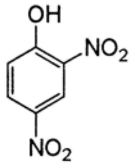
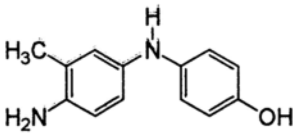
5.2.1 Experimental

5.2.1.1 Materials and Chemicals

Sulphur dyed cotton fabrics (same as base bleached and mercerised cotton fabric used in the dyeing work in this study), were supplied by Mr. Cohen, University of Manchester. All fabrics were dyed at 4% on the weight of the material using exhaust dyeing method. Table 5.2.1 presents the information of the sulphur dyes used in this study. C. I. Sulphur

Black 1 dye was selected due to its great importance in textile dyeing as it offers heavy depth and excellent fastness properties at reasonable costs whilst C. I. Sulphur Blue 7 dye was selected for comparison purposes.

Table 5.2.1 Sulphur dyes used for the research

Code	Generic name; Commercial name	Chemical Class	Molecular structure (monomer unit)
SB1	C. I. Sulphur Black 1; Diresul Black RDT-LS	Unknown	
SB7	C. I. Sulphur Blue 7; Diresul Blue RDT-G	Unknown	

5.2.2 Results and Discussion

The sulphur dyed cotton fabrics were stripped using both sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods as detailed in Section 3.4. Colorimetric parameters were monitored by observing variations in colour strength, CIELAB colour difference and ISO brightness of the stripped fabrics. The results obtained are discussed below.

5.2.2.1 Effect of the sequential Acid/Alkali/Peroxide method on Sulphur dyed cotton fabrics

In the acid/alkali/peroxide method sulphur dyed fabrics were stripped by the hydrolytic actions of the sequential acid and alkali treatment prior to oxidative bleaching reaction of hydrogen peroxide. The obtained colorimetric parameters are discussed below.

5.2.2.1.1 *Colour strength (K/S) of the Sulphur dyed fabrics stripped in the sequential acid/alkali/peroxide method*

The *K/S* values of the sulphur dyed fabrics treated in the sequential acid/alkali/peroxide stripping method are presented in Figure 5.2.1. The acid treatment had no apparent effect on the colour strength of SB1 dyed cotton as the *K/S* value was similar to that of the untreated material. However the treatment slightly stripped dyes from SB7 sample resulting in a *K/S* of 4.4 compared to the original *K/S* of 4.7. Subsequent alkali treatment significantly decreased the *K/S* of SB1 fabric to 4.3, however the effect was moderate on the SB7 fabric resulting in a *K/S* of only 1.5 compared to the original *K/S* of 4.7. Further treatment in the hydrogen peroxide bleaching bath removed additional dye from the SB1 fabric resulting in a *K/S* of 1.0. The effect was again minimal on SB7 fabric resulting in a *K/S* of only 1.1 compared to a *K/S* of 1.5 observed on the fabric stripped by the acid/alkali sequence only.

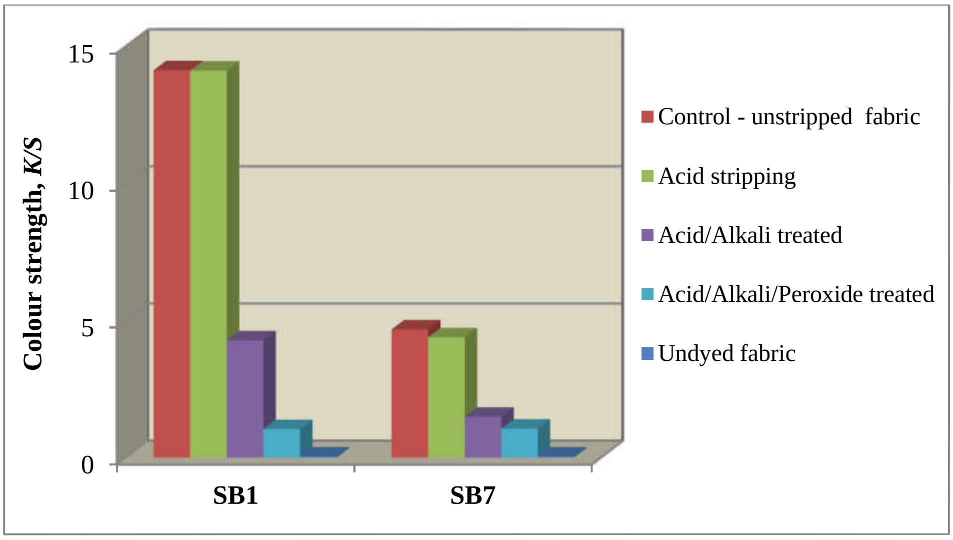


Figure 5.2.1 Changes in the colour strength for the undyed, sulphur dyed and acid/alkali/peroxide stripped cotton fabrics.

Sulphur dyes are reported to be resistant to stripping chemicals because they form insoluble pigments entrapped in the cellulosic substrates [78]. This could have resulted in the relatively lower levels of colour removal as indicated by slightly decreased *K/S* of the two stripped sulphur dyed fabrics.

5.2.2.1.2 *CIELAB colour difference, ΔE, of the sulphur dyed fabrics stripped in the sequential acid/alkali/peroxide method*

The CIELAB colour difference results for the sulphur dyed fabrics treated in the sequential acid/alkali/peroxide method are presented in Figure 5.2.2. The acid treatment had the least effect resulting in Δ*E*s of 0.2 and 0.7 on SB1 and SB7 fabrics, respectively. When further stripped in the alkaline solution, more colorant was removed, resulting in Δ*E*s of 16.3 and 19.1 on the SB1 and SB7 fabrics, respectively. Subsequent peroxide bleaching also removed more colorant from the SB1 dyed fabric resulting in a Δ*E* of 37.3, however the difference was minimal on SB7 fabric resulting in a Δ*E* of only 24.7.

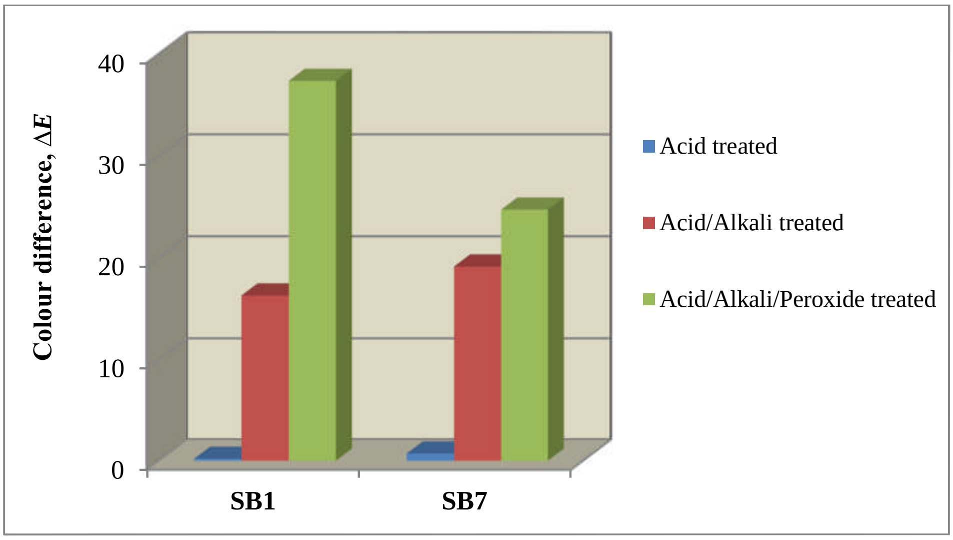


Figure 5.2.2 CIELAB colour difference for the sulphur dyed cotton fabrics stripped in acid/alkali/peroxide treatments.

5.2.2.1.3 *ISO brightness of the sulphur dyed fabrics stripped in the sequential acid/alkali/peroxide method*

Figure 5.2.3 compared the ISO brightness of the sulphur dyed fabrics stripped in the sequential acid/alkali/peroxide method. The brightness of the acid treated SB1 fabric was similar to that of the untreated dyed fabric, however the treatment slightly increased the brightness of the SB7 fabric to 26.1% compared to the original brightness of 25.5%. Further alkali treatment slightly increased the brightness to 11.0% and 38.4% for the SB1 and SB7 dyed materials, respectively. Subsequent peroxide bleaching further increased the brightness of the dyed samples to 28.2% and 49.4%, respectively.

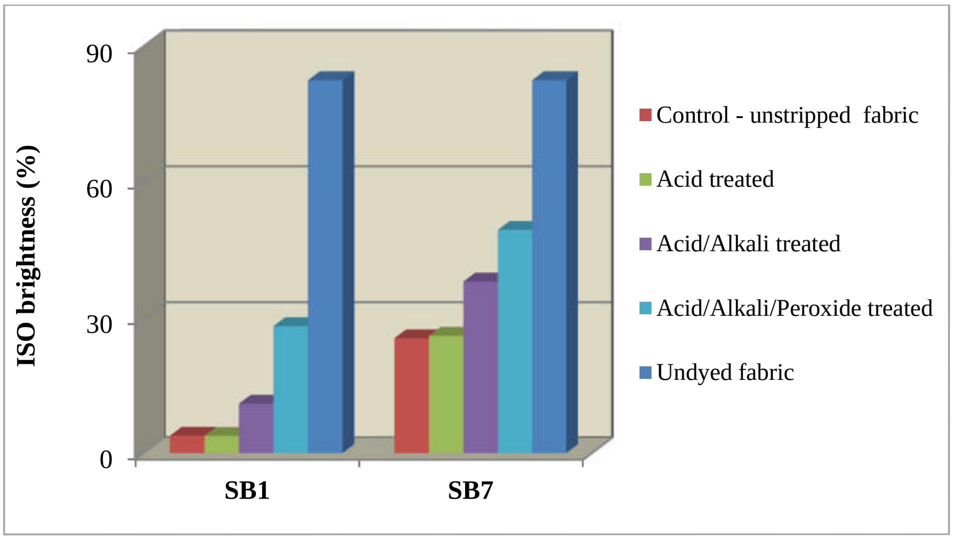
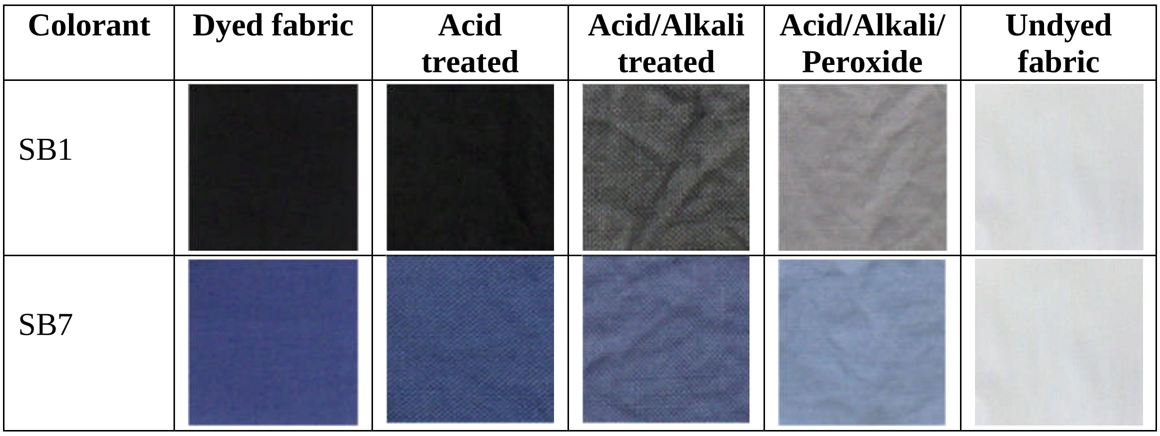


Figure 5.2.3 Comparison of the ISO brightness for the undyed, sulphur dyed and acid/alkali/peroxide stripped cotton fabrics

5.2.2.1.4 Visual comparison of the sulphur dyed fabrics stripped in the sequential acid/alkali/peroxide method

The sulphur dyed fabrics stripped in the sequential acid/alkali/peroxide method are visually compared in Figure 5.2.4. The acid treatment had no apparent effect on the two sulphur dyed materials as they appeared almost similar to their untreated parts. Further alkali treatment and subsequent oxidative peroxide bleaching only resulted in a minor colour change, suggesting the stability of these typical sulphur dyes to the sequential acid/alkali/peroxide treatment.



Colorant	Dyed fabric	Acid treated	Acid/Alkali treated	Acid/Alkali/ Peroxide	Undyed fabric
SB1					
SB7					

Figure 5.2.4 Visual appearance of sulphur dyed cotton fabrics following stripping with the sequential acid/alkali/peroxide treatment.

5.2.2.2 Effect of the sequential Acid/Dithionite/Peroxide method on sulphur dyed cotton fabrics

The sulphur dyed fabrics were also stripped in the sequential acid/dithionite/peroxide treatment as detailed in Section 3.4. Colorimetric parameters of the stripped and unstripped fabrics were monitored and the results obtained are discussed below.

5.2.2.2.1 *Colour strength (K/S) of the sulphur dyed fabrics stripped in the sequential acid/dithionite/peroxide method*

The colour strength of the sulphur dyed fabrics treated in the sequential acid/dithionite/peroxide method are compared in Figure 5.2.5. As previously detailed, the acid treatment of the sulphur dyed fabrics had a minor effect on the colour strength of the SB1 and SB7 fabrics. Subsequent alkaline dithionite treatment significantly decreased the *K/S* values to 0.7 and 0.1 on the SB1 and SB7 dyed fabrics, respectively, compared to the original *K/S* of 14.1 and 4.7, respectively.

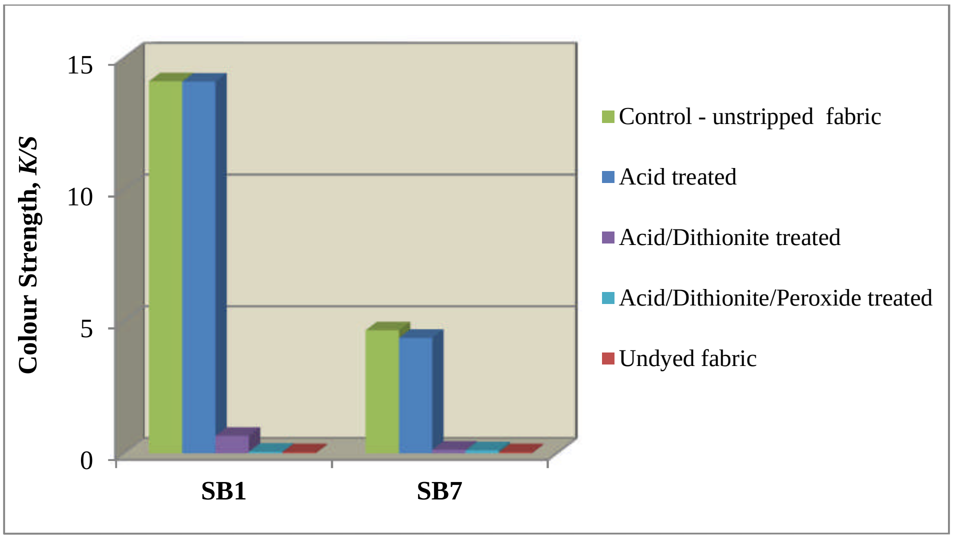


Figure 5.2.5 Comparison of the colour strength for the undyed, sulphur dyed and acid/dithionite/peroxide treated cotton fabrics.

Alkaline dithionite is capable of reducing the disulphide bond of sulphur dyes into the water-soluble (thiol) form [78]. In addition the polyvinylpyrrolidone (PVP) polymer added in the stripping liquor may have prevented the water-soluble sulphur dyes from being redeposited on the fibre surfaces [154, 157, 158]. It is therefore reasonable to conclude that, the high reducing power of the alkaline dithionite solution in combination with the dye binding capacity of the PVP polymer may have attributed to the high colour removal achieved on the two sulphur dyed samples.

Further peroxide treatment removed additional colour from the SB1 dyed fabric resulting in a *K/S* of 0.1. However the treatment had no effect on SB7 fabric resulting in a *K/S* of 0.1, similar to that of its comparable acid/dithionite only treated material. This was unexpected as sulphur dyes are reported to be sensitive to oxidative peroxide bleaching due to possible over-oxidation, resulting from the attack on the disulphide linkage, forming water solubilising sulphinate and sulphonate groups [78].

5.2.2.2.2 CIELAB colour difference of the Sulphur dyed fabrics stripped in a sequential acid/dithionite/peroxide method

The colour difference results for the sulphur dyed fabrics stripped in the sequential acid/dithionite/peroxide method are presented in Figure 5.2.6. The acid treatment had the least effect on the sulphur dyed materials. However following dithionite treatment a large amount of dye was stripped resulting in ΔEs of 43.9 and 47.5 on the SB1 and SB7 dyed samples, respectively. Subsequent oxidative peroxide bleaching further stripped dyes from the SB1 sample resulting in a ΔE of 67.2. However a ΔE value of only 50.5 was obtained on the SB7 fabric.

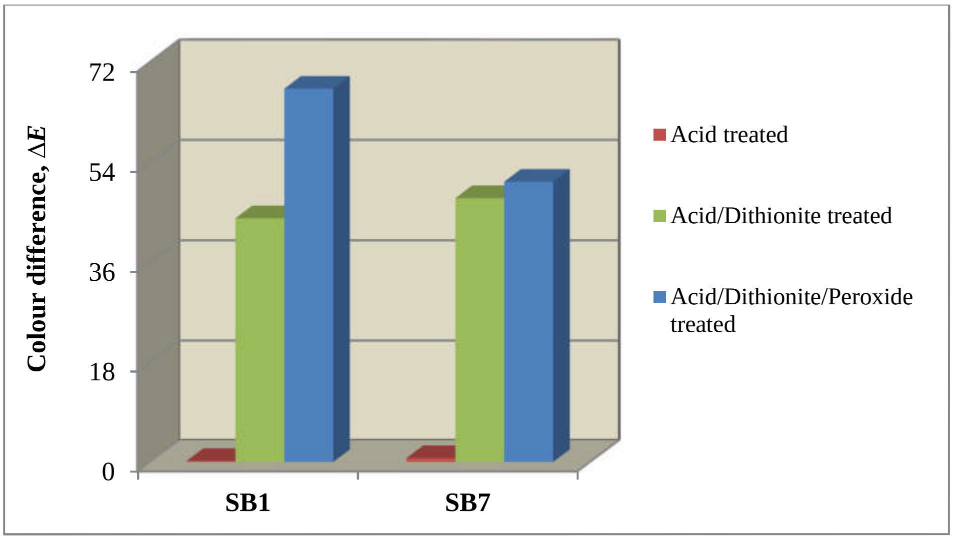


Figure 5.2.6 CIELAB colour difference for the sulphur dyed cotton samples stripped in the sequential acid/dithionite/peroxide treatment.

5.2.2.2.3 ISO brightness of the sulphur dyed samples stripped in the sequential acid/dithionite/peroxide method

The ISO brightness results for the acid/dithionite/peroxide stripped sulphur dyed fabrics are presented in Figure 5.2.7. The acid treatment showed no apparent change on the brightness of the SB1 sample, however the treatment slightly increased the brightness of the SB7 fabric. Subsequent dithionite treatment significantly increased the brightness to 36.3% and 73.8% for both SB1 and SB7 dyed materials, respectively. Further oxidative peroxide bleaching also increased the brightnesses to 74.1% and 82.9%, respectively, compared to a brightness of 82.4% of the white undyed cotton fabric.

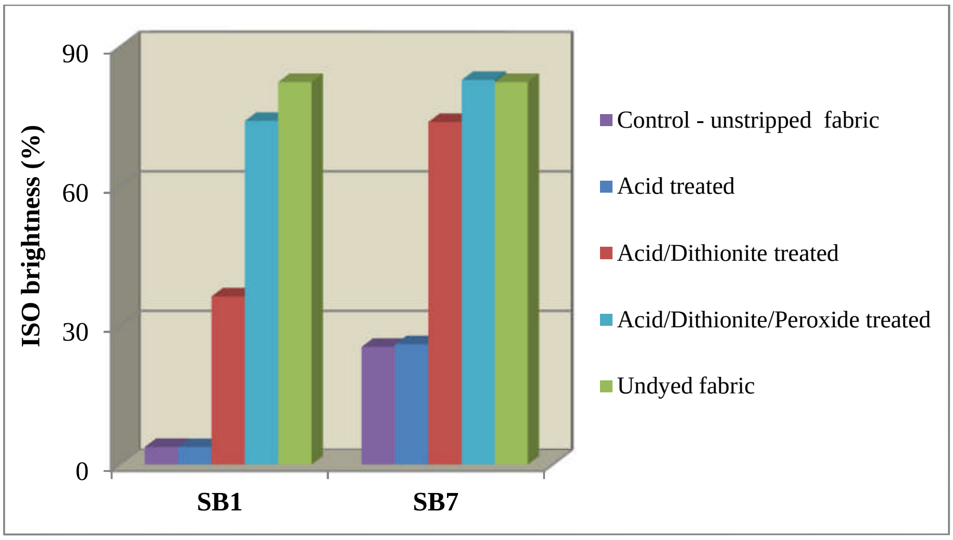


Figure 5.2.7 Comparison of the ISO brightness for the undyed, sulphur dyed and acid/dithionite/peroxide treated cotton fabrics.

It is interesting to note that, although oxidative peroxide bleaching resulted in minor effects on both colour strength (Figure 5.2.5) and colour difference (Figure 5.2.6) of the SB7 sample, the effect was more obvious on the ISO brightness values (Figure 5.2.7). This indicates that the peroxide treatment was able to brighten the base cellulosic substrate of the dyed samples despite the lower amounts of colour removed from the fabrics.

5.2.2.2.4 Visual comparison of the Sulphur dyed fabrics stripped in the sequential acid/dithionite/peroxide method

Figure 5.2.8 visually compares the sulphur dyed fabrics stripped in the sequential acid/dithionite/peroxide method. The acid treatment had no obvious effect on the sulphur dyed samples as the samples looked similar to the untreated fabrics. Subsequent dithionite and peroxide treatment stripped large amounts of the two sulphur dyes as the resultant fabrics appeared almost similar to the undyed cotton fabric.

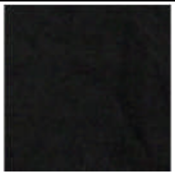
Colorant	Dyed fabric	Acid treated	Acid/Dithionite treated	Acid/Dithionite / Peroxide	Undyed fabric
SB1					
SB7					

Figure 5.2.8 Visual appearance of sulphur dyed cotton fabrics following stripping with the sequential acid/dithionite/peroxide treatments.

5.2.2.3 Comparison of the dye stripping methods on sulphur dyed cotton fabrics

The efficiencies of the sequential acid/alkali/peroxide and the alternative sequential acid/dithionite/peroxide treatments on stripping sulphur dyes from cotton fabrics were determined as per Equation 3.7.4 and the results are presented in Figure 5.2.9. It can be seen that the sequential acid/alkali/peroxide method removed up to 92.7% of the C. I. Sulphur Black 1 dye compared to only 77.5% of the C. I. Sulphur Blue 7 dye stripped by the treatments. However stripping by the sequential acid/dithionite/peroxide treatments stripped larger amounts of both sulphur dyes resulting in stripping efficiencies of 99.6% and 97.5% on the SB1 and SB7 treated fabrics, respectively.

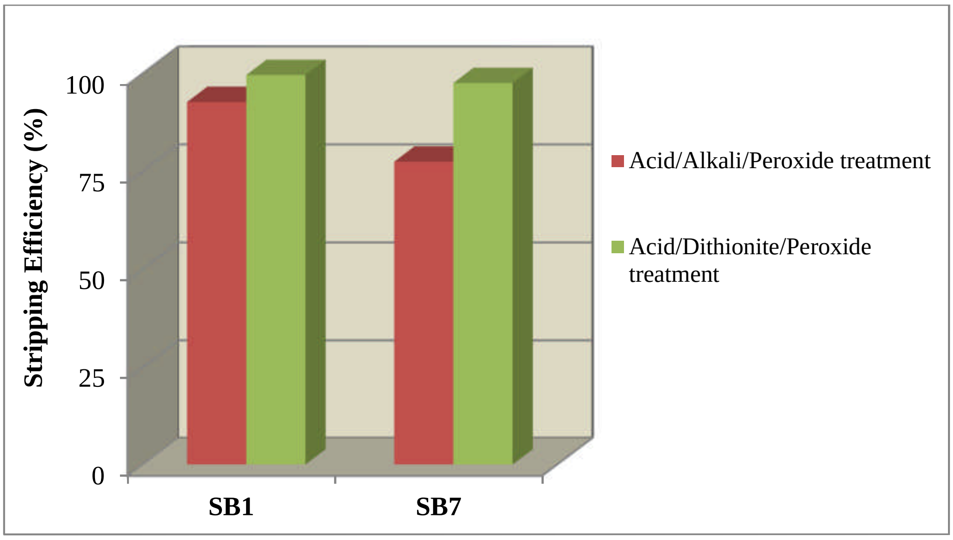


Figure 5.2.9 The stripping efficiencies of the sequential acid/alkali/peroxide and the alternative acid/dithionite/peroxide treatments on sulphur dyed fabrics.

5.3 STRIPPING OF VAT DYES FROM COTTON FABRICS

Vat dyes are an important class of cellulosic dyes that offer the best overall fastness properties including light, wash and chlorine fastness, surpassing the performance of the other cellulosic dye classes (see Section 2.3). In this section the stability of the vat dyes in the sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide dye stripping methods were evaluated.

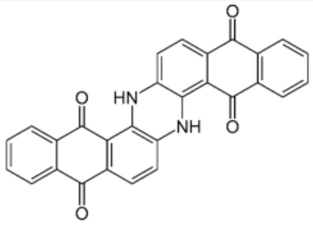
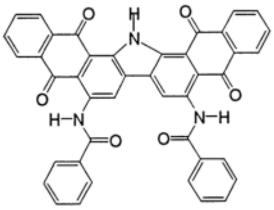
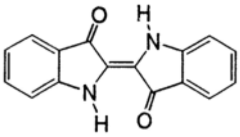
5.3.1 Experimental

5.3.1.1 Materials and Chemicals

C. I. Vat Blue 4 and C. I. Vat Black 27 dyed fabrics (same base bleached, mercerised cotton fabric used throughout this study), were supplied by Mr. Cohen, University of Manchester. These fabrics were dyed at 4% on the weight of the fabric using an exhaustion dyeing method. The indigo dye (C. I. Vat Blue 1) was obtained from Sigma Aldrich Ltd and was applied to cotton fabrics by the researcher using a padding technique detailed in Section 5.3.1.2 below. The scoured, bleached and mercerised cotton fabric described in Section 3.2 was used for indigo dyeing.

The three vat dyes were selected based on their chemical class (anthraquinone and indigo), but C. I. Vat Blue 1 was also selected due to its speciality use in coloration of denim fabrics. Table 5.3.1 provides information on the vat dyes used in this study.

Table 5.3.1 Vat dyes used in this research

Code	Generic name; Commercial name	Chemical Class	Molecular structure
VB4	C. I. Vat Blue 4; Cibanone Blue RS	Anthraquinone	
VB27	C. I. Vat Blue 27; Solanthrene Olive R	Anthraquinone	
VB1	C. I. Vat Blue 1	Indigo	

5.3.1.2 Indigo dyeing of cotton fabric

Cotton fabrics were immersed in the leuco dye liquor, squeezed to about 100% wet pick-up between padding machine roller sets and skied for about 2 minutes to partially oxidise the dye [99]. The process was repeated five times to obtain the required depth. Dyed fabrics were then oxidised by air for 30 minutes prior to washing in 1 mL/L hydrochloric acid followed by cold water rinsing. Soaping of the dyed fabrics was then performed for 15 minutes at 100°C in a liquor containing 2 g/L sodium carbonate and 2 mL/L non-ionic washing detergent. Fabrics were then washed in water prior to air drying.

5.3.2 Results and Discussion

The vat dyed cotton fabrics were stripped using both sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods described in Section 3.4. Colorimetric parameters of the treated and untreated fabrics were monitored by observing changes in colour strength, *K/S*, CIELAB colour difference, ΔE, and ISO brightness obtained by measuring reflectance values at 460 nm wavelength. The results are discussed below.

5.3.2.1 Effect of the sequential Acid/Alkali/Peroxide treatment on vat dyed cotton fabrics

The three vat dyed cotton fabrics were stripped by the hydrolytic actions of the sequential acid and alkali treatment followed by the oxidative bleaching reaction of hydrogen peroxide. Changes observed in colorimetric parameters are hereby discussed.

5.3.2.1.1 Colour strength (K/S) of the vat dyed fabrics stripped in the sequential acid/alkali/peroxide method

Figure 5.3.1 presents the colour strength results of the vat dyed fabrics treated in the sequential acid/alkali/peroxide stripping method. The acid treatment had the least effect on the colour strength of VB27 and VB4 samples resulting in a slightly decreased *K/S* to 9.0 and 26.0, respectively, compared to the original *K/S* of 9.6 and 26.8, respectively. However the treatment stripped more of the dye from VB1 fabric resulting in a *K/S* of 13.4 compared to the original *K/S* of 17.0. The slightly higher level of dye removal observed on VB1 dyed material could be due to easier removal of C. I. Vat Blue 1 dye that had been deposited on the surface of the fabric through multiple padding. Subsequent alkali treatment significantly decreased the *K/S* of the VB1 cotton to 3.6, however the effect was again moderate on VB27 and VB4 fabrics resulting in *K/S* values of 7.9 and 22.1, respectively. The higher dye removal on the VB1 sample was again thought to be due to the hot alkaline solution easily stripping out the dye that was deposited on the surface of the fabric. However the small effect on both VB4 and VB27 dyed fabrics could be due to their anthraquinone chromophore which is highly resistant to most chemicals [204, 205].

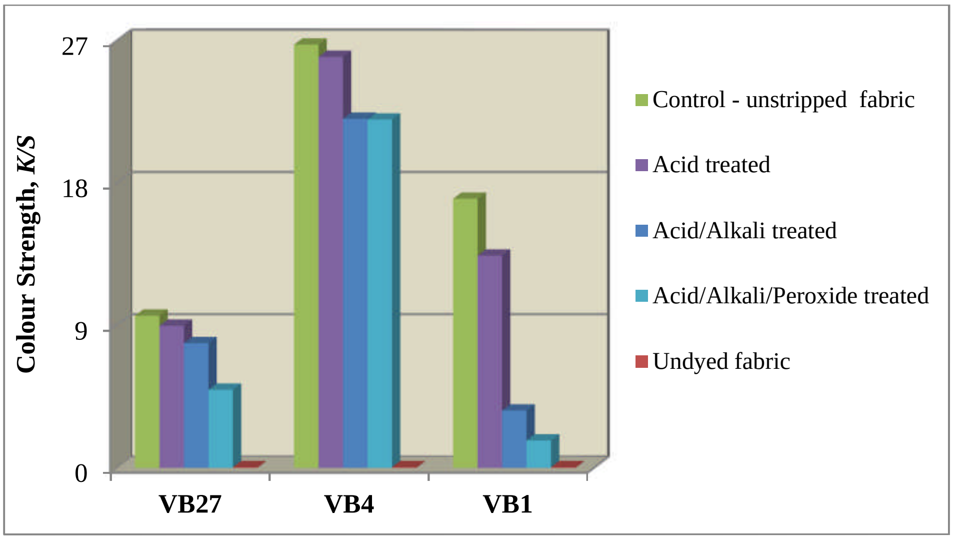


Figure 5.3.1 Comparison of the colour strength for the undyed and vat dyed cotton fabrics stripped in the sequential acid/alkali/peroxide treatments.

It is interesting to mention that during alkali stripping the stripping liquor could remove colorants from the samples as they appeared to have lower colour intensity, however on subsequent washing of the stripped fabrics in warm water, the dyes reoxidised back to their original colour. This could be due to the dye regeneration on the fabric on air exposure [73, 78]. This phenomenon is also thought to have contributed to the relatively lower decrease in colour strength of the VB4 and VB27 dyed materials.

Further peroxide treatment stripped more colour from VB1 and VB27 fabrics resulting in *K/S* values of 1.7 and 4.9, respectively. As expected, the effect was less obvious on VB4 dyed fabric resulting in a *K/S* of only 22.0, which was again attributed to the chemical resistance nature of the anthraquinone structure present in the C. I. Vat Blue 4 dye.

5.3.2.1.2 CIELAB colour difference (ΔE) of the vat dyed fabrics stripped in sequential acid/alkali/peroxide method

The colour difference results for the vat dyed fabrics treated in the acid/alkali/peroxide sequence are presented in Figure 5.3.2. The acid treatment had a minor effect on the vat dyed samples resulting in Δ*E*s of 3.2, 7.3 and 4.5 on VB27, VB4 and VB1 fabrics, respectively. Further stripping in hot alkaline solution removed more dye from the dyed fabrics resulting in Δ*E*s of 5.8, 9.0 and 21.7, respectively. Subsequent peroxide bleaching also removed more dye resulting in Δ*E*s of 12.0, 19.9 and 32.5 on VB27, VB4 and VB1 dyed cottons, respectively. Again the higher colour removal on the VB1 fabric was attributed to the easier removal of the dye padded on the surface of the fabrics while the minor colour removal observed on VB27 and VB4 samples was attributed to the more resistant anthraquinone chromophoric structures of both the C. I. Vat Black 27 and C. I. Vat Blue 4 dyes.

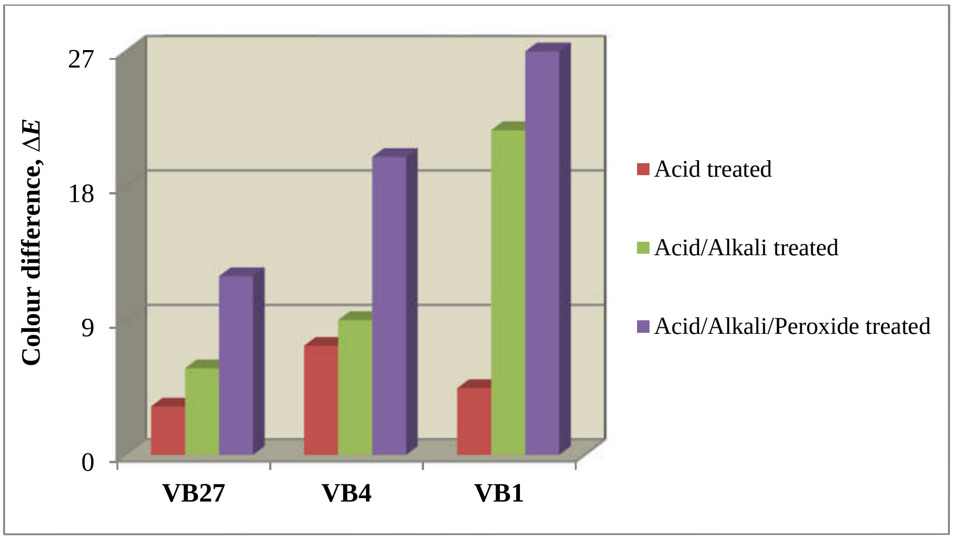


Figure 5.3.2 CIELAB colour difference for the vat dyed cotton fabrics stripped in the sequential acid/alkali/peroxide treatments.

5.3.2.1.3 ISO brightness of the vat dyed fabrics stripped in the sequential acid/alkali/peroxide method

The ISO brightness of the vat dyed fabrics stripped in the sequential acid/alkali/peroxide method are presented in Figure 5.3.3. The acid treatment resulted in brightness values of 5.0%, 11.3% and 11.1% for VB27, VB4 and VB1 dyed cottons, respectively, compared to the original brightness values of 4.7%, 9.9% and 8.6%, respectively. Subsequent alkali treatment had a slight effect on the brightness of the VB27 and VB4 samples resulting in brightness of 5.7% and 12.1%, respectively. However the treatment resulted in a slightly greater increase in brightness of the VB1 fabric to 24.1%. Further oxidative peroxide bleaching also increased the brightness of VB1 to 34.8%. However the effect of the treatment was minimal on the VB27 and VB4 dyed samples resulting in brightness of only 8.5% and 12.1%, respectively.

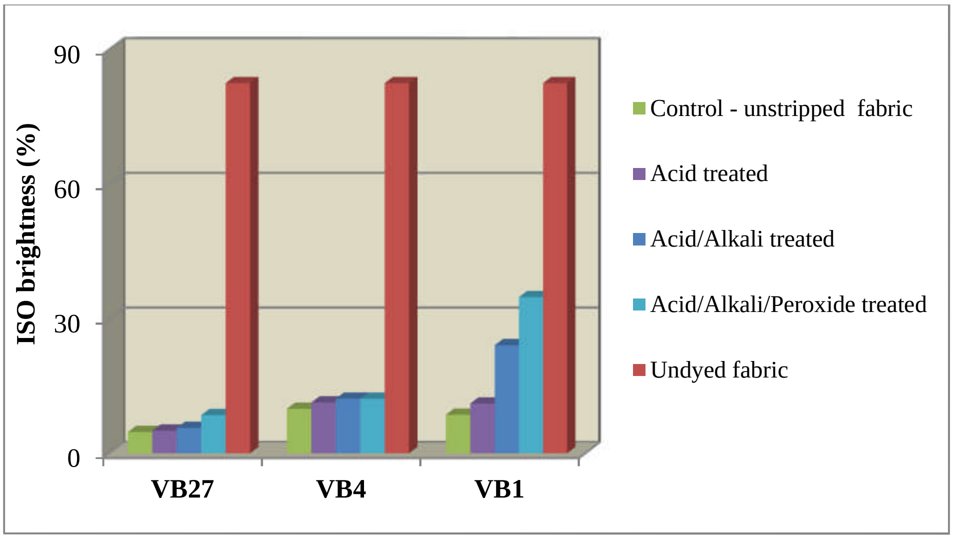


Figure 5.3.3 Comparison of the ISO brightness for the undyed and vat dyed cotton fabrics stripped in the sequential acid/alkali/peroxide treatments.

5.3.2.1.4 *Visual comparison of the Vat dyed fabrics stripped in the sequential acid/alkali/peroxide method*

Figure 5.3.4 visually compares the effects of the sequential acid/alkali/peroxide stripping method on vat dyed fabrics. The acid treatment had no obvious effect on any of the vat dyed fabrics. Similarly subsequent alkali and peroxide treatments did not dramatically affect the VB27 and VB4 dyed materials which is due to the chemical resistant anthraquinone chromophoric structures of the two dyes. The effect was however more obvious on the VB1 dyed cotton which is thought to be due to the easier removal of the surface C. I. Vat Blue 1 dye that was applied to cotton fabrics using multiple padding processes.

Colorant	**Dyed fabric**	**Acid treated**	**Acid/Alkali treated**	**Acid/Alkali/ Peroxide**	**Undyed fabric**
VB27					
VB4					
VB1					

Figure 5.3.4 Visual appearance of vat dyed cotton fabrics that have been stripped with the sequential acid/alkali/peroxide treatments

5.3.2.2 Effect of the Sequential Acid/Dithionite/Peroxide method on vat dyed cotton fabrics

Vat dyed fabrics were stripped in a sequential acid/dithionite/peroxide method as detailed in Section 3.4. The obtained colorimetric parameters are discussed below.

5.3.2.2.1 *Colour strength (K/S) of the vat dyed fabrics stripped in the sequential acid/dithionite/peroxide method*

The colour strength of the vat dyed fabrics treated in the acid/dithionite/peroxide stripping sequence are presented in Figure 5.3.5. As previously stated, the acid treatment only resulted in a small decrease in *K/S* of the vat dyed samples. Subsequent dithionite treatment resulted in a more obvious decrease in colour strength where *K/S* values of 0.1, 0.9 and 0.4 were observed on VB27, VB4 and VB1 treated cottons, respectively, compared to the original *K/S* values of 9.6, 26.8 and 17.0, respectively. As with sulphur dyes, the alkaline sodium dithionite is capable of reducing the water-insoluble vat dye present on the fibre into its water-soluble form [56, 73]. The PVP polymer (a dye transfer inhibitor) present in the stripping liquor could have complexed with the water-soluble leuco vat dye preventing it from redepositing back on the fibre surface hence the higher dye removal observed on the vat dyed and stripped samples.

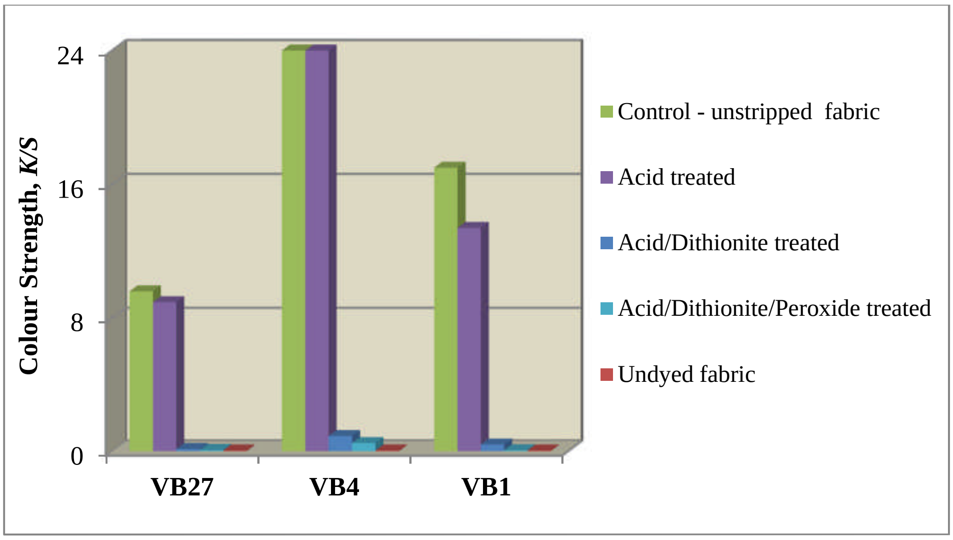


Figure 5.3.5 Comparison of the colour strength for undyed and vat dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatments.

Further oxidative peroxide bleaching resulted in additional colour removal with *K/S* values of 0.07, 0.49 and 0.05 observed on VB27, VB4 and VB1 dyed fabrics, respectively, approaching a *K/S* value of 0.04 for the original undyed cotton.

5.3.2.2.2 CIELAB colour difference (ΔE) of the vat dyed fabrics stripped in the sequential acid/dithionite/peroxide method

The CIELAB colour difference between untreated vat dyed cotton fabrics and those treated in the sequential acid/dithionite/peroxide method are presented in Figure 5.3.6. Again, the acid treatment had a least effect resulting in Δ*E* values of 3.2, 9.0 and 4.5 on VB27, VB4 and VB1 treated fabrics, respectively. Further alkaline dithionite treatment stripped more dye from the samples resulting in Δ*E*s of 55.0, 48.6 and 53.5 on VB27, VB4 and VB1 treated fabrics, respectively. Successive oxidative peroxide bleaching also increased the Δ*E* values of VB27, VB4 and VB1 fabrics to 57.8, 53.4 and 66.5, respectively.

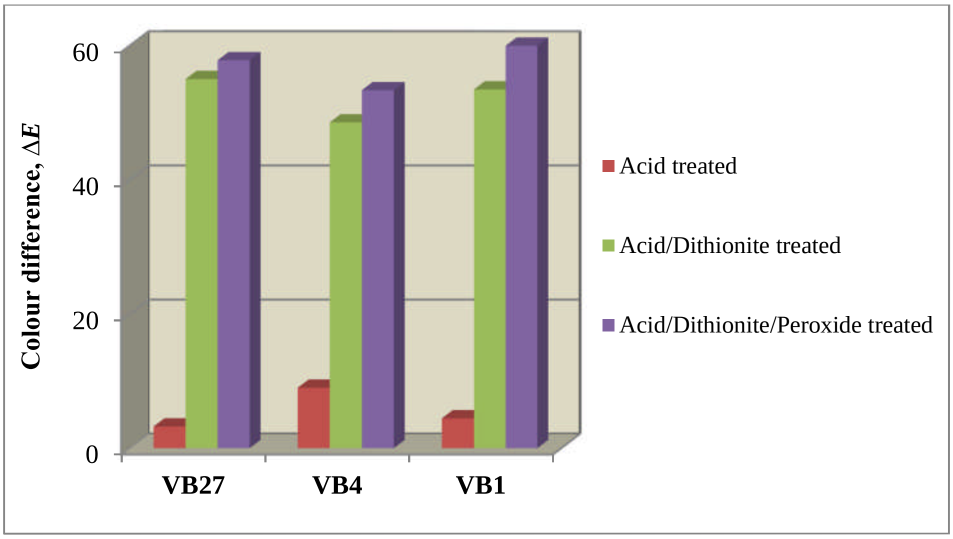


Figure 5.3.6 Comparison of colour difference for the vat dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatment.

5.3.2.2.3 ISO brightness of the vat dyed fabrics stripped in the sequential acid/dithionite/peroxide method

Figure 5.3.7 compares the ISO brightness of the acid/dithionite/peroxide stripped vat dyed fabrics. As observed in previous sections the acid treatment had a little effect on the brightness of the fabrics. Subsequent dithionite treatment significantly increased the brightness of VB27, VB4 and VB1 fabrics to 63.1%, 34.6% and 63.6%, respectively, compared to the original brightnesses of 4.7%, 9.9% and 8.6%, respectively. Further peroxide treatment removed more colorant, increasing the brightness values to 70.1%, 49.8% and 83.4% for the VB27, VB4 and VB1 fabrics, respectively, compared to a brightness of 82.4% of the original undyed cotton fabric. The lowest brightness observed on the VB4 fabric could again be explained as a result of the chemically resistant anthraquinone chromophore of the C. I. Vat Blue 4 dye.

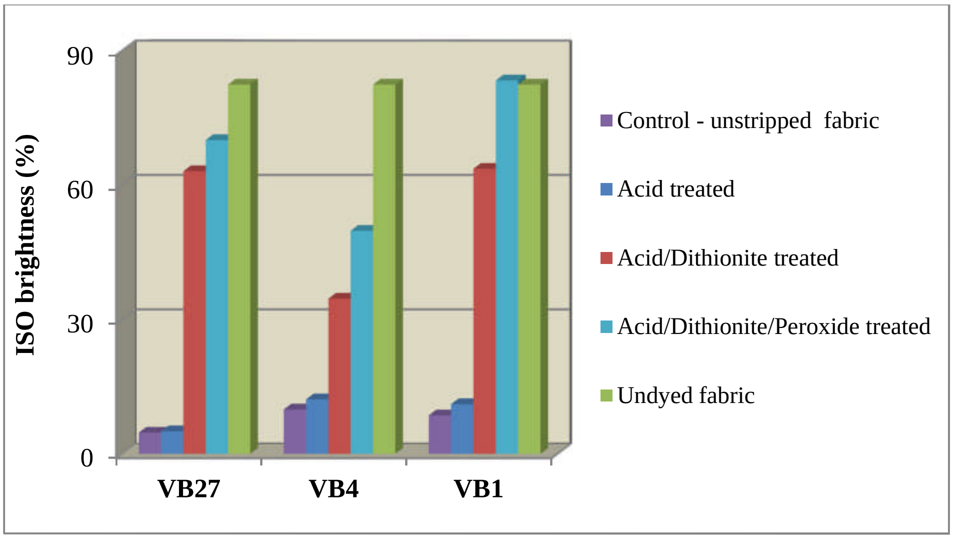


Figure 5.3.7 Comparison of the ISO brightness for the undyed and vat dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatment.

5.3.2.2.4 Visual comparison of the Vat dyed fabrics stripped in the sequential acid/dithionite/peroxide method

Figure 5.3.8 visually compares the vat dyed samples that were stripped in the sequential acid/dithionite/peroxide method. Following the acid treatment further alkaline dithionite treatment resulted in a significant colour change on all the vat dyed samples, the effect which was more pronounced on subsequent oxidative peroxide bleaching resulting in samples approaching those of the white undyed cotton.

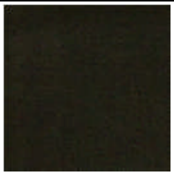
Colorant	**Dyed fabric**	**Acid treated**	**Acid/Dithionite treated**	**Acid/Dithionite/ Peroxide**	**Undyed fabric**
VB27					
VB4					
VB1					

Figure 5.3.8 Visual appearance of vat dyed cotton fabrics following stripping with the sequential acid/dithionite/peroxide treatments.

5.3.2.3 Comparison of the dye stripping methods on vat dyed fabrics

The efficiencies of the sequential acid/alkali/peroxide and the sequential acid/dithionite/peroxide treatments on stripping vat dyes from cotton fabrics were determined as per Equation 3.7.4 and results are presented in Figure 5.3.9. The sequential acid/alkali/peroxide method stripped more of the vat dyes from the VB27 and VB1 fabrics resulting in stripping efficiencies of 48.8% and 89.9%, respectively. The method was however less effective in stripping the C. I. Vat Blue 4 dye from the VB4 fabric removing only 17.7% of the dye. In contrast, the acid/dithionite/peroxide method removed significant amounts of the vat dyes from all samples resulting in stripping efficiencies of 99.3%, 97.8% and 99.7% for VB27, VB4 and VB1 dyed fabrics, respectively.

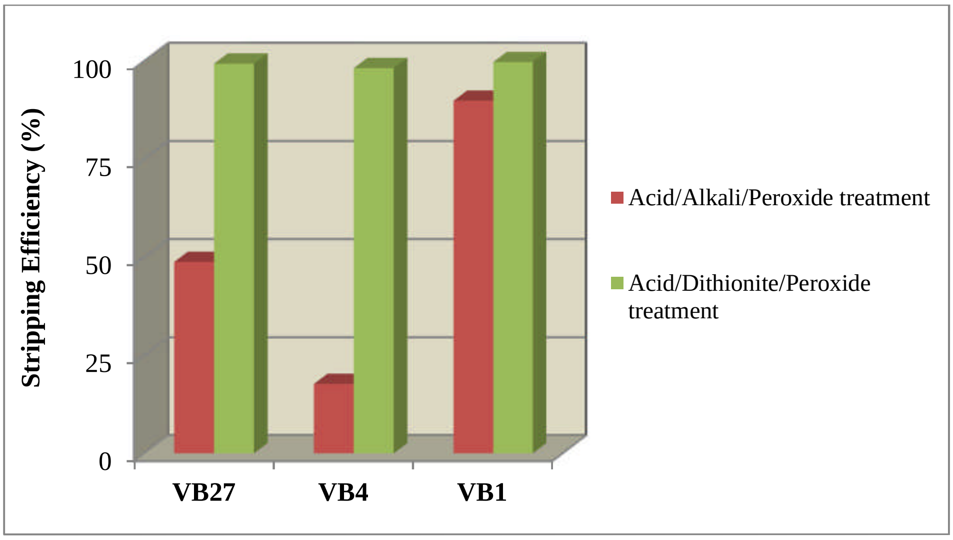


Figure 5.3.9 The stripping efficiencies of the sequential acid/alkali/peroxide and the alternative acid/dithionite/peroxide treatments on vat dyed cotton fabrics.

5.4 STRIPPING OF DIRECT DYES FROM COTTON FABRICS

Direct dyes were the first dyes to be applied directly to cotton substrates without the need for mordanting agents, hence the name *direct cotton dyes* [51]. These dyes are relatively cheap and their application process is relatively simple compared to other cellulosic dyes such as vat dyes [206]. However they are characterised with poor fastness properties and therefore require after-treatment of the dyed articles with cationic fixing agents in order to ensure good wash fastness properties of the material (see Section 2.3). In this section the efficiencies of the established dye stripping methods in stripping direct dyed cotton after-treated with cationic fixing agents were evaluated.

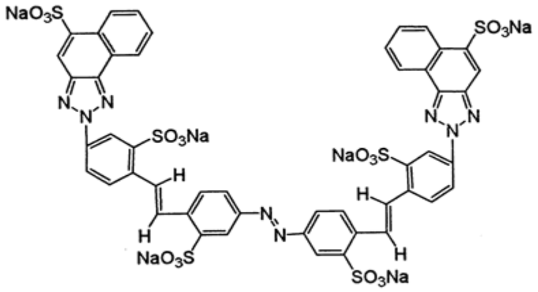
5.4.1 Experimental

5.4.1.1 Materials and Chemicals

Direct dyed cotton fabrics (using the same base bleached and mercerised cotton fabric used in this study) were supplied by Mr. Cohen, University of Manchester. All fabrics were dyed at 4% on the weight of the material by using the exhaustion dyeing technique. The dyed fabrics were aftertreated by using two different cationic agents, namely: Solfix

E (a polyamino-chlorohydrin quaternary ammonium polymer with epoxide reactivity) and Tinofix ECO applied at 6% and 2% concentration, respectively, based on the weight of the material. These agents were selected due to their being commonly used in the after-treatment of direct dyeing. Table 5.4.1 details the information of the direct dye used in this study.

Table 5.4.1 Details of the direct dye used in the study

Generic name; Commercial name	Chemical Class	Molecular structure
C. I. Direct Yellow 106; Solophenyl Yellow Arle	Stillbene	

5.4.2 Results and Discussion

The stripping of direct dyes and their fixing agents from cotton fabrics was performed using both sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods described in Section 3.4. In this study the C. I. Direct Yellow 106 dye fixed with two different cationic fixing agents Solfix E (DSe) and Tinofix ECO (DTe) were used for the analysis. Changes in colour strength, *K/S*, CIELAB colour difference, Δ*E*, and ISO brightness of the treated and untreated materials were monitored.

5.4.2.1 Effect of the sequential Acid/Alkali/Peroxide treatment on direct dyed cotton fabrics

Direct dyed cotton fabrics were stripped by using the hydrolytic actions of acid and alkali treatment followed by an oxidative bleaching with hydrogen peroxide. Colorimetric parameters for the treated and untreated fabrics are discussed below.

5.4.2.1.1 *Colour strength (K/S) of the direct dyed fabrics stripped in the sequential acid/alkali/peroxide method*

The colour strength parameters for the direct dyed samples treated in the sequential acid/alkali/peroxide stripping method are presented in Figure 5.4.1. The figure shows that the acid treatment of the samples slightly decreased the *K/S* of DSe and DTe samples to 18.5 and 17.7, respectively, compared to the original *K/S* values of 21.6 and 18.9, respectively. Subsequent alkali treatment of the dyed fabrics also decreased slightly the *K/S* of the fabrics to 17.6 and 17.2 for DSe and DTe samples, respectively. The small amount of colour removed from the direct dyed materials by the stripping treatments could be due to the presence of Solfix E (DSe) and Tinofix ECO (DTe) cationic fixing agents applied as aftertreatment to the direct dyed fabrics for the purpose of improving their wash fastness properties. The agents possess positive charge which attracts the negatively charged dye resulting in a strong insoluble complex [81, 84] which cannot be easily removed by chemical treatments.

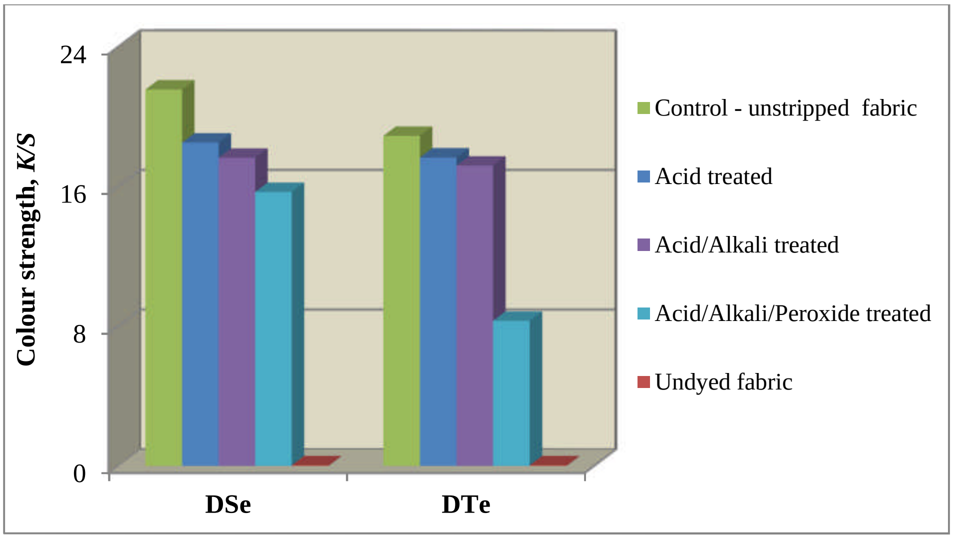


Figure 5.4.1 Comparison of the colour strength for the undyed and direct dyed cotton fabrics stripped in the sequential acid/alkali/peroxide treatment.

Further oxidative peroxide bleaching removed additional dye from the DTe sample resulting in a *K/S* of 8.3 compared to a *K/S* of 17.2 of the acid/alkali treated fabric. However the treatment only removed further 14% of the direct dye from the DSe sample. Solfix E (DSe) is a reactive polymer capable of reacting with cellulosic hydroxyl groups via ether formation, thereby forming a three-dimensional network involving the dye, the fixing agent and the fabric [207]. This could be the reason why the stripping agents could only strip a small amount of the direct dye aftertreated with Solfix E cationic fixing agent. On the other hand, Tinofix ECO (DTe) is a polyethylene imines non-reactive cationic agent that acquires cationic charges under application conditions by protonation [207]. The non-reactive nature of the Tinofix ECO fixing agents could be the reason for a slightly higher colour removal on direct dyed samples aftertreated with the agent.

5.4.2.1.2 *CIELAB colour difference, ΔE, of the direct dyed fabrics stripped in the sequential acid/alkali/peroxide method*

Figure 5.4.2 presents the CIELAB colour differences for the direct dyed fabrics stripped by the sequential acid/alkali/peroxide treatments. The acid treatment only had a slight effect on DSe and DTe samples resulting in Δ*E* values of 1.5 and 1.4, respectively. However further treating of the samples in hot alkaline solution, resulted in a slightly greater increase in Δ*E* to 3.2 and 9.2 on DSe and DTe samples, respectively. Subsequent oxidative peroxide bleaching resulted in a greater colour change on the DTe sample where a Δ*E* of 15.0 was attained. However a lower Δ*E* of only 5.5 was observed on DSe sample which was again thought to be due to the ability of Solfix E cationic fixing agent to form a three-dimensional network between the dye, the fixing agent and the fibre [207] making the formed bond more resistant to chemical treatments.

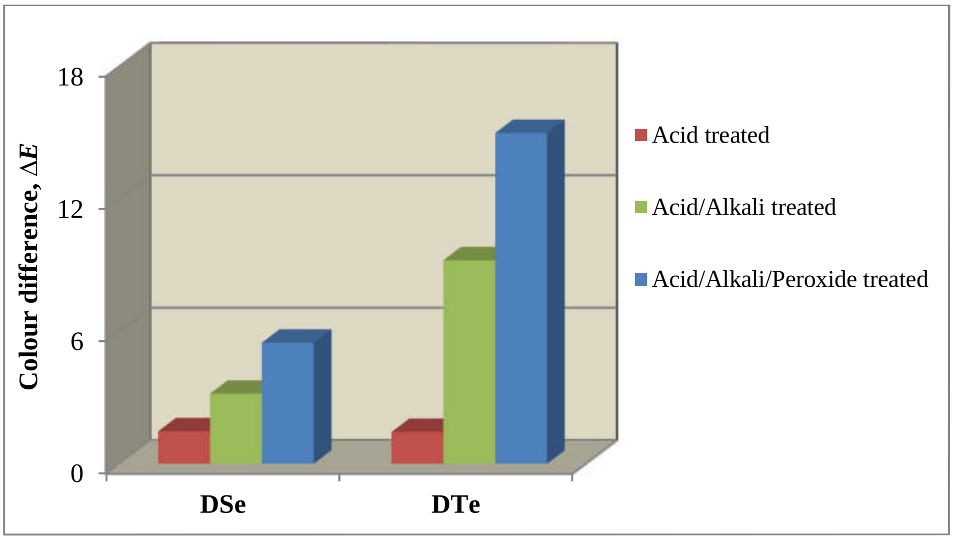


Figure 5.4.2 CIELAB colour difference for the direct dyed cotton fabrics stripped in the sequential acid/alkali/peroxide treatment.

5.4.2.1.3 ISO brightness of the direct dyed fabrics stripped in the sequential acid/alkali/peroxide method

The ISO brightness results for the direct dyed cottons stripped in the sequential acid/alkali/peroxide method are presented in Figure 5.4.3. It can be seen from the figure that the acid/alkali treatment had a little effect on the ISO brightness of the aftertreated direct dyed samples. For instance, the acid treatment resulted in brightness values of only 3.3% and 3.2% for DSe and DTe fabrics, respectively, compared to the original brightness of 3.1% and 3.0%, respectively. Subsequent alkali treatment resulted in a brightness of only 3.4% on both DSe and DTe samples which is again explained by the complex formed between the dye and the cationic fixing agents [81, 84] which could have resisted dye removal by the chemical treatments.

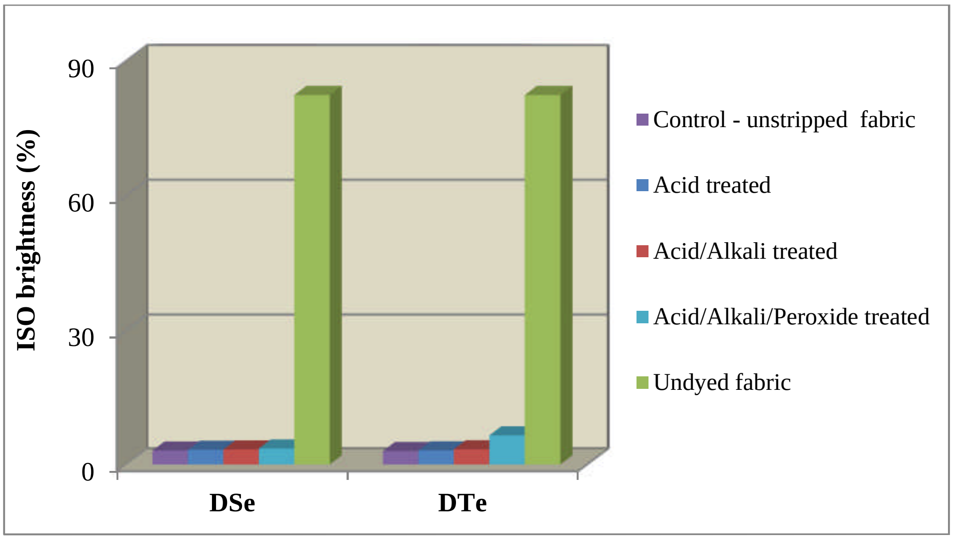


Figure 5.4.3 Comparison of the ISO brightness for the undyed and direct dyed cotton fabrics stripped in the sequential acid/alkali/peroxide treatments.

Further oxidative peroxide bleaching only increased the ISO brightness of the DSe sample to 3.6%, however the effect was slightly greater on the DTe sample resulting in a brightness of 6.5%. This was probably due to the reactive nature of the Solfix E (DSe) cationic fixing agent being more resistant to chemical treatment compared to the non-reactive Tinofix ECO (DTe) fixing agent.

5.4.2.1.4 Visual comparison of the direct dyed fabrics stripped in the sequential acid/alkali/peroxide method

Figure 5.4.4 visually compares the direct dyed samples treated in the acid/alkali/peroxide stripping method. The figure shows that the acid and the subsequent alkali treatment had no obvious effect on the direct dyed samples aftertreated with cationic fixing agents. Further oxidative peroxide treatment resulted in a slight colour change on the less reactive Tinofix ECO cationic fixing agent (DTe). The effect was however minimal on the highly reactive Solfix E cationic fixing agent (DSe).

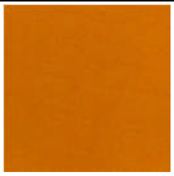
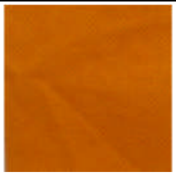
Colorant	**Dyed fabric**	**Acid treated**	**Acid/Alkali treated**	**Acid/Alkali/ Peroxide**	**Undyed fabric**
DSe					
DTe					

Figure 5.4.4 Visual appearance of direct dyed cotton fabrics following stripping with the sequential acid/alkali/peroxide treatments.

5.4.2.2 Effect of the sequential Acid/Dithionite/Peroxide treatment on the direct dyed cotton fabrics

Direct dyed fabrics aftertreated with cationic fixing agents were also stripped by using the sequential acid/dithionite/peroxide treatment and their colorimetric parameters were monitored and the results obtained are discussed below.

5.4.2.2.1 *Colour strength, K/S, of the direct dyed fabrics stripped in the sequential acid/dithionite/peroxide treatment*

The colour strength of the direct dyed fabrics treated in the acid/dithionite/peroxide dye stripping sequence are presented in Figure 5.4.5. As already detailed, the acid treatment only had a marginal effect on the *K/S*, but subsequent dithionite treatment significantly decreased the *K/S* of DSe and DTe samples to 3.1 and 0.5, respectively, compared to the *K/S* values of 18.5 and 17.7, respectively, of the acid only treated samples. The higher stripping effect of the dithionite treatment is thought to be due to the high reduction potential of the agent [56, 73] in conjunction with the PVP dye transfer inhibitor which could have prevented the redepositing of the reduced dye on the fibre surface. Additionally the higher treatment temperatures (80-100°C) used could have also aided in the dissociation of the complex formed between the dye and the cationic fixing agents. Shore reports the dissociation of the dye-cationic fixing agent in detergent solution at temperatures above 60°C [56].

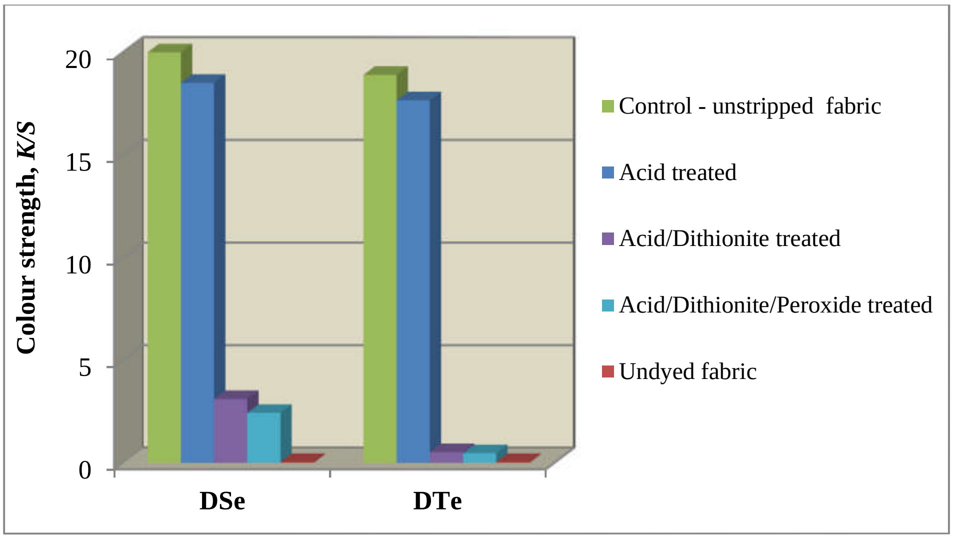


Figure 5.4.5 Changes in the colour strength for the undyed and direct dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatments.

Further oxidative peroxide treatment removed slightly more of the dye from the DSe sample resulting in a *K/S* of 2.4 which could be due to the peroxide removing the dye residues from the fibre surfaces. Surprisingly the treatment had a little effect on the non-reactive DTe treated fabric resulting in a *K/S* of 0.5, similar to that of the acid/dithionite only treated sample.

5.4.2.2.2 CIELAB colour difference, ΔE, of the direct dyed fabrics stripped in the sequential acid/dithionite/peroxide method

The CIELAB colour difference of the direct dyed samples treated in the sequential acid/dithionite/peroxide stripping method are presented in Figure 5.4.6. As already stated the acid treatment had little effect resulting in Δ*E* values of only 1.5 and 1.4 on DSe and DTe treated fabrics, respectively. Further alkaline dithionite treatment significantly increased the Δ*E*s of DSe and DTe samples to 39.9 and 62.5, respectively. This was again attributed to the strong reduction potential of the alkaline dithionite treatment together with the dye transfer inhibiting behaviour of the PVP polymer that was included in the dithionite stripping liquor.

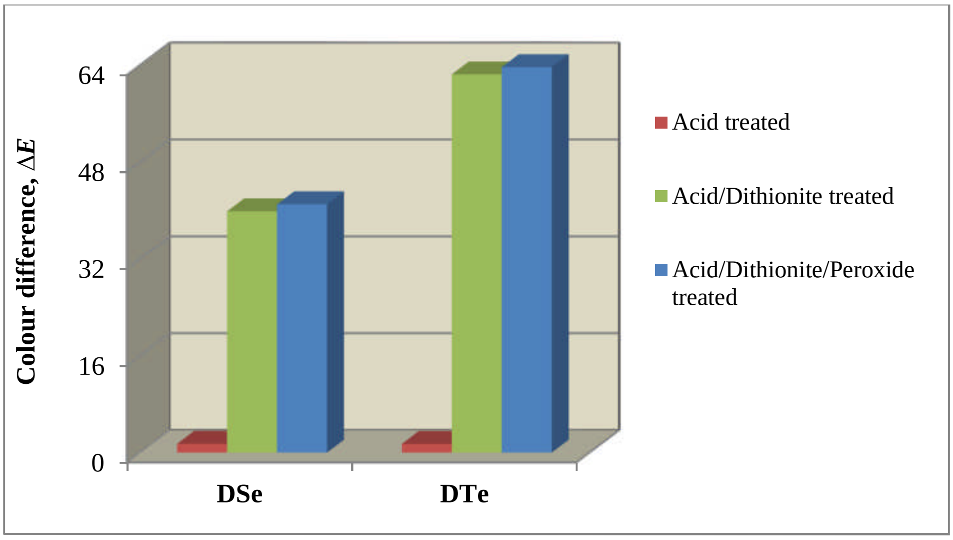


Figure 5.4.6 CIELAB colour difference for the direct dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatment.

Subsequent oxidative peroxide bleaching treatment resulted in a marginally greater colour change with Δ*E* values of 41.0 and 63.7 observed on DSe and DTe, respectively. The slightly lower Δ*E* observed on the DSe sample compared to that of the DTe sample was thought to be due to the higher reactivity properties of the Solfix E cationic fixing agent [207] imparting more resistant to stripping chemicals than the less reactive Tinofix ECO cationic fixing agent.

5.4.2.2.3 ISO brightness of the direct dyed fabrics stripped in the sequential acid/dithionite/peroxide method

Figure 5.4.7 presents the ISO brightness parameters for the direct dyed samples stripped in the sequential acid/dithionite/peroxide method. The acid treatment had an insignificant effect on the brightness of the aftertreated direct dyed samples resulting in brightness of 3.3% and 3.2% on DSe and DTe samples, respectively, compared to the original brightness of 3.1% and 3.0%, respectively. Subsequent dithionite treatment further increased the brightness to 21.4% and 39.8% for DSe and DTe fabrics, respectively, which was again explained by the dithionite agent reducing the dye-cationic complex, thereby freeing some of the dye from the fibre which was then removed by the stripping liquor. Further oxidative peroxide bleaching treatment had little effect resulting in brightness values of only 21.8% and 40.6% on DSe and DTe fabrics, respectively.

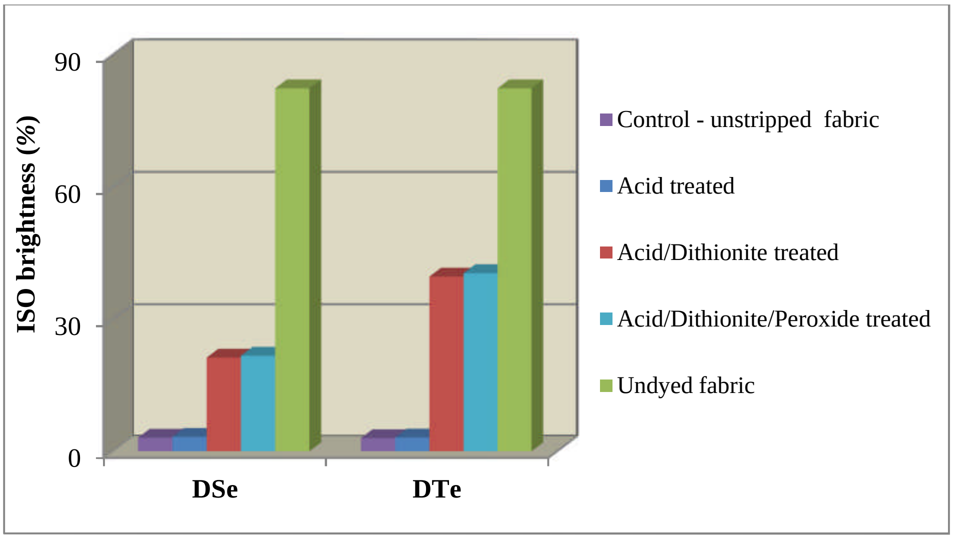


Figure 5.4.7 Comparison of the ISO brightness for the undyed and direct dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatments.

5.4.2.2.4 Visual comparison of the direct dyed fabrics stripped in the sequential acid/dithionite/peroxide method

Figure 5.4.8 visually compares the direct dyed cottons that were treated in the sequential acid/dithionite/peroxide stripping baths. The acid treatment had no apparent effect on the colour change of the aftertreated direct dyed fabrics. Subsequent dithionite treatment resulted in a significant colour change, the effect being more pronounced on the DTe samples aftertreated with Tinofix ECO cationic fixing agent compared to the DSe fabric which was aftertreated with Solfix E cationic fixing agent, perhaps indicating the slightly lower stability of the Tinofix ECO agent in the alkaline dithionite treatment. Further oxidative peroxide bleaching resulted in no obvious colour change with any of the aftertreated direct dyed cotton fabrics.

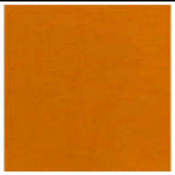
Colorant	**Dyed fabric**	**Acid treated**	**Acid/Dithionite treated**	**Acid/Dithionite /Peroxide**	**Undyed fabric**
DSe					
DTe					

Figure 5.4.8 Visual appearance of direct dyed cotton fabrics following stripping with the sequential acid/dithionite/peroxide treatments.

5.4.2.3 Comparison of the dye stripping methods on direct dyed fabrics

The stripping efficiencies of the sequential acid/alkali/peroxide and the sequential acid/dithionite/peroxide methods on the cationic aftertreated direct dyed cotton fabrics are compared in Figure 5.4.9. The sequential acid/alkali/peroxide method was less efficient in stripping the aftertreated direct dyed samples resulting in stripping efficiencies of only 27.2% and 56.1% on DSe and DTe samples, respectively. In contrast, the acid/dithionite/peroxide method stripped up to 88.7% and 97.5% of the direct dye from DSe and DTe fabrics, respectively.

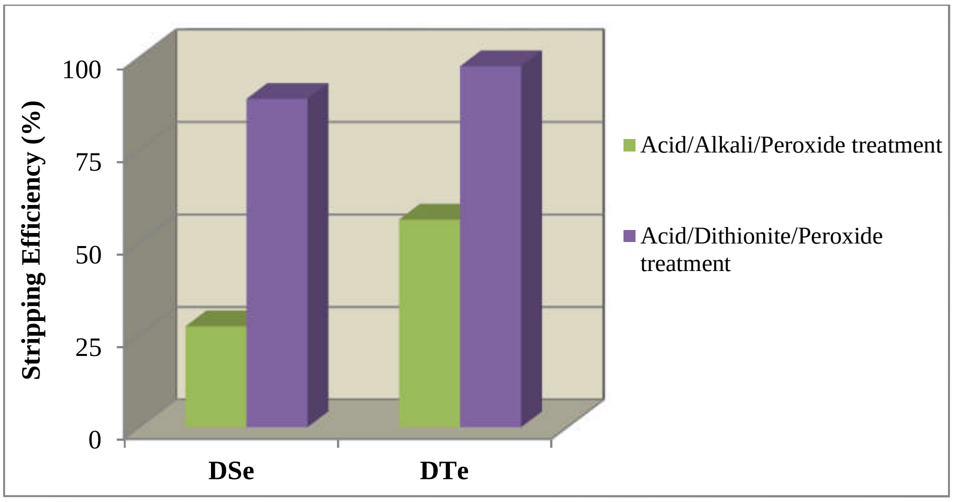


Figure 5.4.9 The Stripping efficiencies of the sequential acid/alkali/peroxide and the comparable sequential acid/dithionite/peroxide treatments on direct dyed cotton fabrics aftertreated with Solfix E (DSe) and Tinofix ECO (DTe).

5.5 STRIPPING OF PIGMENTS FROM COTTON FABRICS

Pigment printing is another important coloration technique that is used to produce multi-coloured effects and designs on textile substrates [52, 96]. The main difference between pigments and dyes is that, the structure of pigments has no solubilising groups making them water-insoluble [96]. They are therefore either applied on the surface of the fabric in the presence, or absence, of a thickening agent and a polymeric binder or incorporated into a polymer melt and extruded. With pigment printing or dyeing, on heat curing, usually through heated air, the binder attaches the pigments to the fibre surface, thereby imparting durability in terms of both wet and dry fastness.

Pigments were included in the scope of this study due to their many applications in the coloration of cotton substrates. Compared to dyeing, their application procedure is relatively simple, economical and requires less equipment for finishing purposes [96, 97]. The process can be combined with resin finishing in a single process, eliminating a process in production and hence reducing the overall production costs [78].

5.5.1 Experimental

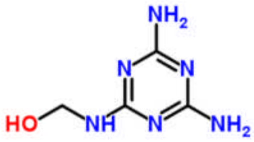
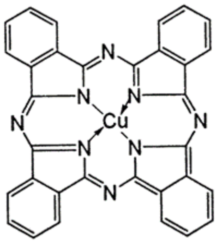
5.5.1.1 Materials and Chemicals

Scoured, bleached and mercerised cotton fabric described in Section 3.2 was used. Details of the pigments and printing auxiliaries used are presented in Tables 5.5.1 and 5.5.2. Due to confidentiality, the chemical structures of most of these chemicals were not disclosed.

Table 5.5.1 Pigments and auxiliaries used in this study

AGENT NAME	FUNCTION	SUPPLIER
Printofix Black T-M (BT)	Pigments	Archroma Co. Ltd
Printofix Blue T-P (BLT)		
Printofix Red T-N01 (RT)		
Printofix Binder 83	Binder	
Printofix Thickener CA	Thickening agent	
Printofix Fixing agent ZF	Fixing agent	
Lyoprint PFL	Formaldehyde-based crosslinking agent	Huntsman
Polymer PAC	Binder	Devan Chemicals Ltd

Table 5.5.2 Chemical properties of pigments and auxiliaries used in this study

Commercial Name	Chemical names/ Chromophore	Chemical structure	Reference
Lyoprint PFL	- Methanol[(4,6-diamino-1,3,5-triazin-2-yl)amino]; - Hydroxymethylmelamine		[208]
Printofix Black T-M	Carbon black	Unknown	Assumption
Printofix Blue T-P	Copper phthalocyanine e.g. C.I. Pigment Blue 15		Assumption
Printofix Red T-N01	Azo	Unknown	Assumption

5.5.1.2 Pigment Printing of cotton fabrics

Pigment printing of cotton fabrics was performed by a conventional screen printing technique [96] using recipes recommended by the suppliers with some modification on the type of binders and fixing agents used.

5.5.1.2.1 Stock paste preparation

Four sets of stock pastes were prepared while varying stock paste contents as shown in Table 5.5.3. Formulation-1 had no fixing agent while Formulation-2 was the standard stock paste containing both the Printofix binder and Printofix fixing agent. Formulation-3 contained both Printofix binder and Lyoprint PFL crosslinking agent while Formulation-4 used Polymer PAC binder. Water was added to each mixture to make a total of 100%.

Table 5.5.3 Stock paste recipes used in the study

Chemical name	**Formulations (% component)**			
	2 - without fixing agent	**1 - Printofix**	**3 - Lyoprint PFL**	**4 - Polymer PAC**
Ammonium hydroxide	1	1	1	1
Printofix Binder 83	24	24	24	-
Printofix fixing agent	-	1.5	-	-
Printofix thickener	1.2	1.2	1.2	1.2
Lyoprint PFL	-	-	1.5	-
Polymer PAC	-	-	-	2
Water	73.8	72.3	72.3	96.8
Total	**100**	**100**	**100**	**100**

5.5.1.2.2 Print paste preparation and printing process

After mixing of the stock paste, 8% of the pigment was added to 92% of the stock paste to make a print paste which was then applied on a cotton fabric using a screen print. The printed fabrics were allowed to dry in air prior to curing for 5 minutes at 150°C temperature in a Mathis Baker. The printed cured samples were then washed with warm water to remove any chemical residues followed by air-drying.

5.5.1.3 Stripping of pigment prints from cotton fabrics

Stripping of pigments from cotton fabrics was done using both sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods described in section 3.4 of this thesis.

5.5.2 Results and Discussion

In this study three water-based pigments, namely: Printofix Black T-M (BT), Printofix Blue T-P (BLT) and Printofix Red T-N01 (RT) were applied to cotton while varying the printing auxiliaries added into the paste. Printed fabrics were then stripped in both the sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments. Colorimetric parameters of the stripped and unstripped fabrics were monitored by assessing the colour strength, *K/S*, CIELAB colour difference ΔE and ISO brightness. Changes in the surface morphology of the cottons was also analysed by using the Scanning Electron Microscopy (SEM) technique. The results obtained are discussed below.

5.5.2.1 The effect of varying the print paste content on the colour strength, K/S, of the pigment prints

Figure 5.5.1 presents the effect of different types of binders and fixing agents on the colour strength of the printed cotton fabrics. It is clear from the figure that the colour strength of the three pigments had a similar trend, with the highest *K/S* of 19.4 obtained on Printofix Blue sample printed by using a traditional print paste. In contrast, both BT and RT printed fabrics showed no significant difference in the *K/S* values of the fabrics printed with print pastes containing varying types of printing auxiliaries. The relatively higher *K/S* value observed on the BLT printed sample was a result of the structure of the Printofix Blue pigment (presumed to be copper phthalocyanine) which is efficiently localised on the fibre surface [139] by the binder and fixing agents. It is also clear that, the lowest *K/S* values of only 9.6 and 9.2 were obtained when polymer PAC binder was used with Printofix BLT and RT treated fabrics, respectively. This was probably due to the weak binding reaction of the polymer PAC binder resulting in less pigments being bound on the fibre surface. A slightly greater *K/S* of 13.7 was however observed with pigment BT treated fabric indicating the possible better interaction between the black pigment/binder and the fibres. The Printofix Black pigment used in this study was presumed to be a carbon black structure, an organic coloured pigment which has a high refractive index resulting from its compact atomic arrangement of its lattice structure [75]. This could have resulted in the higher colour strength observed on the BT printed fabrics.

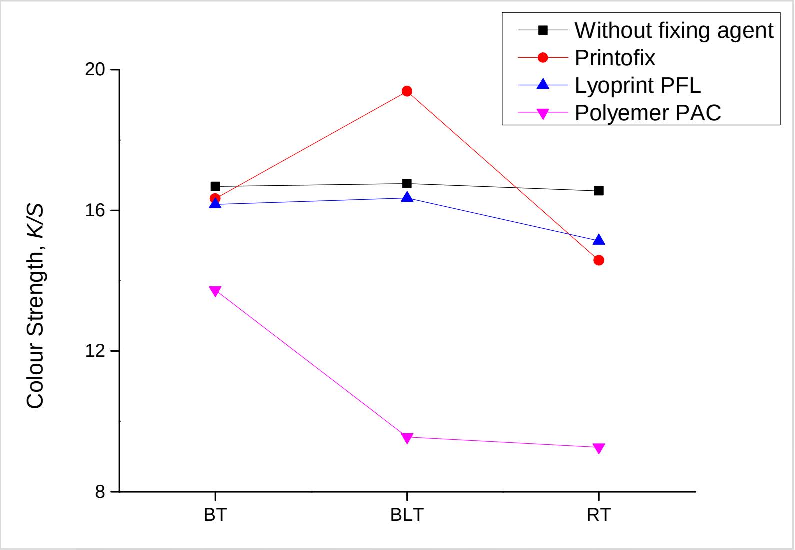


Figure 5.5.1 The effect of varying print paste content on the colour strength of the printed fabrics

5.5.2.2 The effect of the stripping methods on Printofix Black (BT) printed fabrics

In this study a cotton fabric printed by using Printofix Black (BT) pigment, while varying the binder and fixing agent, was stripped by both sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments. Results for changes in colorimetric parameters are discussed below.

Figure 5.5.2 compares the colour strength (*K/S*) of the BT printed fabrics treated in the sequential acid/alkali/peroxide and acid/dithionite/peroxide treatment baths where significant amounts of the pigment was removed from the fabrics resulting in *K/S* values of 0.4 and 2.9, respectively, for the fabrics printed with the Lyoprint PFL crosslinking agent. This was anticipated to be due to the polymer binder weakly crosslinking with the fibres, thereby allowing the chemical agents to attack the binder film and free most of the pigments from the fabric surface. Additionally the formaldehyde present in the Lyoprint PFL agent could have been released during processing [209] again supporting the stripping process. The treatments also stripped large quantities of the BT pigments applied in the presence of the Polymer PAC binder resulting in *K/S* of 1.5 and 0.9 on the fabrics stripped by the acid/alkali/peroxide and acid/dithionite/peroxide baths, respectively. This was again thought to be due to weaker crosslinking properties of the Polymer PAC binder, allowing easier access for the stripping chemicals to the pigments.

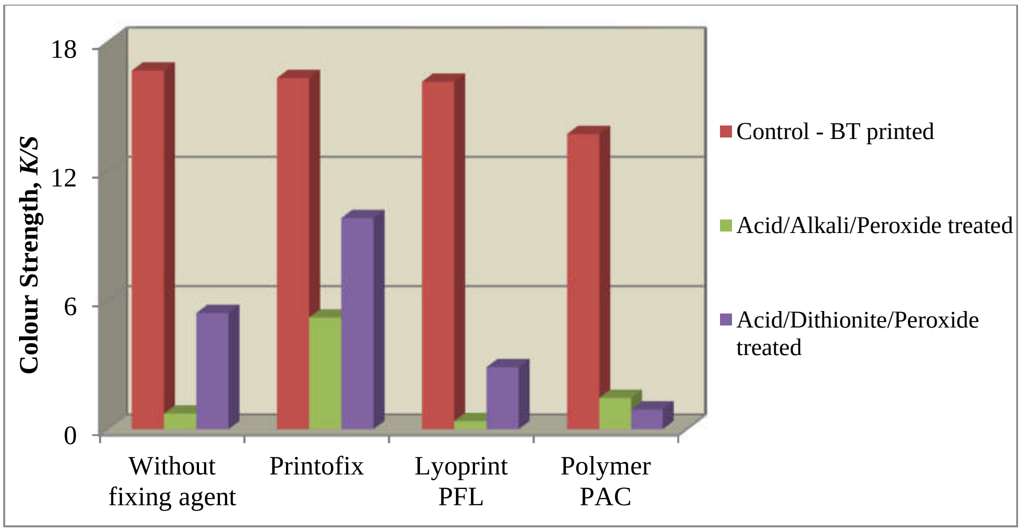


Figure 5.5.2 The colour strength parameters for the Printofix Black printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

The two stripping methods were however less effective on BT fabric printed in the presence of both Printofix binder and fixing agent resulting in *K/S* values of only 5.2 and 9.8 on samples stripped by the sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments, respectively, compared to *K/S* values of 16.3 for the printed unstripped samples. This was due to the strong crosslinking properties of both the binder and fixing agents which could resist chemicals accessing the pigments enclosed within the binder film. Additionally the carbon black structure of the Printofix Black pigment can withstand both high temperature and chemical treatment [74]. This temperature and chemical resistant behaviour of the pigment could have also contributed to lower colour/pigment being stripped from the cotton fabrics.

The sequential acid/alkali/peroxide method removed significant amounts of pigment from the BT pigmented samples that were printed without fixing agents resulting in a *K/S* of 0.7 compared to that of 5.4 observed when the printed fabric was stripped by the acid/dithionite/peroxide method. This could be due to both acid and alkali working together in hydrolysing the unfixed polymeric film, which was not able to be achieved when using the sequential acid/dithionite/peroxide treatment.

Figure 5.5.3 compares the CIELAB colour differences of the BT printed fabrics stripped by the sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments where a high ΔE of 51.6 was again obtained with the acid/alkali/peroxide treatment of the fabric printed with the Lyoprint PFL crosslinking agent. This was followed by the fabrics printed without fixing agents, with a ΔE of 43.4, then those printed in presence of a Polymer PAC binder, where a ΔE of 32.4 was observed. Both treatments had lower effects on fabrics printed in the presence of both Printofix binder and fixing agent which is again due to the strong crosslinked film enclosing the pigment particles allowing them to adhere onto the fibre surfaces.

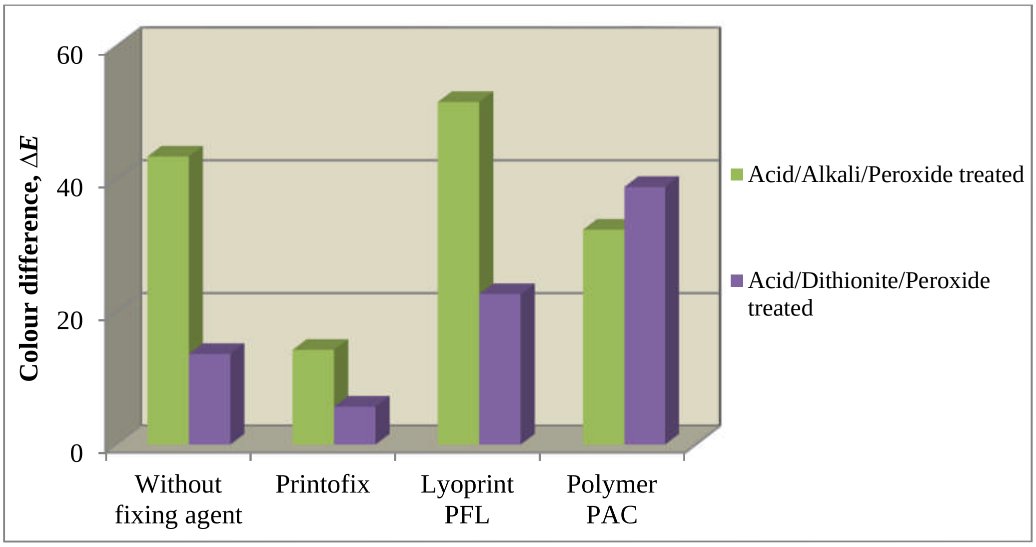


Figure 5.5.3 CIELAB colour differences for the Printofix Black printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

A similar trend was observed with the ISO brightness values of the BT printed fabrics stripped in both acid/alkali/peroxide and acid/dithionite/peroxide baths (Figure 5.5.4) where higher brightness values were again observed with the acid/alkali/peroxide treatment of the BT samples that were printed in the presence of Lyoprint PFL followed by those printed without fixing agents. Both methods stripped a relatively high amount of pigment from BT fabrics printed in the presence of a Polymer PAC binder resulting in brightness values of 21.8% and 28.5%, respectively. However fabrics printed in the presence of both Printofix binder and fixing agent were resistant to the two stripping treatments resulting in brightness values of only 8.1% and 4.6% for acid/alkali/peroxide and acid/dithionite/peroxide, respectively.

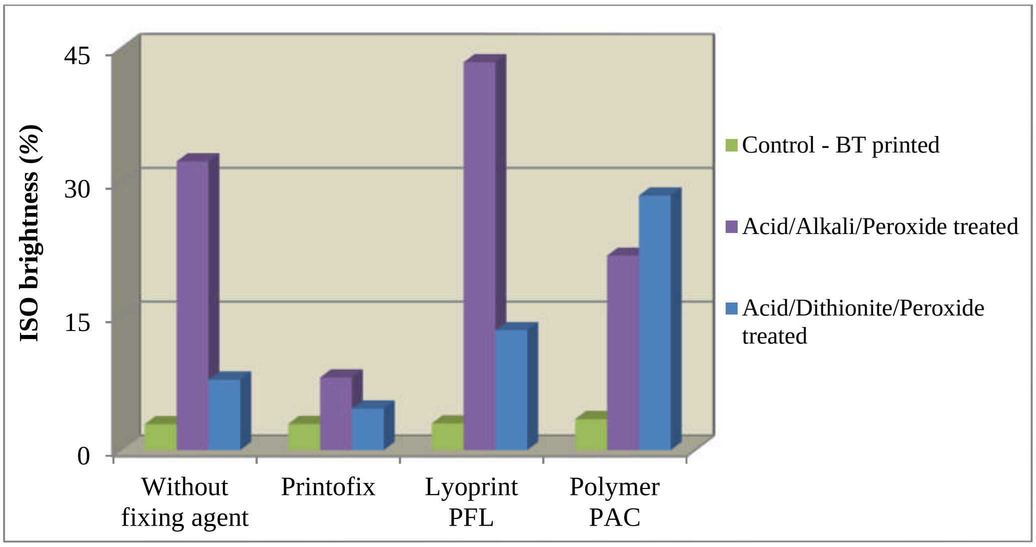


Figure 5.5.4 The ISO brightness for the Printofix Black printed cotton fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

5.5.2.3 The effect of dye stripping methods on Printofix Blue (BLT) printed fabrics

Cotton fabrics were also printed by using Printofix Blue (BLT) pigments while varying the types of binder and fixing agent used and were also stripped in both sequential acid/alkali/peroxide method and in the alternative sequential acid/dithionite/peroxide treatment. Figure 5.5.5 presents the colour strength, *K/S*, for the BLT printed fabrics that were stripped in both sequential acid/alkali/peroxide and in acid/dithionite/peroxide methods. It can be seen that both methods stripped large amounts of the pigment from the BLT cotton that had been printed in the presence of a Polymer PAC binder, resulting in *K/S* values of 0.06 and 0.03 on the acid/alkali/peroxide and acid/dithionite/peroxide treated samples, respectively, compared to the original *K/S* of 9.6. This was again thought to be due to the weakly crosslinking mechanism of the binder, allowing easier chemical attack of the film and subsequent pigment removal by the stripping agents.

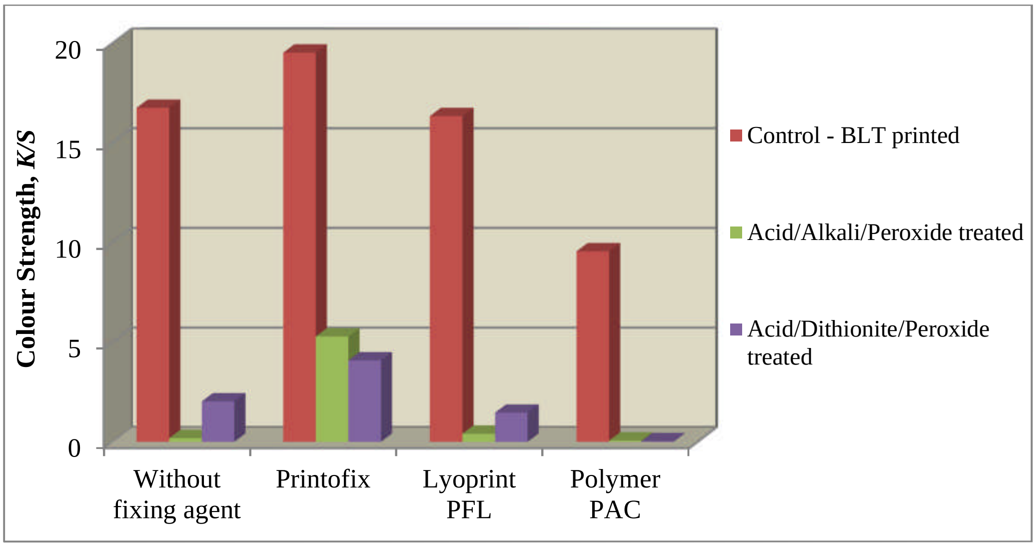


Figure 5.5.5 The colour strength parameters for the Printofix Blue printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

The sequential acid/alkali/peroxide treatment also stripped significant amounts of pigment from the BLT fabrics printed without fixing agents and those printed in the presence of a Lyoprint PFL crosslinking agent resulting in *K/S* values of 0.2 and 0.4, respectively, compared to a *K/S* of 16.8 for the original printed fabrics. The effect was however lower on the fabrics stripped by the sequential acid/dithionite/peroxide method resulting in *K/S* values of only 2.0 and 1.5 for fabrics printed without fixing agents and those printed in the presence of the Lyoprint PFL binder, respectively. The higher stripping levels attained by using the sequential acid/alkali/peroxide route could be due to the combined hydrolysing effects of the acid and alkali on the polymer/pigment film. This was not possible when using the acid/dithionite/peroxide baths.

Both acid/alkali/peroxide and acid/dithionite/peroxide methods could not completely strip the pigment from BLT printed fabrics that had been treated in the presence of both Printofix binder and fixing agent resulting in *K/S* values of only 5.3 and 4.1, respectively, compared to the original *K/S* of 19.5. This was again presumed to be due to the combined power of the binder and fixing agents in protecting the film locating the pigment particles at the fibre surface. In addition the copper phthalocyanine structure of the Printofix Blue pigment used in this study has a highly stable molecular structure that is resistant to chemical attack [74, 75, 78]. This could have also contributed to less colour/pigment being stripped from the fabrics.

Figure 5.5.6 compares the colour difference results for the BLT fabrics stripped by the sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods. Both methods removed significant amounts of pigment from the BLT printed fabric that were printed in the presence of a Polymer PAC resulting in Δ*E* values of 59.6 and 63.7, respectively. The acid/alkali/peroxide method also stripped large amounts of pigment from the samples that were printed without fixing agents resulting in a Δ*E* of 57.4 compared to that of 27.3 observed on the samples stripped in the acid/dithionite/peroxide method. However both methods were not able to strip pigment from the BLT samples printed in the presence of both Printofix binder and fixing agent resulting in Δ*E* of only 15.6 and 19.4 for acid/alkali/peroxide and acid/dithionite/peroxide treatments, respectively.

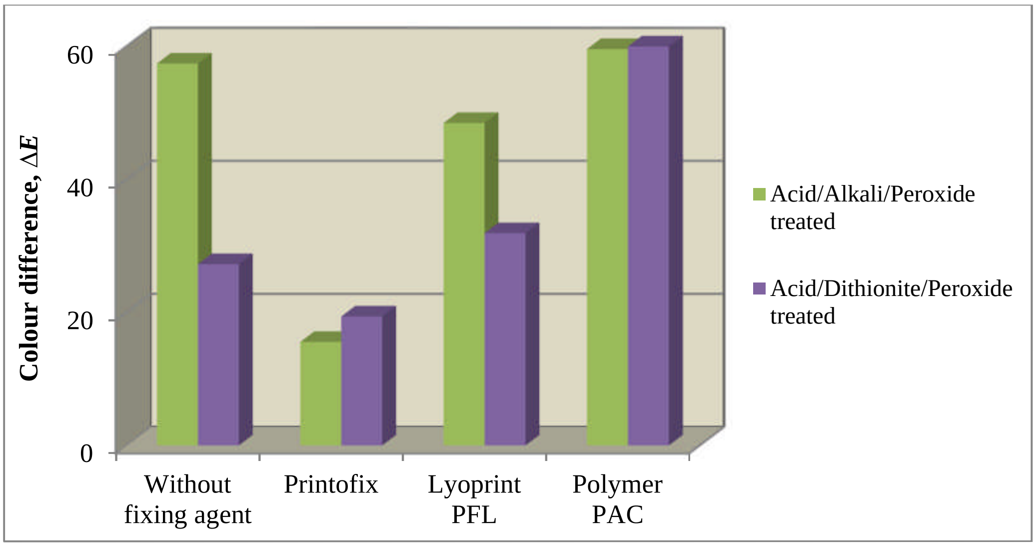


Figure 5.5.6 CIELAB colour difference for the Printofix Blue printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

Analysis of the ISO brightness of the BLT printed stripped samples (Figure 5.5.7) also showed higher brightness when the samples printed in the presence of the Polymer PAC binder were stripped in both sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments resulting in brightnesses of 83.1% and 82.7%, respectively, compared to the original brightness of 32.6%. Again lower amounts of pigment were removed from the samples that were printed in the presence of both Printofix binder and fixing agent resulting in brightnesses of only 29.6% and 34.1% on acid/alkali/peroxide and acid/dithionite/peroxide treatments, respectively.

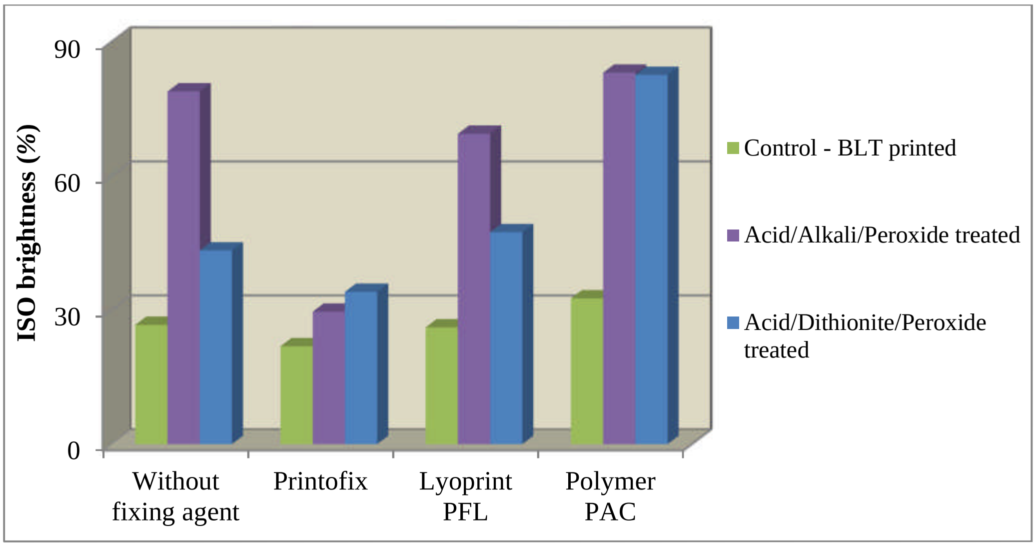


Figure 5.5.7 The ISO brightness for the Printofix Blue printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

5.5.2.4 The effect of dye stripping methods on Printofix Red (RT) printed fabrics

In this study the Printofix Red (RT) pigment was also applied to cotton fabrics while varying the binder and fixing agent used for printing. The printed fabrics were then stripped in both sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments and their efficacies evaluated. Figure 5.5.8 compares the colour strength, *K/S*, data for the RT printed fabrics stripped by the sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide treatments. It is clear that the two methods stripped significant amounts of pigment from the fabrics with the acid/dithionite/peroxide completely stripping the Printofix Red pigments, resulting in a *K/S* of 0.02, even on the fabrics that were printed in the presence of both the Printofix binder and fixing agent. Similarly the acid/alkali/peroxide baths stripped large amounts of pigment from the fabrics, although the effect was less obvious on the cotton printed in the presence of the Printofix binder and fixing agent resulting in a *K/S* of only 5.4.

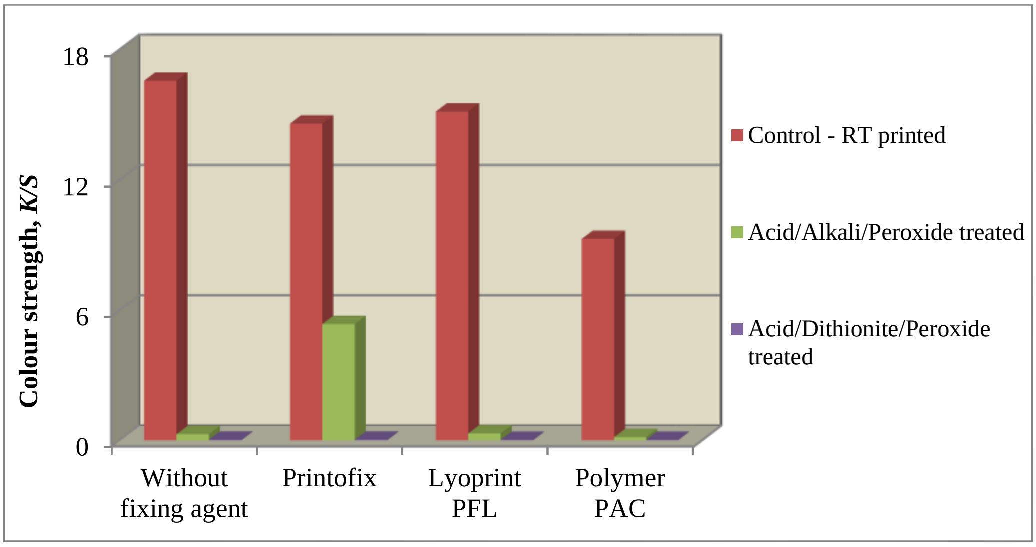


Figure 5.5.8 The colour strength parameters for the Printofix Red printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

The Printofix Red pigment used in this study was presumed to be based on an azo structure. Pigments of these chemical structures are reported to be sensitive to chemical agents [99] due to their low molecular size, the nature of the chromophore and the fact that their intermolecular interactions in the crystal structures is only through the van der Waals' attraction forces [75]. This could be why the stripping agents could relatively easily remove the colour/pigment from the RT printed fabrics.

Figure 5.5.9 presents the CIELAB colour differences for the RT samples stripped by the sequential acid/alkali/peroxide and acid/dithionite/peroxide baths. It can be seen that higher colour differences were observed when the RT printed samples were stripped by the sequential acid/dithionite/peroxide method resulting in a ΔE of approximately 86.0 on fabrics printed without the fixing agents. Similarly the acid/alkali/peroxide treatment stripped relatively large quantities of pigment from all samples resulting in a ΔE of 62.4. The effect was however lower on the RT fabrics printed in the presence of both Printofix binder and fixing agents resulting in a ΔE of only 15.4, indicating the stability of both the binder and fixing agents to the acid/alkali/peroxide stripping sequence.

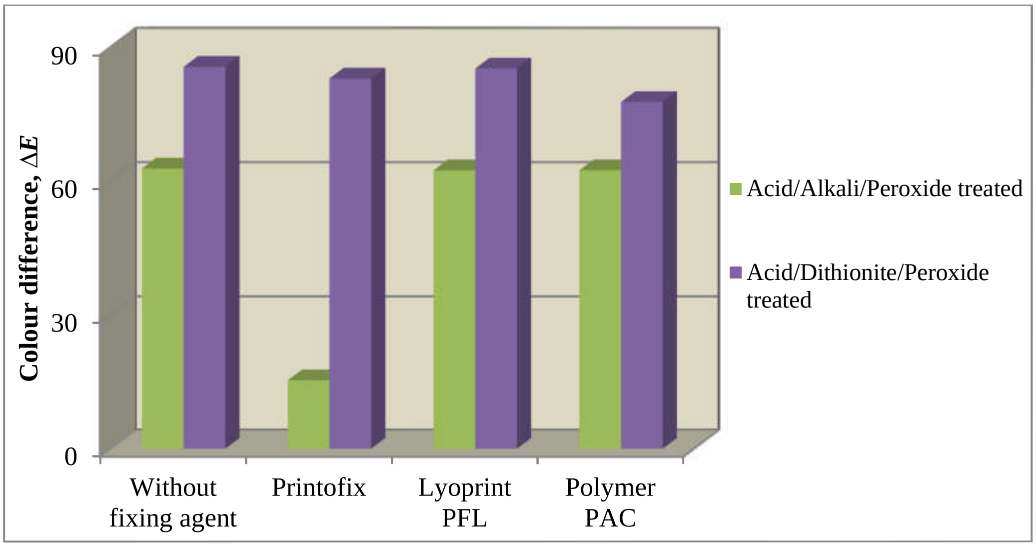


Figure 5.5.9 Colour difference for the Printofix Red printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

Analysis of the ISO brightness (Figure 5.5.10) also showed higher brightness values when the RT samples were stripped by the sequential acid/dithionite/peroxide treatment resulting in brightness of approximately 86% on all fabricss. The sequential acid/alkali/peroxide treatment also resulted in brightness of over 50%, although the effect was again lower on samples that were printed in the presence of both Printofix binder and fixing agent resulting in brightness value of only 9.9%.

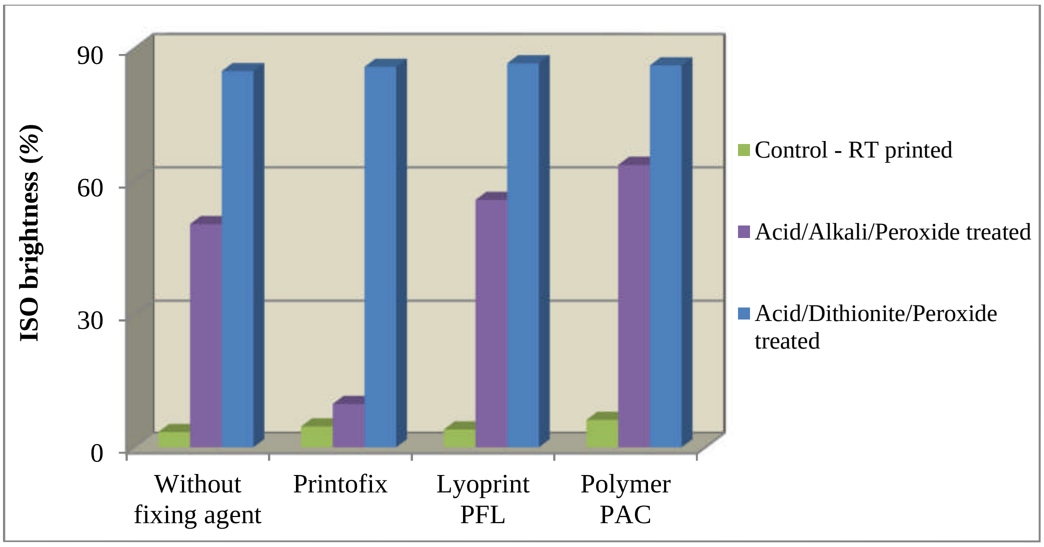
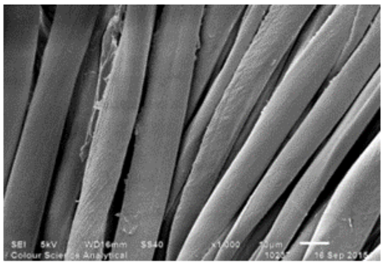


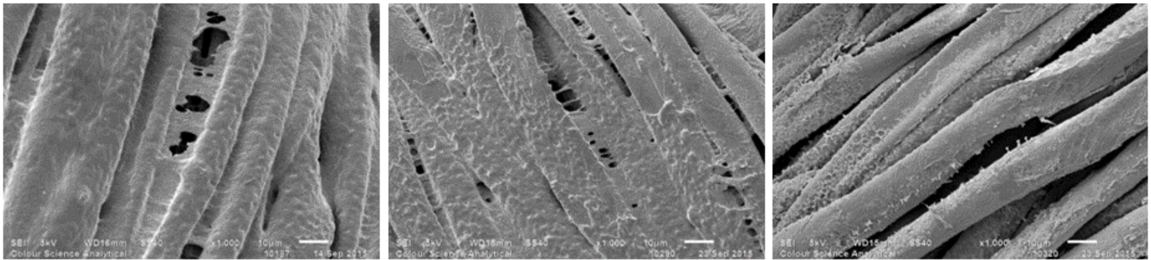
Figure 5.5.10 ISO brightness for the Printofix Red printed fabrics stripped by either sequential acid/alkali/peroxide or acid/dithionite/peroxide treatments.

5.5.2.5 The effect of the sequential Acid/Dithionite/Peroxide treatment on the surface morphology of the pigment printed cotton fabrics

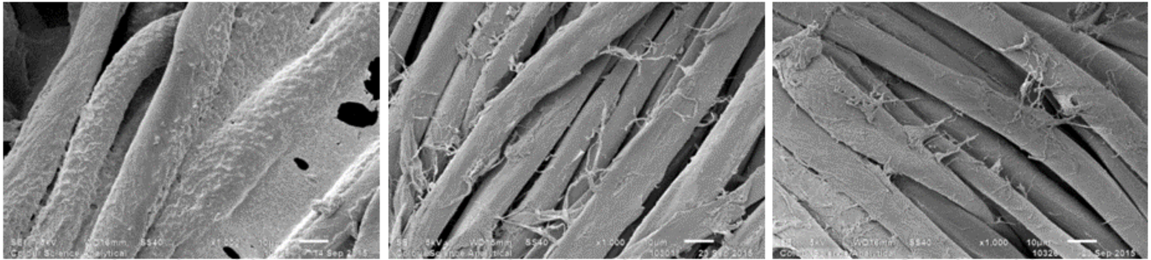
The surface topography of the unprinted, printed and printed-stripped cotton fabrics were characterised by SEM. Only samples that were stripped by the sequential acid/dithionite/peroxide method were analysed due to the overall high stripping efficiency of the method and results are shown in Figures 5.5.11 to 5.5.13. It can be seen that after printing in the presence of the Printofix binder and fixing agent (‘micrograph a’) large amounts of pigment particles were deposited on the fibre surfaces with all images showing fibres covered with a film formed due to the pigment/binder/fibre interaction. The film was more apparent with the Printofix Black (Figure 5.5.11) and Printofix Blue (Figure 5.5.12) printed fabrics compared to the Printofix Red printed fabric (Figure 5.5.13) which could be due to the different chemical structures/size of these pigments.



Before Printing



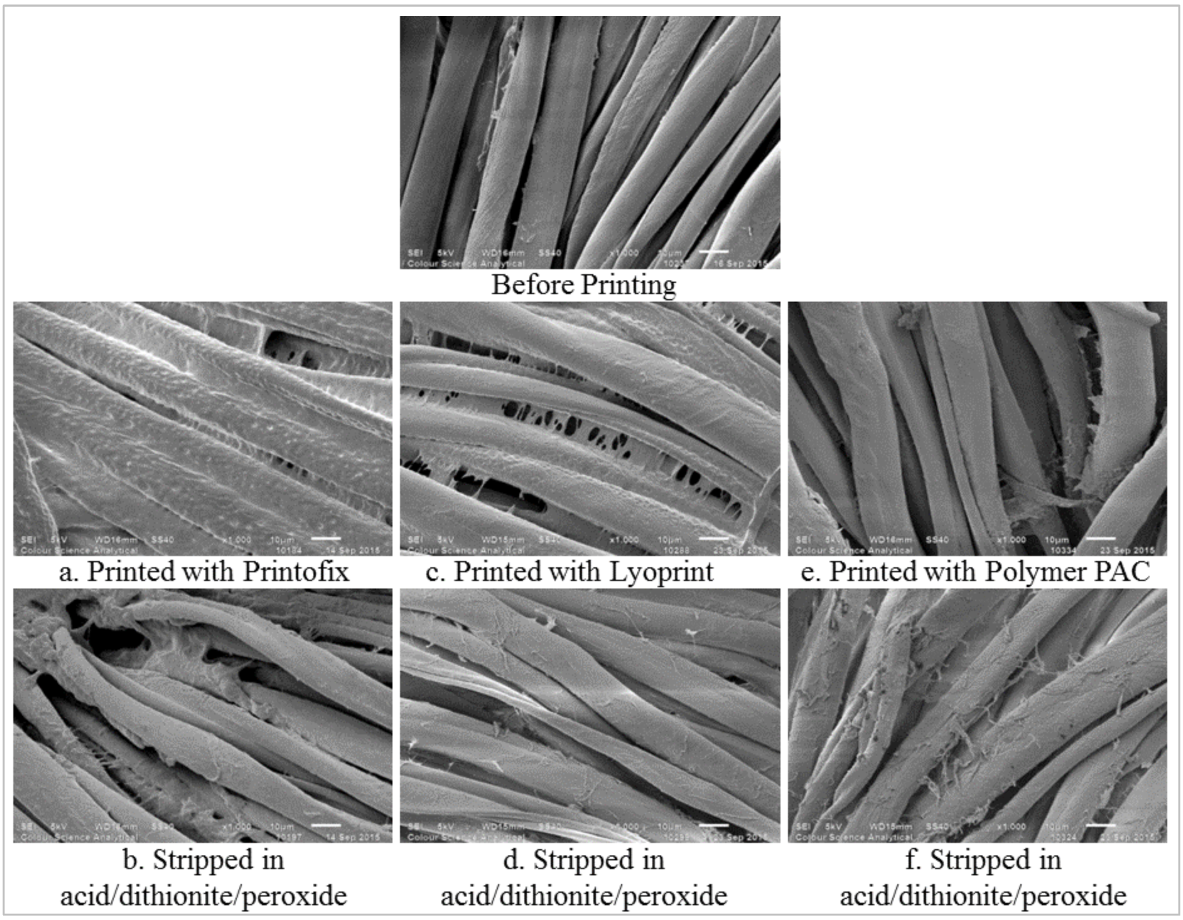
a. Printed with Printofix c. Printed with Lyoprint e. Printed with Polymer PAC



b. Stripped in acid/dithionite/peroxide d. Stripped in acid/dithionite/peroxide f. Stripped in acid/dithionite/peroxide

Figure 5.5.11 SEM micrographs of cotton fabrics printed with Printofix Black pigment then stripped in the sequential acid/dithionite/peroxide treatments.

The structures of the pigments used were thought to be carbon black, copper phthalocyanine and azo-based pigments for the Black, Blue and Red colorants, respectively, which may interact differently with the binder and the fibres. The subsequent sequential acid/dithionite/peroxide treatment of the printed fabrics (‘micrograph b’) stripped almost all the films and pigments from fibre surfaces with only minor traces of the binder remaining on the fibre surfaces. The effect was especially obvious on the azo-based Printofix Red printed fabrics (Figure 5.5.13) where a significant amount of binder was removed from the materials.


Before Printing

a. Printed with Printofix

c. Printed with Lyoprint

e. Printed with Polymer PAC

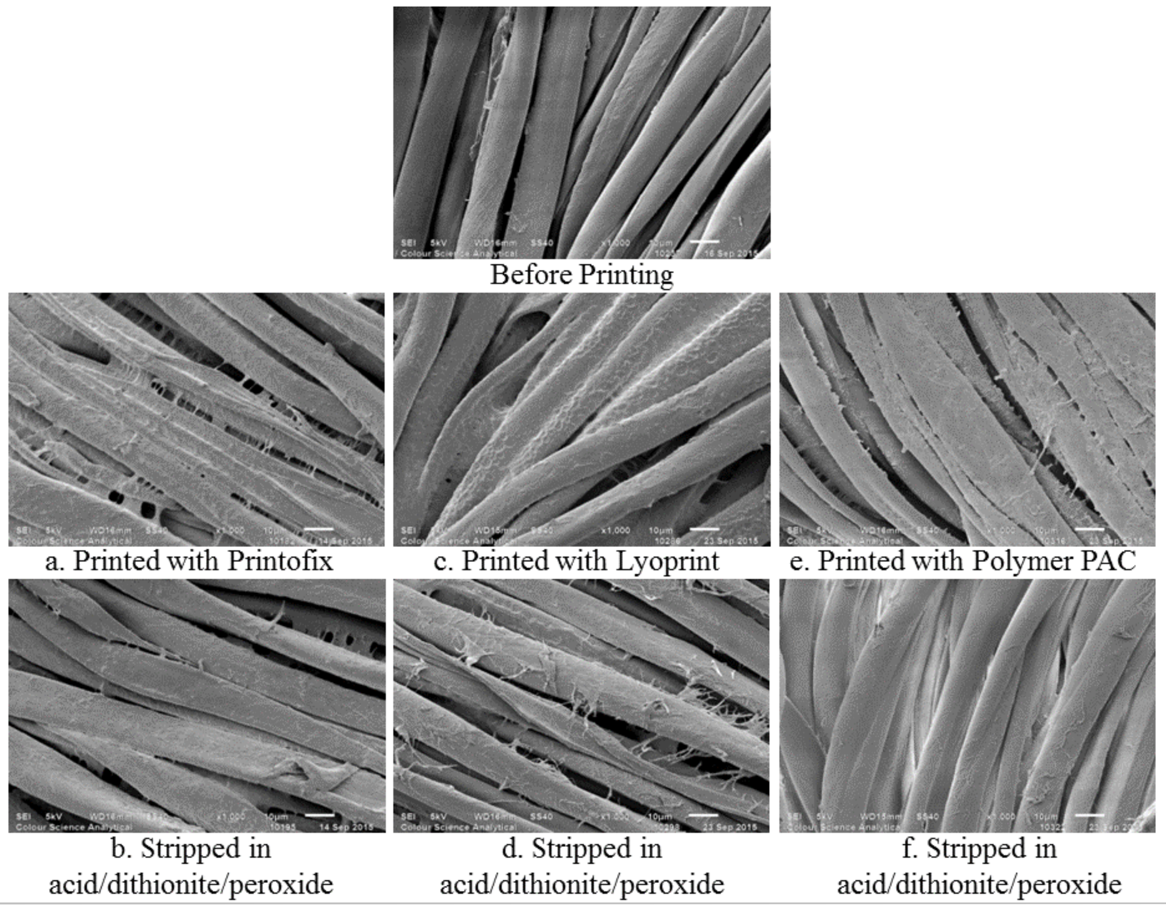
b. Stripped in acid/dithionite/peroxide

d. Stripped in acid/dithionite/peroxide

f. Stripped in acid/dithionite/peroxide

Figure 5.5.12 SEM micrographs of cotton fabrics printed with Printofix Blue pigment then stripped in the sequential acid/dithionite/peroxide treatments.

When Lyoprint PFL was used as the binder, only moderate crosslinking was observed on all the fabrics, as confirmed by the SEM micrographs (‘micrograph c’) of the printed samples. Microscopic analysis also showed large amounts of the binder and pigment was being removed from the cotton fibres after the acid/dithionite/peroxide treatment ('micrograph d') leaving only low levels of residual binder film on the surface of the fibre. A similar effect was also observed when printing was performed in the presence of the polymer PAC binder ('micrograph e') which was again presumed to be due to the weak crosslinking properties of the binder resulting in less pigment/binder/fibre interaction and only small amounts of pigment deposited on all three printed fabrics. Again, the acid/dithionite/peroxide treatment of the printed fabrics ('micrograph f') stripped large amounts of the binder and pigments leaving only small amounts of pigment and residual binder film on the fibre surfaces. The effect was clearly visible on fabric printed with Printofix Red pigment (Figure 5.5.13), which is again thought to be due to the stripping chemicals destroying not only the binder film but also the less chemically resistant azo chromophore.



Before Printing

a. Printed with Printofix

c. Printed with Lyoprint

e. Printed with Polymer PAC

b. Stripped in acid/dithionite/peroxide

d. Stripped in acid/dithionite/peroxide

f. Stripped in acid/dithionite/peroxide

Figure 5.5.13 SEM micrographs of cotton fabrics printed with Printofix Red pigment then stripped in the sequential acid/dithionite/peroxide treatments.

5.5.3 Summary

In this section the effect of the acid/alkali/peroxide and acid/dithionite/peroxide stripping treatments on pigments applied to cotton fabrics in the presence of various types of binders and fixing agents was investigated. It was established that the fabrics that were printed in the presence of both Printofix binder and fixing agents had the highest colour strength and were highly resistant to the two stripping treatments. However application of both Lyoprint PFL and Polymer PAC resulted in moderate colour strength and were more sensitive to the stripping methods.

It was also established that the acid/dithionite/peroxide treatment was particularly effective on the fabrics printed with the Printofix Red pigment, as the treatment removed almost all the colorant and binder from the printed fabrics. The effect was however moderate on the fabrics printed with Printofix Black and Printofix Blue pigments. This was thought to be due to the greater chemical sensitivity of the azo chromophore present in the Printofix Red pigment compared to highly resistant carbon black and copper phthalocyanine structures of the Printofix Black and Blue pigments, respectively. The effects were also confirmed by the analysis of micrographs obtained using the SEM imaging technique.

5.6 STRIPPING OF COLORANTS FROM POST-CONSUMER GARMENTS

The overall increased clothing consumption by consumers in conjunction with the increasing number of fast fashion (characterised by lower costs and clothing with short life spans) seasons has led into a significant increase in waste clothing generation [9]. Since most landfill areas are currently reaching their full capacity [13] and the cost of dumping waste in landfill is also increasing [44], the biggest challenge resulting from this scenario is keeping up with the rate of disposing end-of-life clothing. Recycling of the waste clothing and reuse of the recycled materials as a feedstock for Lyocell fibre regeneration is among the potential ways of reducing the amount of waste clothing sent to landfill. However the presence of any colorants and crosslinking such as those from dye-fibre bonds and finishing agents may prevent the possibility of further processing of these materials for fibre regeneration. These impurities and crosslinks need to be removed prior to fibre dissolution and subsequent material extrusion and new fibre regeneration. In this section the efficiencies of the developed acid/alkali/peroxide and acid/dithionite/peroxide colorant stripping treatments were assessed in terms of their effect of stripping dyes and other impurities from end-of-life garments for the purpose of purifying and preparing the recycled waste garments for Lyocell fibre regeneration.

5.6.1 Experimental

5.6.1.1 Materials

Three ‘first’ generation, 100% cotton garments were used in this study and consisted of denim jean, a black T-shirt and a blue shirt, all obtained from an Oxfam charity shop in Leeds. These garments were selected due to their common use in people’s daily life.

5.6.1.2 Stripping of colorants from the fabrics

Prior to stripping, non-fabric materials such as zippers were removed from the garments using a pair of scissors. Samples were then washed in a domestic washing machine to remove any dirt and were then followed by air drying. Stripping of the colorants from the garments was then performed as described in Section 3.4.

5.6.2 Results and Discussion

In this study three post-consumer garments, namely: T-shirt, denim and shirt were stripped by both the sequential acid/alkali/peroxide and acid/dithionite/peroxide methods in order to assess the efficiency of the methods in stripping colorants from post-consumer garments for the purpose of purifying and preparing materials for new fibre regeneration through the Lyocell process. The colorimetric parameters of the samples were monitored by observing changes in colour strength, *K/S*, CIELAB colour difference, ΔE and ISO brightness.

5.6.2.1 The effect of the sequential acid/alkali/peroxide treatment on the post-consumer garments

The post-consumer garments were stripped by the hydrolytic action of the sequential acid and alkali treatments followed by oxidative bleaching with hydrogen peroxide. Changes in colorimetric parameters of the samples are discussed below.

5.6.2.1.1 Colour strength (K/S) of the post-consumer garments stripped in the sequential acid/alkali/peroxide method

Figure 5.6.1 presents the colour strength for the post-consumer garments treated by sequential acid/alkali/peroxide stripping method. Acid treatment slightly decreased the *K/S* of the fabrics to 18.3, 31.3 and 9.6 for the denim, T-shirt, and shirt, respectively, compared to the original *K/S* of 20.6, 33.2 and 10.3, respectively. Further alkali treatment significantly decrease the *K/S* of the fabrics to 6.9, 2.0 and 4.0 on the denim, T-shirt and shirt, respectively. Subsequent oxidative hydrogen peroxide bleaching further removed colour from the T-shirt resulting in a *K/S* of 0.2. The treatment also removed a significant amount of dye from the denim and shirt fabrics resulting in *K/S* values of 3.9 and 1.7, respectively. From these results it was established that the black colour on a T-shirt was due to an azo-based reactive dye while the blue shirt was dyed with an anthraquinone-based vat dye. The azo dye chromophores are reported to be highly sensitive to most chemical agents while both anthraquinone and indigo chromophores are highly resistant to chemical treatments [56, 203].

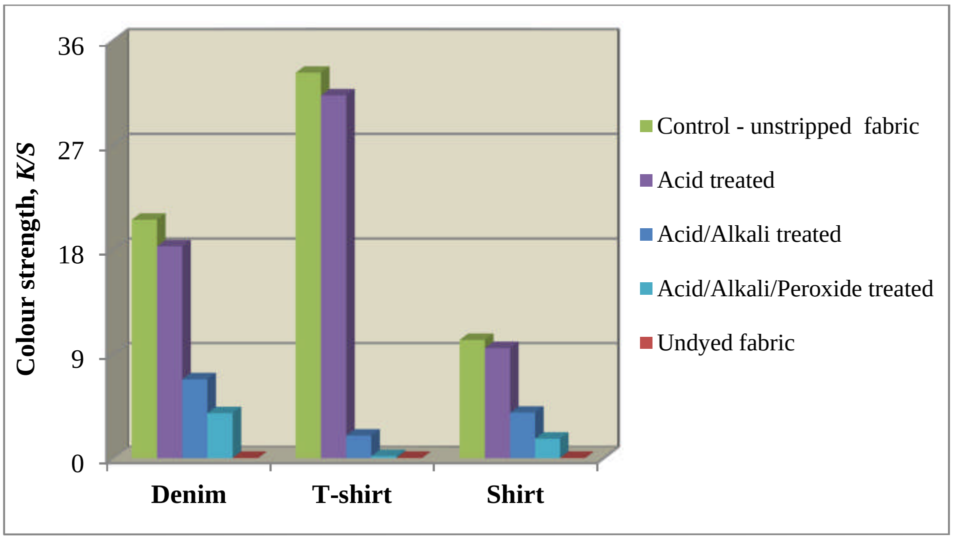


Figure 5.6.1 The colour strength parameters of the post-consumer garments stripped by the sequential acid/alkali/peroxide treatments.

5.6.2.1.2 CIELAB colour difference (ΔE) of the post-consumer garments stripped in the sequential acid/alkali/peroxide method

Figure 5.6.2 presents the CIELAB colour difference results for the post-consumer garments stripped by the sequential acid/alkali/peroxide treatments. The acid treatment had the least effect on the fabrics resulting in ΔEs of 1.4, 0.4, and 0.9 on the denim, T-shirt and shirt, respectively.

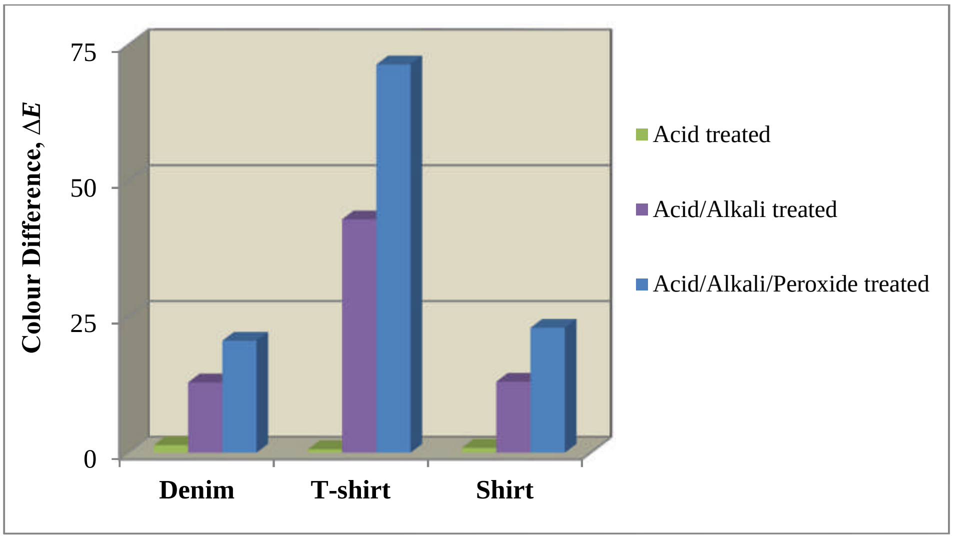


Figure 5.6.2 CIELAB colour difference for the post-consumer garments stripped in the sequential acid/alkali/peroxide treatments.

Further stripping of the fabrics in hot alkaline solution removed more colorant resulting in ΔEs of 12.9, 42.9 and 13.0 on the denim, T-shirt and shirt, respectively. Subsequent oxidative peroxide bleaching also removed greater amounts of colorant from the T-shirt resulting in a ΔE of 71.4. The effect was however slightly lower on the other two materials resulting in ΔEs of only 20.5 and 22.9 on denim and shirt, respectively.

5.6.2.1.3 ISO brightness of the post-consumer garments stripped in the sequential acid/alkali/peroxide method

Figure 5.6.3 presents the ISO brightness of the post-consumer garments stripped in the sequential acid/dithionite/peroxide method. The ISO brightness of the acid treated post-consumer samples were 7.6%, 2.0% and 26.1 for denim, T-shirt and shirt, respectively, compared to the original brightness of 7.0%, 1.8% and 26.0%, respectively. Subsequent alkali treatment slightly increased the brightness of the shirt to 26.9% only, however the brightness of the denim and T-shirt samples were only increased to 14.4% and 18.3%, respectively. Further peroxide oxidative bleaching treatment further increased the brightness of the T-shirt sample to 56.5%, however the effect of the treatment was relatively minimal on denim and shirt samples resulting in brightness values of only 19.9% and 38.9%, respectively.

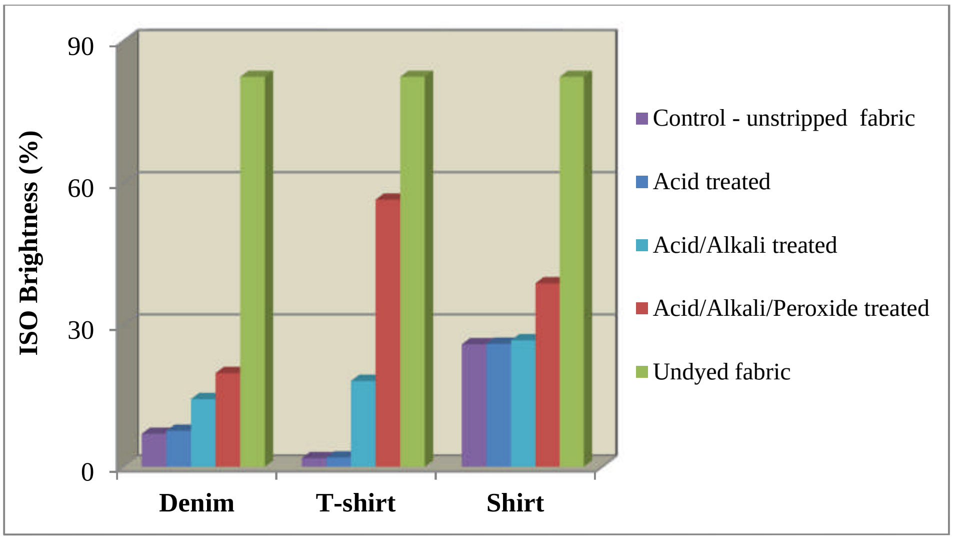


Figure 5.6.3 Comparison of the ISO brightness for the post-consumer garments stripped in the sequential acid/alkali/peroxide treatments.

5.6.2.1.4 Visual comparison of the post-consumer garments stripped in the sequential acid/alkali/peroxide method

Figure 5.6.4 visually compares the effect of the sequential acid/alkali/peroxide treatments on the stripping of colorants from post-consumer garments. It is clear that the acid treatment had no obvious effect on any of the samples as they all appeared similar to their comparable untreated samples. Further alkali treatment and subsequent peroxide treatment of the fabrics resulted in a significant colour change on all samples. The change was more pronounced on the T-shirt which appeared similar to the undyed cotton fabric as compared to the other two materials which is due to the chemically unstable azo chromophore used in dyeing the T-shirt.

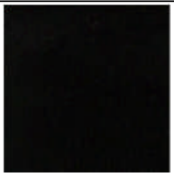
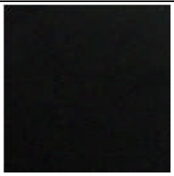
Colorant	**Dyed sample**	**Acid treated**	**Acid/Alkali treated**	**Acid/Alkali/ Peroxide**	**Undyed sample**
Denim					
T-shirt					
Shirt					

Figure 5.6.4 Visual appearance of post-consumer garments that have been stripped with the sequential acid/alkali/peroxide treatments.

5.6.2.2 Effect of the sequential acid/dithionite/peroxide treatment on the post-consumer garments

The post-consumer garments were also stripped using sequential acid/dithionite/peroxide treatments and their colorimetric parameters were again characterised by monitoring changes in colour strength, CIELAB colour difference and ISO brightness. The results obtained are discussed below.

5.6.2.2.1 Colour strength (K/S) of the post-consumer clothing stripped by the sequential acid/dithionite/peroxide treatment

The colour strength for the post-consumer garments treated by the sequential acid/dithionite/peroxide method are presented in Figure 5.6.5. As already stated the acid treatment had only a minor effect on the *K/S* of all fabrics. However further dithionite treatment significantly decreased the *K/S* of the fabrics to 0.8, 0.2 and 0.3 on denim, T-shirt and shirt, respectively, compared to the *K/S* values of 18.3, 21.3 and 9.6, respectively, observed on their acid only treated sample. This is again attributed to the high reductive power of the alkaline dithionite agent [83] in conjunction with the PVP dye transfer inhibitor which is capable of complexing with the reduced dye, thereby preventing it from redepositing on the surface of the fibre [23].

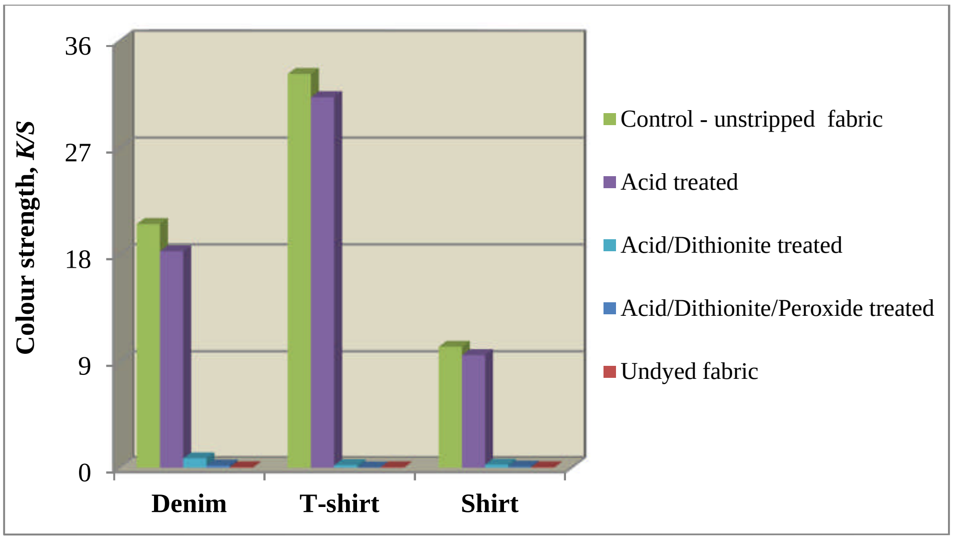


Figure 5.6.5 The colour strength parameters for the post-consumer garments stripped in the sequential acid/dithionite/peroxide treatments.

Subsequent oxidative peroxide bleaching of the post-consumer garments further decreased the *K/S* of the samples to 0.2, 0.03 and 0.09 on denim, T-shirt and shirt samples, respectively, approaching a *K/S* of 0.04 for the undyed cotton sample. This was again thought to be due the removal of colorant residues as a result of the oxidative bleaching action of the hydrogen peroxide stripping liquor.

5.6.2.2.2 *CIELAB colour difference (ΔE) of the post-consumer garment stripped by the sequential acid/dithionite/peroxide method*

Figure 5.6.6 presents the CIELAB colour difference of the post-consumer garments stripped in the sequential acid/dithionite/peroxide method. As seen previously, the acid treatment only resulted in marginal colorant removal on all samples. Subsequent alkaline dithionite treatment removed a significant amount of colorant from the substrates resulting in Δ*E* values of 47.7, 71.5 and 50.0 on the denim, T-shirt and shirt, respectively. Further oxidative peroxide bleaching stripped more colorant resulting in Δ*E*s of 65.5, 79.4 and 62.6 on the denim, T-shirt and shirt, respectively.

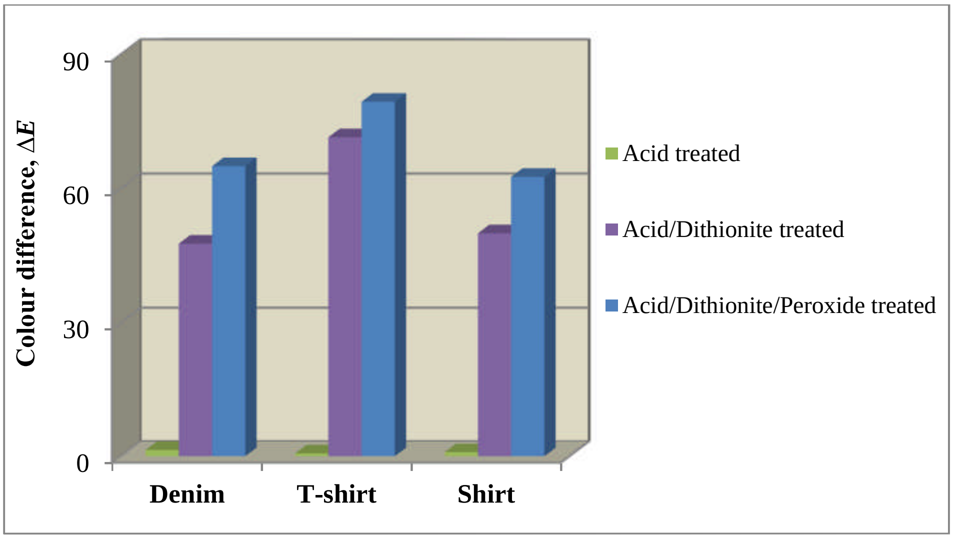


Figure 5.6.6 CIELAB colour difference for the post-consumer garments stripped in the sequential acid/dithionite/peroxide treatments.

5.6.2.2.3 ISO brightness of the post-consumer garments stripped by the sequential acid/dithionite/peroxide method

The ISO brightness of the post-consumer garments stripped in the sequential acid/dithionite/peroxide method are presented in Figure 5.6.7. The acid treatment resulted in brightnesses of 7.6%, 2.0% and 26.1% for the denim, T-shirt and shirt materials, respectively, compared to the original brightnesses of 7.0%, 1.8% and 26.0%, respectively. Subsequent dithionite treatment significantly increased the brightnesses of the coloured fabrics to 53.0%, 60.9% and 56.6% on the denim, T-shirt and shirt materials, respectively. Further peroxide bleaching removed additional colorant resulting in brightnes values of 86.6%, 82.9% and 88.4% on denim, T-shirt and shirt, respectively, higher than a brightness of 82.4% for the undyed cotton fabric.

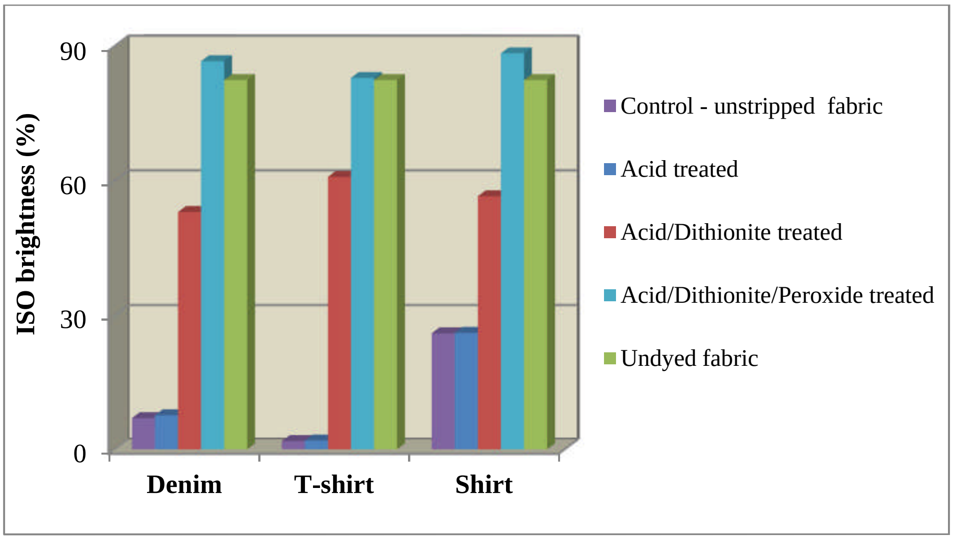


Figure 5.6.7 Comparison of the ISO brightness for the post-consumer garments stripped in the sequential acid/dithionite/peroxide treatments.

5.6.2.2.4 Visual comparison of the post-consumer garments stripped by the sequential acid/dithionite/peroxide method

Figure 5.6.8 visually compares the effect of the sequential acid/dithionite/peroxide treatment on stripping colorant from the post-consumer garments. The acid treatment had no obvious effect as all fabrics appeared similar to their unstripped counterparts. However further dithionite treatment resulted in significant colour change which is again attributed to the powerful reductive properties of the sodium dithionite reducing agent in conjunction with the dye transfer inhibiting properties of the PVP polymer. Further peroxide oxidative bleaching resulted in an additional colour change with the final fabrics appearing almost similar to the original white undyed cotton fabric.

Figure 5.6.8 Visual appearance of the post-consumer garments that have been stripped with the sequential acid/dithionite/peroxide treatments.

5.6.2.3 Comparison of the dye stripping methods on post-consumer garments

The efficiencies of the sequential acid/alkali/peroxide and acid/dithionite/peroxide treatments on stripping colorants from post-consumer cotton garments are compared in Figure 5.6.9. It is clear that the sequential acid/alkali/peroxide method was more effective in removing colorants from the T-shirt resulting in a stripping efficiency of 99.4% compared to only 81.0% and 83.4% colorant removed from the denim and shirt samples, respectively. However the acid/dithionite/peroxide method was effective in removing all colorants from the post-consumer garments resulting in a stripping efficiency of 99.1% on both denim and shirt materials while an efficiency of 99.9% was observed on the T-shirt.

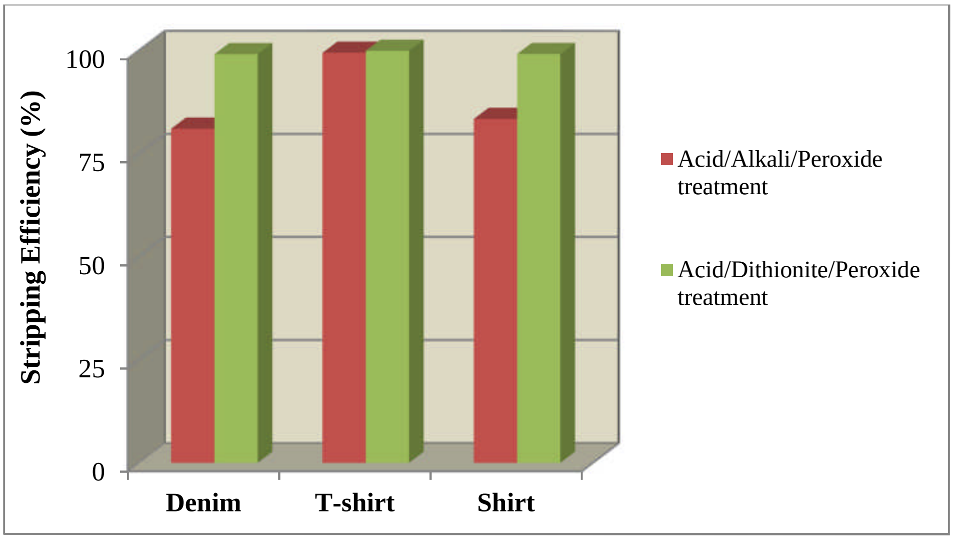


Figure 5.6.9 The stripping efficiency of the sequential acid/alkali/peroxide and the alternative acid/dithionite/peroxide baths on post-consumer garments.

5.7 STRIPPING OF FLUORESCENT WHITENING AGENTS FROM COTTON FABRICS

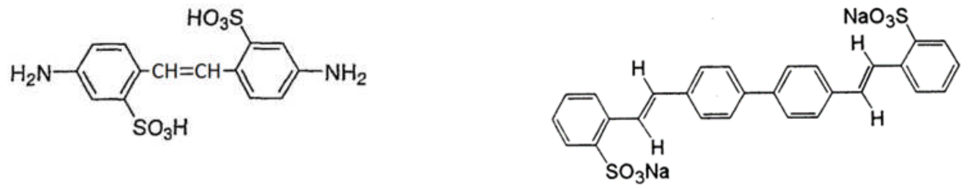
Fluorescent whitening agents (FWAs), also known as fluorescent/optical brighteners, are organic compounds applied to textiles to reduce yellowness of the material by increasing the amount of blue light reflected, thereby improving the apparent whiteness of the material. The agents absorb light in the ultraviolet region (340-370 nm) of the electromagnetic spectrum and re-emit the absorbed light in the blue region (420-470 nm) of the spectrum [83]. They can be applied to textile substrates during manufacturing or they can be incorporated into laundry detergents [104]. For instance, many white cotton substrates are usually treated with FWAs during bleaching or during finishing [102, 210] for the purpose of enhancing their whiteness properties.

As with any other finishing agents, the presence of FWAs on the waste cotton can affect the solubility and subsequent spinnability of the chemically recycled cotton materials. It was therefore necessary for the current study to assess the efficiencies of the established sequential acid/alkali/peroxide and acid/dithionite/peroxide colorants stripping methods in stripping FWA from cotton fabrics.

5.7.1 Experimental

5.7.1.1 Materials and Chemicals

The bleached, mercerised cotton fabric detailed in Section 3.2 was used for the analysis. Three fluorescent whitening agents, namely: Uvitex BLH, Uvitex NFW and Uvitex BHR were supplied by Huntsman, Germany. The structures of the agents were not disclosed, however it was established that Uvitex BLH and Uvitex BHR were derivatives of diaminostilbenesulphonic acid while Uvitex NFW was a distyryldiphenyl type of FWA. These structures are presented in Figure 5.7.1.



Diaminostilbenesulphonic acid *Distyryldiphenyl brighteners*

Figure 5.7.1 General chemical structures for the FWAs used in this study

5.7.1.2 Application of Fluorescent whitening agents onto cotton fabrics

The application of FWA was first carried out using Uvitex BLH at 70°C for 30 minutes using five different concentrations of agent (0.05, 0.1, 0.4, 0.6 and 1% based on the weight of the material). Sodium chloride salt (5 g/L) was used as an auxiliary in the treatment bath to minimize the electrostatic repulsion between anionic FWAs and the negatively charged surface of the cotton substrate, thereby improving the exhaustion of FWAs by cotton substrate. The liquor to goods ratio was adjusted to 30:1 and the temperature was increased at a rate of 3.5°C/min over a period of 15 minutes from 20 to 70°C. The bath was maintained at 70°C for a further 30 minutes followed by cooling the machine to 50°C and stopping the process. Treated samples were removed from the treatment bath, rinsed in cold water and air dried at room temperature.

5.7.1.3 Stripping of FWAs from cotton fabrics

The stripping of the FWAs was done using the sequential acid/dithionite/peroxide and the sequential acid/alkali/peroxide stripping processes detailed in Section 3.4.

5.7.2 Results and Discussion

In this study three fluorescent whitening agents were applied to cotton fabrics and the effect of the established acid/alkali/peroxide and acid/dithionite/peroxide methods in stripping FWAs from cotton fabrics were evaluated. The whiteness of the treated and untreated cotton fabrics were assessed using the CIE whiteness index (*WI*) calculated from reflectance values measured by a Datacolor spectrophotometer.

5.7.2.1 The effect of FWA concentration on Whiteness Index of the treated fabrics

The application of the FWA initially involved varying the concentration of the Uvitex BLH agent so as to determine the amount of FWA required for the complete whitening of the cotton samples and the results are presented in Figure 5.7.2. It can be seen that the highest whiteness index of 168 was obtained when 0.6% (o.w.f) of the agent was used. However further higher application concentrations of the component decreased the overall whiteness index of the material. It has been reported that the level of whiteness of the material increases with increased application levels of FWAs until a maximum level of whiteness is reached; further application of the agent decreases the whiteness level of the material. The phenomenon is reported to be due to increased aggregation of the FWAs on the substrate resulting in a shift in the fluorescence hue and quenching [83, 210].

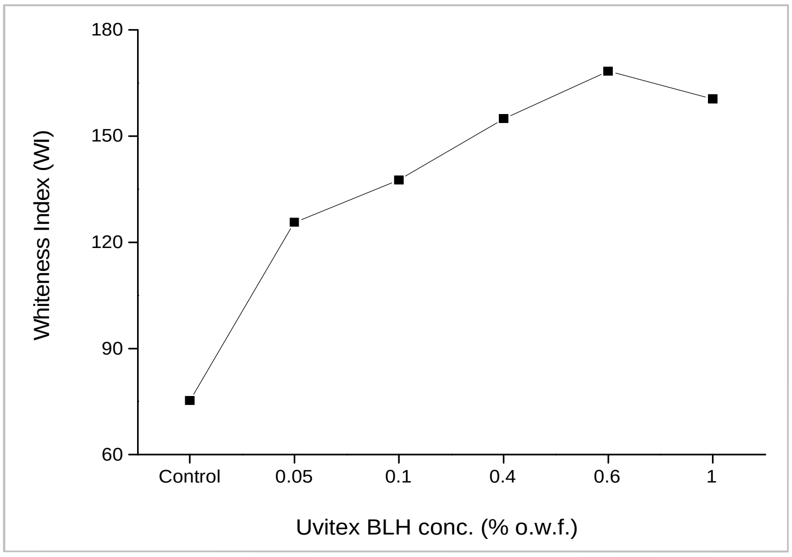


Figure 5.7.2 Effect of FWA concentration on the CIE whiteness of the cotton fabrics.

5.7.2.2 The effect of different types of FWAs on whiteness of the cotton fabrics

Figure 5.7.3 presents the effect of applying different types of whitening agents on cotton fabrics. It is clear from the figure that whitening agents caused a significant increase in whiteness of the materials as the whiteness indices of the treated samples were more than twice that of the unwhitened cotton sample, which had a *WI* of 75.3. This was attributed to the treated fabrics absorbing more light in the UV region than the original untreated white fabric [83].

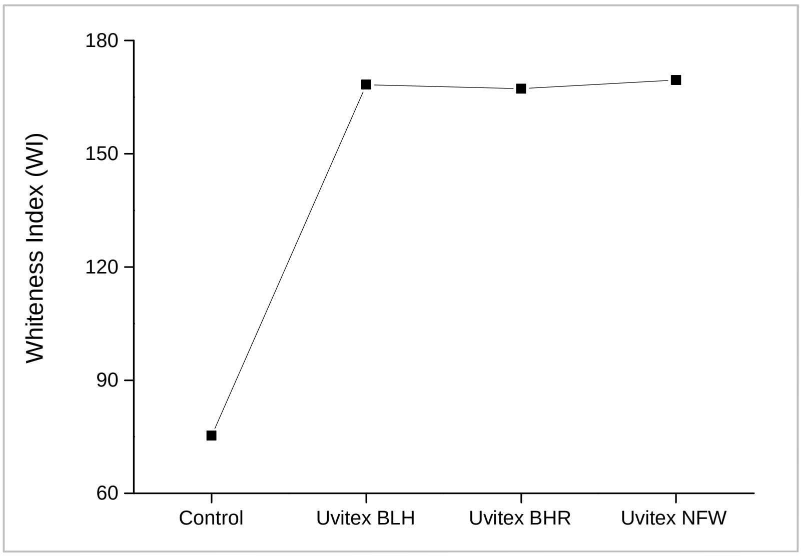


Figure 5.7.3 The effect of different types of FWAs on the CIE whiteness indices of the cotton fabrics.

Although a slightly higher *WI* of 169.5 was observed when using Uvitex NFW, the difference observed on the other two samples were small, resulting in *WI*s of 168.3 and 167.2 for Uvitex BLH and Uvitex BHR, respectively.

5.7.2.3 The effect of the sequential Acid/Alkali/Peroxide treatment on FWA treated cotton samples

Figure 5.7.4 shows the effect of the sequential acid/alkali/peroxide treatment on the FWA treated cotton samples. It can be seen that the acid treatment resulted in a higher decrease in *WI* of Uvitex BLH sample to 153.8 compared to that of Uvitex BHR (*WI* of 163.9) and Uvitex NFW (*WI* of 166.5) treated samples. It has previously been reported that most FWAs are not completely stable to acidic conditions [103, 210] as they tend to form precipitates with subsequent reduction in their whiteness effects [211]. However in this study it is apparent the acid has relatively little effect. Subsequent alkali treatment of the samples only stripped marginally more of the FWAs resulting in *WI*s of 151.8, 148.8 and 164.9 on Uvitex BHR, BLH and NFW treated fabrics, respectively. Further oxidative peroxide bleaching treatment decreased further the *WI* of the Uvitex BHR treated fabric to 120.8, however the treatment resulted in *WI*s of only 141.9 and 156.9 on Uvitex BLH and NFW treated fabrics, respectively.

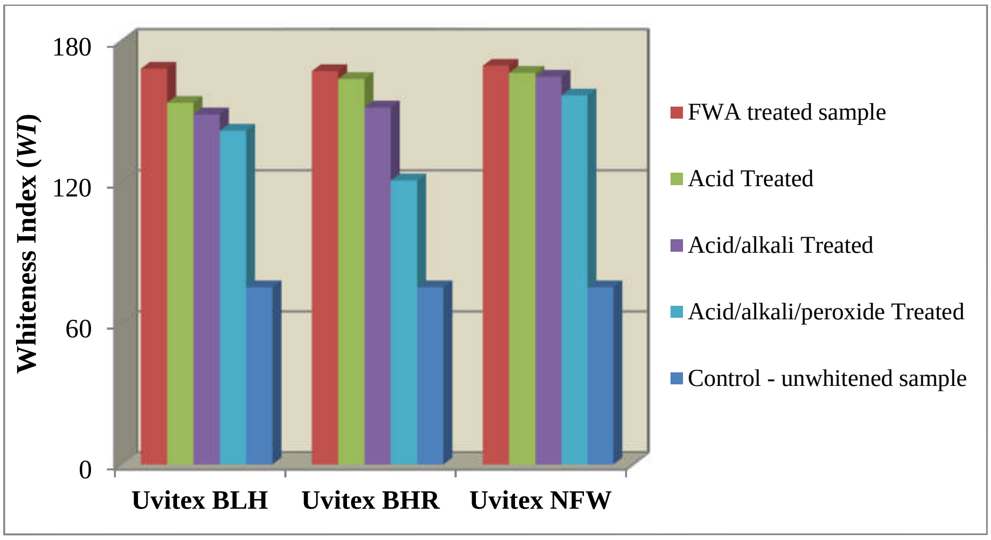


Figure 5.7.4 Effect of the sequential acid/alkali/peroxide treatment on the CIE whiteness index of the cotton fabric treated with different FWAs.

5.7.2.4 The effect of the sequential Acid/Dithionite/Peroxide treatment on FWA treated cotton samples

Figure 5.7.5 shows the effect of the sequential acid/dithionite/peroxide treatment on the FWAs treated cotton fabrics.

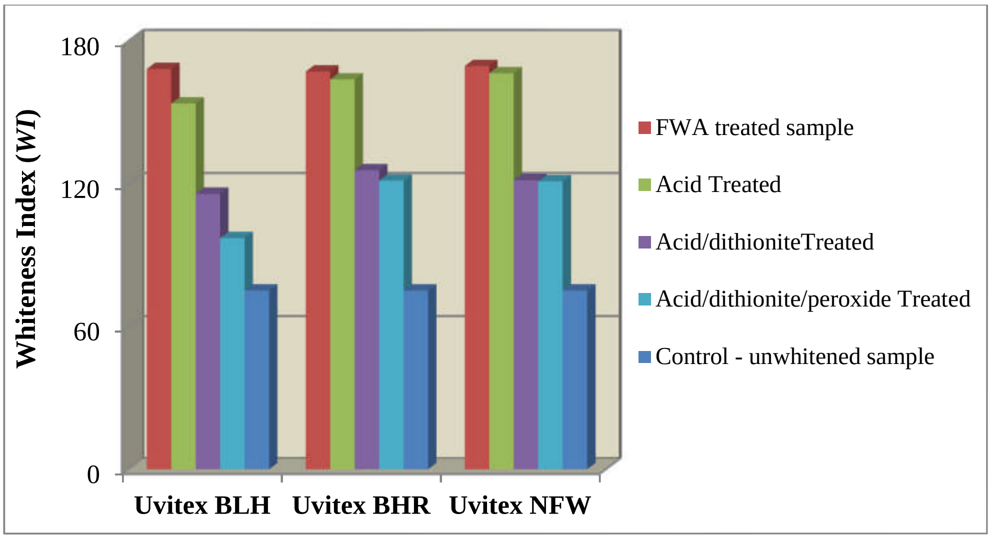


Figure 5.7.5 Effect of the sequential acid/dithionite/peroxide treatment on the CIE whiteness index of the fabrics treated with different types of FWAs

As already established, the acid treatment significantly decreased the WI of the Uvitex BLH treated fabrics, however only a minor decrease was observed on Uvitex BHR and Uvitex NFW treated samples. Further dithionite treatment significantly decreased the *WI*s to 115.9, 125.8 and 121.6 on Uvitex BLH, BHR and NFW cottons, respectively. The alkaline dithionite treatment of the FWA treated cottons could have caused the reduction of the physical and chemical interactions formed between the fibre and the whitening agent, thereby reducing the whiteness levels of the materials. In addition prolonged treatment of the materials at high temperatures (80-100°C) could have also contributed to the reduction of the whiteness level of the stripped materials. Higher treatment temperatures have been previously reported to affect the stability of the FWAs [212].

Subsequent peroxide treatment further decreased the of whiteness of the Uvitex BLH treated material resulting in a *WI* of 97.3. Slightly more of the FWAs were also stripped from the Uvitex BHR treated sample resulting in a *WI* of 121.4, however the effect of the peroxide treatment on Uvitex NFW treated fabric was small. Most cellulosic FWAs are reported to be stable to peroxides and other bleaching baths [103, 105], which could have resulted in a lower effect when the samples were further treated in hydrogen peroxide.

5.7.3 Summary

In this section the efficiency of the established colorant stripping methods were evaluated on their ability to strip FWAs from cotton fabrics. Three FWAs, namely: Uvitex BLH, Uvitex BHR and Uvitex NFW were applied to cotton fabrics and whiteness level analysed. Results indicated the Uvitex NFW treated cotton was more resistant to the sequential acid/alkali/peroxide treatment followed by Uvitex BLH and finally Uvitex BHR treated cotton. However, the acid/dithionite/peroxide treatment was more effective in stripping Uvitex BLH than Uvitex BHR and Uvitex NFW resulting in more of the agents being removed compared to when using the sequential acid/alkali/peroxide method. Nevertheless the FWA treatment was remarkably durable to aqueous chemical treatment and may present a problem in blending with other cellulosic feedctock material for Lyocell manufacture.

5.8 STRIPPING OF THE FINISHING AGENTS FROM REACTIVE DYED COTTON FABRICS

5.8.1 Introduction

In addition to chemical bonds introduced by multi-functional reactive dye molecules into the cellulosic fibres, the application of other functionalising crosslinking agents may also potentially impair not only the processability of the recycled materials but also adversely affect the properties of the final regenerated cellulosic product. For instance, the presence of crosslinks from crease resist finishing agents applied to cotton fabrics for the purpose of improving the easy care properties of the material may also inhibit the initial dissolution of the waste cellulosic feedstock and thereby affecting the overall commercial viability of the new fibre regeneration process [66].

In this section we have investigated the effectiveness of the established dye stripping methods in removing both reactive dyes and DMDHEU based crosslinking agent from cotton fabrics for the purpose of recycling the cotton fabrics and reuse the recycled materials for Lyocell fibre regeneration. Both sequential acid and alkali hydrolysis with subsequent oxidative bleaching treatments were evaluated as potential reactions for delivering cheap and efficient removal of both dyes and crosslinking agents. Sequential acid hydrolysis, dithionite reduction and subsequent oxidative bleaching reaction of the hydrogen peroxide were also investigated.

The efficiencies of the methods in stripping both colorants and crease resist finishes were monitored by observing changes occurring in colour strength as well as their crease resistance performance as per British Standard method [179]. Surface changes as characterised by using Fourier Transform Infrared (FTIR) were also evaluated. Chemical damage to the cellulose polymer as a result of the stripping processes were also assessed by analysing the solubility of the materials in CED solution as well as its limiting viscosity and subsequent degree of polymerisation.

5.8.2 Experimental

5.8.2.1 Materials and Chemicals

Bleached, mercerised cotton fabrics were obtained from Phoenix Calico limited (Section 3.2). These fabrics were dyed with either C. I. Reactive Black 5 (RB5), C. I. Reactive Blue 19 (RBL19) and C. I. Reactive Red 228 (RR228) dyes as described in Chapter 4 of this thesis.

A modified dimethyloldihydroxyethylene urea, (DMDHEU) under the commercial name Fixapret resin ECO (Figure 5.8.1) was kindly supplied by BASF. The modified crosslinker is based on DMDHEU, methanol and diethylene glycol (DEG). It contains low levels of formaldehyde (below the Öko-Tex Standard 100 limit of 75 ppm) while offering overall good physical performances [213].

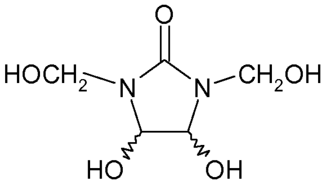


Figure 5.8.1 Structure of Dimethylol dihydroxyethylene urea (DMDHEU)

5.8.2.2 Application of crease resist finishes to Reactive dyed cotton fabrics

Reactive dyed cotton fabrics were padded with DMDHEU solution using a method recommended by the manufacturer [214]. A solution of pH between 4.5-5.5 was prepared using 60 g/L DMDHEU and 12 g/L magnesium chloride as a catalyst and was padded onto a fabric to obtain a wet pick up of 90%. The padded materials were then dried at 100^{o}C for 2.5 minutes followed by curing for 3 minutes at 160^{o}C prior to washing with distilled water to remove unreacted DMDHEU and subsequent air drying.

5.8.2.3 Stripping of the crease resist finishes

The dyed crosslinked cotton samples were stripped as per the sequential acid/alkali/peroxide and acid/dithionite/peroxide methods detailed in Section 3.4.

5.8.3 Results and Discussion

In this study the effect of both the sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide methods in removing dye-fibre bonds due to reactive dyes and crosslinks due to DMDHEU-based crease resist finishes were evaluated. The effectiveness of the stripping methods was determined in terms of colour changes (both visually and instrumentally), crease recovery performance of the samples as well as changes occurring on the surface and chemical composition of the samples. The solubility of the stripped materials in CED solution as well as its limiting viscosity and subsequent degree of polymerisation were also examined. The obtained results are discussed below.

5.8.3.1 Effect of the sequential acid/alkali/peroxide method on crease resist finishes applied on reactive dyed cotton fabrics

The effect of the sequential acid/alkali/peroxide treatment on the colour change of the DMDHEU crosslinked reactive dyed samples was analysed both visually and instrumentally where colour strength, *K/S* values, (Figure 5.8.2) were used to determine the effectiveness of the chemical "stripping" process.

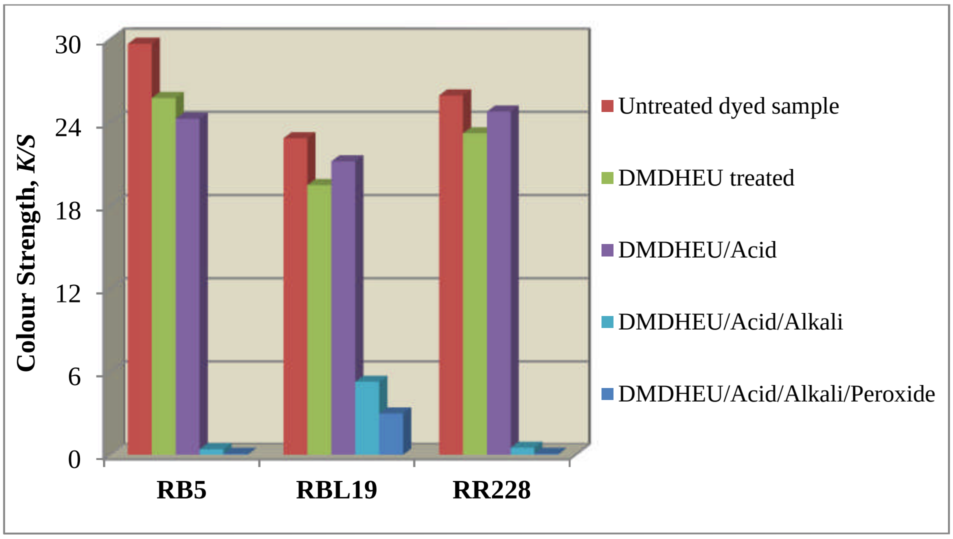


Figure 5.8.2 Comparison of the colour strength for the reactive dyed cotton fabrics treated with DMDHEU then stripped with the sequential acid, alkali and peroxide treatments.

It can be seen from the figure that the DMDHEU treatment slightly decreased the *K/S* of the treated fabrics to 25.8, 19.5 and 23.2 on the RB5, RBL19 and RR228 dyed fabrics, respectively, compared to *K/S* of 29.7, 22.9 and 26.0, respectively, for the original dyed uncrosslinked samples. This decrease in colour strength has previously been observed and can be attributed to the easy care formulation and extended high curing temperature modifying the dyestuff [115, 215]. Previous studies have also reported the sensitivity of the vinylsulphone-based reactive dyes to formaldehyde-based crosslinking agents and their acidic catalysts [115]. This could have also contributed to the decrease in colour strength of the DMDHEU cross-linked reactive dyed cellulosics.

Subsequent acid treatment of the DMDHEU treated samples resulted in a slightly greater loss in colour strength of the RB5 sample resulting in a *K/S* of 23.4 which could be due to the acid hydrolysing the bonds between the dye and cellulosic molecules. Interestingly, the acid treatment slightly increased the *K/S* on both the RBL19 and RR228 dyed samples, resulting in *K/S* of 21.2 and 24.6, respectively, compared to original *K/S* of 19.5 and 23.2 observed on the crosslinked untreated fabrics. The reason for this increase in colour strength is uncertain at present.

When the acid treated samples were further stripped in hot alkaline solution, most of the remaining dyes were removed. The decolourising effect was especially greater on the azo-based (RB5, *K/S* of 0.4 and RR228, *K/S* of 0.5) dyed fabrics, than on the anthraquinone-based RBL19 sample which had a *K/S* of 5.3. This was attributed to the greater stability of the anthraquinone chromophore structure of the C. I. Reactive Blue 19 dye to most chemical treatments [204, 205]. Further hydrogen peroxide treatment stripped even more dyes from the samples as they appeared similar to the original undyed samples. Again the effect was much more obvious on the azo-based dyed samples, resulting in a *K/S* of 0.07 on both the RB5 and RR228 fabrics, approaching a *K/S* of 0.04 observed on the undyed cotton fabric. Again, a *K/S* of only 3.0 was observed on the chemically resistant anthraquinone-based RBL19 fabrics.

Figure 5.8.3 visually compares the effect of the sequential acid/alkali/peroxide stripping method on the reactive dyed cotton fabrics that were cross-linked with DMDHEU crease resist finishing agents. The figure shows a slight decrease in colour after treating the reactive dyed samples with the DMDHEU based crosslinking agent. However the acid treatment resulted to slightly increased colour on RR228 and RBL19 dyed materials.

Further alkali treatment and subsequent peroxide oxidative bleaching resulted in a significant colour decrease on the azo-based RB5 and RR228 dyed fabrics. However the effect was minimal on the anthraquinone based RBL19 fabric.

Figure 5.8.3 Visual appearance of DMDHEU treated reactively dyed cotton samples following stripping with the sequential acid/alkali/peroxide treatments.

The results for the crease recovery angles (warp + weft), Table 5.8.1, indicate that treating cotton samples with DMDHEU easy care finish significantly increased the CRA up to 308° compared to CRA of 130° of the dyed untreated cotton fabric. This effect was due to the crosslinking agent reacting with hydroxyl groups of cellulose to form covalent links between adjacent cellulosic molecular chains within the accessible amorphous region of the fibre, thereby increasing resistance to deformation while improving its elastic recovery from deformation [216, 217]. Subsequently treating the samples in acid decreased the CRA to about 174° which is attributed to the acid hydrolysing the bonds between the crosslinking agent and the hydroxyl groups of cellulose, thereby cleaving the interchenic crosslinks. Further treatment of the samples in hot alkaline solution caused greater hydrolysis of the crosslinking bonds as the CRA decreased to about 139°. Hydrogen peroxide treatment also caused further decreases to the crease recovery angles where values of ~130° were obtained.

Table 5.8.1 Crease recovery angle (warp + weft)° analyses of the treated cotton fabrics

Colorant	**Crease Recovery Angle (W + F)°**				
	Dyed/ untreated	**Dyed/ DMDHEU**	**DMDHEU /Acid**	**DMDHEU/ Acid/Alkali**	**DMDHEU/ Acid/Alkali/ Peroxide**
RB5	141 ± 11	308 ± 10	174 ± 8	139 ± 6	130 ± 13
RBL19	138 ± 14	295 ± 2	180 ± 18	147 ± 9	128 ± 11
RR228	130 ± 11	282 ± 11	175 ± 11	168 ± 13	141 ± 8

Figures 5.8.4 to 5.8.6 present the Infrared Spectra of the DMDHEU treated reactive dyed cotton samples that were stripped in the sequential acid/alkali/peroxide method. The figures indicate that DMDHEU treatment of the reactive dyed cotton fabrics introduced a new spectral peak at about 1706 cm^{-1} which is attributed to the C=O stretch vibration of the easy care finish. This provides confirmation of the covalent bonding of the crease resist finish to the cotton through the reported formation of an ether bond between the hydroxyl groups of cellulose and the crosslinking agent [177]. After acid treatment the IR spectra of the cross-linked samples resembled that of the original uncrosslinked reactive dyed cotton samples, which is probably due to the hydrolysis of the ether bond formed between the cotton and the crosslinking agent [110, 218]. Further treatment of the samples in hot alkaline solution produced only a slight further change to the material’s FTIR spectra. These findings are in agreement with the findings of Haule et al. [66], where they reported hydrolysis of the DMDHEU crosslinks as a result of the sequential acid/alkali treatment. The subsequent oxidation reaction of the hydrogen peroxide had no apparent effect to the FTIR spectra of the samples.

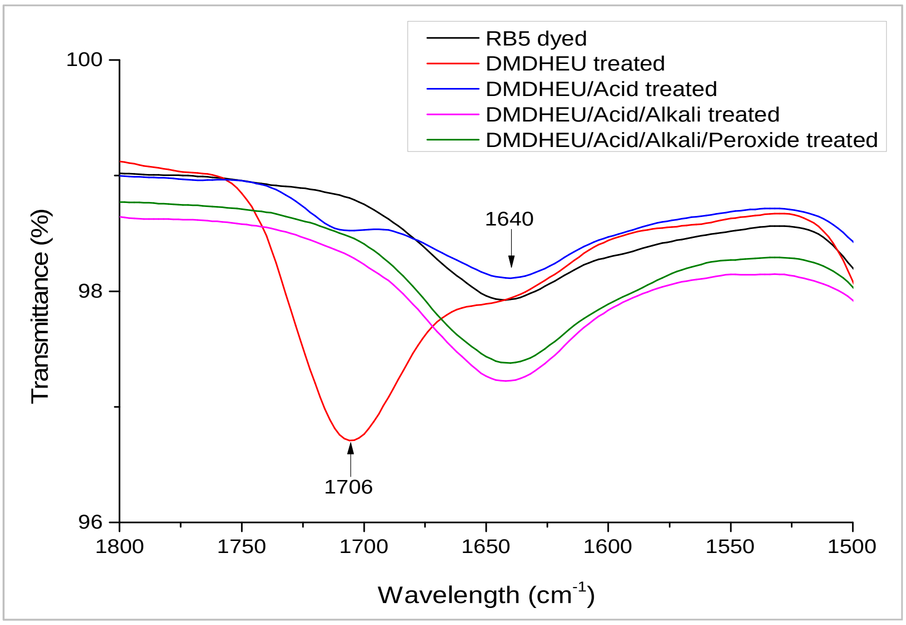


Figure 5.8.4 FTIR spectra of the RB5 fabric modified with DMDHEU easy care finish and then stripped using the sequential acid/alkali/peroxide treatments.

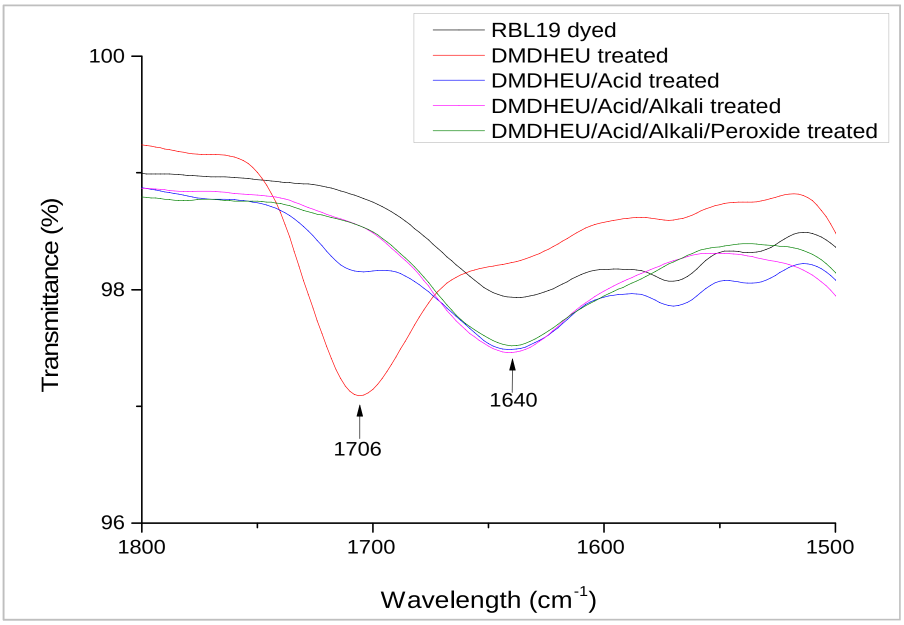


Figure 5.8.5 FTIR spectra of the RBL19 fabric modified with DMDHEU easy care finish and later stripped in the sequential acid/alkali/peroxide treatments.

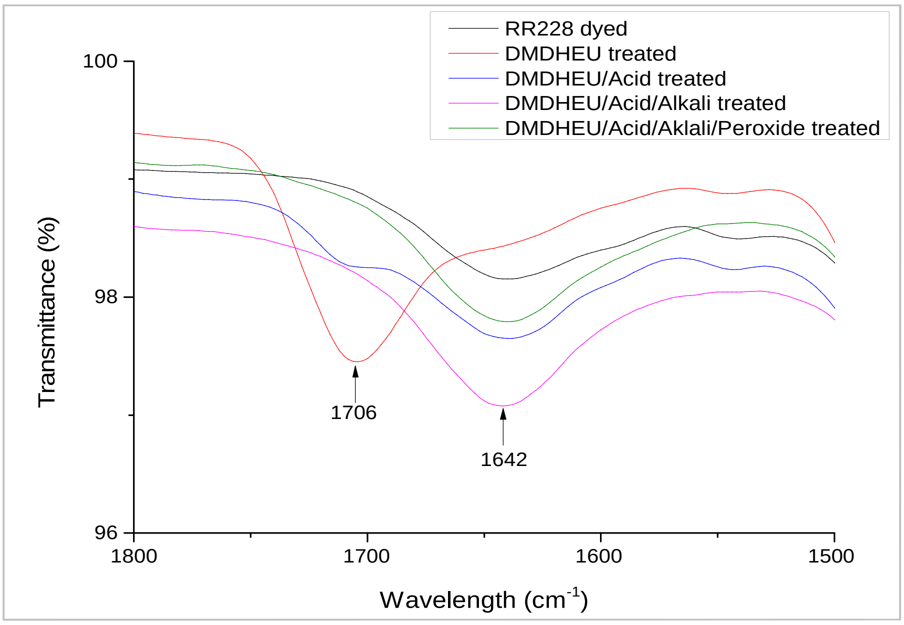


Figure 5.8.6 FTIR spectra for the RR228 fabric modified with DMDHEU easy care finish and later stripped in the sequential acid/alkali/peroxide treatments.

5.8.3.2 Effect of the sequential acid/dithionite/Peroxide method on crease resist finishes applied on reactive dyed cotton fabrics

The effect of the sequential acid/dithionite/peroxide treatment on the colour change of the DMDHEU crosslinked reactive dyed fabrics was analysed both visually and instrumentally where the colour strength, as measured by a Datacolor spectrophotometer were assessed. Figure 5.8.7 presents the changes in *K/S* of the fabrics as they were treated from one chemical agent to another. As already stated, the DMDHEU treatment caused a slight decrease in colour strength of all treated samples which is attributed to the easy care formulation and extended high curing temperature modifying the base fabric and possibly the dyestuff. Acid treatment of the DMDHEU treated dyed materials resulted in a slightly greater loss in colour strength of the RB5 fabric, although the treatment resulted in increased colour strength of both the RBL19 and RR228 dyed crosslinked materials. Subsequent dithionite treatment significantly decreased the *K/S* of the samples to 0.1, 0.4 and 0.5 on the crosslinked RB5, RBL19 and RR228 dyed fabrics, respectively, compared to *K/S* of 25.8, 19.5 and 23.2, respectively, of their crosslinked unstripped samples. The higher decrease in colour strength was again presumed to be due to the strong reductive power of the alkaline dithionite solution in combination with the dye transfer inhibiting properties of the polyvinylpyrrolidone polymer.

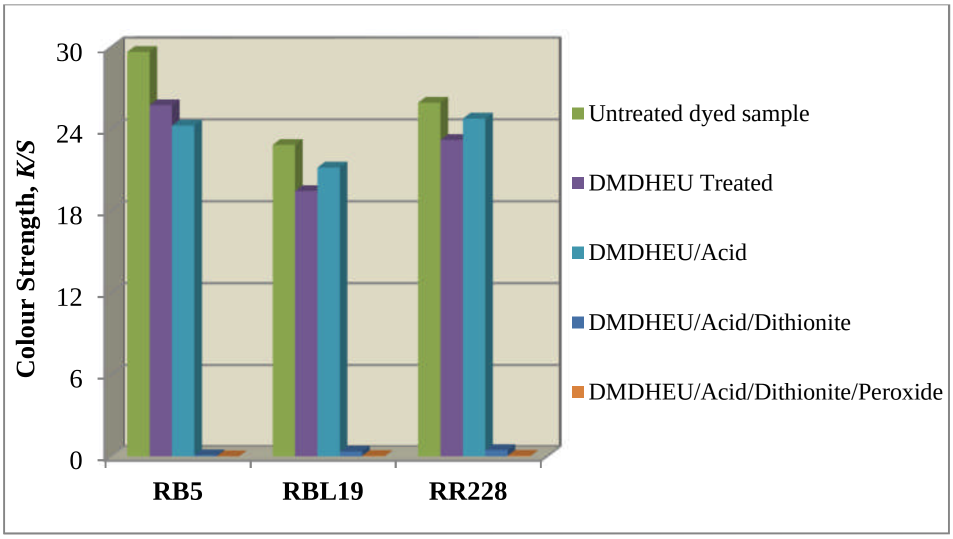


Figure 5.8.7 Comparison of the colour strength for the reactive dyed cotton fabrics treated with DMDHEU easy care finish then stripped with acid, dithionite and peroxide treatments.

Further peroxide treatment also decreased the *K/S* of the samples to 0.01, 0.03 and 0.05 on crosslinked RB5, RBL19 and RR228 fabrics, respectively, compared to a *K/S* of 0.04 of the undyed cotton fabric. This was attributed to the removal of dye residues as a result of the oxidative bleaching reaction of the hydrogen peroxide.

Figure 5.8.8 visually compares the effect of the sequential acid/dithionite/peroxide treatment on the DMDHEU crosslinked reactive dyed samples. The figure shows clearly that the dithionite treatment and subsequent peroxide oxidative bleaching resulted in significant colour removal of all samples as the fabrics appeared similar to the starting material, the undyed cotton sample. This was again attributed to the strong reductive power of the alkaline dithionite treatment, the dye transfer inhibiting properties of the PVP polymer together with the ability of the oxidative peroxide bleaching to remove dye residues from the fabrics.

Figure 5.8.8 Visual appearance of DMDHEU treated reactively dyed cotton fabrics after stripping with acid/dithionite/peroxide treatments.

Table 5.8.2 presents the results for crease recovery angles (warp + weft) for the DMDHEU crosslinked reactive dyed cotton fabrics treated by the sequential acid/dithionite/peroxide stripping treatment. As previously stated, treating cotton with DMDHEU resulted in a significant increase in CRA compared to the CRA observed on the dyed uncrosslinked cotton fabric. This has been reported to be due to the covalent interchenic crosslinking between the hydroxyl groups in the cellulose polymer, thereby increasing resistance to deformation while improving its elastic recovery from deformation [216, 217].

Table 5.8.2 Crease recovery angle (warp + weft) analyses of the treated cotton fabrics

Colorant	**Crease Recovery Angle (W + F)°**				
	Dyed/ untreated	**Dyed/ DMDHEU**	**DMDHEU /Acid**	**DMDHEU/ Acid/ Dithionite**	**DMDHEU/ Acid/Dithionite /Peroxide**
RB5	141 ± 11	308 ± 10	174 ± 8	151 ± 18	131 ± 16
RBL19	138 ± 14	295 ± 2	180 ± 18	132 ± 7	124 ± 7
RR228	130 ± 11	282 ± 11	175 ± 11	147 ± 0.2	129 ± 0.2

Subsequent acid treatment of the DMDHEU crosslinked cotton decreased the CRA to about 174° which was attributed to the acid hydrolysing the bonds formed between the crosslinking agent and the hydroxyl groups of cellulose, thereby cleaving the interchenic crosslinks. Further alkaline dithionite treatment of the fabrics decreased the CRA to about 132° which was thought to be due to the reduction and hydrolysis of the crosslinking bonds as a result of high concentrations of both sodium dithionite and sodium hydroxide present in the stripping liquor. Following hydrogen peroxide treatment also caused additional decreases in the crease recovery angle to ~124°.

Figures 5.8.9 to 5.8.11 presents the IR Spectra of the DMDHEU crosslinked reactive dyed cotton samples treated by the sequential acid/dithionite/peroxide stripping method. The DMDHEU treatment of the cotton fabrics introduced a new spectral peak at about 1706 cm^{-1} which was attributed to the C=O stretch vibration of the easy care finish. Again, after the acid treatment the IR spectra of the crosslinked samples resembled that of the original uncrosslinked reactive dyed cotton fabrics, which is anticipated to be due to the hydrolysis of the bond formed between the fibre and crosslinking agent [218]. Further treatment of the samples in dithionite solution and subsequent peroxide bleaching resulted into a further change to the sample IR spectra. This was again presumed to be due to the strong alkaline conditions (pH>13) of both sodium dithionite and hydrogen peroxide stripping liquors.

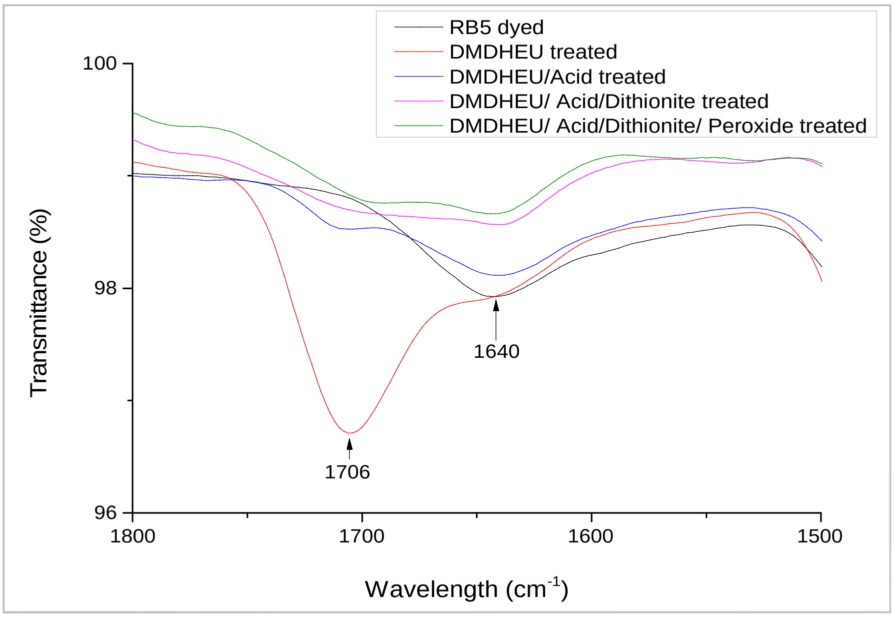


Figure 5.8.9 FTIR spectra of the RB5 fabrics modified with DMDHEU easy care finish and then stripped by the sequential acid/dithionite/peroxide treatments.

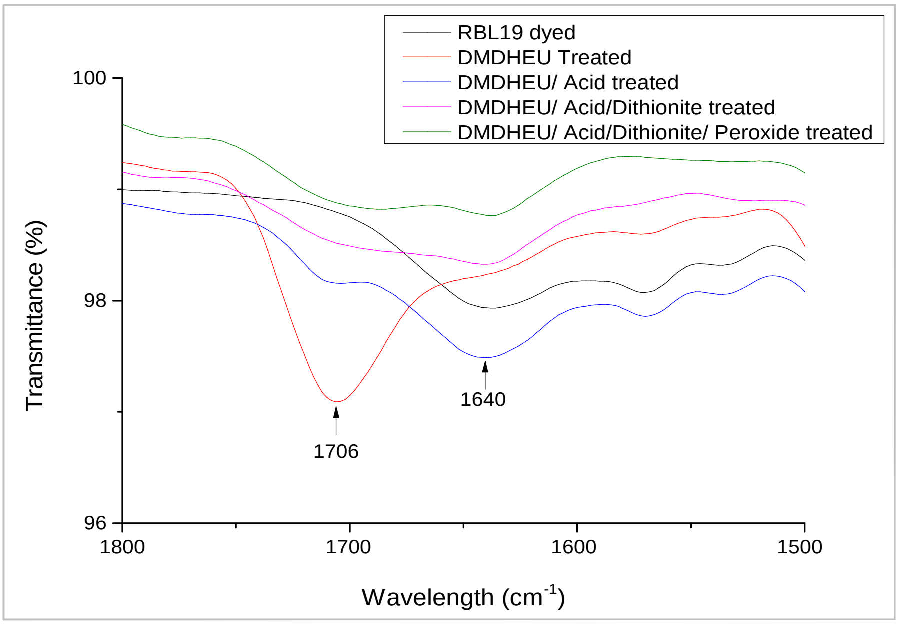


Figure 5.8.10 FTIR spectra of RBL19 fabrics modified with DMDHEU easy care finish and then stripped with the sequential acid/dithionite/peroxide treatments.

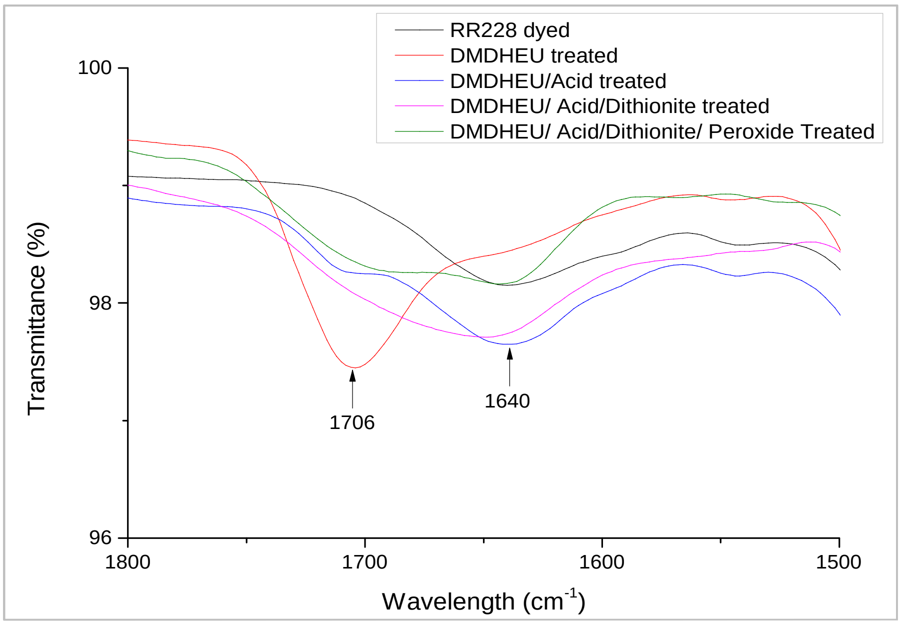


Figure 5.8.11 FTIR spectra of RR228 fabrics modified with DMDHEU easy care finish and later stripped with the sequential acid/dithionite/peroxide treatments.

5.8.3.3 Comparison of the dye stripping methods on the DMDHEU crosslinked reactive dyed cotton fabrics

Figure 5.8.12 compares the stripping efficiencies of the sequential acid/alkali/peroxide treatments to that of the sequential acid/dithionite/peroxide method on stripping DMDHEU treated reactive dyes from cotton fabrics. It can be seen from the figure that although the acid/alkali/peroxide method removed up to 99.7% of dye from the RB5 and RR228 dyed crosslinked fabrics, the treatment was less effective in stripping the anthraquinone based C. I. Reactive Blue 19 dye where only 86.9% of the dye was stripped from the RBL19 fabric. On the other hand, the sequential acid/dithionite/peroxide treatment removed significant amounts of dye from all fabrics resulting in a stripping efficiency of more than 99.8% on all cellulosic fabric.

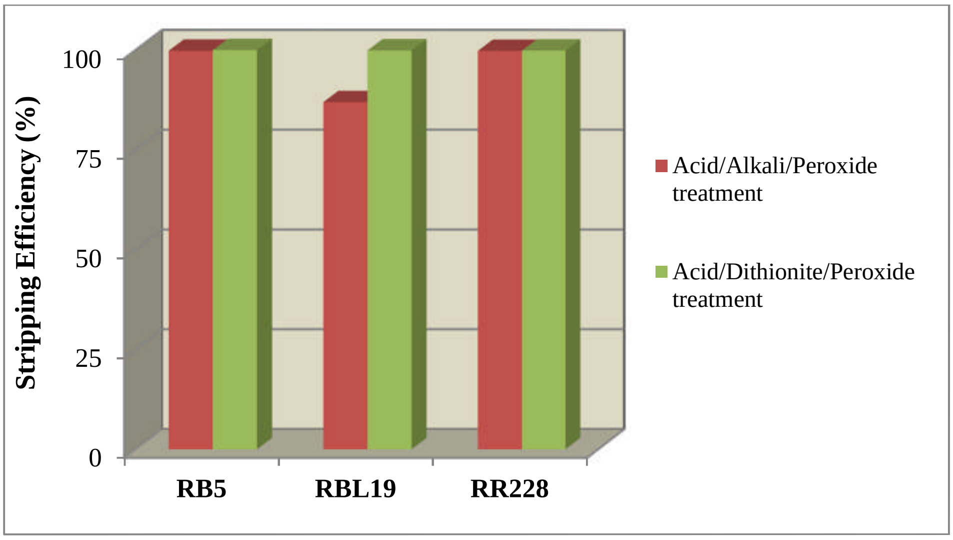


Figure 5.8.12 The stripping efficiencies of the sequential acid/alkali/peroxide and the alternative acid/dithionite/peroxide treatments on DMDHEU crosslinked reactive dyed cotton fabrics.

5.8.3.4 Effect of the sequential acid/dithionite/peroxide stripping method on solubility and cellulose degradation of the DMDHEU treated cotton fabrics

Since the sequential acid/dithionite/peroxide treatment stripped greater amounts of both reactive dyes and DMDHEU easy care finish from cotton fabrics compared to the acid/alkali/peroxide treatment, it was therefore selected for further analysis of the samples. The effect of the stripping method on the solubility of the materials in cupriethylenediamine hydroxide (CED) solvent and its degree of cellulose degradation was assessed by observing changes in limiting viscosity and the degree of polymerisation of the stripped material.

The crosslinked reactive dyed cotton fabrics stripped in the sequential acid/dithionite/peroxide treatment were dissolved in 0.5M CED solution and the results are presented in Table 5.8.3. The table shows that the solvent could dissolve most of the dyed uncrosslinked samples with up to 100% solubility attained on the RR228 samples. The solubility was however slightly lower on the RB5 fabric where only 66.2% of the sample was dissolved. This was presumed to be due to the dye-fibre covalent bonds, which could have reduced accessibility of the cellulose molecules to the CED solvent.

Table 5.8.3 Effect of the acid/dithionite/peroxide treatment on the solubility of the cotton fabrics treated with DMDHEU crease resist finishes.

Sample	Dyed uncrosslinked (%)	DMDHEU treated (%)	Acid treated (%)	Acid/dithionite treated (%)	Acid/dithionite/ peroxide (%)
RB5	66.2	33.1	65.4	96.7	99.8
RBL19	93.9	33.3	61.5	96.4	99.6
RR228	99.6	25.7	46.2	87.6	98.8

DMDHEU treatment of the reactive dyed fabrics significantly reduced the solubility of all the samples to approximately 26-33%. This was due to the agent also crosslinking with the hydroxyl groups of cellulose within the accessible amorphous region of the fibre, thereby limiting its accessibility to the solvent [219]. Acid treatment of the crosslinked samples increased the solubility of the material to about 65%, which was due to the acid hydrolysing the covalent bonds formed between the crosslinking agent and the cellulose hydroxyl groups, allowing the solvent to access some of the freed hydroxyl groups of cellulose and dissolving the material. Further dithionite and subsequent peroxide oxidative bleaching increased the solubility of the crosslinked samples to approximately 99.8%, which was again attributed to both reduction and hydrolysis of the bonds allowing the CED solvent to access the freed hydroxyl groups within the cellulose.

Table 5.8.4 shows the analysis of the limiting viscosity and subsequent degree of polymerisation of the acid/dithionite/peroxide treated samples which could be dissolved completely in CED solution. It can be seen from the table that low values of limiting viscosity and the degree of polymerisation were observed when DMDHEU crosslinked samples were stripped in the complete sequential acid/dithionite/peroxide treatment. The low results could be due to the fact that DMDHEU treatment which requires acidic conditions and high curing temperature for crosslinking to occur could have initiated the degradation of cellulosic material the effect which was more pronounced on chemical stripping process.

Table 5.8.4 Effect of the acid/dithionite/peroxide treatment on the cellulose degradation of the reactive dyed and crosslinked cotton samples

S/No.	Sample Name	Limiting Viscosity (mL/g)	Degree of Polymerisation
1.	Undyed	1051.1 ± 61.7	3193.6 ± 180.0
2.	RB5	294.9 ± 8.6	702.2 ± 20.6
3.	RBL19	296.3 ± 19.4	701.9 ± 41.4
4.	RR228	307.6 ± 17.6	732.0 ± 42.3

Cellulose is highly susceptible to both acidic and oxidative conditions as they tend to attack the glucosidic linkages of the cellulose causing chain scission and subsequent lowered degree of polymerisation [50, 53, 63]. Alkaline conditions are also reported to degrade cellulose materials that have been pre-treated with acid causing loss in strength which can be characterised by reduced viscosity and the degree of polymerisation [50].

5.8.4 Summary

In this section the efficiencies of the sequential acid/alkali/peroxide and sequential acid/dithionite/peroxide in stripping both reactive dyes and DMDHEU-based easy care finishes were evaluated. The results indicated that sequential acid/alkali hydrolysis followed by subsequent hydrogen peroxide oxidation can remove both azo-based reactive dyes and DMDHEU finish applied to cotton fabrics. Subjective and objective analysis of the azo-based C. I. Reactive Black 5 and C. I. Reactive Red 228 dyes indicated the appearance of the final treated fabric was similar to the original untreated fabric. However the C. I. Reactive Blue 19 dye was more resistant to the combined treatment and this was a reflection of the resistance of the reactively bound anthraquinone chromophore to hydrolytic and oxidative processing. In contrast, the acid/dithionite/peroxide method was able to strip both reactive dyes (including the highly resistant C. I. Reactive Blue 19 dye) and the DMDHEU resist finish on all reactive dyed cotton samples, which was attributed to the high reducing power of the alkaline dithionite stripping liquor.

The crease recovery angle results showed a decrease in the CRA of the DMDHEU treated samples following both the acid/alkali/peroxide and the acid/dithionite/peroxide treatments with the final levels similar to the original dyed non-crosslinked cotton samples. The FTIR spectra also showed the disappearance of the C=O vibrational intensity associated with the DMDHEU reacting with the dyed samples following the two chemical stripping processes.

Following the acid/dithionite/peroxide treatment, the solubility parameters of the DMDHEU treated samples were almost identical to those of the uncrosslinked dyed samples. However the treatment significantly degraded the cellulose polymer which was confirmed by the reduced limiting viscosity and subsequent degree of polymerisation.

5.9 STRIPPING OF HEAVY METALS FROM COTTON FABRICS

5.9.1 Introduction

Dyed textile products have been reported to contain organic and inorganic materials, including heavy metal ions [220]. Iron, copper, cadmium, manganese, zinc and nickel are found in textile materials in large quantities, although magnesium, calcium and sodium are also found [221, 222]. Metals found in textile products are usually from various origins [223]. Most metals are naturally introduced into crop-based fibres (particularly cotton, flax and hemp) through the atmosphere during their growing stage [221, 224, 225]. However some metals are introduced into textile fibres during textile processing. For instance, copper, iron, chromium and nickel are sometimes introduced into dyes forming dye-metal complexes (such as chrome mordant and metal-complex dyes) for the purpose of improving their fixation during textile processing and the overall fastness properties of the dyed substrate [74, 83]. Processing water, surfaces of machinery and fittings and other textile processing auxiliaries such as reducing and finishing agents are also potential sources of metals in textile fibres [83, 221].

The presence of transition metals, particularly iron and copper in the pulp have been reported to accelerate the cellulose degradation and thermal instability of the spinning solution during dissolution in the N-methylmorpholine-*N*-oxide (NMMO) solvent and at elevated temperatures. Transition metals are capable of participating in redox processes because they can easily undergo changes in valency [123]. This affects the stability of the NMMO solvent. Both iron and copper promote the cleavage of NMMO into two secondary C-centred radicals, namely: N-methylmorpholine (NMM) and morpholine [123]. The formed radicals attack cellulose by introducing keto groups at the C-2 position of the anhydroglucose unit and eventually cleaving the chain by β-elimination. These metal ions have also been reported to accelerate thermal instability of the NMMO-cellulose solution [32]. Therefore increased concentrations of copper or iron decrease the decomposition temperature of NMMO which in turn can trigger off a runaway decomposition reaction or explosions. More details on the effect of iron and copper on NMMO-cellulose solution can be found in the literature [32, 123].

To prevent the occurrence of side reactions associated with heavy metal contents during cellulose dissolution in NMMO solvent, it was necessary to ensure that all metals were removed from the recycled cotton pulp prior to cellulose dissolution and subsequent extrusion of the spinning solution. In this study chelating agents were included in the alkaline dithionite and peroxide bleaching stripping liquors in order to assist the removal of metals from the materials. To eliminate the possibility of metal contamination resulting from the disintegration equipment, the agents were also added to the material during disintegration.

Chelating or sequestering agents are capable of reacting with metal ions preventing them from interfering with the mainstream process [83]. The agents work by complexing (or bounding) with free metal ions through electron donation to the metal ion forming several stable heteroatom rings around them as shown in Figure 5.9.1. The most common donating atoms are nitrogen found in amines and oxygen from carboxyl, phosphate or ionised hydroxyl groups. The resulting complex blocks the ion's normal reactive sites and prevents it from reacting as it normally would. The formed complex is also soluble under the processing conditions, hence easily washed out after processing.

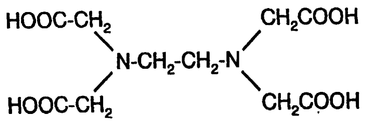
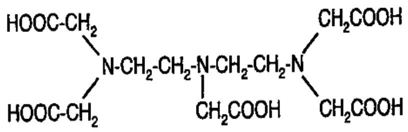
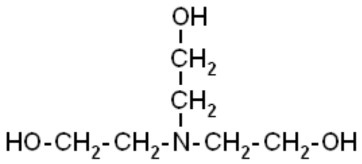
Figure 5.9.1 Formation of a metal chelate, adapted from DRT website [226]

5.9.2 Experimental

5.9.2.1 Materials and chemicals

Scoured, bleached and mercerised cotton fabric dyed with C. I. Reactive Black 5 dye at 4% o.w.f was used for the analysis. All chelating agents were obtained from Sigma Aldrich and their details are presented in Table 5.9.1. The agents were chosen based on their functionality in chelating with metal ions. Ethylenediamine tetraacetic acid (EDTA) was selected due to its relatively cheap price, commercial availability and its popularity as a chelating agent; however the agent is ineffective at controlling iron particularly at higher alkaline pH [83]. Accordingly Diethylenetriamine pentaacetic acid (DTPA) and Triethanolamine (TEA) were also used to assist the removal of metals when higher pH conditions were used. DTPA was also selected due to its ability to offer best chelating properties in the presence of oxidizing agents such as peroxides [83].

Table 5.9.1 Chelating agents used in this study

Code	Name	Details	Structure
EDTA	Ethylenediamine tetraacetic acid	Aminocarboxylic acid Mw= 292.2 g/mol	
DTPA	Diethylenetriamine pentaacetic acid	Aminocarboxylic acid Mw= 393.4 g/mol	
TEA	Triethanolamine	Mw= 149.2 g/mol	 $HO-CH_2-CH_2-\overset{\overset{\overset{\overset{\overset{OH}{\mid}}{CH_2}}{\mid}}{CH_2}}{\overset{\mid}{N}}-CH_2-CH_2-OH$

5.9.2.2 Stripping Procedure

Stripping was performed using the acid/dithionite/peroxide treatment described in Section 3.4. However 2 g/L of a chelating agent was added to the alkaline dithionite and peroxide bleaching stripping solutions in order to aid the removal of metals from cotton fabrics. The other stripping procedures remained the same. To eliminate the possibility of metal contamination resulting from the disintegration equipment, the same amount of chelating agent was also added into the material during disintegration process. Analysis of the samples was performed externally at Hull University using the Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) technique described in Section 3.8. Due to time and facility limitations, the analysis was only performed on C. I. Reactive Black 5 dyed samples (RB5) that were stripped using the sequential acid/dithionite/peroxide treatment.

5.9.3 Results and Discussion

In this section the effect of including chelating agents in the dye stripping liquors was assessed in removing metals from cotton fabrics. The content of heavy metals extracted from the samples by using acid at high temperature and pressure were analysed using the ICP-OES technology and the results are discussed below. Iron (Fe) and copper (Cu) were chosen as representative metals due to the high level of risk they present during dissolution and subsequent spinning of the material using the NMMO Lyocell processing technology. The undyed mercerised cotton fabric was used as the control.

5.9.3.1 Effect of the chelating agents in removing metals from cotton fabrics

Figure 5.9.2 shows the effect of different chelating agents in removing Fe and Cu from RB5 dyed and stripped cotton fabrics. The detection limits, defined as the concentrations corresponding to three times the standard deviation of ten blanks were found to be 0.0003 ppm for both Fe and Cu.

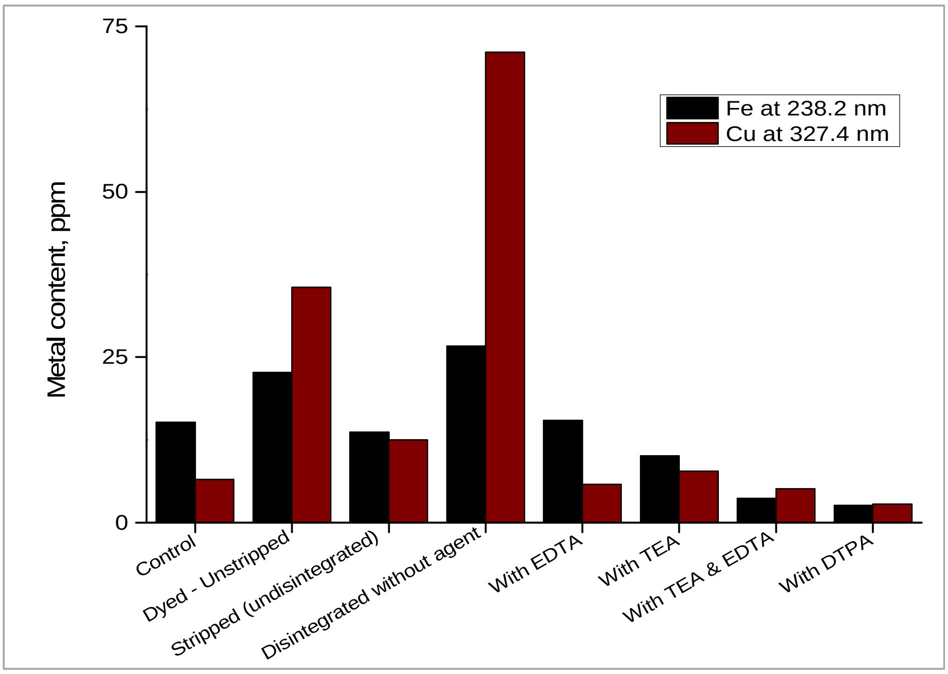


Figure 5.9.2 Metal content of the C. I. Reactive Black 5 dyed cotton fabric following stripping in the presence of various chelating agents.

It can be seen from the figure that the starting cotton material contained a large amount of both Fe and Cu (15.2 ppm and 6.5 ppm, respectively), which increased further to 22.7 ppm and 35.6 ppm, respectively, with dye application. Since the structure of the C. I. Reactive Black 5 dye used showed no presence of heavy metals, the reason for the increased metal content was uncertain, although some reactive dyes were reported to contain coordinated copper atoms [83]. It was however presumed that metals could be coming from the contact points of fabrics and the dyeing tubes despite being made of stainless steel.

Stripping of the dyed samples in the sequential acid/dithionite/peroxide treatment significantly decreased the level of metals on the sample to 13.7 ppm and 12.5 ppm for Fe and Cu, respectively. However disintegrating the stripped materials into a pulp form significantly increased the Cu content of the material to 71.1 ppm compared to that of 12.5 ppm observed on stripped (undisintegrated) sample. Disintegration of the materials also increased the amount of Fe content by 49% more than that observed on the stripped-undisintegrated sample. Again this was thought to be a result of friction between the fibre materials and the blades of the disintegration equipment, despite being made of stainless steel.

Incorporating chelating agents in the stripping liquors and in the disintegration equipment resulted in a significant decrease in metal content. For instance, adding EDTA decreased the amount of Cu to 5.8 ppm compared to 71.1 ppm observed on the sample processed without a chelating agent. However the agent did not remove much of the Fe, resulting in metal content of 15.5 ppm compared to 26.7 ppm observed on samples stripped without chelating agents. EDTA has been reported to be ineffective in controlling Fe metal in highly alkaline solutions, as the metal tends to be precipitated from the complexes formed [83]. Similarly the agent is easily decomposed by hydrogen peroxide, which was among the treatments used in the stripping sequences of this study.

When TEA was used on its own, a significant amount of metals was removed from the samples resulting to 10.1 ppm and 7.8 ppm for Fe and Cu, respectively, compared to 26.7 ppm and 71.1 ppm, respectively, observed on the samples stripped without a chelating agent. TEA has been reported to be a stronger chelating agent which can complex with Fe even in strong alkaline solution (up to 18% NaOH) and remains active [83]. Combining the chelating effect of TEA and EDTA resulted in even greater metal removal where values of 3.7 ppm and 5.1 ppm were observed for Fe and Cu, respectively. The high efficiency of combining TEA and EDTA in complexing with the metals present in the materials have been reported in the literature [83].

The addition of DTPA chelating agent in the stripping liquors and in the disintegration equipment resulted in an obvious beneficial effect in removing both Fe and Cu from the cottons. Metal contents of 2.6 ppm and 2.8 ppm were observed for Fe and Cu, respectively, compared to 15.5 ppm and 5.8 ppm, respectively, obtained on samples stripped in the presence of EDTA alone. The agent was more effective even when compared to the combined effects of TEA and EDTA agents. The DTPA chelating agent was reported to be a higher homologue of EDTA, containing three amino groups and five carboxyl groups [227] compared to only two amino groups and four carboxylic groups present in EDTA. This means, all the three nitrogen atoms of the amino groups present in DTPA can simultaneously coordinate with the metal thereby increasing the stability of the complex formed. This higher stability of the DTPA-metal complexes formed could be the reason for the greater chelating effect with both Fe and Cu ions.

5.9.4 Summary

In this section the efficiency of chelating agents in removing metals from the C. I. Reactive Black 5 dyed and stripped cotton samples have been analysed. EDTA, DTPA and TEA were added in the dithionite and peroxide treatments of the sequential acid/dithionite/peroxide stripping method and in the disintegration equipment for the purpose of aiding the removal of heavy metals, particularly Fe and Cu from the materials. Results indicated that the addition of the chelating agents in the stripping treatment as well as in the disintegration process had a significant effect on metal removal with the best results observed when DTPA chelating agent was used. Accordingly DTPA was selected as the chelating agent in this study and was therefore added to the dithionite and peroxide stripping liquors and during the disintegration of the samples for pulp generation.

5.10 STRIPPING OF COLORANTS FROM COTTON USING OTHER STRIPPING SEQUENCES

In this study the acid/dithionite/peroxide dye stripping sequence was also altered and its effect on colorant stripping evaluated. The results were expressed in terms of colour strength, *K/S*, CIELAB colour difference, ΔE and ISO brightness determined from reflectance values at 460 nm wavelength.

5.10.1 Experimental

5.10.1.1 Materials and chemicals

Two reactive dyed fabrics (C. I. Reactive Black 5 – RB5 and C. I. Reactive Blue 19 – RBL19) and post-consumer denim jeans were analysed. The two reactive dyed fabrics were selected because they represent a large group of dyes used for cotton and other cellulosic fibres while the post-consumer denim jeans was selected because it represents a common garment in people's lifestyle.

5.10.1.2 Stripping process

Stripping was performed as detailed in Section 3.4, but with modification on the treatment sequences (Table 5.10.1), where:

- Sequence 1 = acid/dithionite/peroxide (normal treatment);
- Sequence 2 = acid/peroxide/dithionite (modified);
- Sequence 3 = peroxide/dithionite/acid (modified);
- Sequence 4 = dithionite/peroxide/acid (modified).

Table 5.10.1 Experimental plan for stripping colorants using different sequences

Sequence	Sample	Treatment
1	Group 1	Acid treatment
	Group 2	Dithionite treatment of Group 1 sample
	Group 3	Peroxide treatment of Group 2 sample
2	Group 1	Acid treatment
	Group 2	Peroxide treatment of Group 1 sample
	Group 3	Dithionite treatment of Group 2 sample
3	Group 1	Peroxide treatment
	Group 2	Dithionite treatment of Group 1 sample
	Group 3	Acid treatment of Group 2 sample
4	Group 1	Dithionite treatment
	Group 2	Peroxide treatment of Group 1 sample
	Group 3	Acid treatment of Group 2 sample

5.10.2 Results and Discussion

The colorimetric parameters of the stripped samples were measured by using a Datacolor spectrophotometer where colour strength, CIELAB colour difference and ISO brightness were evaluated and the results are discussed below.

5.10.2.1 The effect of varying the acid/dithionite/peroxide dye stripping sequence on colour strength (K/S) of the stripped samples

Figure 5.10.1 shows the effect of varying the sequence of the stripping treatment on the colour strength of the reactive dyed fabrics and on denim fabrics. It can be seen from the figure that changing the treatment sequences had similar effects on reactive dyed samples resulting in *K/S* values of up to 0.03 on both RB5 and RBL19 samples. However sequence 4 was marginally more effective in stripping colorants from the denim sample resulting in *K/S* of 0.14, followed by sequence 1 which resulted in *K/S* of 0.15. Sequence 2 and 3 also removed significant amounts of colorants from denim sample resulting in *K/S* of 0.4 and 0.2, respectively.

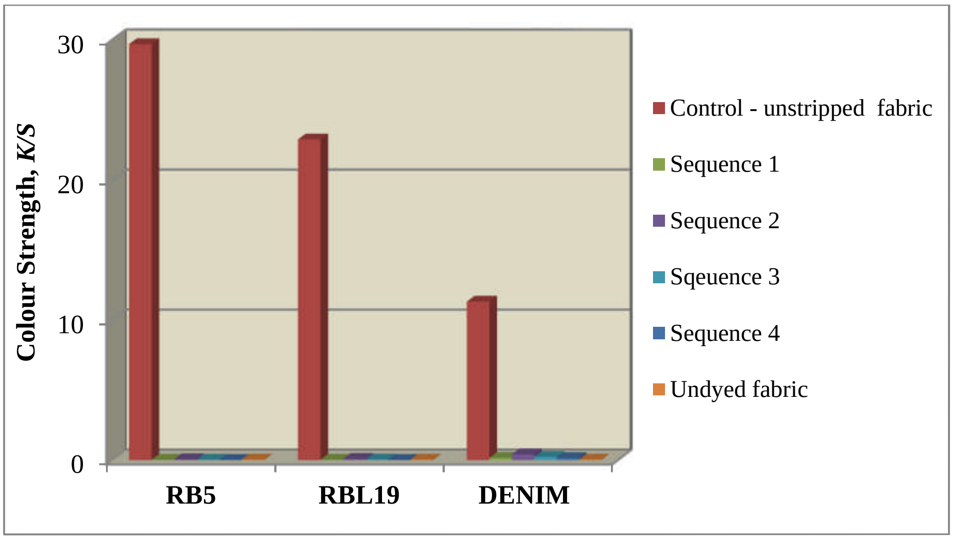


Figure 5.10.1 Effect of varying the acid/dithionite/peroxide stripping sequence on the colour strength of the stripped fabrics.

5.10.2.2 The effect of varying the acid/dithionite/peroxide stripping sequence on the CIELAB colour difference, ΔE, of the stripped fabrics

Figure 5.10.2 shows the effect of varying the acid/dithionite/peroxide stripping sequence on the colour differences of the stripped cottons. It can be seen from the figure that the process of varying stripping sequences resulted in a slight difference on RB5 samples resulting in Δ*E*s of 78.8, 76.5, 78.2 and 79.5 on sequence 1, sequence 2, sequence 3 and sequence 4, respectively. The effect was also minimal on the colour difference of RBL19 fabric stripped in sequence 1, 2 and 4 where Δ*E*s of 78.4, 75.8 and 80.5, respectively, were obtained, however sequence 3 only resulted in a Δ*E* of 72.7. For the denim material greater Δ*E*s of 63.8 and 62.8 were observed on fabrics stripped in sequence 1 and 4, respectively. However sequence 2 and 3 only resulted in Δ*E*s of 49.7 and 53.7, respectively.

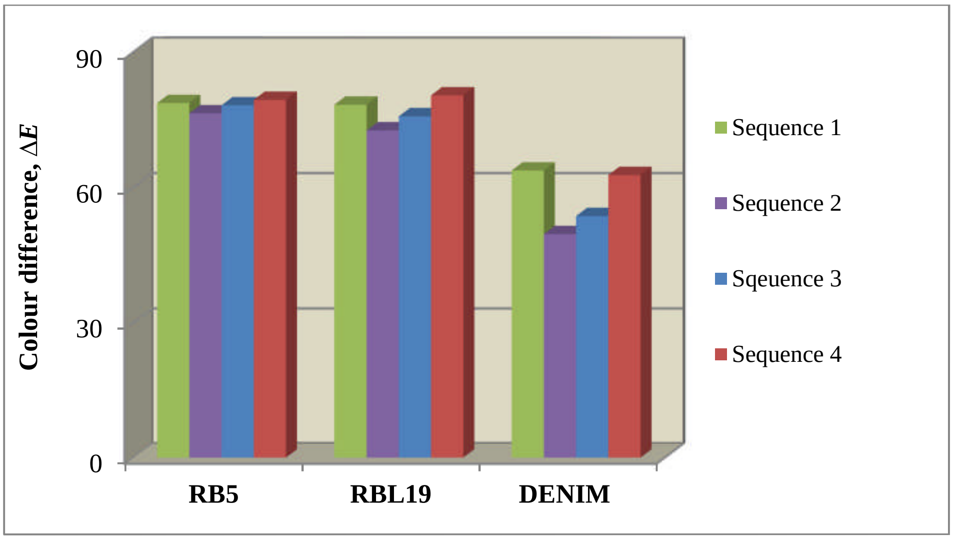


Figure 5.10.2 Effect of varying the acid/dithionite/peroxide stripping sequence on the colour difference, Δ*E*, of the stripped material.

5.10.2.3 The effect of varying the acid/dithionite/peroxide stripping sequence on the ISO brightness of the stripped fabrics

The effect of varying the acid/dithionite/peroxide stripping sequence on the ISO brightness of the stripped samples is compared in Figure 5.10.3. It can be seen that varying the acid/dithionite/peroxide stripping sequence resulted in greater brightness of the RB5 fabric where brightness values of 83.2%, 81.5% and 86.2% were observed with sequence 1, 3 and 4. A slightly lower brightness of 76.9% was however observed when sequence 2 was used. Sequence 2 also resulted in lower brightness on the RBL19 fabric where a brightness of only 67.5% was observed on the stripped material. Similarly the effect of sequence 3 on RBL19 dyed cotton was also minimal resulting in a brightness of only 75.1% compared to the brightness 82.7% and 85.8% attained on sequence 1 and 4, respectively. A similar trend was also observed on denim with greater ISO brightness values of 89.2% and 83.9% attained on using sequence 1 and 4, respectively, compared to the brightness values of 66.4% and 70.1% observed on sequence 2 and 3, respectively.

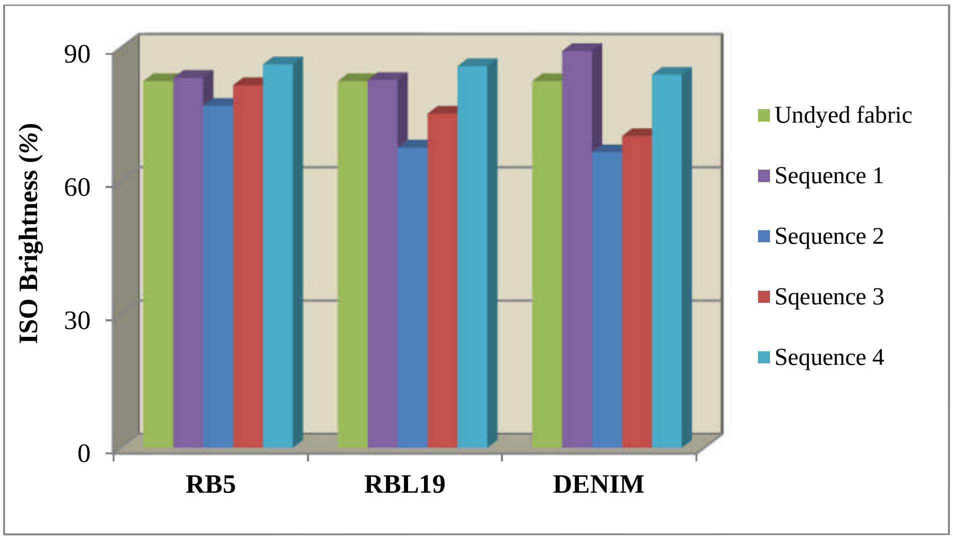


Figure 5.10.3 Effect of varying the acid/dithionite/peroxide stripping sequence on the ISO brightness of the stripped cotton fabrics.

5.10.3 Summary

In this section the acid/dithionite/peroxide stripping sequence was altered in order to assess the effect of varying the treatment sequence on the colorimetric parameters of the stripped fabrics. Two cotton fabrics dyed with C. I. Reactive Black 5 and C. I. Reactive Blue 19 and a post-consumer denim jean were evaluated. It was established that varying the stripping sequence only resulted in a slight difference in the colorimetric parameters of all the fabrics with sequences 1 and 4 offering the overall best results. A slight lower efficiency was however observed when sequence 2 (acid/peroxide/dithionite) and sequence 3 (peroxide/dithionite/acid) were used.

5.11 CONCLUSIONS

Since the presence of impurities, additives and inter-polymer crosslinks, such as those introduced by reactive dye-fibre bonds and finishing agents affects the dissolution and subsequent spinnability of the chemically recycled cotton pulp, it was therefore necessary to develop a method that could remove these impurities/additives and crosslinks as a way of preparing and purifying the waste cotton garments as the pulp for Lyocell fibre regeneration. In this chapter the effect of the sequential acid/alkali/peroxide treatments and that of the alternative sequential acid/dithionite/peroxide method were evaluated in their efficiencies to strip cellulosic colorants including vat dyes, sulphur dyes, direct dyes and pigments from cotton fabrics. End-of-life garments were also treated in the optimised processes so as to determine the efficiency of the stripping sequences in stripping colorants from the actual waste garments. Finishing agents such as the DMDHEU-based easy care finish as well as the fluorescent whitening agents were also evaluated. Heavy metals, specifically iron and copper were also included in the scope of the study due to the safety effects they present when using the NMMO solvent for fibre regeneration.

Results indicated that the acid/alkali/peroxide method could only strip low levels of colorants from all fabrics as after the completion of the stripping process, most colorants were left on the stripped materials. However the acid/dithionite/peroxide stripping process was able to strip over 99% of most cellulosic dyes, including those from end-of-life garments. This was attributed to the strong reducing nature of the alkaline dithionite solutions together with the dye transfer inhibiting properties of the polyvinylpyrrolidone (PVP) polymer. The ability of hydrogen peroxide bleaching to remove dye residues remaining after the dithionite treatment was also thought to contribute to the high stripping efficiency of the sequential acid/dithionite/peroxide method.

Together with the fluorescent whitening agents, the acid/dithionite/peroxide method was also able to strip DMDHEU-based easy care finishes as it was presented by FTIR, CRA and solubility results. With the addition of the chelating agents in the dithionite and peroxide stripping liquors heavy metals (iron and copper) were also removed from the stripped cotton fabrics. Although the reactive dyes used had no heavy metals it was necessary to include the chelating agents in the stripping sequences in order to assist in the removal of any metals resulting from processing water or vessels.

It is also worth mentioning that although the acid treatment included in the two stripping methods was not effective in removing colorants from the cotton materials, the inclusion of the treatment was essential due to its usefulness in breaking bonds resulting from crosslinking agents and in removing impurities such as heavy metals and fluorescent whitening agents.

Chapter Six: Pulp preparation and fibre spinning

6.1 INTRODUCTION

This chapter reports on the activities undertaken to accomplish objective 2 and 3 of this study as detailed in chapter 1.2. These activities involved disintegration of the chemically stripped cotton substrates into a fibrous pulp and further processing the cotton pulps into regenerated Lyocell fibres. Three cotton samples were selected for further processing all of which contained dyes and other colourless reagents capable of crosslinking with the hydroxyl groups of cotton cellulose, and potentially reducing the solubility of the recycled cotton pulp in the N-methylmorpholine-*N*-oxide (NMMO), contaminating the solvent whilst affecting the quality (e.g. brightness and re-dyeability) of the new regenerated fibre. It was therefore necessary to first remove any crosslinks from the selected cotton substrates, prior to producing the pulp and commerce fibre spinning.

To remove colorants and crosslinks such as those resulting from finishing agents, samples were stripped in the sequential acid/dithionite/peroxide treatment, as discussed in Chapter 4 and 5 of this thesis. Together with removing colorants and crosslinks the treatment aimed at purifying the cotton pulps by “freeing” the cellulosic hydroxyl groups in the cotton cellulose, thereby increasing its accessibility to chemical solvents. The efficiency of the treatment in removing both colorants and crosslinks from cotton substrates was assessed by monitoring the change in colour parameters and the extent of solubility of the stripped samples in the CED solvent. Similarly the effect of the stripping process on cotton cellulose degradation was determined by measuring the limiting viscosity of the cotton cellulose in CED solution as per British standards [166] and then calculating the degree of polymerization (DP) using appropriate formulae [121].

The stripped samples were then disintegrated into fibrous pulp materials prior to dissolution in NMMO solvent and subsequent regeneration of new Lyocell fibre. Both mechanical and structural properties of the fibres regenerated from recycled cotton substrates were established and were compared to conventional Lyocell fibres regenerated from wood pulp.

6.2 EXPERIMENTAL

6.2.1 Materials

In this chapter undyed bleached (unmercerised), plain woven 100 % cotton fabric, weighing 135 g/m^2 was supplied by Phoenix Calico, Manchester. The fabric was dyed using two reactive dyes, namely: C. I. Reactive Black 5 (RB5) and C. I. Reactive Blue 19 (RBL19), prior to processing of the dyed fabrics for fibre regeneration. A post-consumer denim jeans (denim) was also used for pulp generation and subsequent fibre regeneration.

The C. I. Reactive Black 5 dye was selected because it provides the basis for a wide range of recipes for heavy navy and black shades for cellulosic fibres. However the C. I. Reactive Blue 19 dye was selected in order to establish the effect of its chemically resistant anthraquinone chromophoric structure on stripping, pulping and the Lyocell fibre regeneration. The post-consumer denim jeans was selected because it is a popular style of wear to people across the social and demographic spectrum.

6.2.2 Pulp preparation

The cotton pulps were prepared by first dyeing the unmercerised cotton fabrics with reactive dyes using the procedure described in Chapter 4 of this thesis. The reactive dyed cotton fabrics and the post-consumer denim jeans were then stripped using the optimised acid/dithionite/peroxide stripping method as described in Chapter 4 and 5 of this thesis. Although the dyes used had no heavy metals, a 2 g/L of diethylenetriamine pentaacetic acid (DTPA) chelating agent was added in each stripping bath to assist the removal of any heavy metals present in the cotton materials as a result of processing water or processing equipment such as the dyeing pots. The DTPA chelating agent was chosen due to the superior properties it offered when compared to other chelating agents, including ethylenediamine tetraacetic (EDTA) and Triethanolamine (TEA) that were used in Chapter 5 of this study.

The acid/dithionite/peroxide stripped fabrics were then disintegrated using the procedure described in Section 3.6 of this thesis. However a 2 g/L of the DTPA chelating agent was added to the disintegration equipment to prevent possible contamination of the pulp with heavy metals from either the processing water or the processing equipment.

6.2.3 Pulp characterisation

The recycled cotton pulp was characterised in terms of its colorimetric parameters (as described in Chapter 4 and 5), its dissolution in cupriethylenediamine hydroxide (CED) solvent and the extent of cellulose degradation as a result of the acid/dithionite/peroxide treatment. The solubility of the stripped cotton fabrics was assessed in the CED solvent using a procedure detailed in Section 3.7 of this thesis. Prior to the addition of the CED solvent, the cotton cellulose materials were first soaked in water in order to initiate the swelling and hence allowing dissolution to occur by enabling penetration of the solvent into the cellulose molecules.

The CED solvent was also used in the determination of the limiting viscosity of the cellulose and in estimating the effect of the acid/dithionite/peroxide stripping treatment to the extent of cellulosic fibre damage through determination of the degree of polymerisation.

6.2.4 Spinning and characterisation of the regenerated fibres

The cotton pulps obtained from the chemically stripped reactive dyed samples and a post-consumer denim jeans were evaluated by Lenzing for dissolution in the NMMO solvent and subsequent fibre spinning as per Lenzing procedures. The spinning solution was prepared by mixing 49.6%v/v NMMO hydrate solution with the pulp and propyl 3,4,5-trihydroxybenzoate (propyl gallate ester) in a suitable ratio (confidential) using a Lenzing knitter mixer. The dissolution process was achieved by mixing the materials at increasing temperature and pressure starting from room temperature and 250 mbar to 110°C and 400 mbar, respectively. The final spinning dope had 9% cellulose concentration, 78% NMMO and 13% water as detailed in Section 3.7 of this thesis.

Fibres were spun in a laboratory scale spinning machine at Lenzing AG, Austria using a spinneret with a single hole of 100µm in size. The dope throughput was 0.03 g/min and the air gap conditions were set at 20 mm, with temperature and relative humidity adjusted to fit the required fibre output. The winding speed was 26 m/min and water was used to precipitate the fibres and regenerate cellulose. Other spinning parameters including the draw ratio, spinning speeds, relative humidity and temperature could not be disclosed due to confidentiality. The spun fibres were then oven-dried overnight at 60°C temperature.

To prepare solutions with the appropriate viscosity properties, 20% of the recycled cotton pulps were blended with 80% of the wood pulp. Five fibres namely: Lyocell-1, Lyocell-2, Lyocell-3, Lyocell-4 and Lyocell-5 were spun as detailed in Table 6.2.1. Lyocell-0 a conventional Lyocell fibre spun from wood pulp is also included.

Table 6.2.1 Description of the Lyocell fibres regenerated from recycled cotton pulp

Fibre name	Description
Lyocell-0	Regenerated from 100% conventional undyed wood pulp pretreated by reductiom and oxidation processes [36].
Lyocell-1	Regenerated from 100% recycled cotton pulp obtained from unmercerised cotton fabrics previously dyed with C. I. Reactive Black 5 then stripped in the sequential acid/dithionite/peroxide method.
Lyocell-2	Regenerated from 100% recycled cotton pulp obtained from unmercerised cotton fabrics previously dyed with C. I. Reactive Blue 19 then stripped in the acid/dithionite/peroxide method.
Lyocell-3	Regenerated from 100% recycled cotton pulp obtained from post-consumer denim jeans, stripped in the sequential acid/dithionite/peroxide treatment.
Lyocell-4	Regenerated from 20% recycled cotton pulp used in Lyocell-1 and 80% wood pulp used in Lyocell-0.
Lyocell-5	Regenerated from 20% recycled denim pulp used in Lyocell-3 and 80% wood pulp used in Lyocell-0

Characterisation of the mechanical properties (linear density, tenacity and elongation at break) of the regenerated fibres was performed at the Lenzing testing facilities in Austria and were compared to the conventional Lyocell fibre (Lyocell-0). Surface and structural properties of the regenerated fibres were also assessed using the SEM, FTIR and XRD analytical techniques available at the University of Leeds.

6.3 RESULTS AND DISCUSSIONS

This chapter details activities conducted to prepare the recycled cotton pulp for spinning and subsequent Lyocell fibre regeneration. The cotton substrates were first treated in the sequential acid/dithionite/peroxide stripping method to remove any colorants and crosslinks resulting from other finishing agents, thereby maximising the dissolution of the pulp for fibre regeneration. The stripped cotton substrates were then broken-down into fibrous pulp materials prior to dissolution of the pulp in the NMMO solvent and subsequent spinning of the solution and Lyocell fibre regeneration. Properties of the recycled cotton pulps were monitored and the new regenerated fibres were characterised and their properties were compared to the conventional Lyocell fibres.

6.3.1 Characterisation of the cotton pulp formed

In this study properties of the recycled cotton pulps were determined by monitoring changes occurring in the colorimetric parameters (ISO brightness and colour strength), fibre lengths and solubility of the stripped materials in CED solvent. The extent of cellulose degradation as a result of the stripping process was also evaluated and the results obtained are discussed below.

6.3.1.1 The effect of the sequential acid/dithionite/peroxide treatment on the colorimetric parameters of the cotton

In this chapter the ISO brightness parameters were used to assess the efficiency of the sequential acid/dithionite/peroxide treatment in stripping colorants from the cotton substrates for the purpose of preparing the recycled materials for subsequent fibre regeneration through the Lyocell process. The parameter is normally used to characterise the level of brightness of pulps [162]. The ISO brightness required for dissolving pulps is typically 90% [36], however the brighter the pulp, the brighter is the regenerated fibre and therefore easier subsequent aftertreatment of the fibre such as redyeing.

Figure 6.3.1 presents the ISO brightness parameters of the cottons following the chemical treatments. The acid treatment had no significant impact on the RB5 dyed cotton resulting in brightness values similar to their comparable dyed untreated cotton. However the treatment partially removed dye from both RBL19 and denim fabrics resulting in brightness values of 31.0% and 7.7%, respectively. Subsequent dithionite and peroxide treatments stripped large amounts of colorant from all the materials resulting in ISO brightnesses of 82.6%, 83% and 86.6% for RB5, RBL19 and denim fabrics, respectively, approaching a brightness of 89.8% for the starting material, the undyed cotton fabric. Although the ISO brightness obtained were slightly lower than the brightness of the conventional wood pulps (90%), the obtained results were within the acceptable brightness range for fibre regeneration through the Lyocell process.

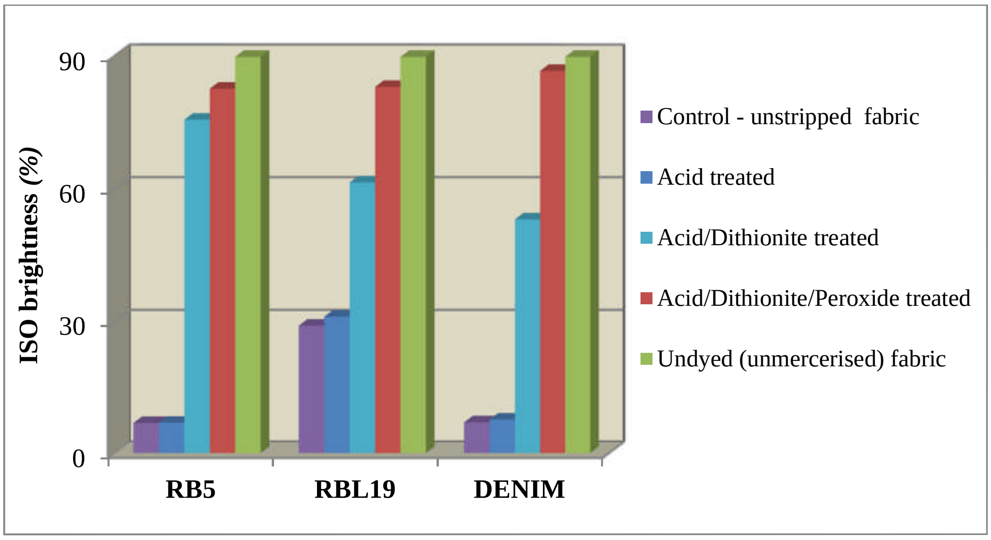


Figure 6.3.1 The ISO brightness parameters for the cotton fabrics stripped in the sequential acid/dithionite/peroxide treatments.

The colour strength results (Figure 6.3.2) also showed significant colour removal as the fabrics were stripped from one treatment to another. Similar results were also obtained when merserised reactive dyed cotton fabrics were stripped in the sequential acid/dithionite/peroxide method as discussed in Chapter 4.

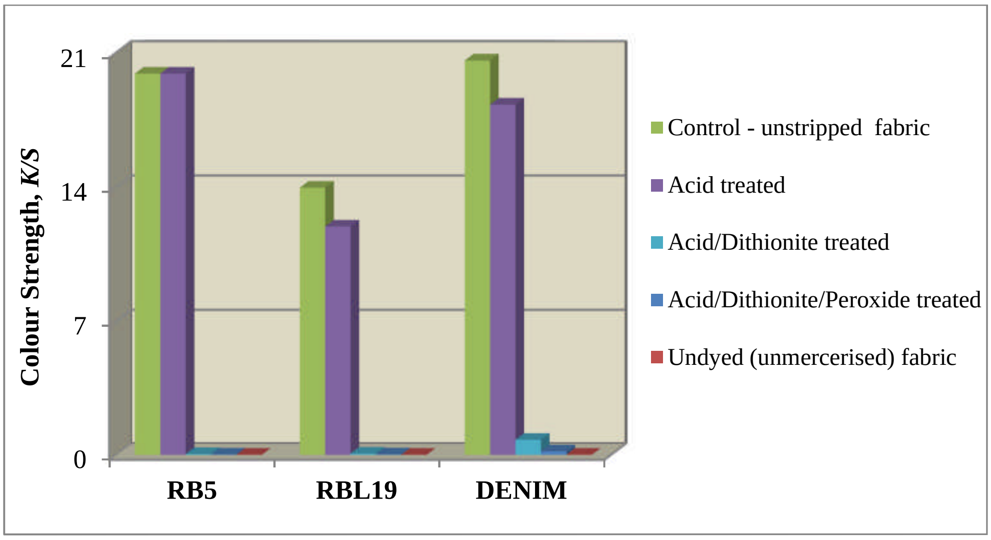


Figure 6.3.2 Comparison of the colour strength for the fabrics stripped in the sequential acid/dithionite/peroxide treatments.

6.3.1.2 The effect of the disintegration process on the fibre length of the recycled cotton pulps

In this study the acid/dithionite/peroxide stripped cotton fabrics were further disintegrated into a fibrous material (pulp) in order to increase the surface area of the materials, thereby increasing their accessibility to chemical solvents. For each resultant cotton pulp, the fibre length was assessed in order to establish the average lengths of fibres generated by the disintegration process.

Figure 6.3.3 presents the mean fibre lengths of the cotton pulps obtained after the disintegration of the recycled cotton materials. The disintegration process produced similar fibre lengths for the RB5 and RBL19 dyed fabrics where an average of 1.9 mm fibre length was observed. However the process resulted in slightly shorter fibres in the denim sample with an average of only 1.0 mm lengths observed. The shorter fibre length observed in denim material could be due to the fact that the post-consumer denim garment had already gone through a number of processes, including wearing, washing and drying during its service time making the fibres weaker and much easier disintegrated. The shorter fibre length observed on denim could also be due to shorter fibres typically used for denim making.

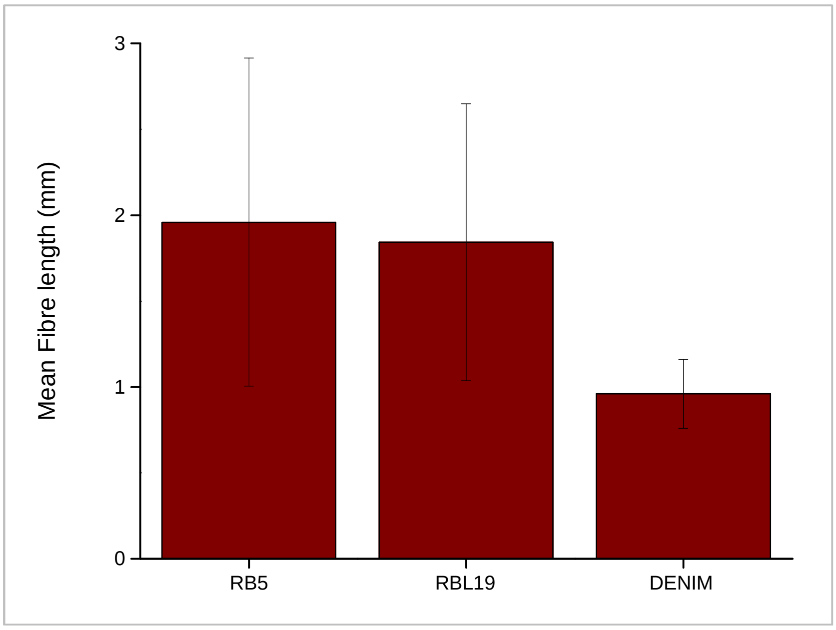


Figure 6.3.3 The effect of the disintegration process on fibre length.

6.3.1.3 The effect of the sequential acid/dithionite/peroxide treatment on the solubility of the stripped cotton in 0.5M CED solution

The accessibility of cellulose by solvents is through its hydroxyl groups present in the amorphous region of the cellulosic material [55, 228]. However the crosslinking nature of most cellulosic dyes and other finishing agents involves chemically bonding with the hydroxyl groups of the cellulose thereby reducing their accessibility to solvents and their subsequent solubility [219]. The purpose of the sequential acid/dithionite/peroxide treatment was therefore not only to strip colorants but to also break the chemical bonds formed between the dyes or finishing agents and cellulosic hydroxyl molecules, thereby, providing a white cotton material with a significant reduction in crosslinking and therefore increased solubility in chemical solvents.

In this section the solubility of the chemically stripped materials was assessed in a 0.5M CED solution. The solubility of the samples was evaluated using both light microscopy and the oven dry weighing.

Table 6.3.1 shows the percentage solubility of the stripped cotton materials in 0.5M CED solution. It can be seen that although the starting material, the undyed cotton fabric could be dissolved completely in the solvent, the situation changed after dye application where the cotton solubility decreased to 44%, 94% and 86% for RB5, RBL19 and denim materials, respectively. For the solvent to dissolve the cellulosic polymer, it must form hydrogen bonds with the hydroxyl groups of the amorphous region of the cellulose, swell the material and finally disrupt the crystalline region of the cellulose to form a polymer solution [55, 228]. Therefore the decreased solubility of the samples was thought to be due to the dye molecules bonding with the hydroxyl groups of the cellulose, thereby reducing their accessibility to the solvent.

Table 6.3.1 The effect of the sequential acid/dithionite/peroxide treatment on the solubility of the stripped cotton in 0.5M CED solution

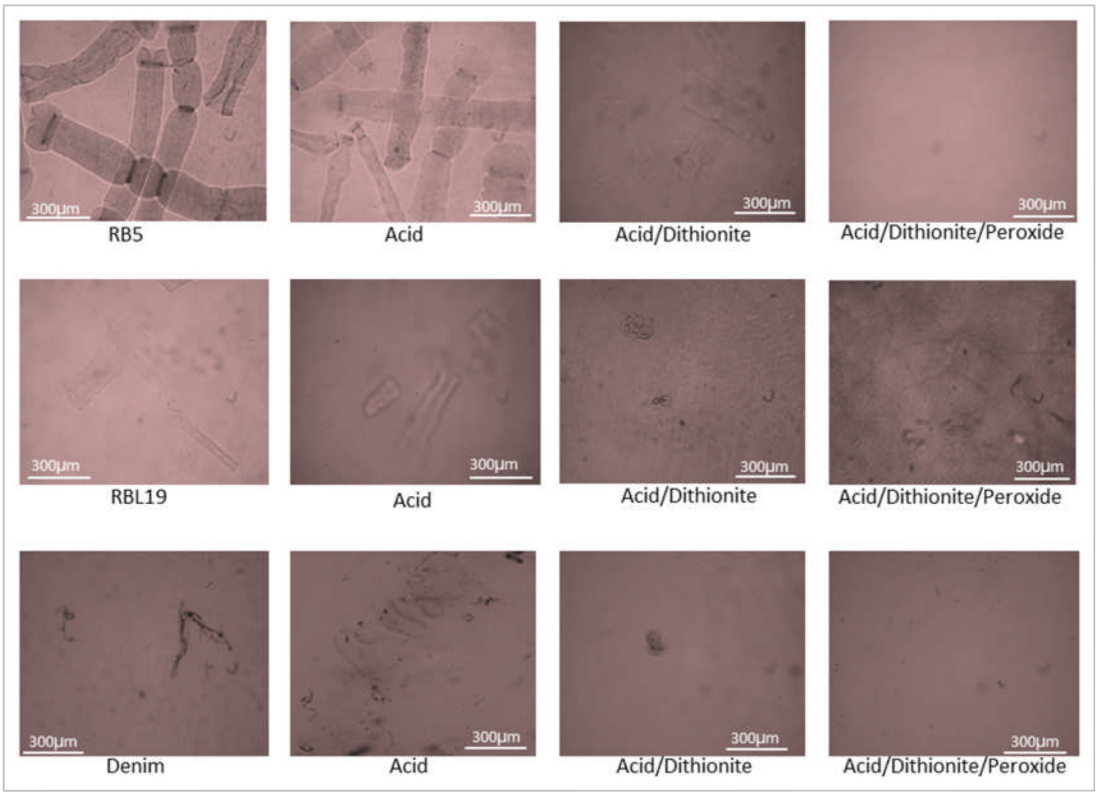
Sample	Solubility in CED				
	Undyed fabric (%)	Dyed untreated (%)	Acid treated (%)	Acid/dithionite treated (%)	Acid/dithionite/ Peroxide treated (%)
RB5	100.0	43.8	70.7	97.9	100.0
RBL19	100.0	94.4	99.3	100.0	100.0
Denim	100.0	86.4	88.1	97.7	99.0

The relatively low solubility of the RB5 dyed cotton could be attributed to the limited swelling ability of the dyed cotton cellulose due to the strong dye-fibre covalent bonds formed as a result of two functional groups present in the C. I. Reactive Black 5 dye. The dye allows the possible formation of multiple bonds between the dye and the hydroxyl groups in the amorphous region of the fibre [204]. These bonds could be strong enough to resist the disruptive action of the solvents hence the reduced solubility. In contrast, the C. I. Reactive Blue 19 dye has only one functional group offering a single dye-fibre bonding option which is more readily to be disrupted by the solvent hence the slightly higher solubility levels observed on the RBL19 cotton. The slightly lower solubility observed with the denim could be due to the coarser warp yarns and the high degree of twist used for making denim yarns [229]. The higher warp yarn twist holds the fibres together, thereby reducing the interspace between fibres which in turn reduce the capillary action in the yarn and limit their accessibility to water and chemicals [230].

Acid treatment of the dyed fabrics slightly increased their solubilities to 70.7%, 99.3% and 88.1% for RB5, RBL19 and denim materials, respectively. This could be due to the acid hydrolysing the bonds formed between the dyes and the cellulosic hydroxyl molecules, thereby exposing some hydroxyl groups in the cotton cellulose [55]. Further dithionite and peroxide treatments of the samples destroyed more of the bonds resulting in solubilities reaching approximately 100% on RB5 and RBL19 cottons while up to 99% of denim being dissolved.

Both acid hydrolysis and oxidation treatments have been reported as activation stages that can be performed prior to cellulose dissolution for the purpose of opening their internal pores and interfibrillar interstices [50, 55, 63]. The treatment can destroy the glucosidic linkages or crystalline structures of cellulose resulting in the increased reactive surface area of the cellulose fibre and their subsequent accessibility to the action of the solvents. Alkaline solutions have also been reported to increase the swelling properties of cellulosic fibres by breaking some hydrogen bonds, thereby resulting in a less ordered cellulose structure with increased numbers of free hydroxyl groups and subsequent increased accessibility to solvents [64, 231].

Figures 6.3.4 presents micrographs of the cellulose-CED solutions as viewed on a glass slide in a Leica optical microscope at 100x magnification. It is clear from the micrographs that the dyed untreated cotton fabrics could not dissolve completely in the CED solvent as fibre fragments were clearly observed on the viewed solution. The effect of the dye-fibre crosslinks was especially obvious with the RB5 dyed cotton which was again thought to be related to the multiple crosslinking nature of the C. I. Reactive Black 5 dye. However following the complete acid/dithionite/peroxide stripping treatment all samples were fully dissolved in the CED solvent.



RB5 | Acid | Acid/Dithionite | Acid/Dithionite/Peroxide

RBL19 | Acid | Acid/Dithionite | Acid/Dithionite/Peroxide

Denim | Acid | Acid/Dithionite | Acid/Dithionite/Peroxide

Figure 6.3.4 Light micrographs showing the effect of the acid/dithionite/peroxide treatment on the solubility of the stripped cotton materials.

6.3.1.4 The effect of the sequential Acid/Dithionite/Peroxide treatment on the limiting viscosity and the degree of polymerization of the stripped cotton materials

Apart from removing dye-fibre bonds and crosslinks from the cotton substrates thereby improving their solvent accessibility, the purpose of the acid/dithionite/peroxide treatment was also to reduce the degree of polymerisation (DP) of the stripped materials. This was important in order to control the viscosity of the spinning dope, thereby minimizing processing difficulties of the dope materials into new cellulosic Lyocell fibres [35]. To obtain accurate and representative results and to avoid blockage of the viscometer used for analysis, only samples that were completely soluble in CED solution were used to assess the extent of cellulose degradation by determining the limiting viscosity and subsequent degree of polymerisation. For instance both dyed and acid treated samples were not completely dissolved in the solvent and were therefore not included in the determination of the limiting viscosity and the subsequent DP.

Figure 6.3.5 shows the limiting viscosity for the coloured cotton substrates that were stripped in the sequential acid/dithionite/peroxide treatment, while Figure 6.3.6 shows the degree of polymerisation data. The treatment resulted in a significant decrease in both limiting viscosity and DP of all cottons, even after the acid/dithionite treatment alone. This decrease could be due to degradation of the cotton cellulose by scission of the glucosidic linkages of the cellulose polymer [63] as a result of the acid hydrolysis and subsequent alkaline dithionite treatment of the materials. Although the dithionite reducing agent alone is unable to chemically modify the cellulose [63], the presence of a strong alkali in the dithionite stripping liquor in conjunction with the acid pre-treatment of the materials could have assisted in the alkali hydrolysis of the glucosidic linkages of the cellulose polymer, resulting in a decrease in the limiting viscosity and the subsequent DP [68]. Treatment of the cotton samples by oxidative peroxide bleaching resulted in a further reduction of the limiting viscosity and DP. This may be a result of the hydrogen peroxide oxidising the alcohol groups of the cellulose resulting in the formation of the reducing and acidic oxycelluloses which cause weakening or scission of the glucosidic linkages and subsequent decrease in limiting viscosity and DP [50, 63]. Similarly the presence of alkali in the peroxide treatment solution could have also contributed to the decreased viscosity and the DP as a result of alkali hydrolysis.

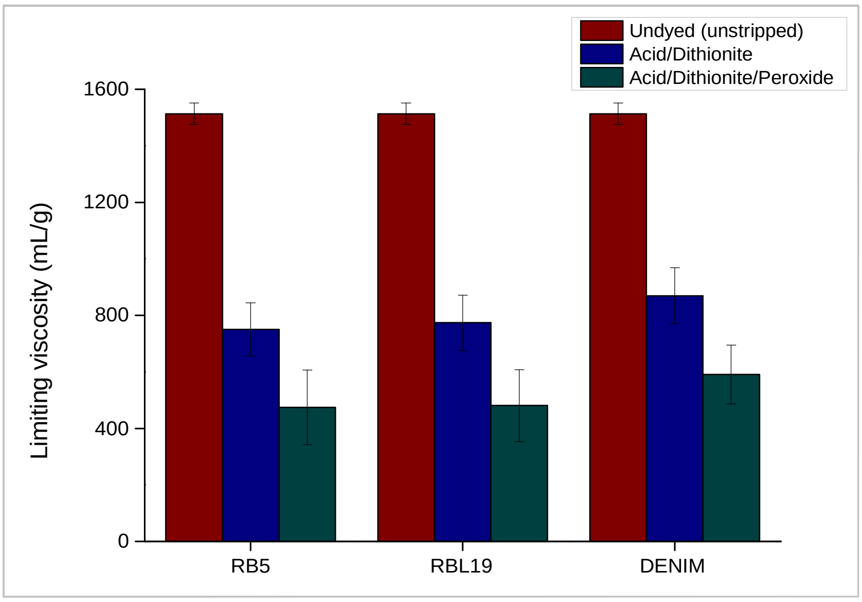


Figure 6.3.5 Effect of the sequential acid/dithionite/peroxide treatment on the limiting viscosity of the recycled cotton pulps stripped in the presence of the DTPA sequestering agent.

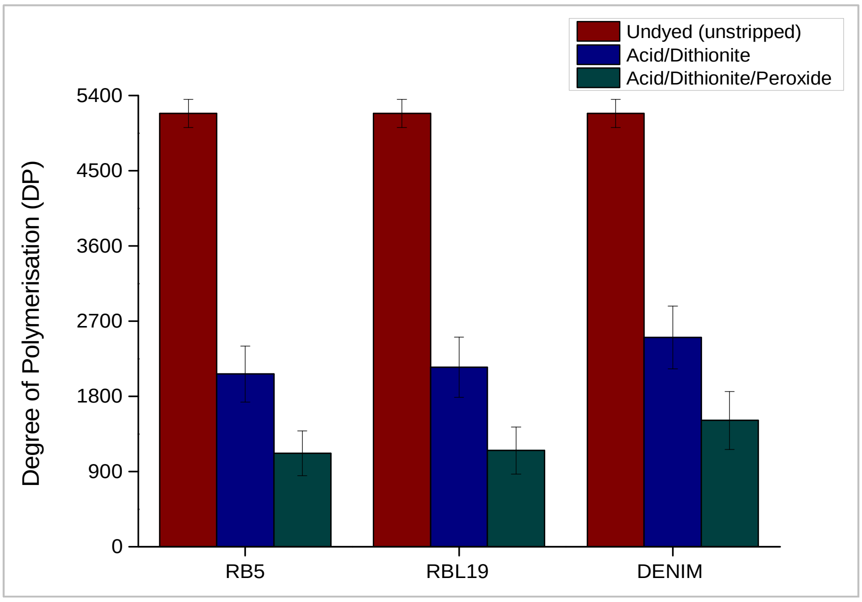


Figure 6.3.6 Effect of the sequential acid/dithionite/peroxide treatment on the degree of polymerisation (DP) of the recycled cotton pulps stripped in the presence of the DTPA sequestering agent.

It is interesting to note the slightly lower effect of the acid/dithionite/peroxide treatment on the limiting viscosity and DP of the denim despite the sample being a post-consumer garment. This could be due to the structure of the denim yarns which are typically stronger and coarser [229] and produce fabrics with higher mass per unit area than normal cotton yarns used in RB5 and RBL19 materials. Accordingly the chemical intake of denim fibres is reduced [230], possibly resulting in lower hydrolysis of their chemical structures hence their slightly higher limiting viscosity and DP.

It is also interesting to consider the effect of DTPA chelating agents on the degradation of the stripped cotton materials. It was found that the addition of the DTPA agent in the stripping liquor significantly reduced the effect of the stripping chemicals on cellulose degradation as higher levels of limiting viscosity and DP were observed on inclusion of the chelating agent (Figure 6.3.7). The presence of some transition metals in oxidative treatment liquors, particularly hydrogen peroxide is sometimes reported to catalyse the redox reactions leading to decomposition of the agent and damaged fibres [36, 83, 227]. Therefore the presence of the DTPA chelating agent in the stripping liquor may have complexed with these metals thereby preventing their catalytic effect and reduced damage to the cotton cellulose.

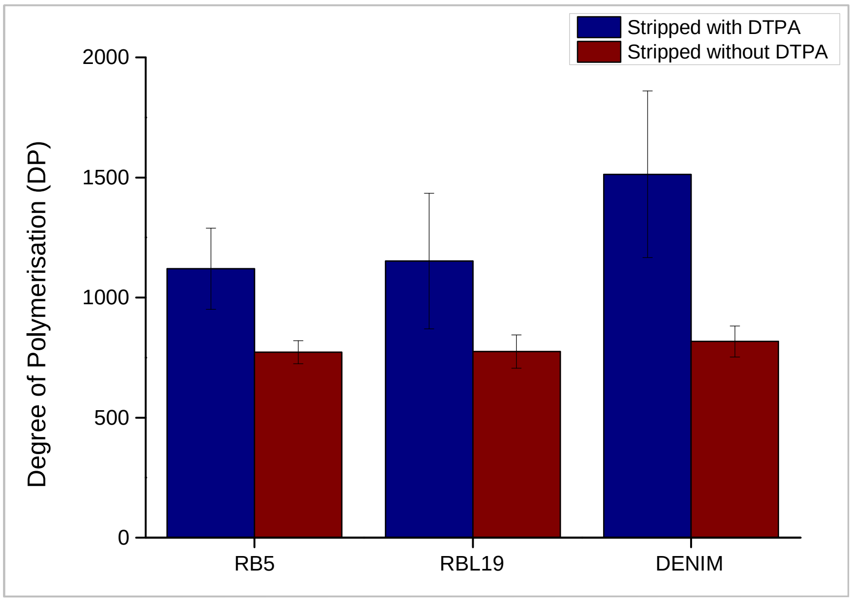


Figure 6.3.7 Comparison of the degree of polymerisation (DP) of cotton fabrics stripped in the sequential acid/dithionite/peroxide method, with and without the DTPA chelating agent.

6.3.1.5 The effect of the sequential acid/dithionite/peroxide treatment on the solubility of the stripped cottons in NMMO solvent

Prior to spinning of the new Lyocell fibres, the recycled cotton pulp was dissolved in the NMMO solvent using the facilities at Lenzing in Austria. The extent of pulp solubility in NMMO was viewed microscopically (Figure 6.3.8). Micrograph ‘a’ shows an example of a spinning dope containing undissolved fibre particles while micrograph ‘b’ shows a complete dissolved spinning dope. The completely dissolved pulps were used for spinning and subsequent Lyocell fibre regeneration.

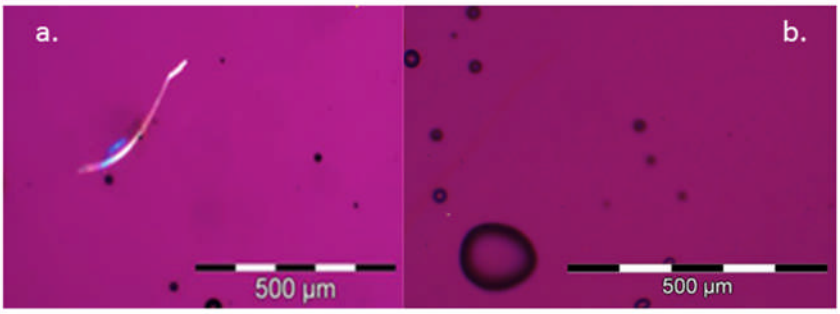


Figure 6.3.8 Micrographs showing a. undissolved particles in spinning dope and b. recycled cotton pulp completely dissolved in NMMO spinning solvent.

From the above results it can be concluded that the sequential acid/dithionite/peroxide treatment was able to strip crosslinks resulting from colorants and other finishing agents, thereby producing a recyclable cotton pulp with the requisite properties required to produce new fibres through the Lyocell NMMO process.

6.3.2 Characterisation of the spun fibres

In this study recycled cotton pulps were spun into Lyocell fibres using the spinning facilities at Lenzing in Austria. Both structural and mechanical properties of the spun fibres were determined and were then compared to the properties of the conventional Lyocell fibres regenerated from wood pulp. Surface and supermolecular structural properties of the fibres were analysed using the SEM, ATR-FTIR and XRD facilities available at the University of Leeds while the mechanical properties (linear density, tenacity and elongation) were assessed in Lenzing.

6.3.2.1 Surface properties of the regenerated fibres

The surface morphology of the Lyocell fibres regenerated from recycled cotton pulp was assessed by the scanning electron microscopy (SEM) technique and were compared to those of fibres regenerated from wood pulp.

Figures 6.3.9 compares the SEM micrographs of the conventional Lyocell fibre (Lyocell-0), fibres made from 100% cotton pulp (Lyocell-1, Lyocell-2 and Lyocell-3) and fibres made from a blend of 80% wood pulp and 20% cotton pulp (Lyocell-4 and Lyocell-5). The micrographs shows that the conventional Lyocell fibre consisted of several straight and smoothly arranged fibre strands. However the surfaces of fibres regenerated from recycled cotton pulp appeared to be slightly rougher. This slight roughness was presumed to be due to different precipitation medium together with contaminants resulting from fibre processing and uneven washing of the spun fibre. In general no significant variations were observed on the surface morphologies of the conventional Lyocell fibres and those regenerated from recycled cotton pulp.

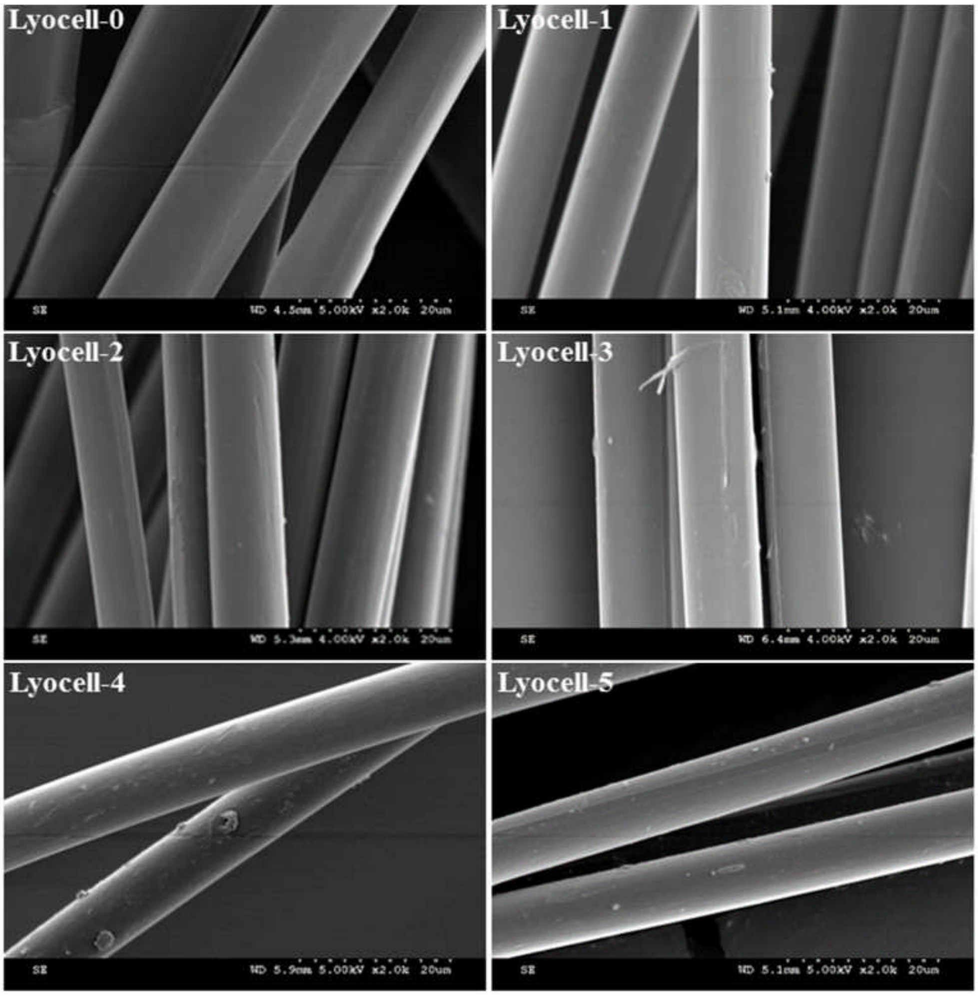


Figure 6.3.9 Comparison of SEM micrographs for the Lyocell fibres regenerated from conventional wood pulp and those from recycled cotton pulp.

6.3.2.2 Supermolecular structural properties of the regenerated fibres

Chemically, all the regenerated cellulosic fibres are the same, with identical chemical formula, however, the different treatment processes causes varieties in their molecular masses, degree of polymerization, degree of crystallinity, crystallite size and orientation as well as crystalline and amorphous dimensions [232, 233]. These variations can lead to differences in accessibility, mechanical and physical properties of cellulosic fibres. In this study the supermolecular structural properties of Lyocell fibres regenerated from recycled cotton pulp were analysed by using ATR-FTIR [175, 178] and WAXD [178, 233] techniques and the results were compared to Lyocell fibres regenerated from conventional wood pulp.

6.3.2.2.1 ATR-FTIR analysis of the regenerated Lyocell fibres

In this study the IR spectra for the Lyocell fibres regenerated from recycled cotton pulp and from wood pulp were recorded in the 3700-2700 cm^{-1} and 2000-800 cm^{-1} regions. The spectra in the 2700-2000 cm^{-1} region did not show any adsorption bands for the regenerated cellulosic fibres and were therefore not reported.

Figure 6.3.10 and Figure 6.3.11 presents the IR spectra in the 3700-2700 cm^{-1} region for the conventional Lyocell fibres and those spun from recycled cotton pulps. The IR spectra of the fibres showed no significant difference between the conventional Lyocell fibres those made with 20% cotton pulp and 80% wood pulp and those regenerated from 100% cotton pulp from the previously C. I. Reactive Black 5 dyed material. Additionally the IR spectra of all samples showed a broad absorption peak centred at 3300 cm^{-1} which was assigned to the stretching vibration of the O-H groups of the cellulose structure [234, 235] which is responsible for intermolecular hydrogen bonding within the cellulose molecule. The peak next to the OH stretching vibration, at the 3000-2800cm^{-1} region corresponds to CH stretching vibrations in the cellulose I and II structures [235]. This indicates that the waste cotton garments can be precipitated and regenerated from NMMO solvents to form cellulose II crystals, as it is with conventional Lyocell fibres from wood pulp.

The spectra of Lyocell-2 and Lyocell-3 (Figure 6.3.10) showed extra peaks at 2918, 2854 and at 2834 cm^{-1}, respectively, which corresponds to the CH_2 asymmetric stretching [174, 234]. These peaks could be due to impurities or contamination resulting from fibre processing and handling.

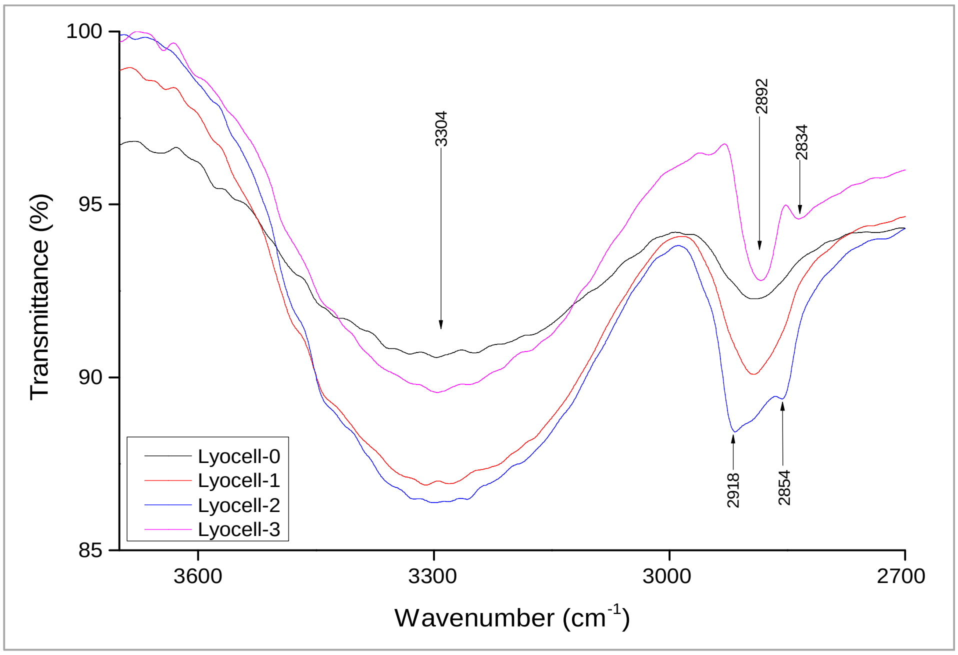


Figure 6.3.10 FTIR Spectra of the Lyocell fibres generated from wood pulp and from 100% recycled cotton pulp in the 3700-2700 cm^{-1} IR region.

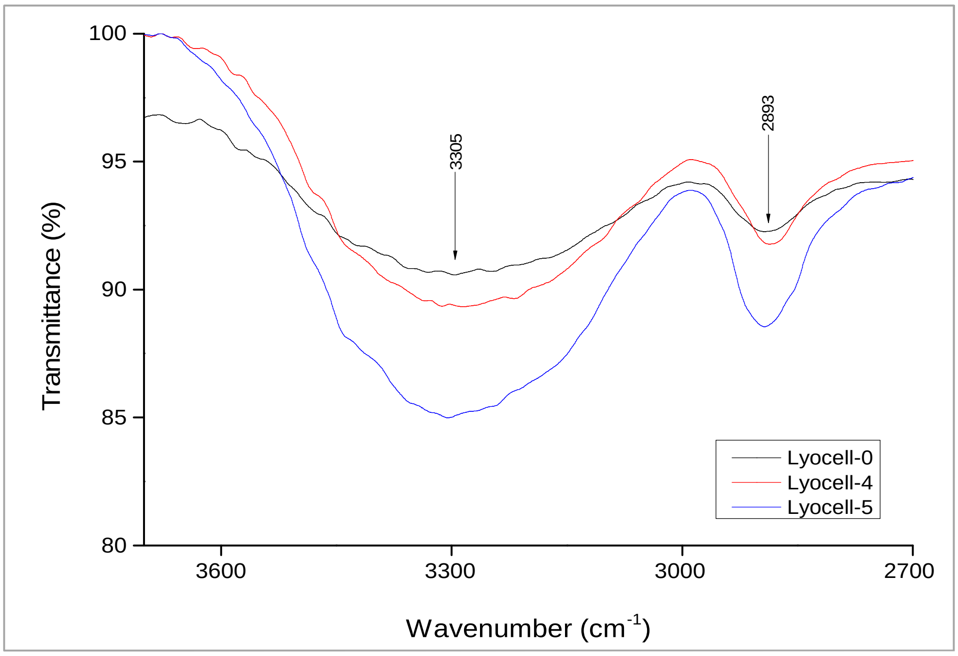


Figure 6.3.11 FTIR Spectra of the Lyocell fibres generated from wood pulp and from 20% recycled cotton pulp in the 3700-2700 cm^{-1} IR region.

Analysis of the IR spectra of the regenerated fibres in the 2000-800 cm^{-1} region (Figures 6.3.12 and 6.3.13) also showed that the fibres regenerated from recycled cotton pulp exhibited similar structures to those of conventional Lyocell fibres. The spectra showed peaks at 1640 cm^{-1} which was attributed to the water molecules absorbed in cellulose while the peak at 1420 cm^{-1} corresponded to the CH_2 symmetrical bending of cellulose II [176, 235]. All IR spectra of the regenerated fibres also showed absorption peaks at 1337, 1314/1315 and 1278 cm^{-1} which are responsible for the crystalline structures of cellulose II present in the Lyocell fibres [175, 178]. The absorption peak at 1420 cm^{-1} was characteristic of crystalline cellulose II and amorphous structure [234]. This peak indicates that both conventional Lyocell fibres and those regenerated from recycled cotton pulp had higher content of cellulose II rather than cellulose I as the peak was shifted away from the 1430 cm^{-1} absorption peak, which is responsible for cellulose I [234]. The peaks at 893/894 cm^{-1} also suggested a near absence of crystalline cellulose I in the regenerated fibres [178, 234].

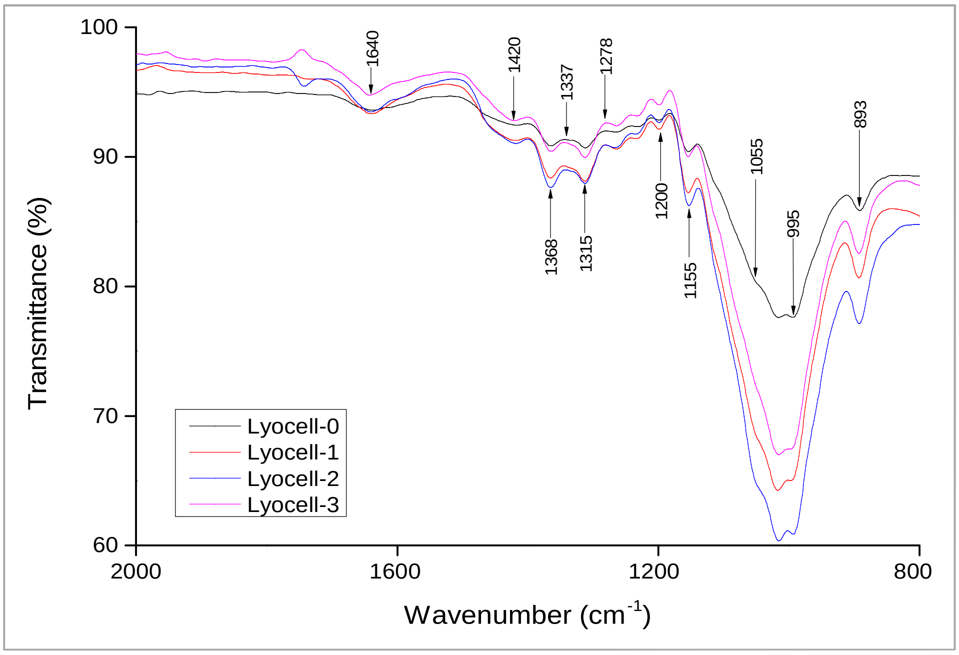


Figure 6.3.12 FTIR Spectra of the Lyocell fibres regenerated from wood pulp and from 100% recycled cotton pulp in the 2000-800 cm^{-1} IR region.

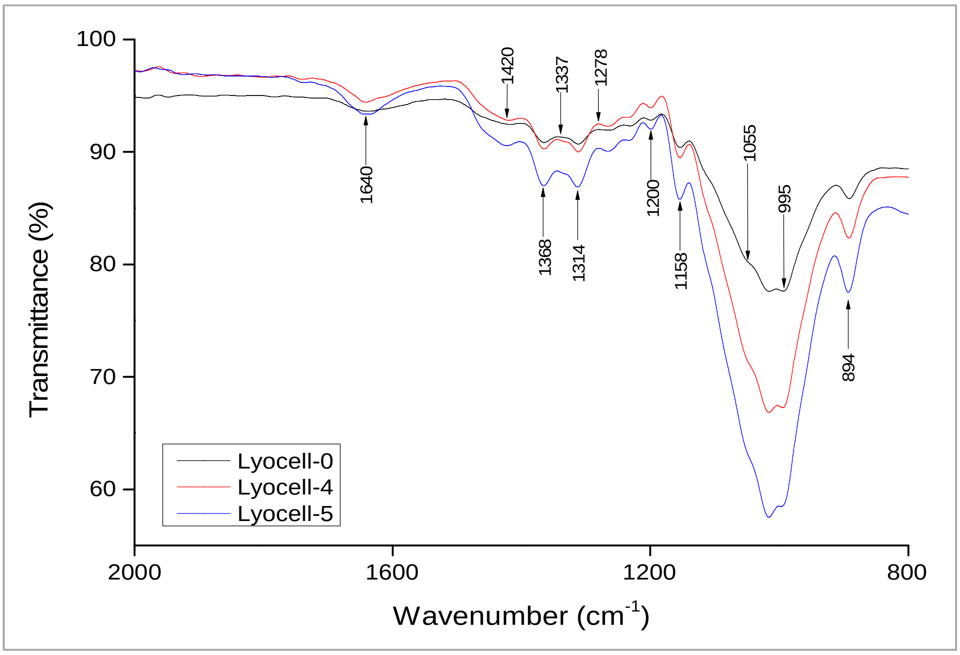


Figure 6.3.13 FTIR Spectra of the Lyocell fibres regenerated from wood pulp and from 20% recycled cotton pulp in the 2000-800 cm^{-1} IR region.

Table 6.3.2 presents the most important characteristic absorption bands observed in Lyocell fibres regenerated from wood pulp and recycled cotton pulp based on the previously published literature.

Table 6.3.2 Interpretation of the characteristic absorption bands of regenerated fibres

Wavenumber (cm^{-1})	**Assignment of the absorption band**	**Reference**
3304/3305	O-H stretching vibration due to inter and intra-molecular hydrogen bonds	[174, 236]
2918	Asymmetric CH_2 stretch	[174, 236]
2892/2893	C–H stretch in cellulose II	[178, 234, 235]
2854	CH_2 asymmetric stretching of Cellulose I and Cellulose II	[234, 236]
2834	Asymmetric CH_2 stretch	[174]
1640	OH of water absorbed from cellulose	[176, 234]
1420	CH_2 symmetric bending of cellulose II	[176, 234, 235]
1368	Symmetric C–H bending	[235]
1337	O–H in-plain deformation	[178, 234, 235]
1314/1315	CH_2 wagging	[175, 178, 234]
1278	C–H deformation	[176, 178, 235]
1200	O–H in-plain deformation	[234, 235]
1155	C–O–C asymmetric from β-glycosidic link in cellulose II	[234, 235]
1055	C–O stretch vibration mainly from C(3)…O(3)H in cellulose II	[234, 235]
995	C–O valence vibration at C(6)	[235]
893/894	C–O–C valence vibration of β-glycosidic link or deformation at C(1) in cellulose II	[176, 234, 235]

The IR crystallinity of the fibres regenerated from recycled cotton pulps were analysed using the ATR-FTIR technique as per Nelson and O'Connor [175, 178], who defined the Total Crystallinity Index (TCI) and the Lateral Order Index (LOI) as the ratios of the FTIR 1372/2900cm^{-1} and 1420/893cm^{-1} peak intensities, respectively. The method has been successfully used to characterise the structure of cellulose-based polymers that consisted of crystalline I, crystalline II and amorphous cellulose [234]. In this study the TCI and LOI were determined at 1368/2892 cm^{-1} and 1420/894cm^{-1}, respectively, due to the position of the peak. The results obtained are tabulated in Table 6.3.3.

Table 6.3.3 Comparison of IR crystallinity ratios for the regenerated Lyocell fibres

FIBRE	**TCI (1368/2892)**		**LOI (1420/894)**	
	Mean	**SD**	**Mean**	**SD**
Lyocell-0	1.20	0.03	0.41	0.03
Lyocell-1	1.09	0.13	0.44	0.02
Lyocell-2	1.02	0.18	0.43	0.04
Lyocell-3	1.20	0.08	0.43	0.00
Lyocell-4	1.13	0.01	0.45	0.02
Lyocell-5	1.13	0.06	0.44	0.02

Analysis of the IR crystallinity parameters of the regenerated fibres indicated that Lyocell fibres from recycled cotton pulp exhibited slightly higher Lateral Order Indices (LOI) of up to 0.45 compared to that of 0.41 obtained for conventional Lyocell fibres. This phenomenon was thought to be due to the greater degree of polymerisation of the cotton cellulose compared to that of wood pulp. Conversely, fibres from the recycled cotton pulp had a slightly lower Total Crystallinity Indices (TCI) where values as low as 1.02 were observed compared to a TCI of 1.2 obtained on the conventional Lyocell fibres. This was unexpected considering the higher DP of the cotton cellulose compared to that of the wood pulp, however the lower cellulose concentration (~9%) used in making the cotton spinning dope is thought to have partially contributed to the slightly lower TCI obtained. In addition Lyocell-3 which was regenerated from post-consumer denim jeans exhibited slightly higher TCI compared to other fibres regenerated from recycled cotton pulp. This is again thought to be due to slightly higher DP of the denim pulp compared to that of a normal cotton pulp. Blending 20% of the recycled cotton pulp with 80% of the wood pulp slightly increased the TCI of both Lyocell-4 and Lyocell-5 resulting in TCI of 1.13.

Conventional Lyocell fibres have previously been reported to have TCI and LOI of 0.76 and 0.35, respectively [176, 234] which is lower than those obtained in this study. These variations could be due to the different spinning conditions used, including the solution state and its composition, air gap length, spinning speed, take off tension, draw ratio, temperature, humidity and the precipitation, drying and post-treatment conditions [35].

6.3.2.2.2 WAXD analysis of the regenerated Lyocell fibres

The crystalline properties of the regenerated Lyocell fibres were also assessed using a wide angle x-ray diffraction (WAXD) technique where crystalline index and crystallite size were determined and were compared to those of the conventional Lyocell fibres. Figure 6.3.14 shows the wide angle x-ray diffraction patterns of the regenerated Lyocell fibres, which shows the recycled cotton pulps with diffraction patterns similar to those of the conventional Lyocell fibres. All the regenerated fibres had diffraction peaks at 12.2°, 20.3° and 21.7° corresponding to 101, 10Ī and 002 reflection planes, respectively, which have been reported to correspond to the characteristic crystalline form of cellulose II [178, 233, 237]. In addition, the 10Ī and 002 reflection planes of all fibres overlapped each other and had higher intensities compared to their 101 reflection planes. This overlapping nature of the 10Ī and 002 reflection planes has also been reported in the literature [233], however, the intensities of the 10Ī and 002 crystalline reflection planes were not compared in this study.

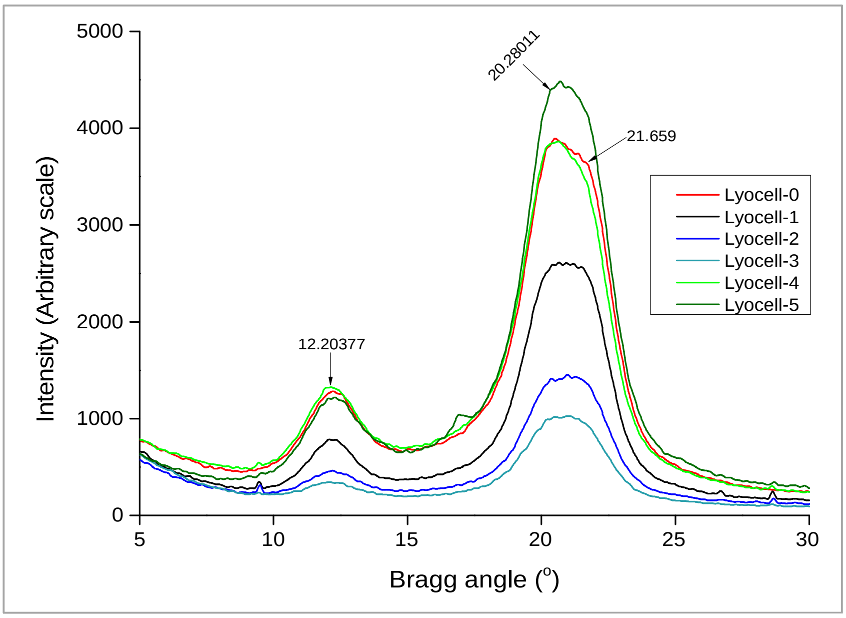


Figure 6.3.14 X-ray diffraction patterns of the regenerated Lyocell fibres.

Table 6.3.4 presents the WAXD crystallinity analysis of the regenerated Lyocell fibres. The crystallinity indices were determined from the height ratios of the crystalline intensity and the total intensity, while the crystallite sizes were calculated using the diffraction angle 2θ of the 002 reflection plane and the breadth of reflection at half maximum intensity *B*° obtained from the wide angle x-ray diffraction patterns.

Table 6.3.4 Comparison of XRD crystallinity of the regenerated Lyocell fibres

FIBRE	***B*°**	**Crystallite size (Å)**	**Crystallinity Index (%)**
Lyocell-0	3.57	22.7 ± 1.5	80.0 ± 0.3
Lyocell-1	3.48	23.3 ± 1.6	83.5 ± 0.2
Lyocell-2	3.45	23.5 ± 1.6	80.3 ± 0.4
Lyocell-3	3.34	24.2 ± 1.7	77.3 ± 0.4
Lyocell-4	3.50	23.1 ± 1.6	82.4 ± 0.3
Lyocell-5	3.46	23.4 ± 1.6	78.0 ± 0.2

Lyocell fibres regenerated from the recycled cotton pulp had up to 6% larger crystallite size than conventional Lyocell fibres, indicating that the structure of the fibres regenerated from recycled cotton pulps were composed of more crystalline than amorphous regions. Similarly, fibres from recycled cotton pulps had a slightly greater crystallinity indices compared to those of conventional Lyocell fibres. The effect was higher on Lyocell-1 (83.5%) and Lyocell-4 (82.4%) which were regenerated from the reactive dyed cotton fabrics which is again attributed to the higher DP of the recycled cotton pulps as compared to that of wood pulp.

The slightly lower crystallinity index of only 77.3%, was however observed on Lyocell-3 fibres regenerated from post-consumer denim jeans. This lower crystallinity index on denim cotton pulp was unexpected considering the higher DP of the pulp used. Blending the denim cotton pulp with 80% wood pulp slightly increased the crystallinity index to about 78.0% as seen on Lyocell-5 fibre.

The higher WAXD crystallinity indices of the fibres regenerated from recycled cotton pulp correlate well with the FTIR crystallinity indices presented in Table 6.3.3. However the difference on the crystallinity values observed when using the two techniques could be a result of the different analytical nature employed by the two techniques. The IR crystallinity depends on the ratio of the FTIR bands to compare the crystallinity of the fibres while the XRD crystallinity depends on the intensities of the diffraction pattern generated from the inter-chain distance of molecules on the fibre [238].

6.3.2.3 Mechanical properties of the regenerated fibres

In this study the mechanical properties of the regenerated fibres were assessed, in order to establish the effectiveness of the recycled cotton pulp in producing Lyocell fibres of acceptable mechanical properties. Linear density, tensile strength and elongation properties of the spun fibres were therefore analysed and were compared to mechanical properties of the conventional Lyocell fibres. Table 6.3.5 presents the obtained mechanical properties of the regenerated Lyocell fibres.

Table 6.3.5 Comparison of the mechanical properties of the regenerated Lyocell fibres

Fibre name	**Linear density (dtex)**		**Conditioned Tenacity (cN/tex)**		**Conditioned Elongation (%)**	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**
Lyocell-0	1.3	0.04	37.0	1.41	13.0	0.00
Lyocell-1	1.3	0.05	42.3	1.27	8.9	0.71
Lyocell-2	1.2	0.10	43.8	0.07	8.5	0.57
Lyocell-3	1.3	0.17	40.6	5.59	9.0	0.28
Lyocell-4	1.1	0.11	41.0	0.14	11.0	0.64
Lyocell-5	1.3	0.02	39.8	0.42	11.1	0.64

Analysis of the linear densities indicates that the recycled cotton pulps can be processed to produce fibres with linear density comparable to those of conventional Lyocell fibres. The slightly lower linear densities on Lyocell-2 and Lyocell-4 could be due to the lower cellulose concentration of 9% in the spinning dope compared to the conventional 13% cellulose used for wood pulps. In addition the higher standard deviation observed on Lyocell-3 could be due to non-uniformity of the post-consumer denim jean resulting from the previous usage phase of the garment. Blending 20% of the denim cotton pulp with 80% of the wood pulp resulted in fibres (Lyocell-5) with similar linear density to that of the Lyocell fibres regenerated from 100% wood pulp. This could be due to levelling of the pulp properties resulting from blending of the two pulps.

Analysis of the elongation at break for the regenerated Lyocell fibres showed slightly decrease in elasticity of the fibres regenerated from 100% cotton pulp where elongation values of 8.9%, 8.5% and 9% were observed on Lyocell-1, Lyocell-2 and Lyocell-3, respectively, compared to that of 13% for the conventional Lyocell fibres. The slightly reduced elasticity of the fibres regenerated from recycled cotton pulp was thought to be due to lower cellulose concentration (only 9%) in the spinning dope together with the higher DP (>950) of the cotton pulps. Blending 20% of the recycled cotton pulp with 80% of the wood pulp slightly increased the elongation at break properties of the regenerated fibres to about 11% compared to that of 13% of the conventional Lyocell fibres.

Analysis of the tensile strength of the fibres indicated greater tenacity values of 42.3 cN/tex and 43.8 cN/tex on Lyocell-1 and Lyocell-2 samples, respectively, compared to that of 37 cN/tex obtained on the conventional Lyocell fibres. The mechanical properties of cellulosic fibres have been reported to depend on the molecular and supermolecular structure of the cellulose including the molecular orientation, degree of crystallinity, crystalline and amorphous dimensions and the shape and size of voids [232]. The cellulose concentration and spinning conditions such as the draw ratio, air gap length, temperatures and humidity have also been reported to influence the tenacity of the spun fibres [35, 239]. It is therefore logical to conclude that the difference in tenacity values observed on the regenerated fibres could be a result of the differences in the structural properties such as degree of crystallinity and size of the crystallites of the fibres as detailed in Section 6.3.2.2. In addition the higher degree of polymerisation (>950) of the recycled cotton pulp together with the lower cellulose concentration (9%) of the spinning solution could have contributed to the observed variations in fibre tenacities.

A slightly lower tenacity of 40.6 cN/tex, was observed on the Lyocell-3 which could be due to the fact that the post-consumer denim jeans material had already completed its ‘first’ lifecycle compared to the new reactive dyed cotton fabrics that were used to regenerate Lyocell-1 and Lyocell-2. Blending 20% of the recycled cotton pulp with 80% of the wood pulp slightly lowered the tenacity of the regenerated fibres to 41 cN/tex and 39.8 cN/tex for Lyocell-4 and Lyocell-5, respectively, approaching that of 37 cN/tex for the conventional Lyocell fibre. It can therefore be concluded that by controlling both the concentration of cellulose and the spinning conditions recycled cotton pulps can be used to produce fibres with mechanical properties similar those of conventional Lyocell fibres.

6.4 CONCLUSIONS

This chapter investigated the use of the acid/dithionite/peroxide stripped cotton substrates for the production of fibres through the Lyocell process. The acid/dithionite/peroxide stripped cotton substrates were disintegrated into fibrous pulp materials prior to dissolution in the NMMO solvents and re-spun into Lyocell fibres. Assessment of the effect of the stripping treatment on the solubility and degree of cellulose damage indicated that the stripped samples could be completely dissolved in the CED solvent and had the limiting viscosity and degree of polymerisation values required for the NMMO Lyocell processing technology. It was also established that the addition of the DTPA chelating agent in both the stripping baths and in the fabric disintegrator assisted in preserving the cellulose structure of the stripped cotton substrates as it resulted in a slightly higher limiting viscosity and degree of polymerisation compared to those stripped in the absence of a chelating agent. These results suggest that the coloured waste cotton garments can be chemically processed through the sequential acid/dithionite/peroxide stripping treatment and yet produce cotton pulp with the characteristics required for producing regenerated fibres through the Lyocell process.

Assessment of the structural and mechanical properties of the new regenerated fibres indicated that the recycled cotton pulp produced Lyocell fibres with properties comparable or better than those of conventional Lyocell fibres. The fibres regenerated from recycled cotton pulps exhibited a higher degree of crystallinity and highly ordered cellulose structure. Similarly the fibres produced were stronger but less elastic compared to conventional Lyocell fibres which was believed to be due to the higher DP of the recycled cotton pulps and the lower cellulose concentration in the spinning dope. Blending of 20% recycled cotton pulp and 80% of wood pulp also resulted in fibres with properties comparable to conventional Lyocell fibres. These results indicate that by optimising the spinning conditions and cellulose concentration in the spinning dope, the cellulose recovered from recycled waste cotton can be used as a potential source of raw material for producing regenerated Lyocell fibres.

Chapter Seven: Final Conclusions and Future Work

7.1 CONCLUSIONS

In the recent years the consumption of clothing has increased significantly, as a result of the expanding population, favourable economic growth prospects and prospects for stronger global consumer demand. In addition the relative fall in the price of clothing as a result of fast fashion has also contributed to the dramatically increased net volumes of clothing purchased. Accordingly the amount of waste clothing generated and hence discarded has increased significantly. The main methods used for handling the generated waste clothing is through reuse, recycling and disposal through landfill or incineration. Currently, most developed countries export used garments to developing countries for reuse as second-hand clothing, however once these garments are no longer serviceable in their new location they are disposed through landfill. Similarly the increased importation of low-cost new clothing from Asian countries like China also offers a new threat to second-hand clothing market in developing countries. In addition the low qualities of the clothing as a result of fast fashion will increase the proportion of recycling grades rather than reuse grades, which will further weaken collection economics and depress the sales and margins of second-hand clothes.

The waste clothing that is not suitable for reuse or for recycling purposes is discarded usually through incineration or landfill, with landfill being the most commonly used route in the UK. Together with the environmental issues associated with the route, it is obvious that the landfill areas are decreasing and the costs of disposing of waste clothing that is not suitable for recycling are increasing. Furthermore in 2014 Zero Waste Europe suggested banning of both landfill and incineration activities by 2030 as a step towards a Circular Economy, which among others requires that resource efficiency is maximised and that waste materials become valuable inputs to other processes instead of being thrown away. Therefore recycling appears to be the only viable method for reusing of waste garments and potentially offering a solution to the circular economy.

The future demand for cotton and cellulosic fibres is also likely to remain high due to the exceptional comfort properties offered. However the future of cotton production will be affected by the population growth whose priority is to improve food crop production. This means, the land that is currently used for cotton production could soon be diverted to food production and with the production of cotton fibre also levelling due to environmental challenges and increased production costs, re-evaluation of recycling strategies is important. Research should therefore be undertaken that responds to the demand for new technologies to produce other cellulosic fibres such as those regenerated from wood pulp.

Waste cotton garments have been identified as potential source of cellulosic materials for fibre regeneration. However the diversity of garment composition in terms of both fibre type and colour components is a challenge for the existing recycling techniques. Traditional mechanical recycling of cotton materials is also difficult because of the resultant recycled fibre length being too short for reuse in many end uses and with low strength and poor colour continuity. The alternative chemical recycling of cotton garments through the pulping technology to produce the precursors to a Lyocell fibre would potentially provide a clothing-to-clothing route albeit from cotton to Lyocell. However the presence of colours, heavy metals and crosslinks resulting from colorants and other performance finishes could present difficulties in the subsequent processability of these waste materials. The current study aimed at processing the waste cotton garments for reuse through fibre regeneration.

The study investigated potential environmental-friendly methods for recycling waste cotton garments with the aim of minimizing the impact of waste textiles on the environment. Accordingly the study investigated ways of reducing the amount of waste textiles that goes into landfill while offering a technically viable feedstock source of regenerated cellulosic fibres, in particular, Lyocell fibres which use an environmentally-friendly processing technology. In order to accomplish the stated main objective of the study, the following specific objectives were established:

Objective I: To develop methods that could chemically remove colorants, crosslinks and impurities from waste cotton garments

Chapter 4 and 5 of this study described how methods optimised in this study could chemically remove colorants, finishing agents and other impurities such as heavy metals from waste cotton garments in order to prepare the waste cotton materials and facilitate the cost effective fibre regeneration process. Initially the stability of the three reactive dyes (C. I. Reactive Black 5, C. I. Reactive Blue 19 and C. I. Reactive Red 228) to various ISO 105 washing conditions was investigated in order to establish if dyes will be present on the garments once they finish their ‘first’ life. It was concluded that the reactive dyes assessed were relatively stable to chemicals used in washing detergent formulations and that most of the initially applied dyes will remain linked to the cellulosic fibres at the end of the garment usage period. Therefore these colorants, finishes and other additives will need to be stripped from waste garments prior to recycling of the materials into pulp for new fibre regeneration. This was necessary in order to allow further processability of the recycled materials, especially on solubilisation and subsequent spinning of the fibres.

To strip colorants from cotton fabrics two methods, based on a combination of acid, alkaline and hydrogen peroxide solutions as well as a combination of acid, dithionite and hydrogen peroxide solutions, were analysed. The treatments were applied to cellulosic colorants including reactive dyes, vat dyes, sulphur dyes, direct dyes and pigments and the effectiveness of the optimised methods in removing these colorants was assessed in terms of changes in colorimetric parameters of the stripped and unstripped samples. Post-consumer garments were also stripped in the methods established in this research in order to determine the efficiency of the stripping sequences in stripping dyes and other crosslinking agents from the actual waste garments. Heavy metals, fluorescent whitening agents and added performance finishes such as crease resist finishes were also included in the scope of the study.

Unlike the combination of acid, alkali and peroxide treatment, the combination of acid, dithionite and peroxide treatment stripped a wide range of colorants from cotton fabrics including those from post-consumer garments resulting in fabrics with colorimetric properties similar to those of a white undyed cotton fabric. The high reductive power of the alkaline dithionite treatment in conjunction with the dye transfer inhibiting properties of the polyvinylpyrrolidone polymer contributed to the greater colorant stripping efficiency of the sequential acid/dithionite/peroxide method. The ability of hydrogen peroxide bleaching to remove dye residues remaining after the dithionite treatment also contributed to the high stripping efficiency of the treatment.

Together with the acid/alkali/peroxide treatment, the acid/dithionite/peroxide method was also able to strip performance finishes such as fluorescent brightening agents and DMDHEU-based easy care finishes as indicated by the FTIR, CRA and solubility results. With the addition of a chelating agent into the dithionite and hydrogen peroxide stripping liquors heavy metals (iron and copper) were also removed from the stripped cotton samples.

The stripping treatments were however unable to completely strip cationic fixing agents from samples that were dyed with C. I. Direct Yellow 106 and aftertreated with the two cationic fixing agents, namely Tinofix ECO and Solfix E. Results showed that samples that were aftertreated with Solfix E cationic fixing agents exhibited especially highly resistance which was thought to arise from the ability of the agent to react with hydroxyl groups of the cellulosic fibre thereby forming a three-dimensional network involving the dye, the fixing agent and the fibre itself. However, the treatments could strip relatively higher amounts of dye from samples that were after-treated with a Tinofix ECO fixing agent which could be attributed to the non-reactive nature of the fixing agent.

Although the acid/dithionite/peroxide treatment could strip significant amount of the azo-based Printofix Red pigment from the cotton fabrics, the treatments could not completely strip the Printfix Black and the Printofix Blue pigments which contain the highly chemical resistant carbon black and copper phthalocyanine chromophores, respectively. The strong crosslinking mechanisms of the binders used in this study were also thought to have contributed to the lower levels of pigments stripped from the printed cotton fabrics.

It is also worth mentioning that in all the two stripping methods the acid treatment was not effective in removing colorants from the cotton materials. However it was necessary to include the treatment in the two stripping sequences due to its usefulness in breaking bonds resulting from crosslinking agents and in removing impurities such as heavy metals and fluorescent whitening agents.

Objective II: Production of a fibrous cotton pulp from the recycled cotton materials

In Chapter 6 of this study the chemically stripped cotton samples were broken down into a fibrous pulp material in order to allow easy dissolution of the pulp in a swelling solvent. The suitability of the resultant pulp was analysed in terms of fibre lengths and the solubility of the pulp through dissolution in a cupriethylenediamine hydroxide (CED) solution. The degree of polymer degradation as a result of the chemical treatment was also analysed through changes in limiting viscosity and the degree of polymerization (DP) of the pulp reclaimed from waste cotton garments.

Examination of the effect of the stripping treatment on the solubility and degree of cellulose damage indicated that the stripped samples could be completely dissolved in the CED solvent and had the requisite limiting viscosity and the DP values suitable for the NMMO Lyocell processing technology. It was also established that the addition of the DTPA chelating agent in both the stripping baths and in the fabric disintegrator assisted in not only stripping metals from the pulp, but also in preserving the cellulose structure of the stripped cotton substrates as it resulted in a slightly higher limiting viscosity and DP compared to those stripped in the absence of a chelating agent. It can therefore be concluded that by including a chelating agent in the stripping process, a far more effective process to chemically process the dyed waste cotton garments through the sequential acid/dithionite/peroxide stripping treatment was established. The process could produce cotton pulp with characteristics suitable for producing regenerated Lyocell fibres.

Objective III: Production of fibres through the Lyocell processing technology

In this study new fibres were generated at the Lenzing facilities in Austria using the environmental-friendly NMMO technology. Five fibre samples were produced; three from 100% recycled cotton pulp and two from a blend of 80% wood pulp and 20% recycled cotton pulp. Analysis of the structural and mechanical properties of the regenerated fibres (Chapter 6) indicated that the recycled cotton pulp produced fibres with properties comparable or better than those of conventional Lyocell fibres. The fibres regenerated from recycled cotton pulps exhibited a higher degree of crystallinity and highly ordered cellulose structure as portrayed by both ATR-FTIR and WAXD techniques. Similarly the fibres produced were stronger but less elastic compared to conventional Lyocell fibres. Blending of 20% recycled cotton pulp and 80% of wood pulp also resulted in fibres with properties comparable to conventional Lyocell fibres.

It can therefore be concluded that the cellulose recovered from recycled waste cotton can be used as a potential source of raw materials for producing regenerated cellulosic fibres through the NMMO Lyocell process. The overall findings of this research have provided a potential alternative use of waste cotton garments rather than incineration or one-lifetime landfill disposal that affects the environment. In addition to the environmental benefits, the research outcomes have also established that waste cotton garments can be processed into a pulp (in a laboratory scale) which can be used (on its own or as a blend with virgin wood pulp) as feedstock for manufacturing of new fibres through the NMMO technology.

7.2 SUGGESTIONS FOR FUTURE WORK

Before the process can be converted into industrial scale, the following suggestions for future work are significant:

1) The use of dithionite in an optimised recycling framework is doubtful in terms of environmental friendliness, especially when large quantities of the agents are used. Although this can be tackled by adding biodegradable polymers such as polyacrylamide which can enhance the stability and efficacy of dithionite thereby reducing the amount to be used, it is still necessary to investigate further alternative stripping chemicals such as the use of enzyme technology which was not included in this study due to time limitations;

2) It would also be useful to explore the possibility of combining the acid/dithionite/peroxide stripping treatments in a single bath, thereby avoiding the three step treatment process. This would potentially reduce the processing temperature and the total time required to provide effective stripping, while making the overall process more energy efficient; with reduced amount of effluent and reduced adverse effect on the environment;

3) In this study the optimised treatments were not able to completely strip direct dyes that were after-treated with cationic fixing agents. Similarly, the treatment could not completely strip pigments from cotton fabrics. It would therefore be valuable and informative to further investigate into ways to strip both after-treated direct dyes and pigments from cotton fabrics. It would also be interesting to develop in fixing agents and binders that would offer high performance of the fibres during usage, but still allow easy removal of the agents during the recycling of the waste garments;

4) It would also be useful to extend the current study to evaluate the redyeing of the new fibres regenerated from recycled cotton pulp and if possible to strip the dyes from the fibres and reprocess the material through the established recycling process thereby practicing a closed loop recycling system;

5) Although the fibres regenerated had properties comparable to the conventional Lyocell fibres, it would still be valuable to investigate the performance of the fabrics/garments produced from fibres regenerated from recycled cotton pulp;

6) Commercial viability (such as cost, logistics to gather waste clothing, dealing with effluent and marketability of the recycled fibres) and the overall environmental impact assessment of the fibres produced in this study (particularly, chemical toxicology, energy and water use) would also be beneficial for the effective implementation of the process;

7) The current study only investigated the use of the recycled cotton fabrics as feedstock for regeneration of Lyocell fibres. However future studies can also be extended into exploring alternative uses of the recycled cotton pulp including non-wovens and the high-end cellulosic materials such as high quality papers and paper products and in production of films and membranes such as cellophanes;

8) Finally, it would be valuable to extend the current research on cotton blends such as polyester/cotton or cotton/lycra, where fibre separation will be essential in order to obtain pure cotton material prior to pulp formation and fibre regeneration. Other performance finishes including flame resistant agents should also be explored.

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APPENDIX

Appendix A - Preliminary study to develop an effective dye stripping method

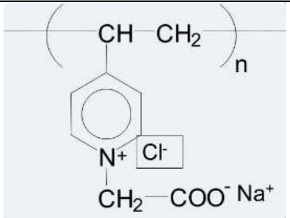
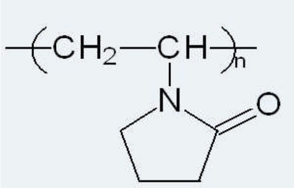
The sequential acid/dithionite/peroxide treatment was used in this study in order to strip colorants and finishing agents for the purpose of purifying and preparing recycled cotton fabrics for reuse as a fibrous pulp for the Lyocell fibre regeneration process. The acid treatment was performed as previously reported [66, 153], while both dithionite and peroxide treatments were optimised prior to their use in this study.

Materials

4% o.m.f. vat dyed fabrics (using the bleached, mercerised base fabric used in this study) were kindly supplied by Mr. Cohen, School of Materials, University of Manchester. Vat dyes (detailed in Chapter 4) were selected for dithionite parameters optimisation as they were highly resistant to the sequential acid/alkali/peroxide stripping treatment used in this study.

Polyvinylpyrrolidone (PVP) and Chromabond dye transfer inhibitors (Table 1) were supplied by Ashland Chemicals Ltd. while all other chemicals were of laboratory grade obtained from different suppliers.

Table 1 Details of the dye transfer inhibitors used in this study [240]

Name	**Structure**
Chromabond S-100 (Polyvinylpyridine betaine)	
Poly(vinylpyrrolidone) – PVP, K-30, average M_w 40,000	

Results and Discussions

The effectiveness of each parameter was determined by examining the decrease in colour strength of the stripped materials as measured by a Datacolor spectrophotometer and the results are detailed below.

Effect of dye transfer inhibitors on colour strength of the samples

Dye transfer inhibitors have been reported to aid in stripping of dyes from fabrics as they prevent the stripped dyes from being redeposited on the surface of the fabrics [56, 79, 83]. In this study both polyvinylpyrrolidone (PVP) and Chromabond S-100 were analysed as potential stripping agents. Samples were stripped for 30 minutes at 80°C using 15g/L dithionite, 20g/L NaOH [151] and varying concentrations of PVP and Chromabond S-100.

Figure 1 and 2 indicate that both lower and higher concentrations of the stripping agents were effective in stripping dyes from fabrics, with the intermediate concentration of 2.5 g/L stripping significant amounts of both C. I. Vat Blue 4 and C. I. Vat Black 27 from cotton fabrics. This concentration was then selected for further processing.

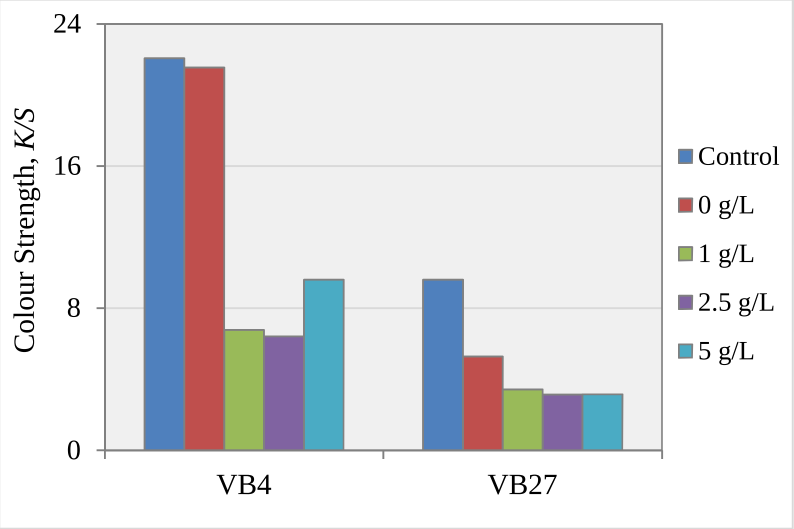


Figure 1 Effect of the PVP concentration on the *K/S* of the vat dyed fabrics

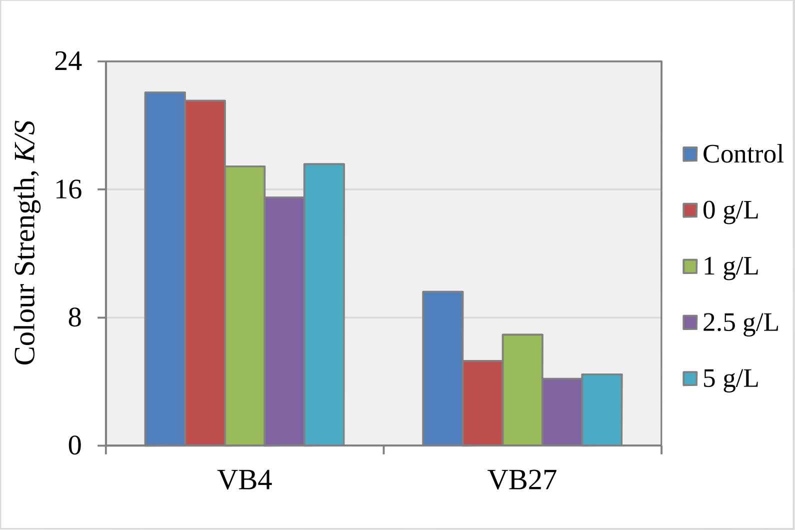


Figure 2 Effect of Chromabond S-100 concentration on the *K/S* of the vat dyed fabrics

Comparison of the efficiency of the two dye transfer inhibitors (Figure 3) indicated that greater dye removal was achieved when using the PVP polymer. The agent was therefore selected for further parameter optimisation.

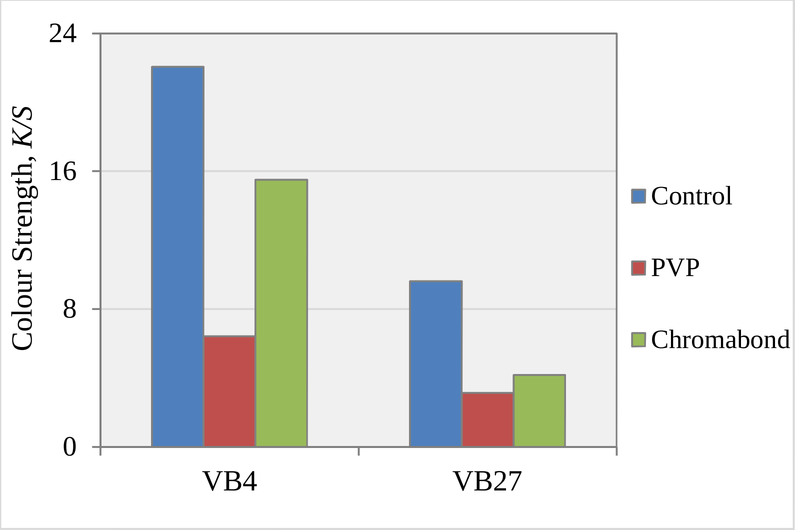


Figure 3 Comparison of Chromabond S-100 and PVP dye transfter inhibitors on the *K/S* of the vat dyed fabrics

Effect of sodium dithionite and sodium hydroxide (NaOH) concentration on the colour strength of the vat dyed fabrics

Three dithionite/NaOH concentrations, identified as high, medium and low, were used in order to establish their effects on stripping vat dyes from cotton fabrics. Samples were stripped for 30 minutes at 80°C temperature. The results (Figure 4) indicated that the standard concentration of the stripping chemicals did not strip much of the dye from the fabric samples. However, both high and medium concentration of the stripping chemicals gave a similar effect on the colour strength of the stripped samples. The medium concentration was therefore selected for further parameter optimization.

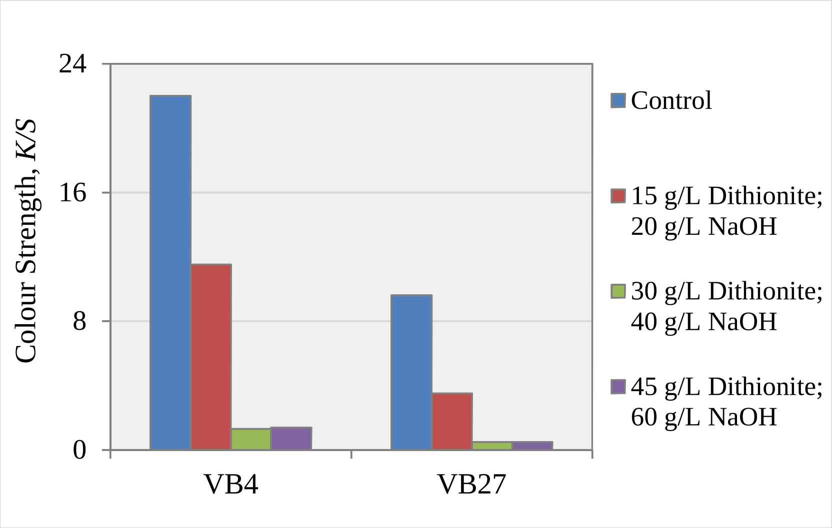


Figure 4 Effect of dithionite and NaOH concentrations on the *K/S* of the vat dyed cotton fabrics

It is worth noting that, although NaOH alone had no significant effect on the stripping, it was necessary to increase the concentration for the purpose of activating the sodium dithionite in the stripping solution by forming the dithionite radicals responsible for the reduction process. In addition the instability of sodium dithionite at higher temperature and particularly in acidic conditions [83] suggested the need for a large amount of sodium hydroxide to ensure the reducing solution remains in the alkaline conditions.

Effect of the treatment time on the colour strength of the vat dyed fabrics

Samples were stripped for 30 minutes [151] and for 60 minutes in order to establish the effect of time in stripping vat dyes from cotton fabrics. The stripping liquor contained 30g/L dithionite, 40 g/L NaOH and 2.5 g/L PVP. The results (Figure 5) indicated that both 30 and 60 minutes stripped large amounts of vat dyes from cotton fabrics. However 60 minutes were selected as the treatment time for this study as it showed more potential in complete dye removal.

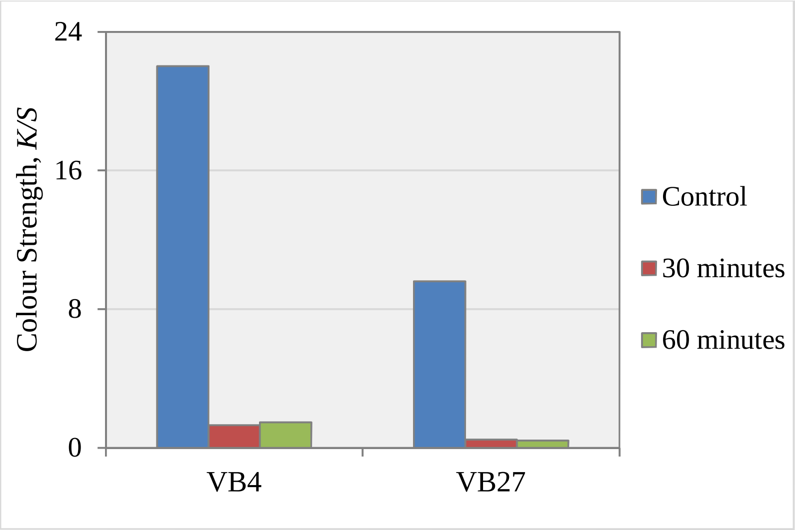


Figure 5 Effect of treatment time on the *K/S* of the vat dyed fabrics

Effect of doubling the dithionite stripping process on the colour strength of the vat dyed cotton fabrics

Samples were stripped twice in the dithionite/NaOH treatment at 80°C and for 60 minutes using 30g/L dithionite, 40 g/L NaOH and 2.5 g/L PVP. After each treatment samples were thoroughly washed in warm water to remove any surplus reducing chemicals.

Figure 6 presents the effect of double stripping process on the colour strength of the vat dyed fabrics where a significant amount of vat dyes was stripped on repeating the stripping process. However the drawback of repeating the dithionite stripping process is the significant amount of the stripping chemicals and therefore significant amounts of effluent that are generated. Additionally the stripping process itself is already a three-step process involving acid hydrolysis, dithionite reduction and peroxide oxidation indicating a higher possibility of significantly destroying the cellulose polymer. It was therefore decided to increase the stripping temperature to 100°C in order to assess its effect on stripping of vat dyes from the samples.

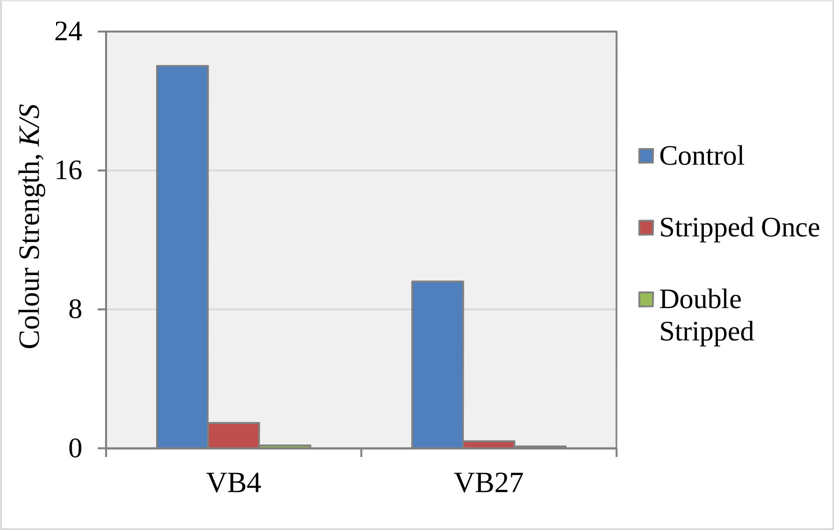


Figure 6 The effect of repeating the stripping process on the *K/S* of the vat dyed fabrics

Effect of the treatment temperature on the colour strength of the vat dyed fabrics

Samples were treated for 60 minutes at 80°C and 100°C temperatures using a solution containing 30 g/L dithionite, 40 g/L NaOH and 2.5 g/L PVP. These temperatures were recommended in the literature as the optimum temperatures required to strip dyes from textile substrates using the alkaline dithionite stripping liquor [56, 79, 130].

It can be seen from Figure 7 that increasing the stripping temperature to 100°C significantly decreased the colour strength of the vat dyed cotton fabrics. Higher stripping efficiency of the increased treatment temperatures is thought to be due to the reduced solubility of oxygen in water, thereby reducing its consumption of the sodium dithionite [36]. Additionally using higher temperature and prolonged stripping process also removed additional dyes from the vat dyed cotton fabrics as presented in Figure 8.

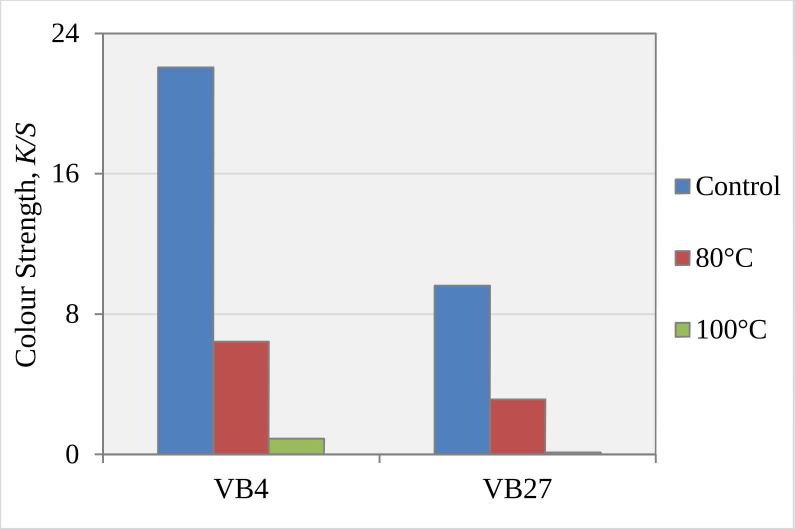


Figure 7 Effect of the temperature on the *K/S* of the vat dyed fabrics

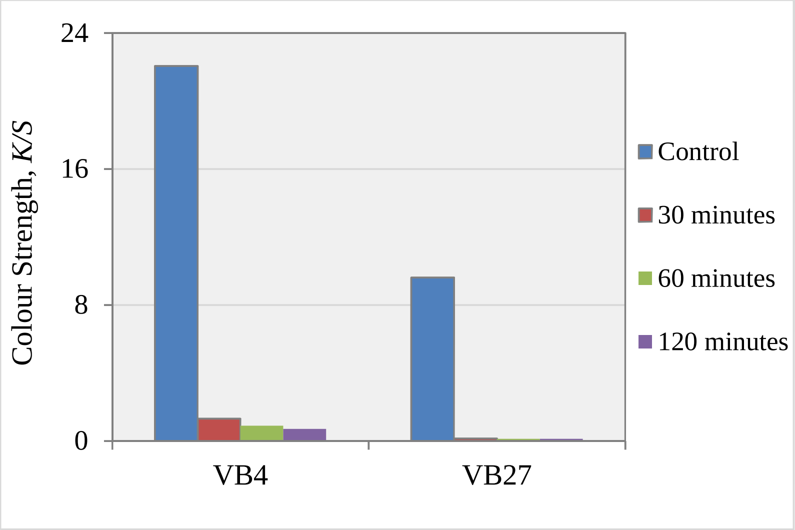


Figure 8 Effect of the stripping time on the *K/S* of the vat dyed fabrics stripped at 100°C temperature

Although higher temperatures (100°C) and prolonged stripping times (120 minutes) stripped greater amounts of dyes from the vat dyed samples, the two extreme conditions had the potential to significantly destroy the cellulosic structure of the fabrics. Additionally the three-step stripping process also suggests possible excessive modification of the cellulose structure. In this study a dithionite stripping process combining both high and medium temperatures and longer and shorter stripping times was selected in order to minimise the effect of the stripping process on the cellulose structure while offering maximum colour removal from the dyed samples. Figure 9 details the optimal dithionite stripping process used in this study.

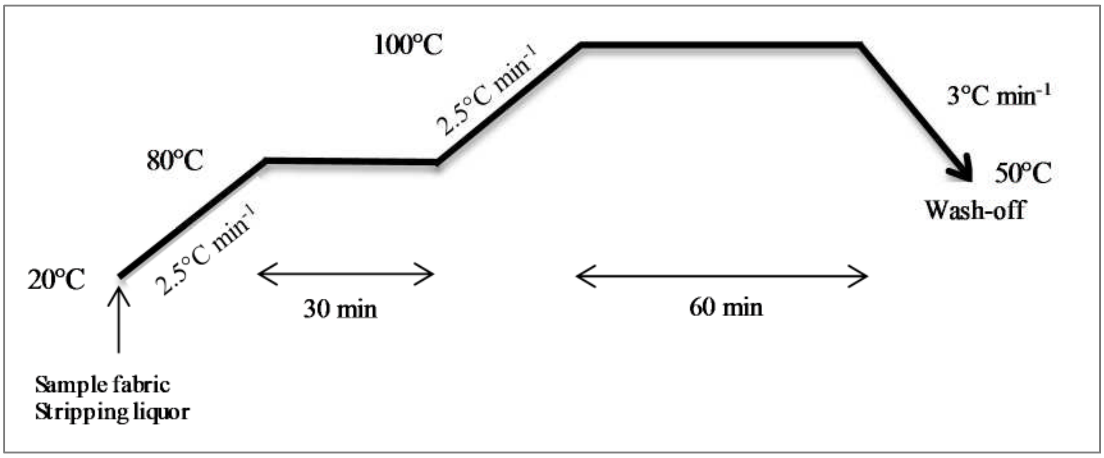
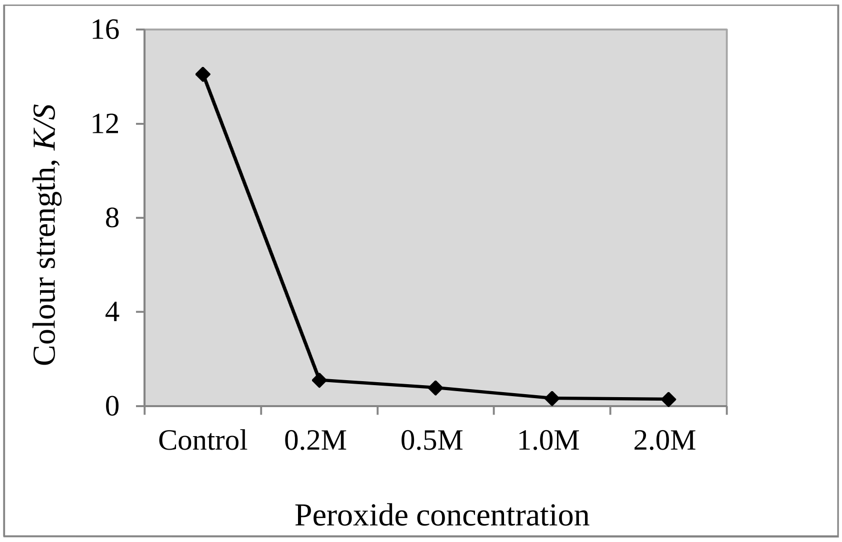


Figure 9 The optimised alkaline dithionite stripping profile

Appendix B - Effect of Hydrogen Peroxide concentration on the colour strength of the cotton fabrics

The concentration of hydrogen peroxide was optimised by using sulphur dyed cotton fabrics (using the same bleached, mercerised base cotton fabrics used throughout this study). C. I. Sulphur Black 1 dyed fabric was selected due to its reported sensitivity to peroxide oxidative bleaching [78]. The oxidation process used the procedure reported in the literature [241] while varying the concentration of hydrogen peroxide to 0.2M, 0.5M, 1.0M and 2.0M in order to obtain optimum colour removal from the samples.

Figure 10 presents the effect of varying the concentration of hydrogen peroxide on the colour strength of the sulphur dyed cotton fabric. Results reveal that increasing the concentration of hydrogen peroxide significantly decreased the colour strength of the samples. However the effect was slightly reduced when higher peroxide concentrations (2M) were used. Additionally too much of the hydrogen peroxide in the stripping liquor suggests a higher potential to cause fabric weight loss, decreased tensile strength [241] and subsequent destruction of the cellulose polymer. Therefore in this study 1M hydrogen peroxide (30%w/v) was selected as the optimum hydrogen peroxide concentration which leads to high colour removal from cotton fabrics.



Figute 10 The effect of varying the hydrogen peroxide concentration on the colour strength of the sulphur dyed cotton fabrics.