

OPTIMIZATION OF SALT FREE DYEING OF COTTON USING HOT AND COLD  
REACTIVE DYES

BY

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of Master of Science in Textile Engineering, Department of Manufacturing, Industrial  
and Textile Engineering, School of Engineering, Moi University-Eldoret,

September, 2020

**DECLARATION BY THE STUDENT**

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## **DEDICATION**

This study is dedicated to my parents and family. Thank you for your support and encouragement towards my goals I appreciate every kind of support you gave me during the entire period of my studies.

## ABSTRACT

Dyeing of cotton with reactive dye requires very high concentration of salt. These salts improve exhaustion by reduction of the repulsion forces between the anionic dye and hydroxyl functional groups of cotton. The salt is released after dyeing process and increases salinity in drain water stream which affects human health and biodiversity in water bodies. To eliminate salt consumption and enhance chicken feather waste utilization, the research aims at using an eco-friendly approach of salt free dyeing of cotton with two types of reactive dyes (cold and hot brand). The aim of the study was to determine the effect of pre-treating the cotton fabric with extracted keratin hydrolysate without the usage of salt on dye exhaustion, to optimize the dyeing parameters, compare dye exhaustion values of hot and cold reactive dyeing and to analyse the effects of dyeing parameters on colourfastness properties of pre-treated cotton fabric dyed with hot and cold reactive dyes. Keratin hydrolysate was extracted from chicken feather waste. Cotton fabric weighing 126.2 g/m<sup>2</sup>, 22.8 warps and 13 wefts per centimetre was used. Central composite experimental design was used to optimize temperature and time in hot and cold reactive dyeing. Dye exhaustion at maximum wavelength were evaluated using spectrophotometer before and after dyeing pre-treated cotton fabric. The experimental data was used to predict optimum dye exhaustion and optimum dyeing parameters. The models for dye exhaustion in hot and cold brand reactive dyeing yielded P value of less than 0.05 and coefficient of determination (R<sup>2</sup>) of 0.9595 and 0.9444 respectively. The model established optimum dye exhaustion of 52.9 % in hot and 48.3 % in cold reactive dyeing. The study established optimum dyeing temperature of 69.7<sup>0</sup>C and time of 75 minutes in hot brand dyeing and 34.4<sup>0</sup>C and 45 minutes in cold brand dyeing. The cotton fabric showed acceptable dye exhaustion in hot and cold reactive dyes in the absence of salt. The untreated sample dyed in absence of salt exhibited low exhaustion values of 21.4 % and 28.7 % for cold and hot dye brands. This is lower when compared with the exhaustion values of treated cotton fabrics. Therefore, the treated cotton fabric dyed in the two types of reactive dyes exhibited high exhaustion values than the control sample dyed in the presence of salt. The research further established that dyed keratin treated cotton samples exhibited better wash fastness and rubbing fastness. While this research has led to the utilization of chicken feather waste and reduction of salt usage in reactive dyeing, more research should be carried out to assess the environmental impact of the effluent which is generated from the salt free reactive dyeing of treated cotton fabrics.

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## **CHAPTER 1: INTRODUCTION**

### **1.1 BACKGROUND OF THE STUDY**

Textiles are elements which coexist with humans. They assist humans in every way by providing comfort and protection. Textiles are used for clothing, carpeting, furnishings, window shades, towels and coverings for tables. Cotton is one of the most important natural fibers in the textile sector used for textiles (Alam et al., 2008). Cotton fibers are characterized by their excellent absorbency, breathability, sanitary property, softness and heat retaining property. They are extensively used in the industries for clothing, decoration, sanitation, and health industry (Zhang, Zheng, & Zheng, 2018). Conventional dyeing process of cotton fabrics is done with water-based dye baths such as reactive dyes and direct dyes (Chavan, R.B, 2007). Reactive dye is one of the most used dyes for cotton fabrics because of its high level of washing fastness, brilliant colours and versatility of application(Lewis, 2011). Dyeing of cotton with reactive dyes requires large amount of salt for better exhaustion of dyes. After dyeing process these dyes are discharged together with salt as effluent (Zhang et al., 2018). These discharge waste water containing high concentration of salt ends up disturbing the marine life.

Chemical modification of cotton in order to improve its dye uptake without the large amount of salt has been considered for a long time. Salt free reactive dyeing of cationized cotton has be known to have several advantages over conventional reactive dyeing such as good colourfastness, reduced usage of salt, improved dye utilization and reduced environmental pollution. This complies with green, ecological and environmental modern manufacturing concept (Chavan, R.B, 2007;Teklemedhin, 2018).

Many studies have been made on the dyeing of cotton fabrics with reactive dyes (Kuo et al. 2008). The effect of dye concentration, electrolyte concentration, dyeing time and

temperature on dyeing performance of cotton fabric dyed has been experimented and it was found that dye absorption increases with the increase in dyeing time and dyeing temperature (Kuo et al., 2008). The effect of different dyeing parameters on colour strength and fastness properties of cotton using conventional dyeing using reactive dyes has been also studied (Wang et al. 2015). Nevertheless, there is few reports on the effects of dyeing parameters on salt free reactive dyeing of cotton. In this research, dyeing parameters that affect dyeing in salt free dyeing of cotton with the use of hot and cold reactive dyes will be investigated. The effect of dyeing temperature, dyeing time and its effect on dye exhaustion and colourfastness was evaluated.

## **1.2 PROBLEM OF STATEMENT**

Cotton is the most used fiber in the world. Reactive dyes are the most used dyes for dyeing cotton. Conventional reactive dyeing of cotton requires large amount of salt used for better exhaustion of dyes and this is considered one of the pollution generation process. Example of textile industry effluent ready to be discharged to the water bodies is shown in Figure 1. Dyeing performance of salt free reactive dyeing is affected by dyeing parameters; temperature, pH and reaction time, however the extent of their effects was established. Important characteristics of colored textiles affected by dyeing parameters include colorfastness and dye exhaustion. It was therefore necessary to evaluate optimum dyeing parameters of salt free dyeing of cotton with hot and cold reactive dyes.



Figure 1: Rivatex Treatment Plant

### **1.3 JUSTIFICATION.OF THE STUDY**

Salt free reactive dyeing is environmentally friendly. Pre-treating the cotton fabrics with reactive cationic agent eliminate the amount of electrolyte required. Efficient control of the critical factors in dyeing helps to improve productivity and performance of its end product. Optimum conditions for salt free dyeing of cotton in hot and cold reactive dyeing was determined.

### **1.4 SIGNIFICANCE OF THE STUDY**

Many challenges in current textile industry are related to pollution and production efficiency. Reactive dyeing with cotton has been considered one of the process that causes environmental problems as huge amount of salt are required and they are neither exhausted or destroyed and end up being discharged as effluents. The large quantity of salt in the effluent causes pollution of rivers and streams and upsets the biological equilibrium. This attempt of salt free reactive dyeing by modifying the cotton fibre using keratin hydrolysate which contains cationic groups, eliminates the usage of salt. Study of optimal dyeing parameters ensures better exhaustion of dyes and good colourfastness

properties. This research will therefore contribute to new knowledge by providing a better understanding of salt free dyeing of cotton with hot and cold reactive dyes.

## **1. 5 OBJECTIVES**

### **1.5.1 MAIN OBJECTIVES**

The main objective of the study was to optimize the dyeing parameters of salt free dyeing of cotton fabric in hot and cold reactive dyes. To be able to accomplish this, the project was guided by the following specific objectives:

- i. To characterize and pre-treat grey cotton fabric
- ii. To obtain keratin hydrolysate extracts from chicken feathers waste and pre-treat the cotton fabric with the extracts.
- iii. To carry out salt free dyeing of treated cotton fabrics in hot and cold reactive dyes by varying temperature and reaction time
- iv. To evaluate and optimize the dyeing parameters on exhaustion of dyes on the cotton fabric and compare the dye exhaustion values of hot and cold reactive dyes.
- v. To analyse the effects of dyeing parameters on colourfastness properties; light, rubbing and washing

### **1.6 SCOPE OF THE STUDY**

In this research, the coverage was; extraction of keratin hydrolysate from chicken feather waste, pre-treatment of cotton fabric with the extracts, dyeing of pre-treated cotton fabric with hot and cold brand reactive dyes, analysing dye exhaustion percentages and colourfastness and comparing of results using statistical methods.

## CHAPTER 2: LITERATURE REVIEW

### 2.1 INTRODUCTION

Dyeing is a process of coloration of textile fabric by using synthetic and organic dyes according to the required shade and colour. It is applied in aqueous solution to the textile substrate. Dyes can be absorbed on to the substrate in solution form through covalent bond with salts or metals by chemical retention or physical adsorption (Faridulhasan et al; 2016). The dyeing process is one of the key factors in the successful trading of textile products and affects the quality of the end product. In addition to the design and beautiful colour, the consumer usually looks for some basic product characteristics such as colour fastness properties. To obtain an uniform depth of colour suitable for the end use of the fabric, chemical aids such as surfactants, acids, alkali, electrolytes, carriers, levelling agents, promoting agents, chelating agents, emulsifying oils, softening agents are applied to the textile during dyeing process (Moore SB, 2004).

Before the dyeing process, the fabric goes through pre-treatment process whereby unwanted impurities are removed from the fabrics before. This is done by desizing and scouring followed by bleaching to remove the natural colour. These processes improve the dye uptake of the substrate. Dyeing can be carried out as a continuous or batch process (P.Choquette, 2016). In Continuous dyeing, the fabric is passed through a trough containing dye solution and then squeezed through a padding nip at controlled pressure. The dyestuff is therefore applied to the fabric by physical means rather than by exhaustion. In batch processing, sometimes called exhaust dyeing, the dye is gradually transferred from the dye bath to the material being dyed over a relatively long period of time (WS, 1991). Dyeing occurs in the presence of dilute chemicals in a closed equipment such as a kier, kettle, beam, jet or beck (Maria et al., 2013). Unlike the continuous process, instead of being passed through various baths in a long series of equipment sections, the



batch process the fabric remains in a single piece of equipment, which is alternately filled with water and then drained at each step of the process (Maria et al., 2013).

## **2.2 DYEING PROCESS**

Dyeing involves colouration of various forms of textile materials which are fiber, yarn, fabric in knitted or woven form, and garments. Dyeing is a process in which a textile fiber absorbs the molecules of dye from its solution so that the dyed product retains the dye and prevents it from being released back to the solution from which it has been absorbed. Dyeing processes take place in water solutions and involve four stages; diffusion of the dye in the dye solution during which individual dye molecules move within the liquid phase towards the fiber, absorption of the dye on the fiber surface where dye molecules pass from dye solution to the fiber. Fiber surface contains pores which allow dyes to penetrate into the interior. Molecular diffusion of the dye from the fiber surface towards the interior of the fiber takes place after the absorption process. This is a slow process and it can be increased by raising the temperature of the dye solution. Higher temperature also helps in increasing fiber swelling. The last stage is fixation of dye molecules on the fiber molecules by the formation of bonds between the molecules of dye and the fiber (Grishanov, 2011). There are various dyeing methods and machinery for each textile material.

### **2.2.1 BATCH PROCESSES**

This is the process whereby a textile substrate is immersed in a bath of water in which dye is dissolved as shown in Figure 2.1. With heat, the dyestuff diffuses through the solution and is absorbed at the fiber surface and then diffuses into the fiber. For diffusion of dyes to take place the dyes must be broken down into aggregates in the presence of heat.

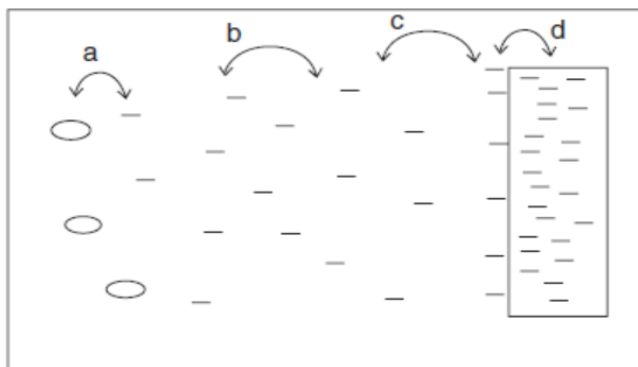


Figure 2.1: Schematic dyeing process (G. P. Nair, 2011)

### 2.2.1.1 EXHAUSTION.

This is the process whereby the dye moves from the dye bath to the fiber until a point whereby the dye bath becomes depleted of dye. This is also referred to as a percentage of dye that has moved from the bath to the substrate. Exhaustion over time may be illustrated by an exhaustion diagram in Figure 2.2. Dye is initially absorbed rapidly but the rate of uptake decreases as the dye bath is depleted of dye. Eventually, an equilibrium is reached and no further uptake occurs. In equivalent situations, percentage exhaustion at equilibrium decreases as the amount of dye applied increases (Pauet al , 2017).

### 2.2.1.2 EQUILIBRIUM.

Dyeing is the process in which a dye equilibrates between the dye bath and the substrate. While most dyeing's reach a point at which the concentration of dye in the dye bath is changing very little as seen in Figure 2.2 (Choquette, 2016).

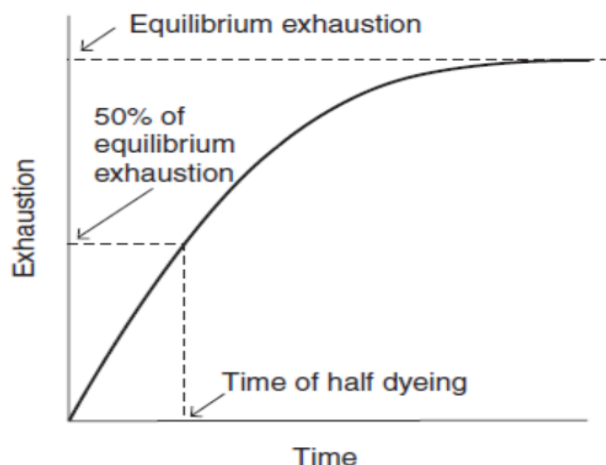


Figure 2.2: Exhaustion/Time Plot of a Dyeing Process  
(Choquette, 2016)

## 2.2.2 CONTINUOUS DYEING PROCESS

When large amounts of a single colour shade are required, continuous processing is more efficient than batch processing (Choquette, 2016). White fabric material is fed into the system and coloured material withdrawn continuously. The various steps are accomplished in successive units of a continuous range.

### 2.2.2.1 PADDING

The substrate is impregnated initially with dye solution typically by dipping and squeezing between rollers to remove excess dye and leave a consistent amount of dye on the substrate (Choquette, 2016). This dip and squeeze sequence is referred to as “padding.” All the chemicals required for dyeing may be present in the pad bath; alternatively, some may be applied in a second padding step usually after an intermediate drying. As the pad is continuously filled, an equilibrium is established, but the first length fabric dyed are darker than the bulk. The extent of relative darkness and length affected depends on the substantivity of the dye, temperature and volume of the pad bath (Clark, 2011).

### **2.2.2.2 FIXATION**

The penetration of fiber by dye is similar to that which happens in a batch dyeing. This might be accomplished continuously with steam or dry heat. It may also be convenient to apply dyestuff continuously and then divide the material into batches and allow fixation to occur over time typically 8–12 hours while the fabric is stored on a roll. This is the basis of semi continuous or pad-batch processing (Choquette, 2016).

### **2.2.2.3 WASHING OFF AND DRYING**

Dye auxiliaries and unfixed dyes are removed in one or more washing steps, followed by drying over heated cylinders or in a continuous oven. If fixation is accomplished in batches, this step may also be carried out batch wise or the batches may be combined and subjected to continuous washing (Choquette, 2016).

### **2.2.1.3 AFFINITY OF THE DYEING PROCESS**

The standard affinity of the dyeing process is a measure of the desire of the dye to move from its standard state in the dye bath to its standard state in the fiber and it can be considered as the driving force of the dyeing process (Ferus-comelo, 2002). It is often referred to simply as affinity (Ferus-comelo, 2002). A high affinity describes a dye that has a strong tendency to move from the dye bath to the fiber and to stay there. A high affinity dye, under a given set of conditions will tend to have a high equilibrium exhaustion. On the other hand, a low affinity dye has a low tendency to move to the fiber phase, and it is desorbed more easily than a high affinity dye. Since the affinity value is generally derived from an isothermal system, it is not unexpected that affinity varies with temperature; since dyeing is exothermic, affinity declines as temperature increases (Choquette, 2016). Along with the decrease in affinity, as temperature increases the equilibrium exhaustion decreases as illustrated in Figure 2.3 (Coquette, 2016).

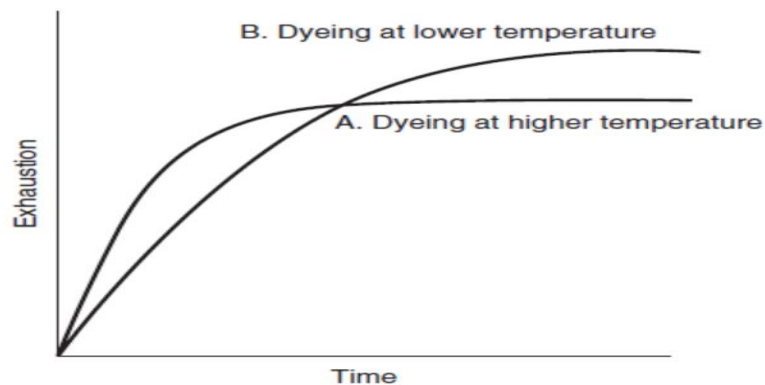


Figure 2.3: Effect of Temperature and Dyeing Rate & Equilibrium Exhaustion (Choquette, 2016)

## 2.3 DYEING MACHINES

### 2.3.1 JIGGERS

Jigger is a dyeing machine in which fabric in open width is moved from one roller to another and passes each time through a dye bath. Full width piece goods may be dyed in jiggers (Nair, 2011). The cloth is passed from the feed roller through the dye bath, and by means of another roller, is given a thorough treatment in the liquor (Nair, 2011). The jigger is one of the oldest types of machines used for dyeing woven fabrics up to boiling temperatures. Fabric is wound onto the take-up roller then run through the dye bath located in the lower part of the machine and onto the second main roller. When the roller is fully loaded, the fabric passage is reversed and runs back through the dye bath before being batched again on the first main roller. The movement of fabric from one main roller to the second main roller is called one turn. The dye bath trough has a guide roller or rollers at the bottom through which the fabric passes during dyeing while picking up fresh dye liquor. During rotation on the rollers, the dye liquor penetrates and percolates through the fabric facilitating the dyeing process (Nair, 2011).

### **2.3.2 BEAM DYEING MACHINES**

Before the invention of jigger machine, beam dyeing machines were used for dyeing polyester and are suitable for dyeing warp knit fabrics, light-weight woven filament fabrics and polyester blended fabrics. In this machine, the fabric batch remains stationary during dyeing while the dye liquor is circulated through the batch (Nair, 2011).

### **2.3.3 WINCHES**

This is the oldest rope dyeing machine with stationary liquor and material moved via a winch reel. This machine exerts only a low tension on the fabric much lower than that exerted by a jigger, and hence was considered an ideal dyeing machine for delicate and tension-sensitive fabrics such as viscose rayon and the knitted substrates (Nair, 2011). However, its liquor requirement is greater than the jigger with a material to liquor ratio (M: L) of 1:20–40, resulting in high effluent generation. In this machine, the fabric is in the form of loops or ropes immersed in the dye bath. The upper part of the rope runs over two reels mounted over the dye bath. There is a smaller reel at the front of the machine above the surface of the dye bath. The winch consists of a power-driven elliptical reel mounted on a tank that has a perforated partition between a small and a large compartment. The small compartment is at the front of the machine and has a perforated steam pipe, water inlet and outlet. There is a guide roller to move the cloth (Nair, 2011).

### **2.3.4 AIR JET DYEING**

Jet dyeing machines which is widely used for the dyeing of polyester in rope form. In this machine, both the fabric and the dye liquor are in motion, thereby facilitating a faster and more uniform dyeing. In rope form, fabrics can be run at higher speeds and in multiple strands for rapid dyeing and higher productivity. Jet nozzles can be of various sizes and shapes to suit different fabric qualities from heavy woven to knits and other delicate materials (Nair, 2011).

## 2.4 COTTON FIBER

Cotton fiber is one of the most used natural textile fibers and accounts for about one third of the total world production of textile fibers (Grishanov, 2011). Cotton fibers grow on the surface of the seed of cotton plant. Cotton consist of cellulosic and non-cellulosic material. Cotton fiber contains 90–95% cellulose which is an organic compound with the general formula  $(C_6H_{10}O_5)_n$  (Grishanov, 2011). A morphological structure of cotton fiber is shown in Figure2.4.

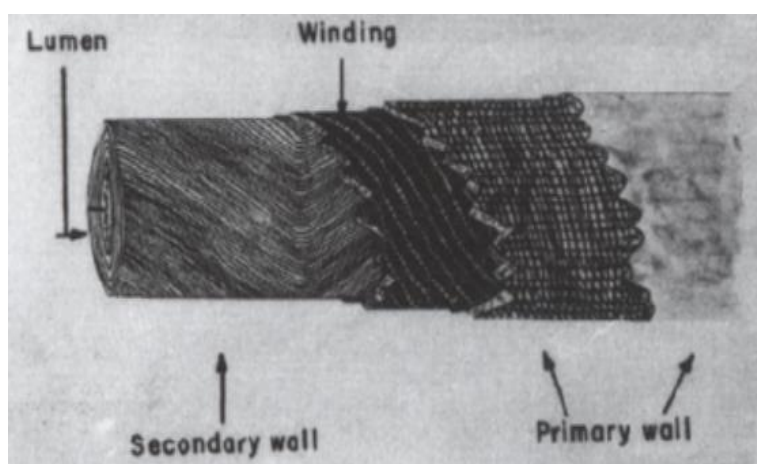


Figure 2.4:A Morphological Structure of the Cotton (Grishanov, 2011)

The outer most layer of the cotton fiber is the cuticle, covered by waxes and pectin and it surrounds a primary wall built of cellulose and protein material. The inner part of the cotton fiber consists of the secondary wall comprised of fibril and the lumen. The fibrils consist of densely packed bundles of cellulose chains. Micro-capillary system is developed inside the micro fibrils. The capillary system is used for swelling and absorption processes (Grishanov, 2011).

Cellulose is a linear polymer of 1,4- $\beta$ -D-glucose units linked together by valence bonds between the carbon atoms number 1 of one glucose molecule and number 4 of another molecule as shown in Figure2.5. The hydroxyl groups (OH) protruding from the sides of

the molecule chain link neighbouring chains together by hydrogen bond and form ribbon-like micro fibrils which are further arranged into larger building blocks of the fiber. (Nair, 2011). The natural cellulosic fibers contain 3000-5000 glucose units joined together with molecular weight of the order of 300,000 -500,000 (Grishanov, 2011).

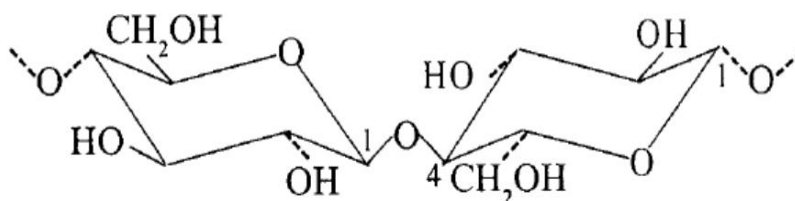


Figure 2.5: Molecular Structure of Cellulose (Karmakar, 1999)

#### 2.4.1 COTTON IMPURITIES

Cotton fibers contain impurities in the range from 4 to 12% (o.w.f.) and the overall composition of cotton fibers are shown in Table 2.1 (Karmakar, 1999). The impurities in cotton fiber vary according to the fiber maturity. Cotton impurities are located on the outer side of the fiber. The secondary wall is mainly composed of cellulose (Karmakar, 1999).



Table 2.1: Composition of Cotton Fibers

Constituents	Percentage by Dry Weight
$\alpha$ – cellulose	88.0-96.5
Protein	1.0-1.9
Wax	0.4-1.2
Ash (inorganic salts)	0.7-1.6
Pectin	0.4-1.2
Others (resins, pigments, hemi-cellulose, sugars, organic acids, incrusted ligneous substance)	0.5-8.0

## 2.5 PRE-TREATMENT PROCESS OF COTTON MATERIALS

Pre-treatment is a process that is meant to prepare the textile materials prior to dyeing process. This process involves removal of cotton impurities which have negative influence on dyeing process. The different stages for preparatory processing of cotton fabrics are shown in Figure 2.6. The pre-treatment process must meet the requirements of the dyeing and finishing stages and the intended end-use of the textile material (Karmakar, 1999).

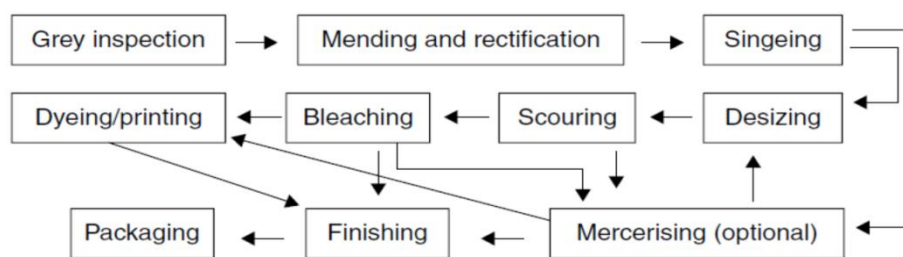


Figure 2.6: Pre-treatment Process of Cotton (Karmakar, 1999)

### 2.4.1 SHEARING AND CROPPING

This is the removal of projected yarns on the surface of the fabric which obstruct adsorption of dyes on the fabric surface during dyeing and printing processes. They may also be entangled within machine parts causing damage of the materials. The projected fibers or yarns are cut from the fabric surface (Nair, 2011).

### 2.4.2 SINGEING

During yarn formation from short staple fibers, the two ends of the fiber may not be formed in the yarn and they get projected due to twist imparted during spinning. Singeing or gassing is a very effective method for removal of these projected fibers as shown in Figure 2.7 (Nair, 2011).



Figure 2.7: Singeing Machine( Nair, 2011)

### 2.4.3 DESIZING PROCESS

This is removal of size material imparted to the warp yarn before weaving to prevent breakage warp yarns during weaving due to abrasion. The presence of size on the fabric makes it stiff and render its treatment with different liquors used in dyeing and finishing difficult (Ammayappan, Mathukrishnan, & Prabakar, 2003). This process therefore facilitate the penetration of dyes and chemicals in the subsequent wet processing operations. About 65% of the cotton fibres used for textiles is made into woven fabric (Karmakar, 1999).

The surface coating of size is stiff, hard, smooth and less absorbent to water. The size recipe contains other additives such as humectants, binders and lubricants. Starch and tallow based lubricants have been used as sizing components for cotton because they are readily available, cheap and are based on natural sustainable materials (Karmakar,

1999). The removal of hydrophobic part of the sizes is difficult and are not removed during desizing, but removed in alkali scouring by being emulsified (Tzanov et al., 2001).

#### 2.4.4 SCOURING OF COTTON AND OTHER CELLULOSIC FIBERS

This is the most important process in wet process applied to textile materials before dyeing or printing. It is a process whereby matter or impurities are removed. The scouring process, purifies the  $\alpha$ -cellulose, imparts the hydrophilic character and permeability necessary for bleaching, mercerising, dyeing or printing. During scouring, oils, waxes and free fatty acids are emulsified by the soaps. Proteins are degraded to simple soluble amino acids and mineral matter is dissolved. Dirt is removed and other added impurities are broken into soluble products. The recommended weight loss in scouring is 4-8% in which the scoured fabric is absorbent (Grishanov, 2011). There are two types of machines that are shown in Figure 2.8 and 2.9 that are used for scouring; kier and j-box.

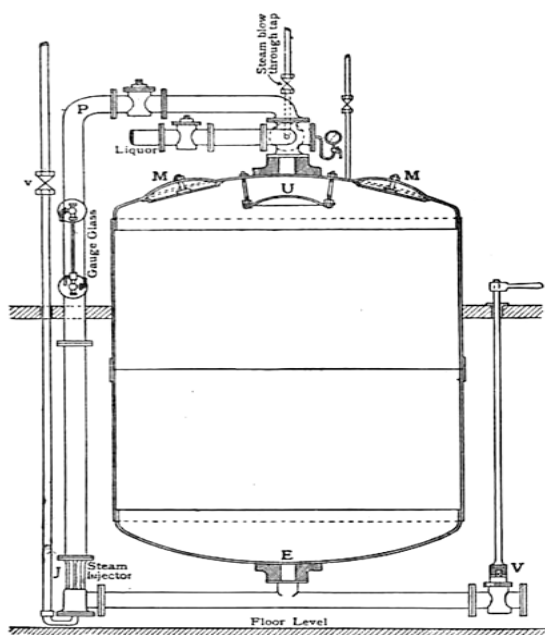


Figure 2.8: Kier Boiler (Nair, 2011)



Figure 2.9: J-Boxes (Nair, 2011)

#### **2.4.5 COMBINED DESIZING, SCOURING AND BLEACHING**

This is a process whereby desizing, scouring and bleaching are combined into a single stage by using process equipment as shown in Figure 2.10. This technique is effective in minimising time, energy and labour (Ammayappan et al., 2003). In this method, the fabric is padded with the enzyme bath and then passed into a wet steam chamber at 96°C- 100°C where the desizing takes place in less than a minute. The fabric after desizing is impregnated in a solution of 40-60 g/l of sodium hydroxide at 130-135°C, 1-3 g/l wetting agent, and 1-3 g/l emulsifier at the period of 2 minutes (Karmakar, 1999)

The fabric after impregnation is taken out and piled into J-box, steam chamber or pad roll chamber at 98°C and allowed to remain there for two hours during which period the alkali reacts with the impurities. The fabric is then rinsed.

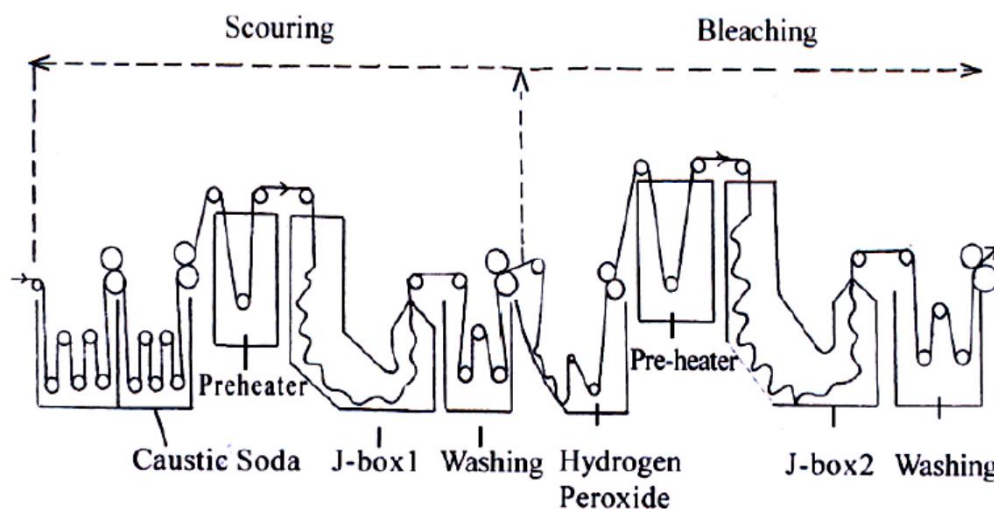


Figure 2.10: Process Equipment for Combined Desizing, Scouring and bleaching  
(Karmakar, 1999)

#### 2.4.6 MERCERISATION

This is the treatment of cotton fabrics with caustic soda solution to improve lustre and dye uptake and more without tension to produce stretch materials. Cotton fabrics are mercerised in grey or bleached condition. The main purpose of mercerisation is to swell the cotton increasing its lustre, tensile strength, dimensional stability and dye ability (Karmakar, 1999). Mercerization improves the following properties; modifies the internal reorientation of cellulose structure, increases the strength by 15-25%, improves elasticity and dimensional stability, enhances luster and feel, improves absorbency of water, dyes and other finishing chemicals, increases the uniformity of dyeing and improves the dye affinity (Karmakar, 1999).

#### 2.5 REACTIVE DYES

Reactive dyes are the most commonly used dye for dyeing of cotton fabrics. These dyes operate under alkaline conditions. They react with the ionized hydroxyl groups in cotton cellulose forming a covalent bond with the fiber. The strong bond between the reactive dye and the cellulose ensures good fastness to washing. The simple chemical structures

of the dyes often result in bright colours. These dyes have also other advantages such as good levelness, high affinity for cellulose, good stability of the dye-fiber bond and simple dyeing procedures (Jstršek, Oliška, & Akin, 2008).

Reactive dyes are used for dyeing wool, cotton, nylon, silk, and modified acrylics due to their strong interaction with many surfaces of synthetic and natural fabrics (Mottaleb & LittleJohn, 2001). The reactive site of the dyes reacts with functional group on fiber under influence of heat and alkali. One of the major factors determining the release of a dye into environment is its degree of fixation on the fiber. Reactive dye is hydrolysed to some extent during application processes. Reactive dyes in dyeing wastewater have been identified as one of the pollutant compounds since they are highly alkaline, have high concentration of organic materials and strong colour in comparison with other dyes (Saeed & Abbas, 2012). Reactive dyes are characterised by nitrogen to nitrogen double bonds and azo bonds. The colour of the azo dyes is due to this azo bond and associated chromophores (Saeed & Abbas, 2012). The dyes are first absorbed onto the cellulose and then react with the fiber. The reactive systems of these dyes react with ionised hydroxyl groups on the cellulose substrate (Saeed & Abbas, 2012). However hydroxyl ions present in the dye bath due to alkaline dyeing conditions compete with the cellulose substrate resulting in a percentage of hydrolysed dyes which can no longer react with the fiber (Ahmad et al., 2012).

### **2.5.1 CLASSIFICATION OF REACTIVE DYES**

Reactive dyes can be classified according to the type of reaction and application temperature (Chinta & Vijaykumar, 2013). According to type of reaction they are classified as; dyes reacting through the nucleophilic substitution reaction and nucleophilic addition reaction. The cold brand dyes contain a highly reactive dichlorotriazine group which reacts with cellulose fiber at 25<sup>0</sup>C to 40<sup>0</sup>C in the presence of an alkali (Lewis,

2011;Jstršek, Oliška, & Akin, 2008). Hot brand dyes with lower reactivity contain monochlorotriazine which require hot temperatures have also been developed (Lewis, 2011).

They are also remazol dyes which are considered as warm dyes possessing vinyl sulphonyl group. The reactive dyes with the presence of both vinyl sulphone and monochlorotriazine reactive groups in the same dye molecule allows higher fixation of the dye on the fabric in the temperature range of 50-80<sup>0</sup>C (Jstršek et al., 2008).

### **2.5.1.2 DYES REACTING THROUGH THE NUCLEOPHILIC SUBSTITUTION REACTION**

Triazine-based reactive groups react through the nucleophilic substitution reaction. There are mostly chlorotriazines of either the dichlorotriazine or monochlorotriazine .The reactivity of dichlorotriazine-based dyes is higher than the monochlorotriazine dyes so they require temperature of 25<sup>0</sup>C-40<sup>0</sup>C (Jstršek et al., 2008;Lewis, 2011) and a milder alkali for their application when compared to the monochlorotriazine dyes. These dyes are known as cold brand reactive dyes. The general structure of cold brand are as shown in Figure 2.11(Lewis, 2011).

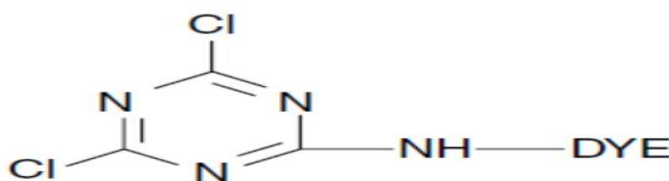


Figure 2.11:General structure of cold brand reactive dye (Lewis, 2011)

Monochlorotriazine dyes require a higher temperature and a stronger alkali application than the dichlorotriazine-based dyes. The general structure of monochlorotriazine-based hot brand reactive dyes is shown presented in Figure 2.12 (Lewis, 2011).

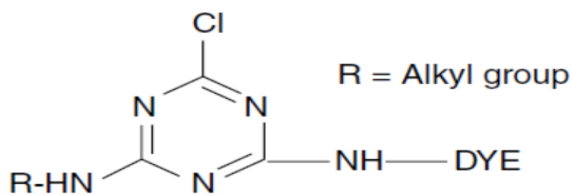


Figure 2.12: General structure of Hot brand reactive dye (Lewis, 2011)

The reaction of triazine dyes with cellulose is shown in Figure 2.13. The chlorine of the triazine ring is replaced by cellulose thus the dyes form a covalent bond with the fiber, which accounts for the high wash-fastness of reactive dyes. The reactive dyes can react with water molecules as well. The reaction of the dyes with water is called hydrolysis as shown in Figure 2.14. The hydrolysed dyes lose their power to react with the fiber. These dyes remain loosely held on the fiber and if not properly removed through soaping, they deteriorate the wash fastness of the dyes (Choquette, 2016).

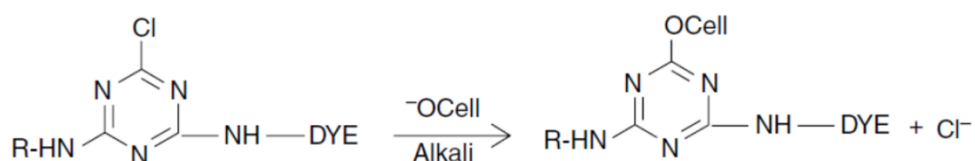


Figure 2.13: Reaction of Cotton Cellulose with Reactive Dye (Choquette, 2016)

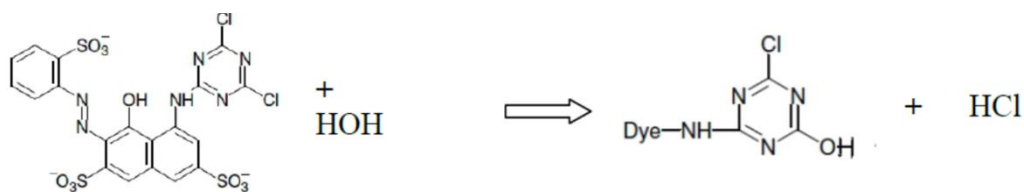


Figure 2.14: Hydrolysis of reactive dye (Choquette, 2016)

### 2.5.1.3 DYES REACTING THROUGH THE NUCLEOPHILIC ADDITION REACTION.

The majority of the dyes that react through nucleophilic addition reactions are based on vinyl sulphone. The bond between vinyl sulphone and cellulose is very strong and is stable to acid hydrolysis.



## 2.5.2 PROPERTIES OF REACTIVE DYES

Reactive dye is anionic in nature and a water-soluble dye. They have better wash and light fastness properties and better substantivity. They form strong covalent bond with the cellulosic fiber in alkaline condition. Wide range of colour can be produced with reactive and are comparatively cheaper in price (Nair, 2011). These dyes form covalent bond with cellulose fiber by nucleophilic substitution and addition reactions as shown in Figure 2.15 and 2.16.

### 2.5.2.1 Substitution reaction:

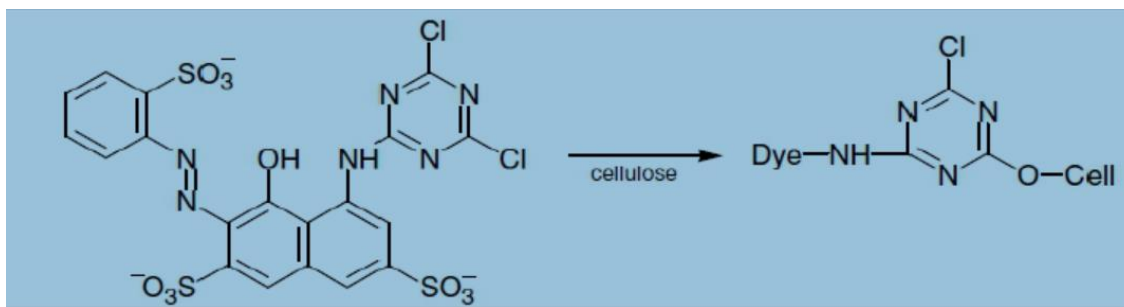
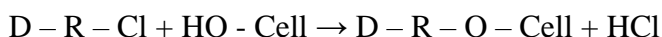


Figure 2.15: Reactive Bonding with Cellulose by Substitution Reaction (Nair, 2011)

### 2.5.2.2 Addition reaction:

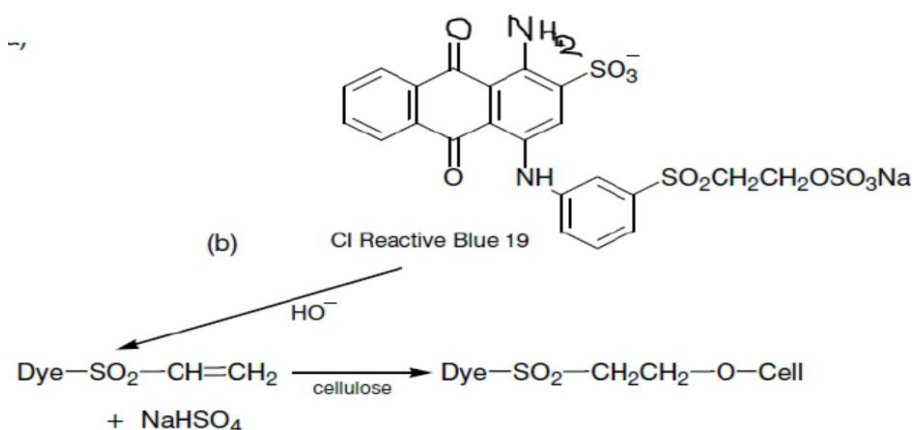


Figure 2.16: Cellulose Bonding with Reactive Dye by Addition Reaction

### **2.5.3 DYEING OF COTTON WITH REACTIVE DYES**

Cotton is one of the important and mostly used natural fiber in the world (Paul et al., 2017). Reactive dye is one of the most used dyes for dyeing cotton items because of its high level of washing fastness and versatility of application (Lewis, 2011). Reactive dyes are mostly used in dyeing cotton fabrics and contributes most to the effluent discharged to the environment (Khatri & White, 2015). Dyeing of cotton garments with reactive dyes involves two stages, namely; exhaustion and fixation of dyes.

When Cellulose fiber come in contact with water they produce slightly negative charge due to the ionization of hydroxyl groups and reactive dyes also became anionic in solution (Teklemedhin, 2018). The negative charge developed on the fibers results in repulsion of anionic reactive dyestuffs and thus limitation of the exhaustion of dyes. Therefore in dyeing of cotton with reactive dyes and other anionic dyes, large amount of electrolyte, such as sodium sulphate (Glauber's salt) or sodium chloride is required to reduce the charge repulsion between the negatively charged cotton and the reactive dyes (Montazer, Malek, & Rahimi, 2007).

These salts are fully dissociated in water to lose ion pairs. The positive sodium ion travels to the fiber and water interface and effectively negating the zeta potential destroying the barrier to the initial dye and fiber interaction (Chavan, 2007).

In reactive dyeing of cellulosic substrate, approximately 70–80 % of reactive dye is only exhausted and large quantities of electrolytes are required for exhaustion. The electrolyte used in dying process is discharged as effluent and increases the total dissolved solids (TDS). The effluents require advanced treatment for its removal. A lot of attempts have been made by researchers to improve the dye uptake of reactive dyes and reduce the usage of salt in reactive dyeing process. The efforts on reduction of salt usage has been done by

modification of substrate which is cotton to take up dyes without usage of salt (Bhuiyan, Shaid, & Khan, 2014).

## **2.5.4 APPLICATION OF REACTIVE DYES**

### **2.5.4.1 EXHAUST TECHNIQUE**

The exhaust technique is the most used method for application of reactive dyes as it is resistant to small changes of system variables. It has two steps; exhaustion and fixation. During exhaustion the dyes are exhausted from the dye bath and come into the fiber phase. High electrolyte concentration is required to have adequate exhaustion of the dye (Nair, 2011).

#### **2.5.4.1.1 COLD EXHAUST DYEING**

In this method dyeing begins at 25–30°C and maintained while dye is added. Salt is added in 3–4 portions over 30–60 min, the size of the addition is increased each time. The amount of salt used depends on the depth of shade. Dyeing continues for 15 min after the final addition of salt, then soda ash is added portion wise over 15 min. Dyeing continues for 30–45 min.

#### **2.5.4.1.2 WARM, HOT EXHAUST DYEING DYES.**

This is an isothermal technique for depths of shade above 0.5 % of the weight of the fabric(owf). The process begins at 40°C with salt at pH 7.0. The temperature is brought rapidly up to the dyeing temperature of 60–80°C depending on the dye. The dye is added over 10–15 min and the dyeing run for 30 min before adding alkali portion wise over 10–20 min. Dyeing continues for 45–60 min before dropping the dye bath and starting the wash-off sequence (Nair, 2011).

#### **2.5.4.1.3 MIGRATION EXHAUST TECHNIQUE.**

This method is preferred for pale shades below 0.5 % of the weight of the fabric. Dyeing starts at 50°C with salt at pH 7.0. Dye is added over 20 min and the temperature is raised to the temperature of 95°C. After 20 min of this temperature, the dye bath is cooled to 60–80°C and alkali is added portion wise over 20 min. After another 30 min, the dyebath is drained and the washing sequence is started (Nair, 2011).

#### **2.5.4.1.4 ALL-IN METHOD.**

Dyeing starts at 25°C with salt and alkali which is mixed soda ash and caustic soda and runs for 15 min, before adding dyes over 10 min. After a further 15 min, the temperature is brought up to 80°C and maintained at this temperature for 30–60 min before draining the dye bath and starting the washing process (Nair, 2011).

#### **2.5.4.2 PADDING TECHNIQUE**

One of the padding techniques is continuous dyeing, where the fabric is passed through bath containing dye solution and then squeezed through a padding nip at controlled pressure. This process of squeezing applies dyestuff to the fabric by physical means. The alkali is added to the dye solution in a second padding treatment. The fabric is dried to a moisture content below that at which migration can occur and then steamed followed by a washing-off process (Maria et al., 2013; Sivaraja, 2001).

There is also cold pad-batch dyeing technique where the fabric is padded with dye and alkali solution and the whole batched for 4–24 hours at an ambient temperature. Pad batch dyeing is possible on grey minimally prepared fabric followed by washing on the same perforated beam used to batch the fabric after dyeing (Faridulhasan et al., 2016).

## **2.6 EFFECT OF DYEING PARAMETERS ON DYE EXHAUSTION IN REACTIVE DYEING OF COTTON**

Dyeing with reactive dyes depends upon different parameters like electrolyte, alkali, liquor ratio and temperature (Haque, 2015). A highly reactive dye has higher probability to react with fiber but also possess strong chances to get hydrolysed. That is why the behaviour of any dyestuff in different parameters should be studied for getting the optimum results from the process. Several researchers studied the influence of dyeing parameters on dyeing with reactive dye. One of the studies by Miljkovic et al., 2007 on the effect of dyeing parameter on dyeing with vinyl sulphone dyes, indicated that the desired colour hue may be attained by reducing dye concentration or shortening dyeing time for 20 min with reduction of salt concentration .

## **2.7 VARIABLES THAT ARE CONTROLLED IN REACTIVE DYEING**

The process variables which are temperature, time, pH concentration of alkali, dye and salt require dynamic monitoring and control for effective dyeing. The absorption phase is dependent on the substantivity of dyes. Dyestuffs with very low and high substantivity in a recipe will cause problems of uneven dyeing and shade variation.

The absorption phase is very critical, where the curve is steep the dyestuff will be absorbed quickly causing uneven application. This is solved by the addition of electrolyte for exhaustion purposes. Electrolyte is also controlled, if not properly controlled the salt concentration may exceed at times and aggregation of the colour can take place, which would cause deposition of colour on the substrate in clusters causing skittery dyeing. The sodium chloride is freely soluble and unaffected by an increase in temperatures whereas sodium sulphate (glaubers salt) solubility decreases at higher temperatures (Chinta & Vijaykumar, 2013).

In the fixation phase, the alkali used and their concentrations are also controlled and monitored. The temperature and the alkali chosen would depend on the reactivity of the dyestuffs in the recipe and the pH parameter need to be carefully controlled and maintained over the fixation period. The degree of levelness of a reactive dye depends on the tolerable amount of dye which is bonded to the fiber per bath material contact; beyond this limit the dyeing is uneven. The phase at which rate of fiber dyestuff bonding is accelerated, pH level need to be controlled for even results (Chinta & Vijaykumar, 2013).

### 2.7.1 EFFECT OF TEMPERATURE AND REACTION TIME IN REACTIVE DYEING

The rate of dyeing increases with increase in temperature. Dye uptake at equilibrium decreases since dyeing is an exothermic process. Since practical dyeing is carried out at shorter time intervals than required for equilibrium dyeing. The amount of dye taken up is influenced by the dyeing time. Figure 2.17 shows that in the case of slow-dyeing dyes, dye uptake can be a maximum within normal dyeing time (time A) at about 100°C, whereas rapid dyeing dyes will have maximum adsorption at about 40°C (Sivaraja, 2001).

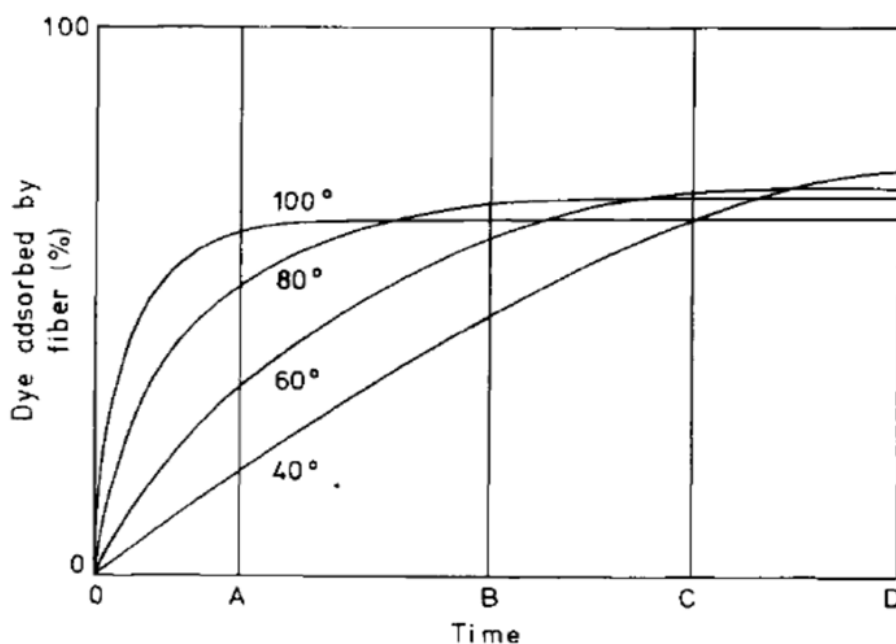


Figure 2.17: Effect of temperature on dyeing time and equilibrium (Sivaraja, 2001)

Diffusion inside the textile substrate has a greater temperature coefficient than dye diffusion in the dye bath. Diffusion in the fiber is regarded as an activated process, hence only that fraction of the total number of dye molecules having an activation energy in excess of the average energy of the diffusing molecules will be able to overcome the restraints to diffusion and move inside the fiber. Practical dyeing in short time intervals is possible only by raising the temperature (Sivaraja, 2001).

#### **2.7.1.2 EFFECT OF TEMPERATURE IN REACTIVE DYEING OF COTTON**

Temperature has a great influence on the dyeing performance (Haque, 2015). The dyeing rate increases with an increase in temperature up to an equilibrium point as shown in Figure 2.18. Initial dyeing rate increases with the increase of temperature. This is an effect of temperature on the rate of dying process. Dyeing is usually an exothermic process because of the heat released during the reaction of the dye with the fiber. The interaction between the dye and fiber molecules is stronger than between the dye and water molecules in solution (Pawadeetanaset & Rukijkanpanich, 2015).

Dye exists in solution as an aggregate of various sizes. The fabric absorbs the small aggregates. The larger aggregates break down to maintain an overall dynamic equilibrium of dye solution. When the temperature of the solution is increased the thermal energy coming from outside impedes aggregation and therefore the amount of the non-aggregated dye particles in the solution increases. Hence, the increase in temperature and consequently the increase in the kinetic energy of the molecule tend to break-up large aggregates into smaller units. Thus, the small dye particles penetrate into the fabric pores at high temperature. When the dye bath cools, the pore of the fabric contracts thus retaining the dye particles (Alam et al., 2008).

The increase in dye diffusion coefficients at higher temperature due to the greater kinetic energy acquired by the dye molecules and the increase in the frequency and amplitude of thermal oscillation in the separate sections of the macromolecule chain, provoke an increase in the number of the pores in the fabric structure and their diameter (Alam et al., 2008).

Most reactive dyes require the temperature of the dye liquor to be increased for the reaction to take place between the dye molecule and fiber. Reactive dyes have specific temperatures at which reaction between dye and fiber are optimum. For some of reactive dyes this reaction with alkali can take place at room temperature (Islam, Paul, Das, & Science, 2017).

The effect of temperature in reactive dyeing of cotton fabrics with have been studied by several researchers. The effect of dyeing temperature on colour strength was studied (Shahid et al., 2016). The result was that the colour strength of reactive dyed fabrics increased gradually with the increase of temperature from 40°C to 60°C. Agrawal (2015) performed conventional dyeing of cotton using reactive dyes by raising slowly the dye bath temperature to 80<sup>0</sup> C and dyeing continued at this temperature for about 60 minutes. The result indicated that the fabric exhibited good to excellent fastness. Dye exhaustion of cotton fabric increased with the increase in temperature and it reached optimum point at 60°C in 60 minutes when dyed with reactive dyes as shown in Figure 2.18 (Alam et al., 2008). Patel et al. (2014) also carried out dyeing of cotton fabric with monochlorotriazine reactive dye at 80<sup>0</sup>C and good colour yield was achieved.



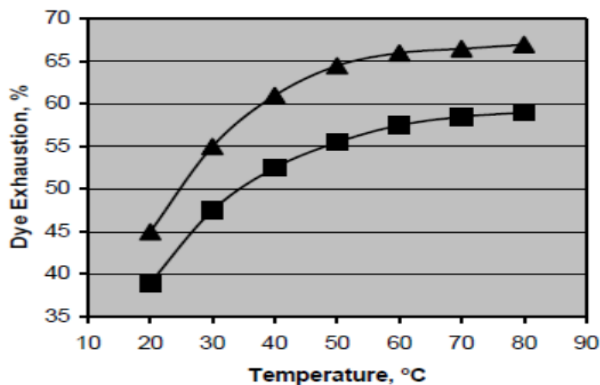


Figure 2.18: Effect of Temperature on Dye Exhaustion in Reactive Dyeing of Cotton  
(Alam et al., 2008)

The influence of the dye-fixing temperature on dyeing was investigated in reactive dyeing with dyeing promoters; neutral Nano liposomes and cationic Nano liposomes used instead of salt had colour strength increased as dye-fixing temperature increased from 70 to 100 °C. The colour strength values all first increased and then decreased, and the optimum colour strength was achieved at 85 °C in 70 minutes (Ru et al., 2018).

#### 2.7.1.2 EFFECT OF REACTION TIME IN REACTIVE DYEING OF COTTON

The dye absorption by cotton fabric increased with increase in dyeing time as shown in Figure 2.19. The dye absorption remains nearly the same on further increase in dyeing time (Zhang et al., 2018). The result of this behaviour is that when cellulosic fabric is immersed in a dye solution, it absorbs dye till the equilibrium is reached. Under any temperature and electrolyte concentration, the equilibrium is reached when each fabric is evenly dyed throughout its cross-section, and even after the lapse of a long period of time, no further exchange of dye in the fabric and in the solution takes place (Alam et al., 2008). The effect of temperature and dyeing time on natural cotton was investigated by (Wang et al., 2015) and optimum dyeing conditions was achieved at 90°C at 35 minutes. This time was close to the final dye uptake with the limited change for results. To save

the time in practice, the dyeing time of 35 minutes can lead to the satisfactory result (Wang et al., 2015).

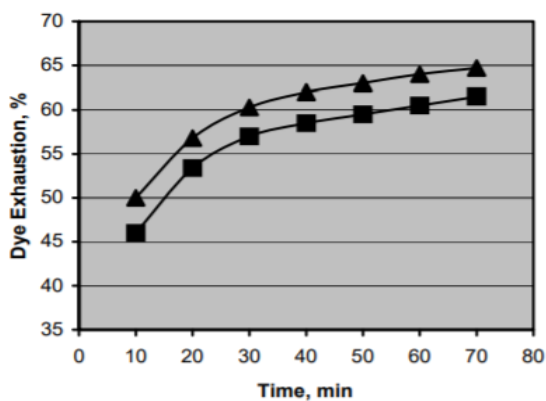


Figure 2.19: Effect of Reaction Time on Dye Exhaustion in Reactive Dyeing of Cotton (Alam et al., 2008)

Reactive dyes can be applied to textile products by exhaust method on jigger or winch and padding. Conventional reactive dyeing of cotton by exhaust method is shown in Figure 2.20.

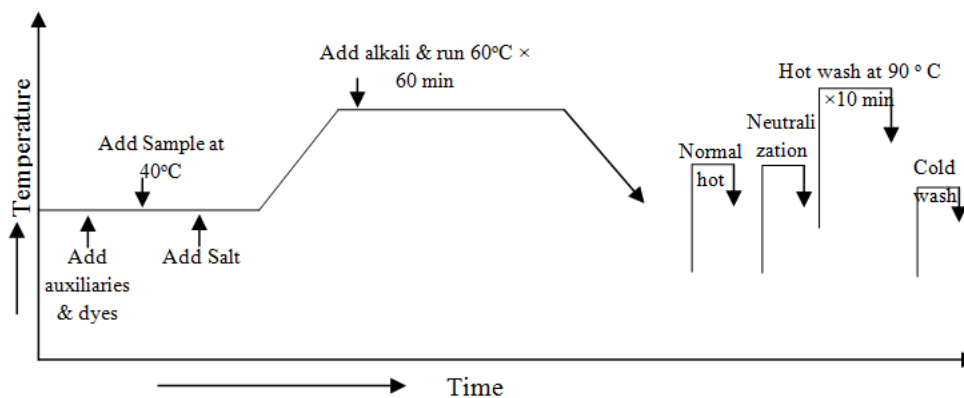


Figure 2.20: Conventional reactive dyeing of cotton (Bhuiyan et al., 2014)

## 2.8 COLOURFASTNESS

Colourfastness is the resistance of a material to change in any of its colour characteristics to the transfer of its colorants to adjacent materials or both (Schindler & Hauser, 2004).

Fading means that the colour changes and lightens. Fabric is dyed in order to produce

desirable colour shade. During dyeing, dyeing parameters are controlled to ensure the fastness of colour of fabric is obtained. The fastness is one of the most important property of colours to customers among all other qualities. When the fabric is in use it is exposed to environmental agencies that can cause its colour to fade. These happens because of the decomposition of the dye molecules in the fabric or when they are removed from their external medium. The dyed material exhibit different resistance power to different agencies (Alam et al., 2008).

The various dyes used in textiles are not fast to factors such as light, heat, intense rubbing or washing with detergents, which results in fading of colour as well as the staining of adjacent garments in selective cases. Fading can make a garment unusable due to a change in look and aesthetic value. The extent a specific dyeing can withstand these influences can be ascertained by conducting fastness tests on that particular garment or fabric as a prerequisite to marketing. The most of the factors that influence colourfastness are related to dye chemistry and the mode of attachment of the dye with the fiber (Nair, 2011).

## **2.8.1 FACTORS INFLUENCING DYE FASTNESS**

### **2.8.1.1 LIGHT FASTNESS**

Light fastness is an important property of dyed textiles and determined by wavelength of incident radiation, compactness of dye and fiber structures, dye–fiber system, degree of dye aggregation and dye particle size, effective humidity, dye induced catalytic action, temperature, availability of oxygen or UV light (photo-reduction), amount of colorant on fiber, deep or light shades, presence of impurities, namely carriers, dispersing agents, dye-fixing agent, metals and various solvents, time of exposure, exposed surface area under light, photoconductivity of dyes and fibers, substituent present in dye structure and stability of aromatic compound (Nair, 2011).

The shorter the incident wavelength, the higher the energy release on the coloured fabric surface and the higher the rate of fading. Vat dyes show an excellent light fastness on cotton due to the compactness of the dye structures (Chakraborty, 2011). A more compact structure obstructs pores and does not allow the passage of oxygen or moisture inside the fabric, thereby suppressing fading. Dyes of bigger sizes generally take more time to initiate fading. Fading is inversely proportional to the radius of the dye particle due to the photochemical layer effect. Effective humidity facilitates the diffusion of oxygen to the excited dye structure or acts as a highly dielectric reaction medium.

The higher the temperature the faster the rate of fading. Prolonged exposure to visible light causes photo-oxidation depending on the availability of oxygen. The presence of impurities, some of which are essential to the dyeing process, like carrier, dispersing agent or metals in the fiber or dye structure promotes fading. The total time of exposure is a vital parameter too; short exposure gives dyed textiles enough time to release energy to go back to their ground state from an excited one. (Chakraborty, 2011). The minimum acceptable quality standards for colourfastness following exposure to light compared with the blue wool standard are shown in Table 2.2 (J. Geršak, 2013).

Table 2.2: The minimum quality standards for fabric colourfastness following exposure to light

Trouser , shorts	Skirts, Jacket, coat	Knitwear	Anoraks, Skiwear, sport wear	Shirts, dresses, blouses	Lingerie, lining	Swim -wear	Pyjama, nightwear
5	5	5	5	5	4	5	4

### 2.8.1.2 WASH FASTNESS

The washing performance of dyed textiles depends on numerous factors, such as dye chemistry, size and solubility of dye, nature of dye fiber attachment, dye solvent interaction, location of dye on fiber structure and detergent used in washing (G. P. Nair,

2011). Reactive dyes are water soluble as well as hydrolysable in the dye bath due to the water dye interaction. Monochlorotriazine and vinyl sulphone dyes are monofunctional they attach to the fiber through covalent bonds but also undergo competing hydrolysis reaction with the water in the dye bath. Washing after dyeing removes hydrolysed dyes completely thus giving excellent wash fastness. This is the reason why these dyes are highly preferred in dyeing and printing. In contrast, dichlorotriazine reactive dyes form partially hydrolysed dyes and therefore show poor wash fastness (Lewis, 2011). The final structure of the dye must be big enough to be inside the fiber. This may be achieved by allowing aggregation of dye.

### **2.8.1.3 RUBBING FASTNESS**

Rubbing of two different coloured fabrics or one coloured and another white fabric may cause transfer of colour from one to the other. This is caused by the presence of; superficial dyes, inadequate washing at the end of dyeing, formation of few coloured molecules at the textile air interface, water solubility of dyes or weak dye fiber attachment on the surface layer. Wet rubbing fastness produces a lower result when compared to dry rubbing. This may be due to solubilisation of a part of the dye and its migration to the surface of coloured fabric (Nair, 2011).

### **2.8.2 GRADING OF FASTNESS PROPERTIES**

The extent of change in colour change and staining is assessed with two different grey scales graded from 1 to 5, where 1 is very poor and 5 is excellent. Generally, a grade of 4 or above is deemed acceptable for commercial use (J. Geršak, 2013).

Light fastness is graded on a system from 1 to 8, where 1 is very poor and 8 is excellent.

## **2.9 SALT FREE REACTIVE DYEING OF COTTON**

Reactive dyeing with cotton has been considered one of the process that causes environmental problems as huge amount of salt are required and they are neither exhausted or destroyed and end up being discharged as effluents (Teklemedhin, 2018).

A number of studies have been done from 1930 till date to improve the absorption of anionic dyes towards cellulosic fibers by introducing cationic sites on the fibers through chemical modification of cotton (Chavan, , 2007). This process is known as cationization as seen in Figure 2.21 (Tutak, 2011). This process is done by reaction with the functional groups (hydroxyl groups) already present in the fiber. The use of reverse micelles as the medium for non-aqueous reactive dyeing of cotton have been also studied to reduce the usage of salt (Yiu et al., 2018).

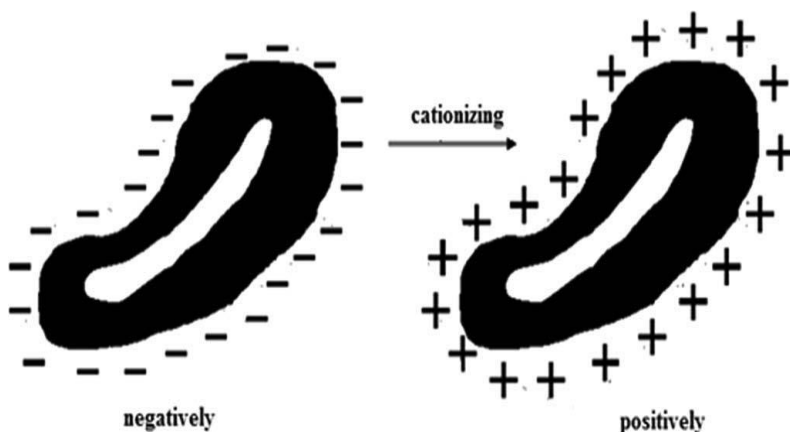


Figure 2.21: Negative And Positive Surface Charges Of Cotton Fibers (Tutak, 2011)

### 2.9.1 CATIONIZATION OF COTTON

This process of cationization improve affinity toward anionic substances such as dyes. They are also cationizing agent used in conventional textile processing that is used to treat cotton fabrics before dyeing to reduces the surface negative charge resulting in attraction of anionic dyes towards the fabric increasing dye uptake (Montazer et al., 2007). This process of cationisation of cotton also improves dye strength and wash fastness (Shahin, 2015).

In one of the report (Bhuiyan et al., 2014), cotton was treated with chitosan to increase the cationic sites in the fiber and the results indicated higher absorption of reactive dye. Attempt was also made to treat Cotton cellulose with 1, 2 dichloroethane(DCE) followed by methyl amine to introduce free amino groups in the cellulose structure (Chavan, 2007). A number of Studies have also reported an increase in dye exhaustion and good colourfastness of cotton fabrics treated with the use extracts from wool and cattle horns (Teklemedhin, 2018;Wangatia & Tseghai, 2015).

The extracts from these sources are known to have good reactive properties due to the presence of a large number of reactive amino hydrophilic polar groups (nucleophilic groups) within its molecular structures. The primary hydroxyl group of cotton react with carboxylic group of keratin hydrolysate as shown in Figure 2.22 and as a result water molecule are formed.

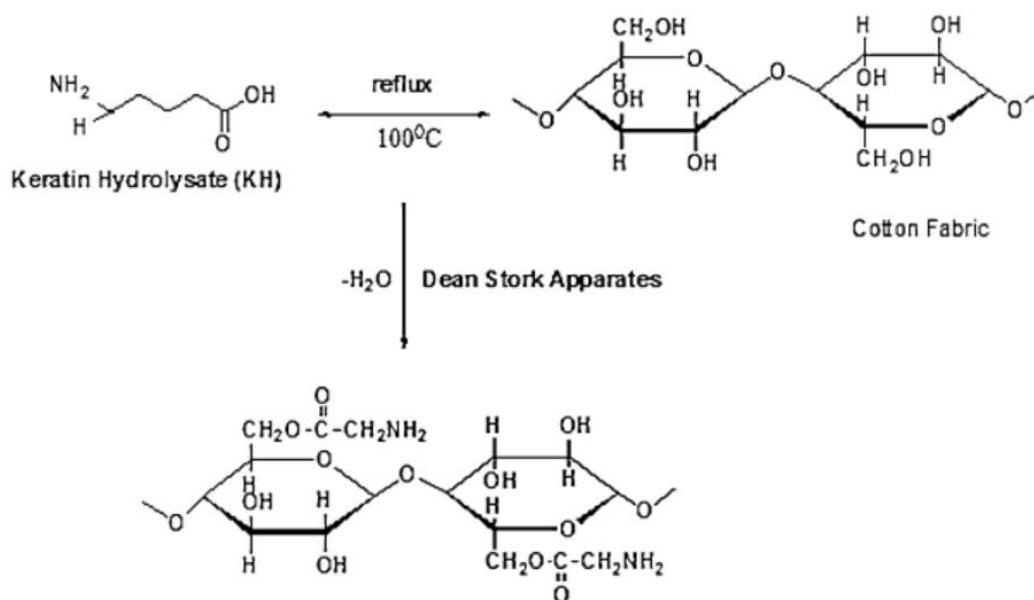


Figure 2.22: Fixation of Keratin Hydrolysate in Cotton Fabric (Bhuiyan et al., 2014)

## 2.10 KERATIN

Keratin is a protein found in feathers, wool, hair, nails and hooves. The food industry, Slaughterhouses, meat processing and the tanning industry produce large amounts of solid feather waste (Mokrejs., 2010). Keratin waste contains a high amount of proteins. The nitrogen content related to dry matter of feathers is 15%, of wool it is 15.8% and of horns it is 16.6% (Graham et al. 1949; Fahnenstock & Steinbuchel 2003).

Keratin properties has been studied as shown in Table2.3(Wattie, 2016). Keratin has a high percentage of the amino acid cysteine in its composition. Feathers have up to 7% of cysteine. The high cysteine content results in the formation of a high number of crosslinks of disulphide bonds.

These crosslinks render keratin insoluble in water. Feather keratins are reported to have a molecular weight of 10 kDa as shown in. Table2.3. Thermal degradation temperature of 201<sup>0</sup>C is recommended to preserve the native keratin structure ((Wattie, 2016). Cysteine can impart strength to any materials they are added to due to the presence of the numerous disulphide bonds.

Table 2.3: Physical properties of Keratins

<b>Physical properties</b>	<b>Measured value</b>	<b>Additional comments</b>
E (Young's Modulus)	2.5 GPa	Native feather
Degradation temperature	201 <sup>0</sup> C	-
Cysteine content	7%	Forms disulphide bonds
Hydroxyl containing groups	22%	Seine, threonine, tyrosine
Molecular weight	10-14kDa	90-100 amino acids in sequence
Density	1.15g/cm <sup>3</sup>	Compacted
Fracture stress	226 N/m <sup>2</sup>	
Isoelectric point	pH4.5-5.5	

Source:(Wattie, 2016)



### **2.10.1 CHICKEN FEATHER WASTE**

Feathers consist of 90% keratin and they make up 5-7% of the total weight of adult chicken (Staroń et al., 2014). The feather waste are composed of 90% keratin proteins which are small and uniform in size (Mokrejs.P et al., 2010) as shown in Table 2.4. There are a lot of chicken being consumed per year in Kenya and other countries as shown in Table 2.5 which leads to production of chicken feather waste. In this regard, chicken feather waste was the preferred choice for extracting keratin hydrolysate. Disposal of these waste feathers is a major concern for poultry industry and accumulation of this huge volume of the waste feathers results in environmental pollution and protein wastage (Mokrejs.P et al., 2010).

Table 2.4: Amino Composition of Chicken Feather

Amino Acid	uM/mg Protein*1	%Amino Acid in Protein
Aspartic Acid	0.358	4.76
Threonine	0.345	4.11
Serine	1.292	13.57
Proline	0.875	1.01
Glutamic Acid	0.624	9.18
Glycine	1.008	7.57
Alanine	0.411	3.66
Valine	0.618	7.24
Cystine	0.088	2.11
Methionine	0.017	0.025
Isoleucine	0.376	4.93
Leucine	0.570	7.48
Tyrosine	0.102	1.85
Phenylalanine	0.267	4.11
Lysine	0.039	0.57
Histidine	0.001	0.016
Argin	0.377	6.57

Source:(Mokrejs. P et al., 2010)

## 2.11 KERATIN HYDROLYSATE

Keratin hydrolysates are partial grafts of protein. Keratins contain several amino acid types which are bonded together via peptide bonds. Each amino acid has different reactive sites such as hydroxyl group, carboxylic groups, amine group, thiol group and aromatic group. Besides, keratins are bonded together via covalent disulphide bonds, ionic bonds, hydrogen bonds and hydrophobic (Gupta et al., 2012). From this reason, the extraction of keratin requires many chemicals for breaking those bonds. The presence of these reactive functional groups, peptide backbone, disulphide (-S-S) bridges, amino (-NH<sub>2</sub>) and

carboxylic acid (-COOH), make it chemically reactive under favourable reaction conditions (Teklemedhin, 2018).

### **2.11.1 EXTRACTION OF KERATIN HYDROLYSATES**

Keratin is the most abundant structural fibrous protein of hair, skins, bristles, horns, hooves, and bird feathers (Staroszczyk & Sinkiewicz, 2017). Keratin hydrolysates are reduced to soluble protein. Keratin hydrolysates can be prepared by acid, alkali, enzymatic or reduction method (Mokrejs et al., 2010). These methods have been known for many years and were described by many authors. Prepared keratin hydrolysates have good physical properties and better treatability than keratin protein. During hydrolysis chemicals break both types of keratin bonds (disulphide and peptide). The structure of keratin hydrolysates is different from the structure of keratin protein (Krejci, Mokrejs, & Sukop, 2011).

The extracts are insoluble in water due to highly cross-linked structure. Alkaline hydrolysis is the preferred method for production of extracts as the loss of functional group like amino acids are lower (Staroń et al., 2014). The production of the hydrolytic processes depends on pH, temperature and reaction time, and also on the type and concentration of acid or base (Staroszczyk & Sinkiewicz, 2017). These hydrolysate contains reactive amino compounds that can be used for cationization of cotton fabrics (Chavan., 2007). The optimal time for extracting keratin hydrolysate from 20g of chicken feathers waste using 3% w/v of sodium hydroxide at boil was reported to be 8 minutes (Abouheif et al., 1985).

### **2.11.2 EXTRACTION TECHNIQUES OF KERATIN HYDROLYSATE**

The dry and wet processing methods are methods used to convert proteins into free amino acids, films, coating and thermoplastics (Wattie, 2016). Dry processing which is

thermomechanical process, involves blending of the reagents, such as plasticizers, and cross-linkers, with proteins without the use of solvent. The thermomechanical energy is used to activate the reaction and form the final product. Wet processing involves the proteins being dissolved in solution by mixing it with the appropriate solvent and reagents(Wattie, 2016). This process allows for more varied modification of the protein through copolymerization and functional group modification.

#### **2.11.2.1 OXIDATIVE HYDROLYSIS**

Oxidation reaction for hydrolysis of proteins can be done by using peroxy acids such as performic acid and per acetic acid. Hydrolysis with strong acids limits the reactions to the scission of ester and peptide bonds and does not break the disulphide bonds. In the presence of peroxy acids the peptide bonds are broken to a lesser degree and the disulphide bridges undergo oxidation. The yield of soluble proteins from the acid hydrolysis method is quite low in the range of 7-40% of the initial mass with longer treatment times of 6 hours giving the highest yield (Wattie, 2016).

#### **2.11.2.2 SULFITOLYSIS**

This is an approach used to cleave disulphide bonds using a redox mechanism with sulphite anions (Wattie, 2016). Each disulphide bond is broken into one sulphite derivative and one thiol group. This process of sulfitolysis continues until all the sulphite are converted. This process is having an advantage of disulfide bonds being broken without hydrolysis of the protein chains. Also, negative charges on the cysteine groups is introduced which promotes solubility. The process occurs at 65°C for 0.5-2 hours. Sulfitolysis procedure has one main disadvantage in that the extensive dialysis is required after extraction. This dialysis is also costly and time consuming and there is also a low

yield of up to 30% soluble protein as compared to the initial mass of the untreated keratin (Wattie, 2016).

#### **2.11.2.3 REDUCTION WITH 2-MERCAPTOETHANOL**

This technique of extracting keratin involves reducing condition with 2-mercaptoethanol as a reducing agent, sodium dodecyl sulphate as a stabilizing surfactant and urea to disrupt hydrogen bonds. Yields of 75% has been reported in this method within a short reaction time of 30 minutes which is much larger when compared to the yield of sulfitolysis (Wattie, 2016).

#### **2.11.2.4 ENZYMATIC HYDROLYSIS**

Enzymes are a special kind of proteins which are biologically active and act on specific substrates. The type of enzymes that act on keratin are called keratinases. They are both sulfitolytic and proteolytic. This enzymatic hydrolysis is often combined with a pre-treatment step. (Eslahi, Dadashian, & Nejad, 2013). These pre-treatment step by which include alkaline hydrolysis using potassium hydroxide or sodium sulphite to reduce cysteine bonds have been used (Mokrejs. et al., 2010). Eslahi et al. (2013) reported a yield of keratin hydrolysate of 21.6% in this method. Enzymatic hydrolysis is expensive at the industrial scale due to the cost of producing the enzyme and the difficulty involved in reusing the enzyme.

#### **2.11.2.5 ALKALI HYDROLYSIS**

Keratin is solubilised by hot diluted sodium hydroxide solution because of the hydrolysis of the molecule. The alkali attacks feather keratin molecule in the mode and it produces modified free amino acids. The solubilised materials in the reaction mixture are proved to be amino acids by paper and column chromatography. Their behaviour in the column chromatography are different from that of standard amino acids, indicating that the amino

acid residues which constituted feather keratin molecule are set free (Nagai & Nishikawa, 1970).

## **2.12 APPLICATIONS OF KERATIN HYDROLYSATE**

Keratin hydrolysate is a soluble natural fibrous protein available as a by-product from several industries such as wool from textile industry, horns and hooves from slaughterhouse, feathers from poultry, animal's hair from tanneries. Keratin hydrolysate has been found to have many applications such as modification of cotton fabrics, used in pharmaceutical, medical cosmetic, and biotechnological industry (Staroń et al., 2014).

Keratin is non-antigenic which is used to heal wounds and reconstruct tissue. Non-antigenic keratin has a positive effect on wound healing and tissue reconstruction. One potential alternative for utilizing keratin hydrolysates has also been utilized in packaging techniques which are films, coatings and encapsulates (Mokrejs et al., 2010).

Waste chicken feather has been used as reinforcement in cement bonded composites that can be used for non-structural applications in low cost housing projects in developing countries (Acda, 2016). Feather boards are comparable to dimensional stability (water absorption and thickness swelling) to commercial wood fiber-cement board of similar thickness and density. Cement bonded chicken feather boards have showed excellent decay fungi resistance which made them very attractive as construction materials in the tropics as shown in Figure 2.24 (Acda, 2016).



Figure 2.23 :Feather Board (Acda, 2016)

The high protein content of feathers makes them a viable feed ingredient and fertilizer after undergoing hydrolysis to make them have free amino acids and oligopeptides which have been shown to have a beneficial effect on the growth of plants as fertilizer. Reports have indicated improvement in harvest times, antioxidant content, and yields in banana crops testing both root and stem dosages. These studies have demonstrated the potential of feather hydrolysates as fertilizer for crops (Wattie, 2016). Keratin materials such as membranes, fibers and powders have adsorption capabilities which have been used in waste water treatment in textile industries to remove dyes such as Azo dyes (Ghosh & Collie, 2014).

Natural feather has regular  $\alpha$ -helix and  $\beta$ -sheet structures which are converted into a random coil structure by disrupting the bond network and protein structure as shown in Figure 2.25 (Ghosh & Collie, 2014). A random coil is a looser structure of protein and hence more sites are available for pollutant absorption. Even though there are diverse applications of these by products containing keratin hydrolysate their consumption is very low and large amount of these products are wasted and disposed to the environment (Ghosh & Collie, 2014).

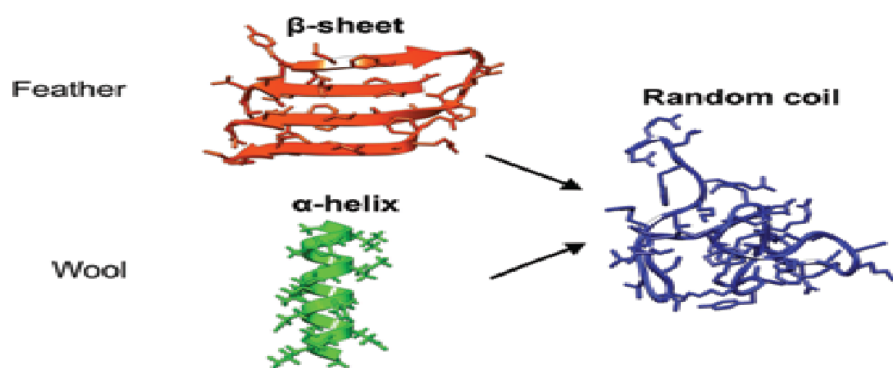


Figure 2.24: Chemically Extracted Keratin has more Loose Structure with Greater Accessibility to Reactive Groups Compared to  $\alpha$ -Helix and  $\beta$ -Sheet Structures of Natural Keratins (Ghosh & Collie, 2014).



## CHAPTER 3: MATERIALS AND METHODS

### 3.1 INTRODUCTION

In this research, keratin hydrolysate was extracted from chicken feathers waste. The pre-treated cotton fabric was pre-treated with keratin hydrolysate to introduce positive sites on the surface for dyeing with hot and cold reactive dyeing. The effect of dyeing temperature and time on dye exhaustion was studied on the two types of reactive dyes; hot and cold reactive dyes. Colourfastness properties of dyed fabrics were also studied. A summary of methodology is given in Figure 3.1.

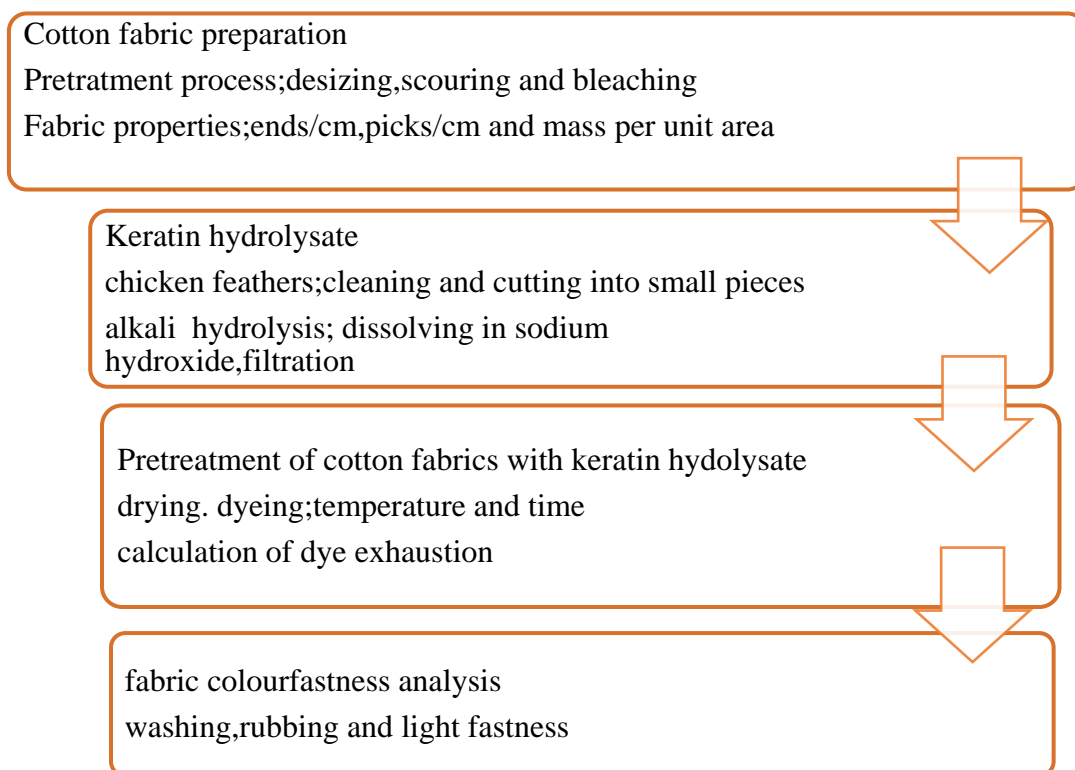


Figure 3. 1: Summary of Methodology

### **3.2 COTTON FABRIC PRE-TREATMENT AND CHARACTERIZATION**

Grey cotton plain weave fabric weighing 500g was collected from Rivatex. Grey cotton fabric contains natural impurities and size added prior to the weaving. Grey cotton fabrics are pre-treated to remove the natural impurities and size added. Pre-treatment processes include desizing which removes the size applied to warp yarns prior to weaving; scouring which breaks down pectin and waxes and helps remove other impurities present in cotton fibers. This pre-treatment process improves dye absorbance of cotton fabrics. The three-pre-treatment process that is; desizing, scouring and bleaching were combined into a single stage.

#### **3.2.1 COMBINED DESIZING, SCOURING AND BLEACHING**

The removal of size, natural impurities and colouring matter was achieved by combining three pretreatment process that is; desizing, scouring and bleaching into a single stage. Sodium hydroxide was used as conventional scouring agent and hydrogen peroxide used as desizing and bleaching agent. The treatment bath containing 5% (of weight of the fabric) sodium hydroxide, 3% (of weight of the fabric) hydrogen peroxide, 1ml/L wetting agent and 1ml/L detergent and a material to liquor ratio of 1:20 was used. Fabric sample weighing 250g were soaked in treatment bath by use of stainless-steel container. The pretreatment of cotton was carried out at a temperature of 80<sup>0</sup>C for 2 hours. The treated fabric samples were cold washed with soap at room temperature for 4 minutes and then dried in oven at a temperature of 60<sup>0</sup>C.

### **3.2.2 EVALUATION OF SCOURING**

To determine the effectiveness of combined desizing scouring and bleaching, weight loss percentage was done on the pre-treated fabric using the following formula.

$$\text{Weight loss\%} = \frac{\text{weight of unscoured sample} - \text{weight of scoured sample}}{\text{weight of unscoured sample}} \times 100$$

### **3.2.3 COTTON FABRIC CHARACTERIZATION**

#### **3.2.3.1 WEAVE DENSITY OF COTTON FABRIC**

The fabric weave density refers to the ends per inch and the picks per inch of the fabric.

The fabric was placed flat on a horizontal surface and number of threads per cm in warp and weft direction were counted using pick glass. The mean values of ends/cm and picks/cm were calculated and recorded

#### **3.2.3.2 MASS PER UNIT AREA OF COTTON FABRIC**

Mass of the cotton fabrics in unit area was determined by five samples being cut from the fabric, each measuring approximately 10 cm x 10 cm. The samples were preconditioned at atmosphere of relative humidity of  $65 \pm 2\%$  and a temperature of  $20 \pm 2^{\circ}\text{C}$ . The samples were weighed and mass in  $\text{g/m}^2$  recorded.

### **3.3 EXTRACTION OF RAW KERATIN HYDROLYSATE KERATIN FROM CHICKEN FEATHERS**

Chicken feathers waste was the best choice in this study for extraction of keratin hydrolysate as they were available in large quantities in Eldoret market. The extracts from feather waste are composed of keratin proteins 90% which are small and uniform in size (Mokrejs.P et al., 2010). The presence of these reactive functional groups; peptide backbone, disulphide (-S-S) bridges, amino (-NH<sub>2</sub>) and carboxylic acid (-COOH), make it chemically reactive under favourable reaction conditions (Teklemedhin, 2018).

### **3.3.1 PRE-TREATMENT OF THE FEATHERS**

The chicken feather waste collected were washed with soap water and dried under sunlight. The main purpose was to clean the feathers from blood stains, oil and grease before processing it. The feathers were then washed with soap water and dried under sunlight. The feathers were then cut into small pieces as shown in Figure 3.2 and kept in sealed plastic bag.



Figure 3.2: Chicken Feather Waste

### **3.3.2 DISSOLVING OF CHICKEN FEATHERS**

Keratin hydrolysates were extracted by alkaline hydrolysis by use of two litres of (3% w/v) sodium hydroxide solution. Blended chicken feathers weighing 30g were added to the sodium hydroxide solution as shown in Figure.3. 3. The solution was heated to boil; pH was maintained about 10-13 and the solution was continuously stirred for 8 minutes. The solution was then filtered and supernatant liquid collected and then filtered using filter paper to make it particle free.



Figure 3.3 Dissolving of Chicken Feathers in Sodium Hydroxide Solution

### **3.3.3 CONFIRMATION OF THE PRESENCE OF PROTEINS**

The solution was subjected to the confirmatory test to confirm the presence of proteins (Gupta et al., 2012). Biuret test was used to confirm the presence of the proteins.

#### **3.3.3.1 BIURET TEST**

1% copper sulphate solution and 1% potassium hydroxide solution were prepared. Few drops of potassium hydroxide solution were added to 5ml of test solution followed by addition of three drops of copper sulphate solution. Changes in solution were observed and recorded.

### **3.4 PRE-TREATING COTTON WITH RAW KERATIN HYDROLYSATE KERATIN FROM CHICKEN FEATHERS WASTE**

The cotton samples size of 5g were treated with extract solution by using dip-dry cure method. It was dried at 80<sup>0</sup> C and cured at 135<sup>0</sup>C for 4 min (Wangatia & Tseghai, 2015).

### **3.5 DESIGN OF EXPERIMENT**

Response surface methodology was used to optimize the dyeing conditions of salt free reactive dyeing. Central composite design was used whereby two factors temperature and time were studied in salt free dyeing by use of hot and cold brand reactive dyes. A total of 26 experiments were done for the estimation of various coefficients of the model. To

establish the functional relationship between independent variables and the response surface, a model was utilized as follow

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_1 X_1^2 + \beta_2 X_2^2 + \beta_{12} X_1 X_2$$

where  $X_1, X_2$  are the input factors that influence the response  $Y$

$\beta_0, \beta_1, \beta_2$  and  $\beta_{12}$  are constant parameters

The actual values of independent variables in factorial design are as in Table 3.1 and Table 3.2 for hot brand reactive dyeing and cold brand reactive dyeing respectively. Design for experimental runs are shown in Table 3.3.

Where  $\alpha = 1.414$

$-\alpha$  (Lower axial point), 0 (centre point), -1 (lower level), 1 (upper level)  $+\alpha$  (upper axial point),

Table 3.1: Actual levels of factors for hot brand reactive dyeing

Factor	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
X1: Temperature	41.72	50	70	90	98.28
X2: Reaction time	31.72	40	60	80	88.28

Table 3.2: Actual levels of factors for cold brand reactive dyeing

Factor	Levels				
	$-\alpha$	-1	0	+1	$+\alpha$
X1: Temperature	15.9	20	30	40	44.14
X2: Reaction time	11.7	20	40	60	68.3

Table 3. 3: Experimental runs

Runs	Coded factors			
	Hot brand reactive dyeing		Cold brand reactive dyeing	
	X <sub>1</sub>	X <sub>2</sub>	X <sub>1</sub>	X <sub>2</sub>
1	1	1	$\alpha$	0
2	0	0	$-\alpha$	0
3	-1	1	0	$\alpha$
4	0	0	1	1
5	$-\alpha$	0	-1	-1
6	0	0	0	0
7	0	$-\alpha$	-1	1
8	-1	-1	0	0
9	$\alpha$	0	0	0
10	0	0	0	0
11	0	0	1	-1
12	1	-1	0	0
13	0	$\alpha$	0	$-\alpha$

### 3.6 RESPONSE SURFACE METHODOLOGY

Response surface methodology is a collection of statistical and mathematical methods that is useful for modelling and analysing engineering process. This technique optimizes the response surface that is influenced by various process parameters. It enables trials to be done at the extreme level settings of the variables and also trials in which one or more of the variables is set at the midpoint of the study range. These designs provide information on direct effects, pairwise interaction effects and curvilinear variable effects. Central composite design is a response surface design which apart from the two levels factors has axial or star point. The axial or star point usually denoted as ( $\alpha$ ) increases the number of levels to five levels thereby giving the experimental design flexibility (Baxter, Hastings, Law, & Glass, 2008). For model and statistical fitting analysis, a three-dimensional response surface and contour plots of the independent variables and their interactions will be generated.

### **3.7 OPTIMIZATION OF SALT FREE REACTIVE DYEING**

Response surface methodology was used to find optimal set of experimental parameters that produces maximum value of response. This method is more advantageous than other approaches in terms of saving time, working space and raw material. The study will establish the optimum conditions of key variables for maximum salt free reactive dyeing. The number of experimental trials needed to evaluate multiple parameters and their interactions is less laborious and time-consuming than other approaches. The process variables used were the temperature ( $X_1$ ) and reactive time ( $X_2$ ).

All the experiments were conducted to evaluate multiple parameters and their interactions to obtain their optimum values using central composite design. The results were analysed by multiple regression analysis. The main aim of the optimization of salt free reactive dyeing was to establish maximum levels within independent variables which are temperature and time that will provide maximum percentage of dye exhaustion with accepted colourfastness values.

### **3.8 DYEING OF COTTON WITH VARYING TEMPERATURE AND REACTION TIME**

The pre-treated cotton fabrics each weighing 5 grams were dyed with varying temperature and time. Dyeing was carried out in both dyes at varying temperature and constant dyeing time of 60 minutes. Shade of 2 % was used in hot brand and cold brand reactive dye solution in a liquor ratio of 1:20. Dye bath in the two types of dyes comprised of 20g/l of sodium carbonate and 2 ml/l of wetting agent. The samples were rinsed with cold water and finally washed with hot soapy water using 5 g/l standard detergent.

For comparison purposes three samples of cotton fabric scoured were used in each of the dye type. The samples were dyed at temperature of 70<sup>0</sup>C and time of 60 minutes in hot



brand and 30<sup>0</sup>C and time of 60 minutes in cold brand reactive dye. One sample in each of the dye type was treated and dyed without salt in a dye solution containing 2% shade of reactive dye, 20g/l of sodium carbonate and 2ml/litre of wetting agent. One sample was dyed using conventional method (use of salt) in a dye solution containing 2% shade of reactive dye, 20g/l of sodium carbonate, 30g/l of sodium sulphate(salt) and 2ml/litre of wetting agent. The remaining sample was untreated and dyed without sodium sulphate(salt) in a dye bath solution containing 2% shade of reactive dye, 20g/l of sodium carbonate and 2ml/litre of wetting agent. After dyeing all the samples were rinsed with cold water and finally washed with hot water using 5g/L. Dye exhaustion of the dyed samples were calculated and compared.

### 3.8.1 DYE EXHAUSTION

The percentage dye exhaustion for the two types reactive dye was determined by comparing concentration of dye in dye bath before and after dyeing. The solution was placed in glass bottles and tightly closed as shown in Figure 3.4.

The dye absorbance of each sample was measured using UV/Vis spectrophotometer Figure 3.5. The dye-bath absorbance was measured at the wavelength of maximum dye absorption ( $\lambda_{max}$ ). The exhaustion was calculated using equation:

Determination of dye exhaustion (E%)

$$E\% = \frac{A_0 - A_1}{A_0} \times 100$$

Where,  $A_0$  and  $A_1$  indicate the absorbencies at maximum wavelength ( $\lambda_{max}$ ) of the dye originally in the dye bath and of residual dye after dyeing respectively. The obtained dye exhaustion from the methods of dyeing hot brand and cold brand were then compared.



Figure 3.4: Dye ready for measuring absorbance in UV/Vis spectrophotometer



Figure 3.5: UV/Vis spectrophotometer ready for measuring dye absorbance

The dye solution was subjected to wavelength range from 200 to 800nm. The dye absorbance of the dye solution before and after dyeing were measured and recorded at maximum wavelength.

### **3.9 DETERMINATION OF COLOUR FASTNESS**

Wash fastness tests were performed according to ISO 105C06 standard, rubbing fastness tests according to ISO 105-X12 and light fastness measured according to ISO 105 B02. Colour fastness to washing, light and was assessed using the grey scale.

#### **3.9.1 COLOURFASTNESS TO RUBBING**

Dry and wet rubbing fastness was tested in accordance to ISO 105-X12. Two pieces of each sample size of 50mm X 140mm were used for testing dry rubbing and wet rubbing.

### 3.9.1.1 DRY AND WET RUBBING TEST

Each test specimen was fastened to crock meter machine as shown in Figure 3.6 by means of clamps to the baseboard of the testing device so that the long direction of the specimen follows the track of the device.



Figure 3.6: Mounting of Samples on Crock Meter

A soft- paper back waterproof abrasive was placed between the baseboard of the crock meter machine and the specimen to help reduce movement of the specimen.

With the dry rubbing cloth flat in place over the end of the finger of the testing device, rubbing was done to and fro in a straight line 20 times; 10 times to and 10 times fro, a long track on the dry specimen. Test specimen were removed and air dried. The cotton rubbing cloths were assessed with grey scale. For testing the wet rubbing fastness, test samples were dipped in distilled water and were squeezed and then the entire process of dry rubbing fastness was repeated.

### 3.9.2 COLOURFASTNESS TO WASHING

Wash fastness of the dyed samples were analysed as per ISO 105 C06. Specimen of 100 mm × 40 mm was attached to a piece of the multifiber adjacent fabric with dimensions of 100 mm × 40 mm. by sewing along one of the shorter edges followed with the multifiber adjacent fabric next to the face side of the specimen. A detergent solution was prepared

using detergent at concentration of 5 g/l and sodium carbonate of 2g/L. The prepared samples were then placed in the steel containers Soap solution was added in a liquor ratio of 50:1 ml/g and preheated to the test temperature of  $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . The steel containers were closed and fixed in the gyrowash machine as shown in Figure3.7.



Figure 3.7: Gyrowash Machine for Carrying out Colourfastness to Washing

The machine was operated at the temperature of  $60^{\circ}\text{C}$  for 30 minutes. Timing was started as soon as the container was closed. Composite specimens were removed at the end of the wash and each placed separately in a beaker half filled with. They were gently agitated and rinsed for 1 min and then placed in the beaker under a cold running tap for 1 min. Excess water was removed by squeezing the test specimen by hand. The specimens were dried by pressing it flat between new filter papers to remove excess water and left in air to dry at room temperature. The change in colour of the specimen and the staining of the adjacent fabric were assessed with reference to the original specimen using the grey scales.

### **3.9.3 COLOURFASTNESS TO LIGHT**

The colourfastness following exposure to light of a material is defined as the level of change in colour it undergoes when exposed to light. Light fastness of the dyed samples was analysed as per ISO 105 B01. The eight cotton specimens dyed at optimum dyeing

conditions and a range of eight blue wool standards were simultaneously exposed to the daylight for 5, 10, 15 and 20 hrs. Light fastness was graded on a system from 1 to 8, where 1 is very poor and 8 is excellent. The change was compared with the original specimen and assessed by grey scale.

## **CHAPTER 4: RESULTS AND DISCUSSION**

### **4.1 PRE-TREATMENT AND CHARACTERIZATION OF COTTON FABRIC**

Grey Cotton fabric characteristics were first determined before carrying out dyeing. The number of ends and picks per centimetre were found to be 22.8 and 13 respectively. The mass per unit area was also found to be 126.2g/m<sup>2</sup> as shown in Table 4.1.

To remove size, natural impurities and colouring matter, pre-treatment process was undertaken. The effectiveness of scouring was evaluated by determining the weight loss percentage. The recommended weight loss percentage of scoured cotton fabric is 4-8% (Grishanov, 2011). The percentage weight loss of 5.9 was achieved on scoured cotton fabric which implies that the sample was well scoured.

Table 4.1: Pre-treatment and Characterization Results

<b>Fabric property</b>	<b>Test result</b>
<b>Ends/cm</b>	22.8
<b>Picks/cm</b>	13
<b>Weight loss (%)</b>	5.9
<b>Mass per unit area, g/m<sup>2</sup></b>	126.2

### **4.2 EXTRACTION OF KERATIN HYDROLYSATE FROM CHICKEN FEATHERS WASTE**

Keratin hydrolysate extract was prepared by reacting 3% sodium hydroxide with 30 grams of chicken feather waste. The alkali attacked feather keratin molecule producing free amino acids.

#### **4.2.1 CONFIRMATION OF THE PRESENCE OF PROTEINS**

To confirm the presence of proteins in the extract biuret test was utilised by mixing chicken feathers in sodium hydroxide solution which dissolved completely. The solution

turned violet in colour as shown in Figure 4.1 indicating the existence of amino acids and the presence of peptide linkages in the extracts.

Peptide linkages are the bonds which binds the protein molecules. Sodium hydroxide reduced chicken feathers effectively. The alkali attacked feather keratin molecule by breaking it down to free amino acid.

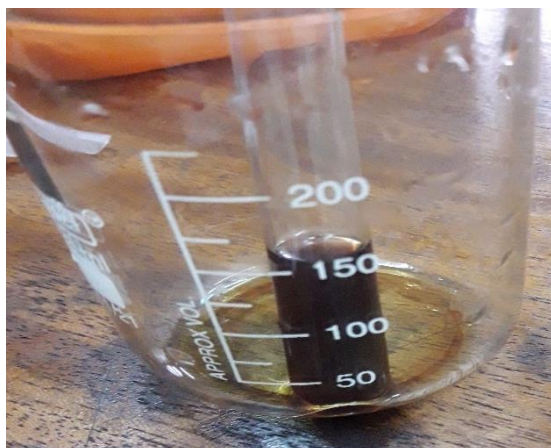


Figure 4.1 Confirmation of Proteins from the Feather Extract Solution

### **4.3 PRE-TREATMENT OF COTTON FABRICS WITH EXTRACTED KERATIN HYDROLYSATE**

To analyse the effect of keratin hydrolysate concentration on cotton fabric, pre-treatment of cotton fabric with the hydrolysate was done.

#### **4.3.1 PRE-TREATMENT OF KERATIN HYDROLYSATE ON COTTON FABRICS**

Preliminary study was carried out to establish the effect of varying concentration of keratin hydrolysate on dye exhaustion of cotton fabrics. Figure 4.2 shows the exhaustion of dyed samples pre-treated with different concentrations of keratin hydrolysate. The results indicated improved dye exhaustion with increase in keratin hydrolysate.

The exhaustion of dye in the dyed samples increased with increase in concentration of keratin hydrolysate because of formation of more additional hydroxyl groups in the cotton

fabric. The effect of keratin hydrolysate on cotton fabrics is in agreement with the study of cationization of cotton with chitosan (Bhuiyan et al., 2014). The results also shown that the treated fabric with lower concentration did not absorb much of dye compared to untreated control samples which was dyed in the presence of salt.

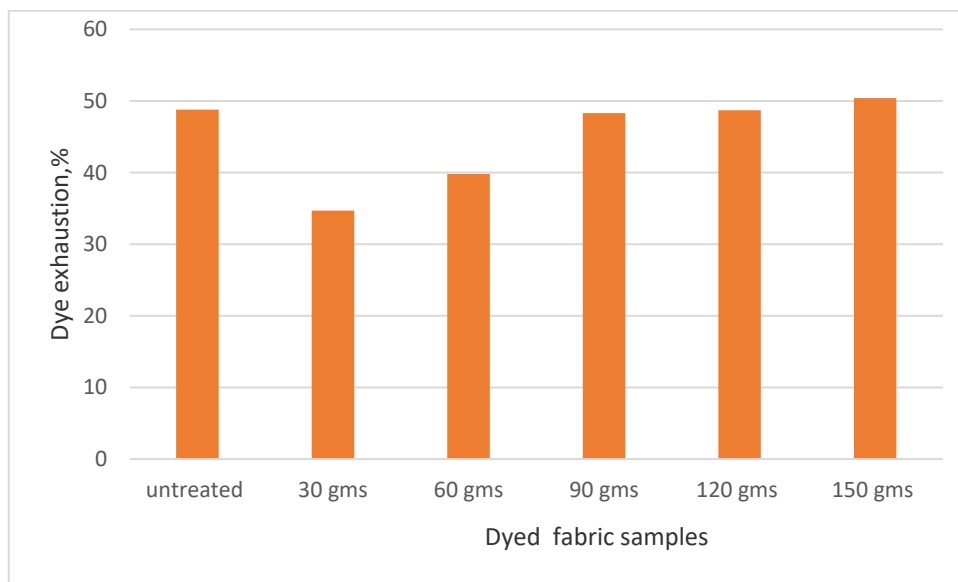


Figure 4.2: Effect of Keratin Hydrolysate

Cationization of chicken feathers on cotton fabrics took place resulting to H-bonding being formed between free hydroxyl groups of the cellulose with carboxylate anion of the amino acid as shown in the following Figure 4.3. The cotton fabric acquired the positive charge when reacted with keratin hydrolysate. This indicates the presence of cationic dye sites in the cotton fabric which will strongly attract anionic reactive dyes.

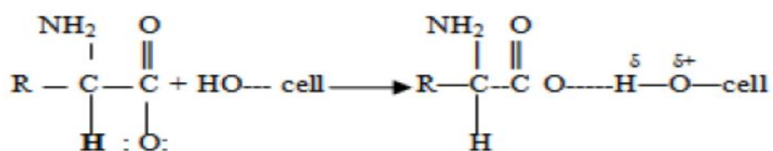


Figure 4.3: Cationization of Cotton Fabric with Extracted Keratin Hydrolysate



#### **4.4 EFFECT OF DYEING PARAMETERS IN SALT FREE DYEING OF COTTON FABRICS IN HOT AND COLD REACTIVE DYES**

Colour strength and colourfastness are the end desirable characteristics on the finished textile fabric and are determined by the dyeing parameters. Dye exhaustion determines the degree of colour strength to be achieved on the fabric. The effect of temperature and reactive time on dye exhaustion and colourfastness were investigated by utilising the two types of reactive dyes; hot brand and cold brand both carried out at different temperature and time.

The effects of the different combination of the factors on dye exhaustion on each type of reactive dye was studied using statistically designed experiments.

##### **4.4.1 EFFECT OF TEMPERATURE ON DYE EXHAUSTION**

The effect of temperature on dye exhaustion in hot and cold reactive dye is shown in Table 4.2 and Table 4.3. The results as illustrated in Figure 4.4 and Figure 4.5 shows that the dye exhaustion increases with increase in temperature from 41.1<sup>0</sup>C to 78.6<sup>0</sup>C and 20<sup>0</sup>C to 35<sup>0</sup>C in hot and cold brand respectively. This is because reactive dyes become more soluble with increase in temperature. Dye exists in solution as an aggregate of various sizes and these aggregates break down to maintain an overall dynamic equilibrium of dye solution. Increase in temperature leads to an increase in the kinetic energy of the molecule which break-up large aggregates into smaller units hence solubility of the dye.

Increase in temperature also provoke an increase in the number of the pores in the fabric structure and their diameter(Zhang et al., 2018), thus the small dye particles penetrate into the fabric pores at high temperature leading to an increase in the dye uptake.

Dye solubility reached equilibrium state at 78.6<sup>0</sup>C in hot brand reactive dyeing and 35<sup>0</sup>C in cold brand reactive dyeing. Beyond these equilibrium states dye hydrolysis took place

hence lower dye exhaustion values. This is because beyond these temperatures; 78.6°C and 35°C the dyes react with water before it gets into the fiber. Research has also shown that increase in temperature increases dye uptake up to an equilibrium point (Taylor et al., 2016).

Table 4.2 Effect of Dyeing Temperature on Dye Exhaustion-Hot brand

	<b>Hot brand reactive dyeing</b>												
Dyeing temperature, °C	90	70	50	70	41.7	70	70	50	98.2	70	70	90	70
Dye exhaustion, %	44	16	30	40	20	30	20	30	30	30	40	30	30

Table 4.3 Effect of Dyeing Temperature on Dye Exhaustion-Cold Brand

	<b>Cold brand reactive Dyeing</b>												
Dyeing temperature, °C	44.1	15.9	30	40	20	30	20	30	30	30	40	30	30
Dye exhaustion, %	39	19	38	37	23	37	24	38	41	37	40	40	39

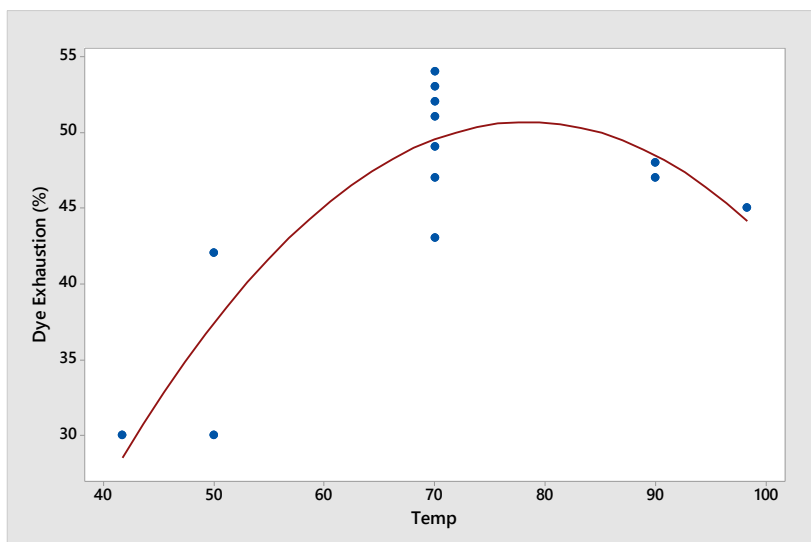


Figure 4.4: Effect of Temperature on Dye Exhaustion-Hot Brand

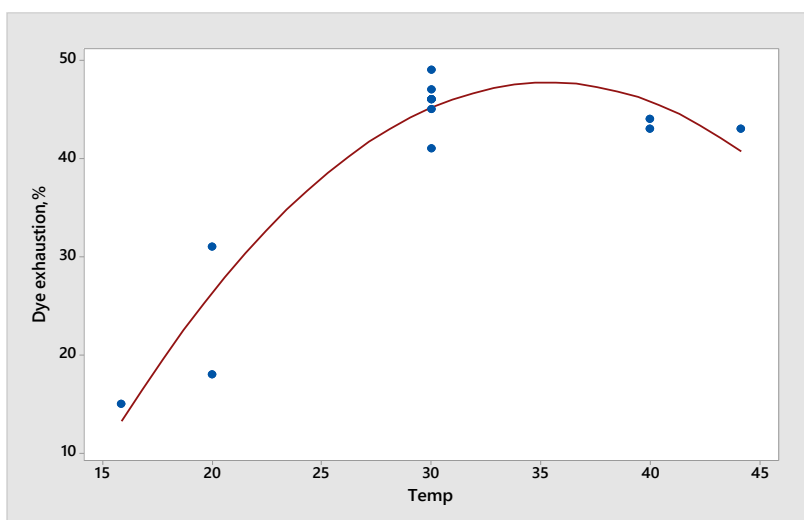


Figure 4.5: Effect of Temperature on Dye Exhaustion-Cold brand

#### 4.4.2 EFFECT OF TIME ON DYE EXHAUSTION

The results of dyeing time on dye exhaustion is shown in Table 4.4 and Table 4.5. Figure 4.6 and 4.7 illustrate that dye exhaustion increases with increase in time from 32 to 74 minutes in hot brand and 12 to 47 minutes in cold reactive dyeing. This is because when cotton fabric is immersed in a dye solution, it absorbs dye till an equilibrium is reached. The dye exhaustion decreased with dyeing time increasing from 74 to 90 minutes and 47 to 70 minutes in hot and cold reactive dyeing respectively. This is because the dyes got hydrolysed due to prolonged time and they were no further exchange of dyes in the

fabric taking place. This is in agreement to the study carried out on eco-friendly reactive dyeing of cotton (Zhang et al., 2018).

Table 4.4:Effect of Dyeing Time on Dye Exhaustion-Hot Brand

	Hot brand reactive dyeing													
Dyeing Time (Mins)	32	80	60	88	40	60	60	40	80	60	60	60	60	60
Dye exhaustion, %	34	44	46	43	36	45	46	34	43	44	44	41	39	

Table 4.5:Effect of Dyeing Time on Dye Exhaustion-Cold Brand

	Cold brand reactive dyeing													
Dyeing Time (Mins)	4	60	40	12	40	40	60	40	40	20	40	68	20	
Dye exhaustion, %	38	35	37	22	37	38	34	35	36	29	37	34	25	

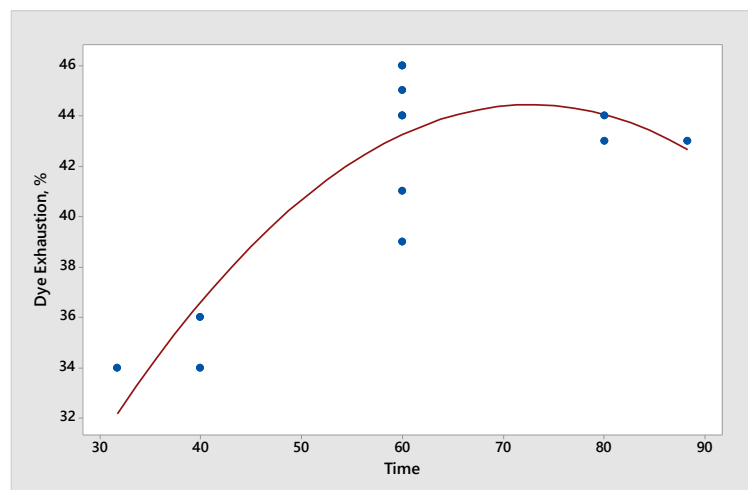


Figure 4.6: Effect of Time on Dye Exhaustion-Hot Brand

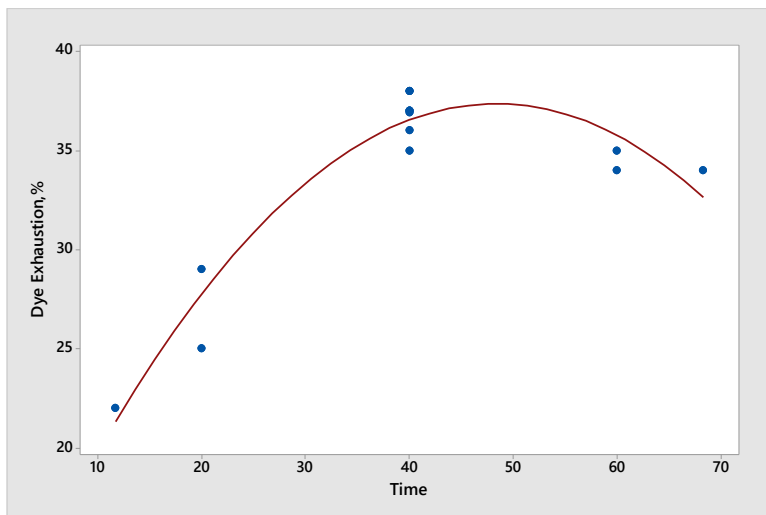


Figure 4.7: Effect of Time on Dye Exhaustion-Cold Brand

#### 4.5 DEVELOPMENT OF REGRESSION MODEL FOR DYE EXHAUSTION

From the experimental results, the regression model equations relating the response which is the dye exhaustion percentage and input variables which are the dyeing parameters was generated by Response Surface Methodology (RSM). The model equations are shown in Equation 1 and 2 for hot (Y1%) and cold (Y2%) brand respectively. RSM generated equation in terms of coded factors which reflected the interaction and significance of variables towards response. The significance and accuracy of the model were justified through the analysis of Variance (ANOVA).

The p-values were used as a tool to check the significance of the model and each of the model terms and the interactions to response. Low P- value of less than 0.05 means that result has a significant effect to the response (Kumar et al., 2018). The ANOVA for the quadratic model of dye exhaustion is given in Table 4.8 and Table 4.9 for hot and cold brand respectively.

From the Table 4.8 and 4.9, the model obtained F value of 33.1 and 23.8 in hot and cold reactive dyes respectively and P value of 0.0000 in both hot and cold reactive dyes. This implies that the two models were significant because P-value was less than 0.05 and

adequate to represent the actual relationship between the response (dye exhaustion) and variables (temperature and time). From the Tables, temperature (X1), time (X2) and the interaction term of temperature and time ( $X_1X_2$ ) were significant.

The temperature in hot and cold reactive dyeing had P-value of 0.000 and 0.000 respectively which implies that temperature had a major effect on dye exhaustion. The reactive time and interaction of temperature and time also had an effect on the dye exhaustion with P-values of 0.003 and 0.016 in hot reactive dyeing and p-values of 0.008 and 0.005 in cold reactive dyeing. The predicted values using the equations were compared with experimental results for both types of dye and the data are shown in Table 4.6 and Table 4.7

Table 4. 6 Experimental design and results for dye exhaustion of cotton fabric dyed with hot brand reactive dyes

Runs	Temp(X1, <sup>0</sup> C)	Time (X2, min)	Dye exhaustion, %	
			Experimental	Predicted
1.	1	1	47	48.4
2.	0	0	53	50.7
3.	-1	1	42	43.7
4.	0	0	52	50.7
5.	- $\alpha$	0	30	29.3
6.	0	0	49	50.7
7.	0	- $\alpha$	43	43.5
8.	-1	-1	30	30.6
9.	A	0	45	45.1
10	0	0	51	50.7
11	0	0	47	50.7
12	1	-1	48	48.2
13	0	$\alpha$	54	52.9

Table 4. 7 Experimental design and results for dye exhaustion of cotton fabric dyed with cold brand reactive dyes

Runs	Dye exhaustion, %			
	Temp(X1, <sup>0</sup> C)	Time (X2, min)	Experimental	Predicted
1.	A	0	43.4	43.3
2.	- $\alpha$	0	28.1	24.4
3.	0	$\alpha$	46.5	45.8
4.	1	1	43.5	43.1
5.	-1	-1	18.8	22.8
6.	0	0	46.5	46.3
7.	-1	1	36.2	38.5
8.	0	0	47.1	46.3
9.	0	0	46.0	46.3
10	0	0	45.5	46.3
11	1	-1	43.7	45.0
12	0	0	46.4	46.3
13	0	- $\alpha$	39.1	36.0

$$Y1, \% = -107 + 3.131X_1 + 1.113X_2 - 0.01691X_1^2 - 0.00316X_2^2 - 0.00813X_1X_2 \dots \dots \text{Equation (1)}$$

$$Y2, \% = -73.8 + 5.277 X_1 + 1.369X_2 - 0.0621 X_1^2 - 0.00670 X_2^2 - 0.02200 X_1X_2 \dots \text{Equation (2)}$$

Table 4.8: Analysis of Variance (ANOVA) for Response Surface Quadratic Model for Dye Exhaustion –Hot Brand

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value	Percentage contribution (%)
<b>Regression</b>	693.9	5	138.8	33.1	0.000	
<b>X1</b>	244.4	1	244.4	58.3	0.000	33.70.
<b>X2</b>	88.2	1	88.2	21.1	0.003	12.20.
$X_1^2$	318.1	1	318.1	76.0	0.000	43.90.
$X_2^2$	42.3	1	42.3	2.7	0.148	5.80.
$X_1X_2$	42.3	1	42.3	10.1	0.016	5.80.
<b>Lack of fit</b>	6.1	3	6.1	0.35		0.84
<b>Pure error</b>	23.2	4	23.2			3.20.
<b>Total</b>	723.2	12	723.2			100

From Table 4.2 & 4.3, temperature was found to have a major effect on dye exhaustion than time, because it had a high percentage values of 33.7 and 50.3 in hot and cold brand respectively.

Table 4.9: Analysis of Variance (ANOVA) for Response Surface Quadratic Model for Dye Exhaustion –Cold Brand

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value	Percentage contribution (%)
<b>Regression</b>	828.2	5	165.6	23.8	0.000	
<b>X1</b>	362.3	1	362.3	52	0.000	40.1
<b>X2</b>	95.7	1	95.7	13.7	0.008	10.6
$X_1^2$	268	1	268	38.5	0.000	29.7
$X_2^2$	50	1	50	7.2	0.032	5.5
$X_1X_2$	77.4	1	77.4	11.1	0.005	8.6
<b>Lack of fit</b>	47.4	3	15.8	44.5	0.013	5.3
<b>Pure error</b>	1.4	4	0.4			0.2
<b>Total</b>	902.2	12	869.6			100

The  $R^2$  for equation 1 and 2 are 0.9595 and 0.9444 respectively. This indicates the total variation in the model. The  $R^2$  shows how much the change in an independent variable affects the dependent variable. Normal probability plot of residuals was used to check if the data was normally distributed Figure 4.8 and 4.9 shows that the data in hot and cold reactive dyeing were normally distributed as it lies close to the line.



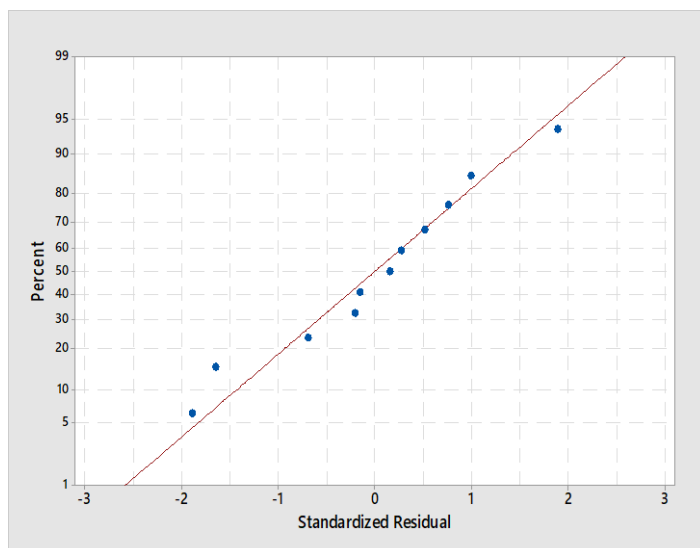


Figure 4. 8:The Normal Probability Plot for Dye Exhaustion-Hot Brand Reactive Dyeing

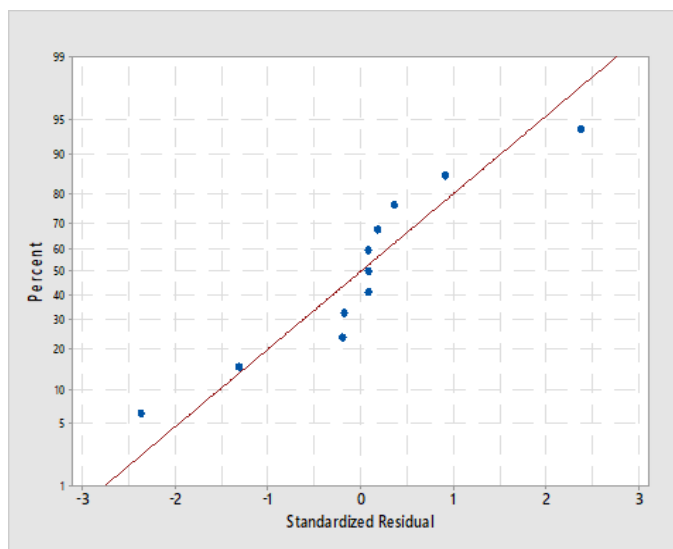


Figure 4.9:The Normal Probability Plot for Dye Exhaustion-Cold Brand Reactive Dyeing.

#### 4.6 COMBINED EFFECT OF TEMPERATURE AND TIME ON DYE EXHAUSTION

Table 4.8 and Table 4.9 indicated that X1(temperature) had the most significant effect on dye exhaustion in hot and cold reactive dye, followed by time. As seen in Table 4.8 and Table 4.9, interaction of temperature and time, denoted by X1X2 was also significant. Figure 4.10 and Figure4.11 illustrate three-dimensional response surface which show the

effects of the two significant variables on the dye exhaustion. It was observed that maximum dye exhaustion of 53% in hot brand reactive dyeing is achieved at the temperature range between 60<sup>0</sup>C -80 <sup>0</sup>C and time of 60-80 minutes as shown in Figure 4.10 and 48.5% in cold brand reactive dyeing in temperature range between 25<sup>0</sup>C -35 <sup>0</sup>C and time of 40-60 minutes as shown in Figure 4.11.

The dye exhaustion in Figure 4.10 and Figure 4.11 increased with increase in temperature and time which indicates that temperature and time are key factors in reactive dyeing of cotton. These results are in line with the study carried by Chengchen Fu et al. (2015) which studied the effect of temperature and dyeing duration on the colour depth of the fabric in a non-aqueous dyeing process of reactive dye on cotton.

Increase in temperature and activation time increase solubility of the dye and increases the pores size in the fabric molecule chain (Zhang et al., 2018) which enhanced dye exhaustion. In addition, increased of temperature causes rapid adsorption of the dye molecules on the fiber surfaces to occur within a short time. However, beyond the equilibrium points the values of dye exhaustion reduced because dye hydrolysis took place. This is because at high temperatures beyond 80<sup>0</sup>C the dyes get hydrolysed and formation of the bond between the fiber and dye is limited. The dye exhaustion could not also improve efficiently with dyeing time increasing from 60 min to 80 minutes in hot brand reactive and 40-60 minutes in cold brand reactive. This indicates that the dyes on the fibers got saturated.

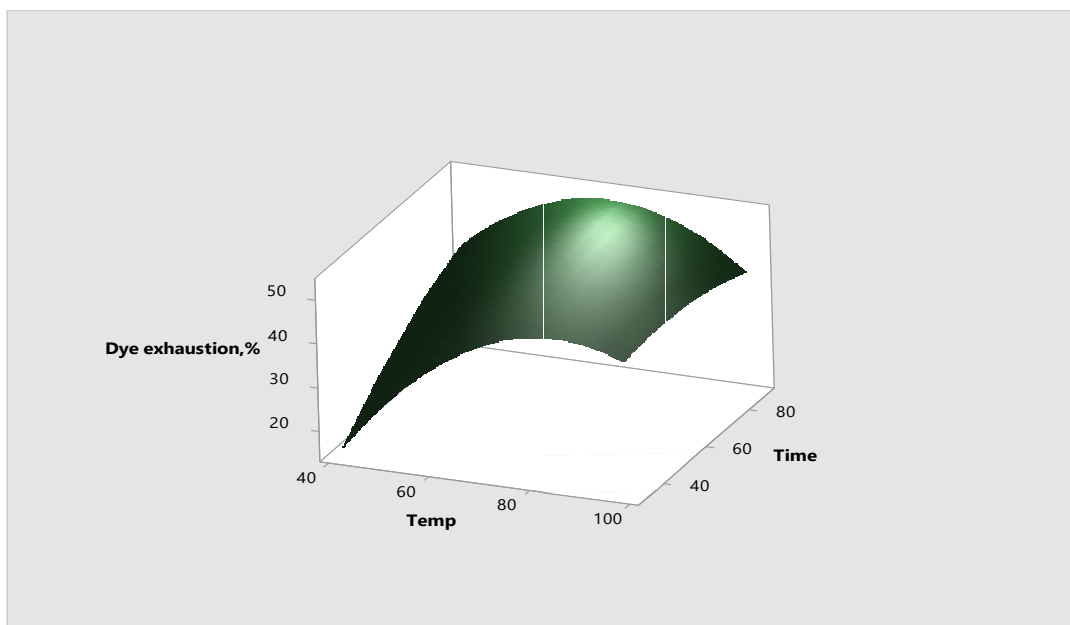


Figure 4.10: Combined Effect of Temperature and Time on Dye Exhaustion-Hot Brand

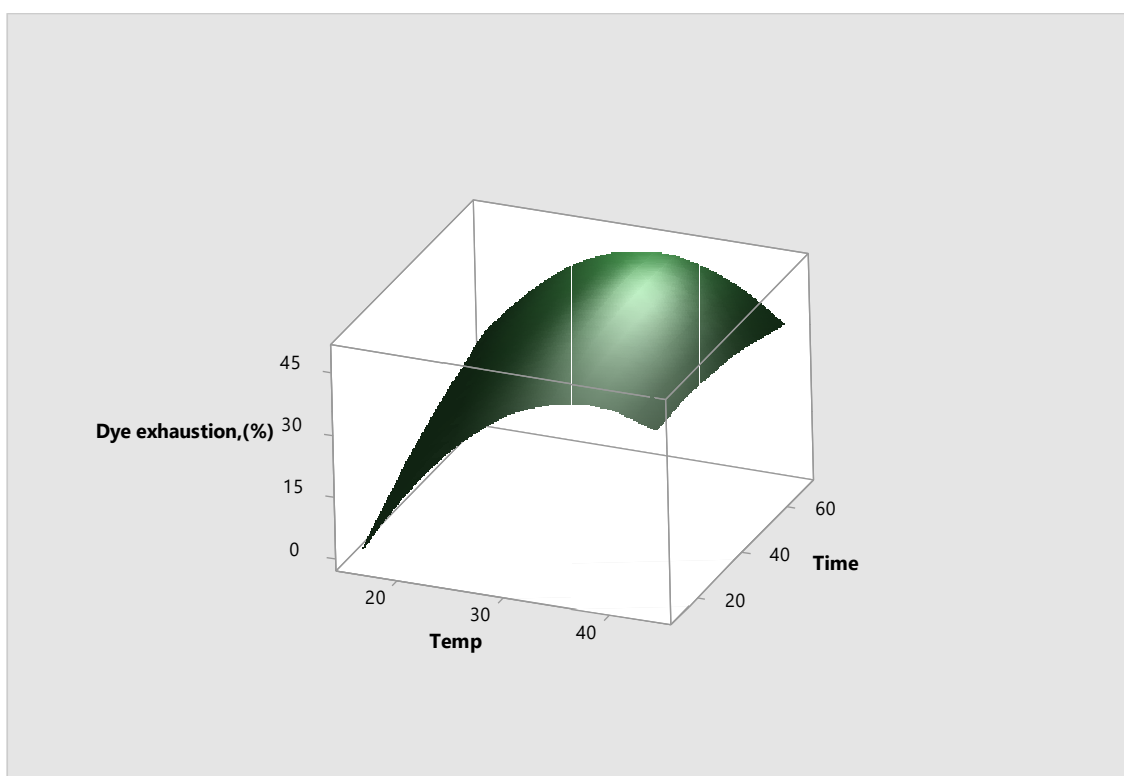


Figure 4.11: Combined Effect of Temperature and Time on Dye Exhaustion-Cold Brand

#### 4.7 OPTIMIZATION OF DYING PROCESS PARAMETERS

The objective of the experimental design was to find the optimum dyeing conditions so that the optimum dye exhaustion can be achieved. Optimal dyeing conditions were

established at 69.7 °C and 75 minutes in hot brand reactive dyeing and 34.4°C and 45minutes in cold reactive dyeing as illustrated inTable4.10

The dye exhaustion achieved at optimum dyeing condition was 52.9%. and 48.3 % for hot and cold respectively.

Table 4.10:Optimal Dyeing Conditions for Dye Exhaustion

Parameters	Temperature(°C)		Time (Min)		Dye exhaustion, %	
	Hot	Cold	Hot	Cold	Hot	Cold
Optimal conditions	69.7	34.4	75	45	52.9	48.3

#### **4.8 COMPARISON OF EXHAUSTION PROPERTIES OF HOT AND COLD REACTIVE DYES**

The exhaustion properties of modified cotton fabric dyed with two types of reactive dye; hot and cold reactive dye were studied and compared. The control sample(untreated)dyed with cold brand reactive dyes in absence of salt exhibited low exhaustion percentage as shown in Table 4.11. Control sample dyed in cold reactive dye in presence of salt increased its dye exhaustion from 21.4% to 35.1%. The treated samples, on the other hand, obtained a high value of 38.6 % in dye uptake in the absence of salt in comparison with control and untreated sample. The treated samples dyed with cold reactive dye had exhaustion values close to control samples dyed in the presence of salt. The dye exhaustion percentages of the two dyes are plotted in the y axis as shown in Figure 4.12.

Dye exhaustion values of control samples dyed with hot brand dyes were better than for cold brand reactive dyeing even in the presence of salt. Addition of salt during dyeing caused improvement from 28.7 % to 37.8 %. The hot brand reactive dyes were exhausted more on treated cotton fabric with values of 41.4 % than cold reactive dyes which had exhaustion value of 38.6 %.

This is because cold brand reactive dyes have high reactivity which makes them to react with water. Research has found that hot brand reactive dyes have lower reactivity and thus lower tendency for dye hydrolysis(Naser et al., 2015). The hydrolysed dye has a very low substantivity for the cellulose fiber which gets attached to the fiber surface after dyeing. This study indicated that pre-treated cotton fabric showed a remarkable improvement in dye exhaustion when compared with control sample dyed in presence of salt. These results are in agreement with study made on compatibility analysis of reactive dye and salt free reactive dyeing using methyl amine as pre-treatment (Naser et al., 2015;Chavan, R.B, 2007).

Table 4.11:Comparison of dye exhaustion in hot and cold reactive dyes

	Dye exhaustion, %		
	Treated (without salt)	Untreated (without salt)	Control (with salt)
<b>Hot brand reactive dye</b>	41.4	28.7	37.8
<b>Cold brand reactive dye</b>	38.6	21.4	35.1

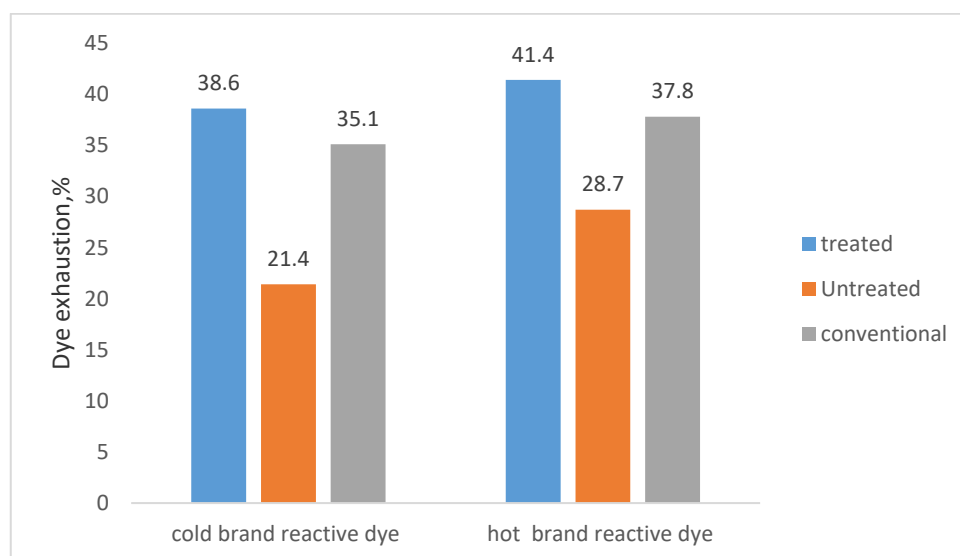


Figure 4.12: Dye Exhaustion Values for Hot and Cold Reactive Dyeing

#### **4.9. EFFECT OF DYEING PARAMETERS ON COLOURFASTNESS**

Dyeing fabric is generally done in order to produce a desired colour and does not only impart the desired colour but also ensures the fastness of colour of the fabric. Colourfastness is the most important colour property to the consumers among all other qualities in dyed woven fabrics. Dyeing parameters which includes temperature and time affects colourfastness which is one of the qualities required in dyed fabrics. Colour fastness to washing, light and rubbing were conducted in gyrowash machine, xenotest machine and crock meter respectively. The colour change in the samples and staining in multi-fiber were assessed using grey scale in colourfastness to washing. Staining of the adjacent fabric in colourfastness to rubbing was also assessed using grey scale.

##### **4.9.1 EFFECT OF TEMPERATURE ON COLOURFASTNESS TO WASHING**

The evaluation of the change in colour of the test specimen and degree of staining of two pieces of adjacent fabrics was done using the grey scales. The Grading was given on a scale of 1–5, where 1 is very poor and 5 is excellent.

Fabric dyed with hot reactive dyeing at 68<sup>0</sup>C shows good grade of 3.9 in colour change and 4.0 in staining as shown in Figure 4.13.and 4.15. Cold brand reactive dyeing at 32<sup>0</sup>C displays good grade of 3.8 in colour change and 4.0 in staining as shown in Figure 4.14. and 4.16. At high temperatures, the dye solubility increases resulting in faster diffusion of dyes into the fibers and good fixation of dyes takes place leading to wash fastness.

Beyond 68<sup>0</sup>C which is the equilibrium point, dissolution of dye particles from the fiber surface took place and hence more dye particles were easily washed off from the fabric resulting in high colour change and staining.

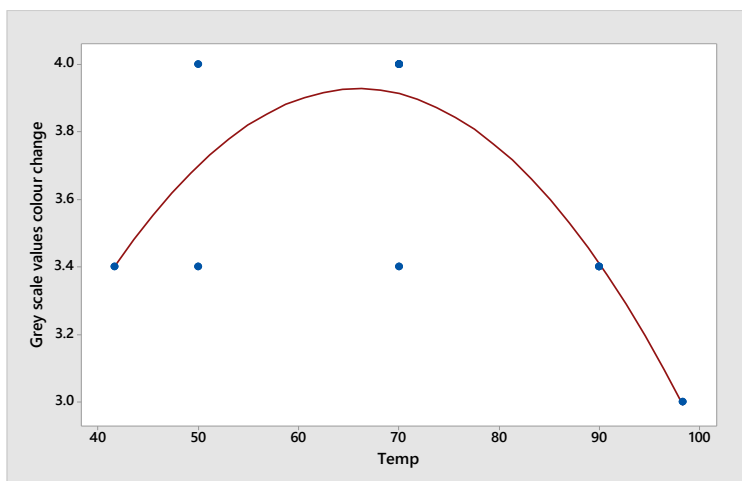


Figure 4.13:Effect of Temperature on Colour Change-Hot Brand

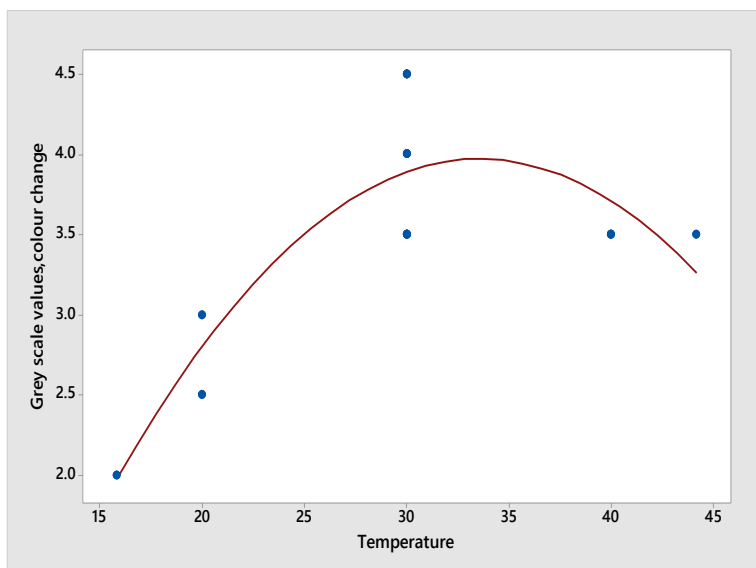


Figure 4.14:Effect of Temperature on Colour Change-Cold Brand

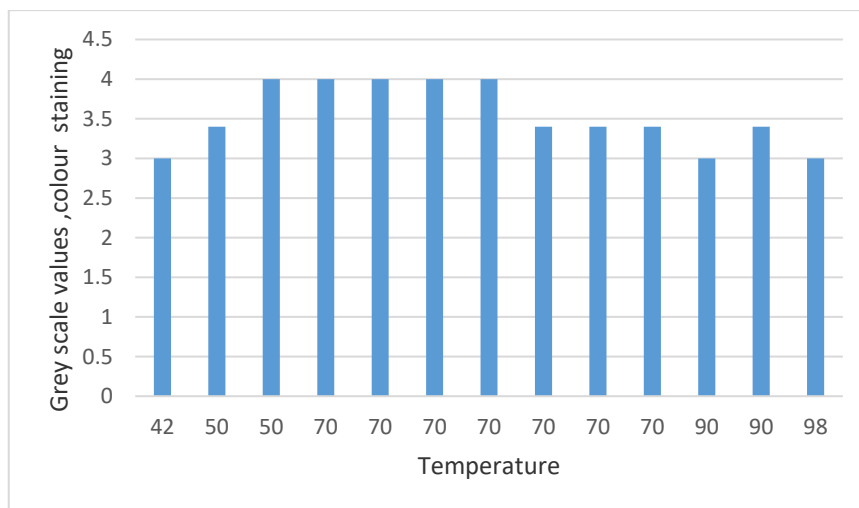


Figure 4.15: Effect of Temperature on Colour Change-Hot Brand

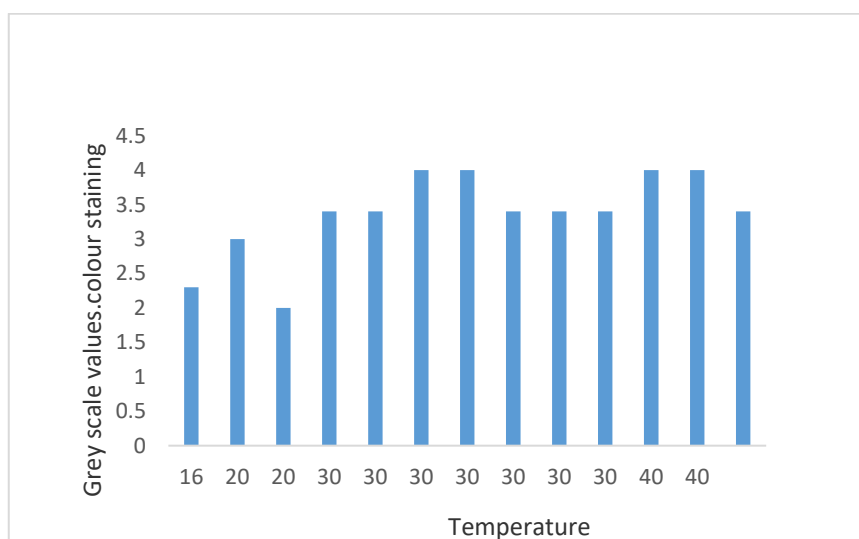


Figure 4.16: Effect of Temperature on Colour Change-Cold Brand

#### 4.9.2 EFFECT OF TEMPERATURE ON COLOURFASTNESS TO RUBBING

From Figure 4.17 and 4.18 the staining values for rubbing in dry conditions were found to be good; 5 and 4 at the temperature of 70 °C and 30°C in hot and cold reactive dyes respectively. The higher values mean good rubbing fastness. The wet rubbing value was 4 for both hot and cold reactive dyeing at the temperature of 70 °C and 30°C, respectively. The rubbing fastness value increases with temperature due to good fixation of the dye molecule.



Beyond the optimum temperature of 70 °C and 30 °C the depth of shade is increased and as a result, when the dyed samples were rubbed against a white fabric, more dye molecules come out from the fabric surface hence the staining value becomes less. From this study, the wet rubbing staining values are lower than dry rubbing values. This study also shows that the fabrics exhibited better colourfastness to rubbing than colourfastness to washing.

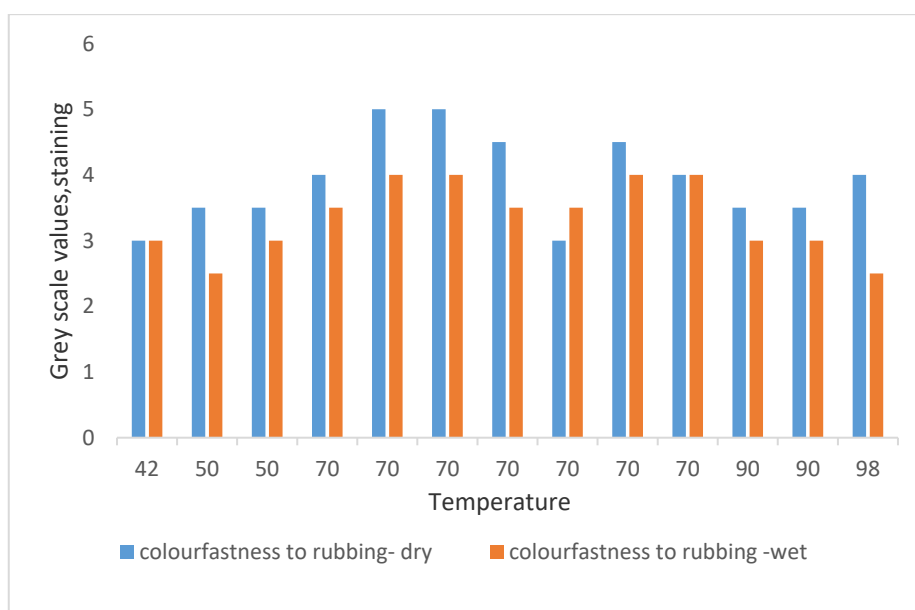


Figure 4.17: Effect of Temperature on Colourfastness to Rubbing-Hot brand

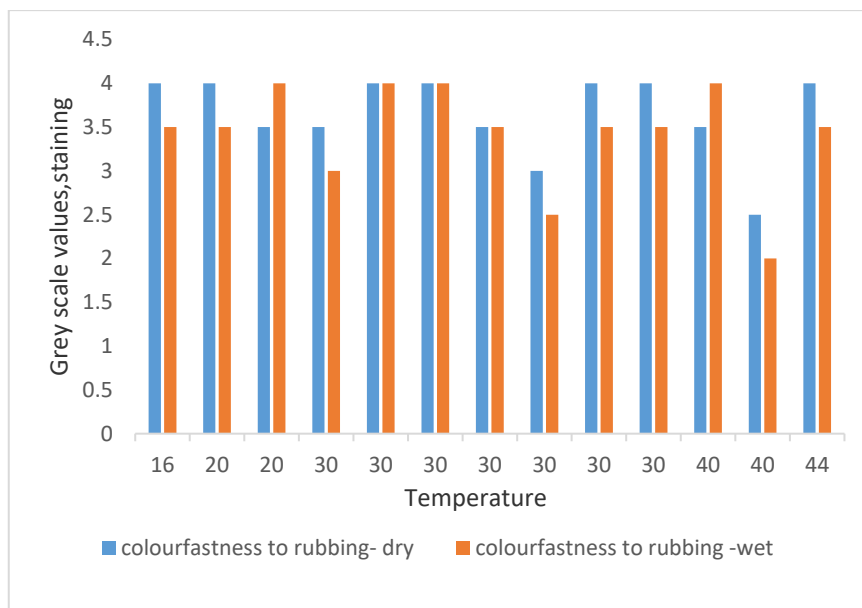


Figure 4.18: Effect of Temperature on Colourfastness to Rubbing-Cold brand

#### 4.9.3 COLOURFASTNESS TO LIGHT

Colourfastness to light was graded on a scale of 1 to 8, where 1 is very poor and 8 is excellent. The dyed cotton specimens and a range of eight blue wool standards were simultaneously exposed to light for 5, 10, 15 and 20 hrs. Table 4.12 shows that light fastness of dyed treated cotton fabric to increase in exposure time decreases from 8 to 6 and 5 to 5-4 in hot and 7 to 6-5 and 5-4 to 4 in cold reactive dyeing. Earlier results have showed that the colourfastness of cotton fabric to exposure under light decreases with the increase in exposure time (Alam et al., 2008).

It is also found from this study that colourfastness to light of cotton fabric dyed with hot reactive dyeing is better than that of the fabric dyed with cold reactive dyeing. The fastness of a dyed fabric depends upon the dye-fiber interaction and the intensity of light. An intensive oxidation of the fiber occurs due to the capacity of the dye molecule excited by the light, this oxidation reaction rapidly occurs at the earlier time of light exposure and hence the colour of the dyed fiber abruptly changes.

Table 4.12: Fastness Properties to Light

	<b>Hot dyeing</b>	<b>reactive</b>	<b>Cold dyeing</b>	<b>reactive</b>
<b>Exposure time, hrs</b>	Grade		Grade	
<b>5</b>	8		7	
<b>10</b>	6		6-5	
<b>15</b>	5		5-4	
<b>20</b>	5-4		4	

## CHAPTER 5: CONCLUSION AND RECOMMENDATION

### 5.1 CONCLUSIONS

The main objective of the study was to optimize dyeing parameters of treated cotton fabric in dyeing with hot and cold reactive dyeing without the use of salt and compared with control sample. The dyeing behaviours of the treated cotton fabric in cold and hot reactive dyeing were also compared. The cotton fabric was treated with chicken feather waste keratin hydrolysate which provided a cationic site which was dyed with hot and cold reactive dyes without the salt.

The regression model was built by taking in temperature and time as input variables and dye exhaustion as response variable. The two models developed in hot and cold reactive dyeing presents dyeing parameters interaction and their effects on the dye exhaustion. The optimal dyeing parameters were found to be 69.7<sup>0</sup>C and 75 minutes with dye exhaustion of 52.9 % in hot reactive dyeing and 34.4<sup>0</sup>C and 45 minutes with dye exhaustion of 48.3 % in cold reactive dyeing. The comparison was made on dye exhaustion between the hot and cold reactive dyeing. The treated cotton fabric shows greater dye exhaustion results of 52.9% in hot brand reactive dyeing than in cold reactive dyeing with dye exhaustion values of 48.3%. From the models the temperature had the greatest effect on dye exhaustion with the percentage contribution of 33.7 and 40.1 in hot and cold reactive dyeing respectively.

The study also showed that treated cotton fabrics exhibited good dye exhaustion values for all the dyes in the absence of salt. The untreated sample dyed in absence of salt exhibited low exhaustion values of 21.4% and 28.7 % when compared with treated cotton fabrics. The treated cotton fabric dyed in the two types of reactive dyes exhibited high exhaustion values than the control sample dyed in the presence of salt. The research further established that dyed keratin treated cotton samples exhibited better colourfastness

to washing light and rubbing fastness. It also established that the dyed treated cotton fabric exhibited better colour fastness to rubbing than washing.

Based on the results it is evident that treatment of cotton fabrics with keratin hydrolysate caused improvement in dye exhaustion for the two types of reactive dyes. From the study the cotton fabrics can be pre-treated and environmentally dyed with reactive dyes without the use of salt thus reducing the dye effluent load.

## **5.2 RECOMMENDATION**

From the study, scanning electron microscope (SME) is recommended for purchase. This equipment can be used for further research in establishing morphological changes on the surface of treated cotton fabrics. This will enable comparison of the changes that have taken place in treated and untreated cotton fabrics.

Further research to be carried out to assess the environmental impact of the effluent which is generated from the salt free reactive dyeing of treated cotton fabrics. The analysis of effluent content to be carried out in terms of biological oxygen demand (BOD), chemical oxygen demand (COD) and total dissolved solids (TDS). Fabric physical tests such as breaking strength, tearing strength, and crease recovery could be studied on the pre-treated cotton fabrics. These physical tests on treated cotton fabrics can be compared with untreated cotton fabrics and the effect of cationization on cotton fabrics quality established.

Furthermore, the use of alkali in cotton reactive is necessary for fixation of dye on the fabric. Treated cotton fabrics have cationic sites for dye fixation, therefore, future study is recommended on optimal alkali concentration for salt free reactive dyeing.

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## APPENDICES



Figure 5. 1: Extracted Keratin Hydrolysate



Figure 5. 2: Pre-Treated Cotton Fabrics with Keratin Hydrolysate