OPTIMIZATION OF MERCERIZING CONDITIONS FOR ENHANCED COTTON FABRIC DYEABILITY

BY

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DECLARATION

Declaration by the Candidate

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DEDICATION

I hereby dedicate this thesis to my lovely family. Thank you for never giving up on me and encouraging me towards my goals because your sincere sacrifice towards my education has exposed me to the world of Engineering. If it were not for your love, encouragement, support and sacrifices, I would have never made it this far. I love and appreciate you.

ABSTRACT

Pretreatment of cotton fabrics prior to dyeing involves a number of processes consisting of desizing, scouring, bleaching and mercerisation. Mercerisation process is among the pretreatment processes that have a great impact on dyeing properties of cotton fabrics. The mercerisation process is the treatment of cotton fabric with strong sodium hydroxide solution. The dyed fabrics at Rivatex, Kenya presented uneven dyeing faults and the absorbance preliminary study confirmed that the practical cause was improper mercerisation. The main aim of this study was to optimize mercerizing conditions for enhanced fabric dyeability by mercerizing the cotton fabric with varying conditions of sodium hydroxide concentration and treatment time; determining optimum mercerizing conditions for enhanced fabric dyeability and eventually analysing and comparing dye exhaustion and colour fastness properties of mercerized and un-mercerized fabric. This was accomplished by pretreatment of the cotton fabric using 3% o.w.f hydrogen peroxide and 5% o.w.f sodium hydroxide at a temperature of 80^0C for 2 hours. The pretreated samples were then subjected to mercerization experiments in slack state. A two-variable, five level circumscribed central composite design with two replicates which yielded 26 experiments was used. The variables were; sodium hydroxide concentration in a range of 13%-27% w/v and treatment time in a range of 2-7 minutes at room temperature. After mercerization, the samples were measured for absorbance. Un-mercerized (control) and mercerized samples were dyed using similar dyeing conditions. The samples were dyed with a reactive red HE 3B dye using 3% shade (o.w.f), 20g/L sodium carbonate, 55g/L sodium sulphate, 0.5g/L sodium hydroxide and 2ml/l wetting agent. The dyed samples were tested for dye exhaustion and colour fastness. The results were subjected to statistical analysis to establish the appropriate sodium hydroxide concentration and treatment time. The combined pretreatment process gave acceptable values of absorbance of wetting time of 78 seconds and sinking time of 108 seconds. The experimental data was used to develop regression models to establish the relationship between the mercerizing conditions and the fabric properties. The model for dye exhaustion of mercerised samples yielded a coefficient of determination (R^2) value of 0.64, a P value of less than 0.05 and an optimum exhaustion of 64.4%. This showed a realistic improvement in comparison to the unmercerised dyed samples which yielded 34% dye exhaustion. On the other hand, mercerized dyed samples highlighted a substantial improvement in colour fastness as they yielded acceptable colour fastness rates of 4 to 4/5 for washing and rubbing and 7 light colour fastness as compared to 2/3 to 3 for unmercerised samples Statistically, the optimum conditions were established as 23.4% sodium hydroxide and 4.9 minutes treatment time. From the results of this study, it was concluded that the optimal conditions of mercerization can yield improved dye uptake and uniform dyeing. However, to maximize the full research potential, there is a need for further investigations about; the effect of mercerisation on the fibre surface morphology, effect of mercerisation on natural dyeing, mercerisation study using cotton blended fabric and a study which involve variation of mercerizing temperature are recommended.

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ACRONYMS AND ABBREVIATIONS

[NaOH]	Concentration of sodium hydroxide
AATCC	American Association of Textile Chemists and Colourists
CC	Colour change
CCCD	Circumscribed Central Composite Design
CS	Colour staining
HE	Highly exhaustive
LCF	Light colour fastness
MLR	Material to liquor ratio
P value	Significance value
RSM	Response surface methodology
Time (min)	Treatment time in minutes
UV-Vis	Ultraviolet visible
w/v	Weight over volume

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CHAPTER 1: INTRODUCTION

1.1 Background of the Study

In textile wet processing, the production sequence normally starts with fabric pretreatment, proceeds with colouration (dyeing and printing) and ends with finishing. Various cotton fabric pretreatment processes are in existence to improve the fabric performance characteristics (Nur et al., 2016). These include desizing, scouring, bleaching and mercerization. Among these, mercerization is a major field of interest to researchers with respect to fabric dyeing and colour chemistry as it improves on the quality of dyed products (Akhbari et al., 2012; Moghassem & Valipour, 2016). Mercerization, a textile process named after its inventor, the English chemist John Mercer (1791-1866), was first developed in 1844. In 1889 Horace Lowe discovered the additional effect of enhancing the lustre by stretching the swollen materials while wet with caustic alkali and then washing off (Dinand et al., 2002). Mercerization is done additionally for cotton goods either as pretreatment process for dyed materials or as finishing process for white goods (Alam, 2016; Ayatollahi et al., 2013)

Mercerization is a process of irreversibly altering the physical characteristics and appearance of natural cellulosic fibres by swelling in a strong alkali solution (Patil et al., 2019). Different alkali solutions have been used for efficient mercerization, however, sodium hydroxide solution demonstrates the best applicability (Ibanescu et al., 2006; Semeii et al., 2008). The material is then treated with water or acid to neutralize the alkali solution and finally dried. In natural condition the cotton fibre is a flat, twisted, ribbon-like filament and when immersed in sodium hydroxide solution, it swells out and takes on a round and a hair like appearance, and becomes plump instead of flat. The cellulose is changed into hydro-cellulose or cellulose-hydrate (Ayatollahi et al., 2013). Sodium hydroxide solution actually rearranges the cellulose at both

molecular and macromolecular levels to produce these changes in fibre cellulose from cellulose I to cellulose II (Elizabeth, 2002).

Mercerization of cotton fabric is a common practice in the preparation process that enhances dye uptake and facilitates uniform dyeing in addition to improving dimensional stability, strength, and lustre (the fibres are swelled) thus enhancing appearance, making it similar to silk (Alam, 2016; Ayatollahi et al., 2013; Dinand et al., 2002). The enhancement in fabric properties is brought about by the changes in microstructure, morphology, and conformation of the cellulose chains as illustrated in Figure 1.1 after mercerization. The changes in the microstructure of the fibres, alters the sorption properties of mercerized fibres which lead to an increased accessibility of the reactive hydroxyl groups of cellulose fibres (Sauperl & Brezocnik, 2013).

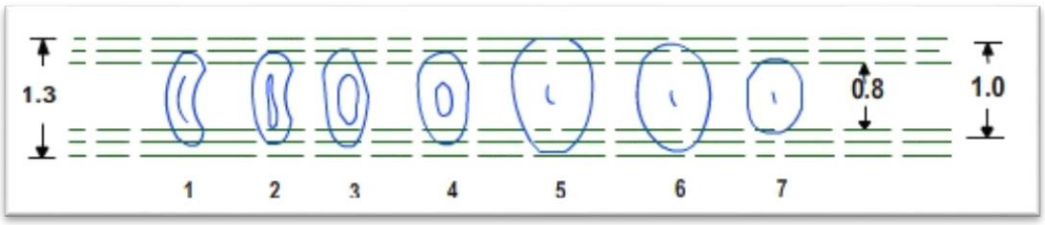

Figure 1.1: Gradual change in cross section of cotton fibre on mercerization (Gemci & Cebicci, 2011)

The extent of the changes that occur in fibre cellulose depends on the treatment time, sodium hydroxide concentration, temperature, degree of polymerization, source of cellulose, slack or without tension treatment, the degree of applied tension during the treatment and physical state of cellulose (Clark, 2011; El-Sayed & Saleh, 2015). However, the chemical (sodium hydroxide) concentration and time of treatment were given attention in this study.

Uneven fabric dyeing is caused by a number of factors which include; incorrect pH of treatment, inadequate desizing, scouring and bleaching of the grey fabric, water hardness, uneven mercerization, uneven heat setting, improper soda dosing, quick addition of dyes & chemicals (Samanta & Agarwal, 2009). Preliminary survey at local textile industries in Kenya indicates that uneven dyeing occurs in the dyed cotton fabrics. For uniform dyeing, the fabric's absorbance must be uniform. The absorbance test AATCC-79-2006 (Moghassem & Valipour, 2016) was carried out on mercerized fabric samples and preliminary results showed that mercerized samples had variations in fabric absorbance. The fault was thus found out to be caused by variations in fabric absorbance which is as a result of improper cotton fabric mercerization.

Plethora of research has been published on the influence of mercerization treatment on the properties of woven fabrics. The findings of all the researches confirmed improvement in tensile characteristics, sorption properties, and dimensional stability of the fabric samples after treatment (Moghassem & Valipour, 2016). However, the volume of literature available on the effects and optimization of chemical treatment and its parameters on fabric dye exhaustion, absorbance and colour fastness of cotton plain woven fabric is grossly inadequate. Against this background, the present study was proposed to investigate the effect as well as optimization of mercerization with respect to dye absorption properties. The purpose of this experimental study was to test the theory of mercerization that relates the sodium hydroxide concentration and treatment time to fabric dyeability. The independent variables (factors) were sodium hydroxide concentration and treatment time. The main responses were fabric dye exhaustion, absorbance and colour fastness properties. Other responses were weight loss, shrinkage and tensile strength. Untreated (unmercerized) fabric was served as control and compared with all mercerized fabrics for the stated response. The results obtained in

this research work were used to determine the optimum mercerizing conditions using RSM. According to RSM experiment design, 26 different samples were produced to identify and optimize the effective parameters influencing the mentioned responses of mercerization. Analysis and comparisons of dye exhaustion and colour fastness properties of mercerized and un-mercerized fabric was also conducted.

1.2 Statement of the Problem

Mercerization processes applied in different working conditions have different effects. In other words, structural and physical properties of a mercerized fabric are completely different from those of the grey fabric. These changes are observed in terms of luster, degree of whiteness, hydrophilicity, and strength. Basing on hydrophilicity effect, mercerization leads to an improvement in dye uptake and uniformity of the dyeing of the cotton fabrics hence preventing shade variation and saving on the dye stuff. This is because it brings about improved fabric absorbance. Currently, most dyed fabrics from local textile industries in Kenya have reported a lot of complaints because the colour properties of dyed fabrics have uneven dyeing faults as shown in Figure 1.2. The absorbance test AATCC-79-2006 (the American Association of Textile Chemists and Colorists test method 79) was carried out on mercerized fabric samples and the fault was found out to be caused by variations in fabric absorbance which is as a result of improper cotton fabric mercerization. This leads to rejects and hence company losses. The main focus of this present research is limited to systematically establish the optimum sodium hydroxide concentration and treatment time for mercerization to avoid uneven dyeing faults of a cotton woven fabric.

Figure 1.1: Defects in dyed fabrics (taken from local textile industries in Kenya)

1.3 Justification of the Study

The overall expectation of this research states that optimization of mercerization conditions in terms of sodium hydroxide concentration and treatment time would result in improved dye exhaustion percentages and colour fatness grades. This is because mercerization leads to an increase in absorption. The effect is as a result of increase in the proportion of amorphous part in the cotton fibre and increased availability of hydroxyl groups. On the other hand, mercerization also influences the initial portion of the breaking load frequency curve of a fabric by strengthening the weak fibres.

The findings of this study would contribute greatly to the benefit of local textile processing industries considering that mercerization plays an important role in fabric quality and thus cost. The need to supply high quality finished fabrics at relatively low manufacturing costs justifies the need for adjusting on some of the processing treatments without compromising on the quality. Thus, when local textile processing industries apply the recommended approach derived from the results of this study, will be able to register a reasonable reduction in manufacturing cost.

1.4 Objectives of the Research

1.4.1 Main objective

To optimize mercerizing conditions for enhanced cotton woven fabric dyeability

1.4.2 Specific objectives

i. To determine the effect of varying mercerizing conditions of sodium hydroxide concentration and treatment time on fabric properties.

ii. To determine the optimum mercerizing conditions for enhanced fabric dyeability.

iii. To analyze and compare dye exhaustion and colour fastness properties of mercerized and un-mercerized fabric.

1.5 Scope

Cotton fabric pretreatment involves desizing, scouring, bleaching and mercerization. However, this study focused on mercerization which emphasizes improvement in absorbance, dye exhaustion and colour fastness. The study also focused on mercerization using sodium hydroxide solution. The factors considered were sodium hydroxide concentration and treatment time. The factors were varied and optimized to bring about improved absorbance, dye exhaustion and colour fastness as the main responses. Other responses included weight loss, shrinkage, and tensile strength. This study involved the use of 100% plain woven cotton fabric. The study was carried out from Rivatex textile laboratory and Moi University textile laboratories.

CHAPTER 2: LITERATURE REVIEW

2.1 Mercerization of Cotton

Textile industry conventional processing as illustrated in Figure 2.1 consist of several stages which include desizing, scouring, bleaching, mercerization and colouration (dyeing and printing) and finishing (Bhatti et al., 2012; Karim-nejad et al., 2015; Zebic et al., 2017).

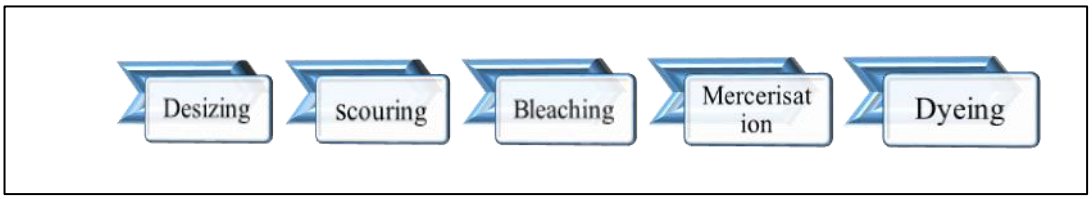

Figure 2.1: Wet processing sequence (Choudhury, 2011)

Most important pretreatment operation that alter the quality characteristics and physical properties of cotton is Mercerization (Zahid et al., 2017). Mercerization stage of textile treatment includes the treatment of textile with caustic alkaline solution of sodium hydroxide and auxiliary chemicals. Mercerization is the swelling of cotton fibres in 15-25% (Bhatti et al., 2012) aqueous solution of sodium hydroxide. This swelling results in reorganization of the cellulose fibre, which becomes cellulose II from cellulose I when the swelling agent is removed (Moharram & Mahmoud, 2007, 2008) . The native form of cellulose which occurs in cotton and other natural cellulosic fibres, is known as cellulose I. It has a unique crystal diffraction pattern (monoclinic). It is a thermodynamically less stable form of cellulose. During Mercerization, some native cellulose gets converted to cellulose II as shown in Figure 2.2. The extent of this conversion depends on process conditions like temperature, tension, time and alkali concentration (Kafle et al., 2014)

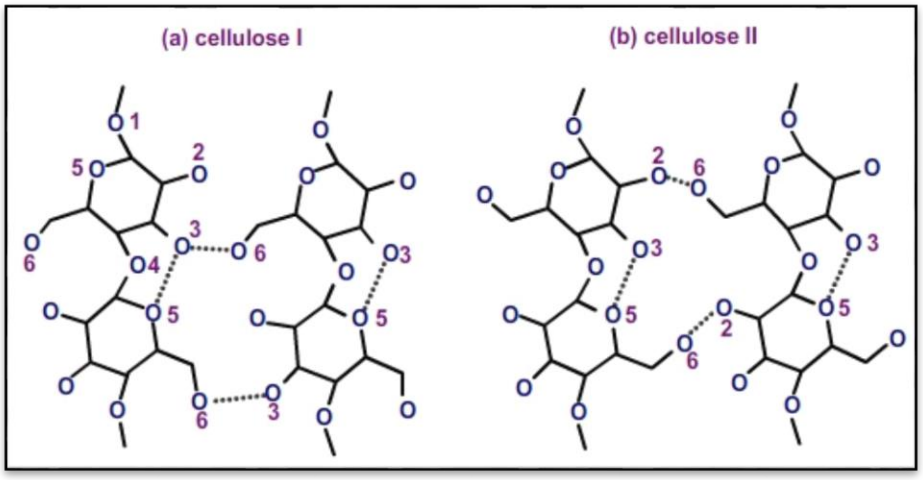

Figure 2.2: Arrangement of cellulosic chains in cellulose I and II (Yusuf et al., 2017)

Figure 2.2: The swelling in sodium hydroxide breaks hydrogen bonds and weak van der Waal's forces between the cellulose chain molecules. Once the forces are broken between chains during swelling, the chains are freed to rearrange, expand, and reorient (El-naggar et al., 2017). In this case the dimensions of cellulose I unit cell undergoes transformation as illustrated in Table 2.1. When the sodium hydroxide is removed, these chains form new bonds in this reorganized state thus cellulose II unit cell as shown in Figure 2.2 is formed (Moharram & Mahmoud, 2008).

Table 2.1: The dimensions of unit cells of cellulose I and II (Moharram & Mahmoud, 2008)

Crystal form	Dimension a (Å)	Dimension b (Å)	Dimension c (Å)	B (degrees)
Cellulose I	8.35	10.30	7.9	84
Cellulose II	8.14	10.3	9.14	64

Mercerization changes cellulose at either molecular or macromolecular level. For instance, absorbance of mercerized fibres increases because of the changes seen on fibre structure. Reduction in crystallinity and increase in amorphous region lead to increase in reactivity of hydroxyl groups of cellulosic fibres. Some structural changes are

observed during Mercerization process, such as increase in solubility, absorption of fibre, and reaction with oxygen (Gemci & Cebicci, 2011).

The process of mercerization is accompanied by important changes in the microscopic appearance of the fibre as shown in Figure 2.3. The mercerization is used to give increased luster, smoothness, increased dye and finishing chemical uptake, dimensional constancy and better mechanical properties (Bhatti et al., 2012). Mercerization of yarn or fabric is normally accomplished either in the slack state to obtain, for example, stretch properties, or under tension to improve properties such as textile fibre strength, dye efficiency degree of whiteness (luster), hydrophilicity by rearranging the cellulose molecules in the fibres (Gemci & Cebicci, 2011; Ibanescu et al., 2006; Zebic et al., 2017).

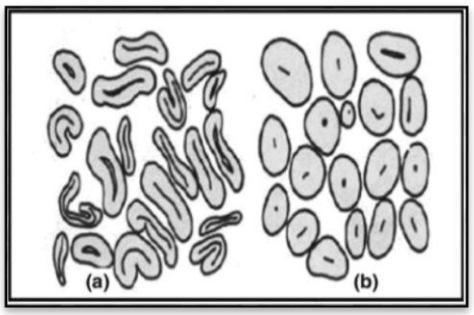

Figure 2.3: Cross-sectional views of cotton fibre (a) without Mercerization and (b) after Mercerization (Gemci & Cebicci, 2011)

2.1.1 Mercerization of cotton with sodium hydroxide solution

Sodium hydroxide (NaOH) solution of 15 to 25% concentration is the most commonly used mercerizing agent. The cotton is immersed in a bath containing this concentration of sodium hydroxide and wetting agent solution (anionic and nonionic surfactants) for a certain period of time, and then it is washed with hot and cold water before final drying (Gemci & Cebicci, 2011; Zebic et al., 2017). The swelling of cellulose in alkali solutions causes changes in the crystallinity, accessibility, unit cell structure, and

orientation of fibrils in cellulosic fibres. The extent to which mercerization solutions change these properties depend on factors such as the concentration of the solution, the additives mixed with alkalis, the temperature, the degree of polymerization, the source of cellulose, the physical state of the cellulose (i.e. fibre, yarn, or fabric), and the degree of tension employed to restrict fibre shrinkage and swelling (Ibanescu et al., 2006). These variables should be effectively controlled for the mercerization of cotton to improve one or more of the following properties: dimensional stability, affinity for dyes, tensile strength, higher add-on of finishing agents, luster, and fabric smoothness (Ibanescu et al., 2006).

2.2 Parameters of Mercerization Process

Mercerization changes both the crystalline and amorphous regions in cellulose that depends upon the concentration of the alkali solution, the time of treatment, temperature, additives as well as the tension applied to the materials(Zahid et al., 2017).

2.2.1 Temperature

The higher the dipping temperature, the lower the strength retention, owing to the fact that mercerization is an exothermic reaction. Hence raising the temperature decreases sodium hydroxide absorption and swelling. Conversely, when the dipping temperature is low, the fibres become swollen. Interaction between fibre molecules subsequently improved the cohesiveness and the strength retention of the fibres. The study by (Akhbari & Zahiri, 2012) demonstrated that raising the temperature has no significant effect on the extent of amorphous regions and added that mercerization degree in the same fibres change very little when the temperature of the process rises from 5 to 55 ^{0}C. However, for optimum swelling, the temperature should be kept between 15^{0}C and 25^{0}C because the viscosity of the chemical (sodium hydroxide) decreases at low

temperature (Gemci & Cebicci, 2011). Temperature of drying after mercerization also influences the dye and water uptake ability of cotton fabric. The increase in the temperature of drying decreases the dye uptake and water absorption (Zahid et al., 2017).

2.2.2 Treatment time

Controlling the mercerization time facilitates the absorption of sodium hydroxide and converting cellulose I to cellulose II, and at the same time increases the efficiency of the treatment (Akhbari et al., 2012). By using optimum treatment time, the strength and dye absorption properties of the fabric are enhanced. The required time for swelling is 60 s when a scoured cotton fabric is immersed into mercerization solution under tension. In a chainless mercerizing machine, required time for dry product is 12 seconds to supply full impregnation with sodium hydroxide solution, and it is 20 seconds for wet product (Gemci et al., 2011). For tension mercerization, up to 300 s of time of treatment with 20% [NaOH] is recommended (Moghassem & Valipour, 2016). However, mercerization without tension (slack) requires 3 to 5 minutes of treatment time for the effective swelling of a scoured and bleached cotton fabric (Mori et al., 1997; Semeii et al., 2008).

2.2.3 Concentration of sodium hydroxide solution

When fabric samples having same structural and physical properties are subjected to mercerization with different concentrations, it is seen that mercerization results are not the same in different concentrations (Gemci & Cebicci, 2011). At a given dipping temperature, fabrics pretreated with a high concentration of sodium hydroxide retain more of their strength, particularly over the sodium hydroxide concentration ranges between 16 and 25% (Zahid et al., 2017). The theoretical concentration of sodium

hydroxide for mercerization is 18% although practically 15-30% concentration of sodium hydroxide is recommended (Ammayappan et al., 2016) with 20% being the optimum (Zahid et al., 2017). At 20 to 30% concentration of sodium hydroxide, swelling of the outermost fibres forms a barrier, inhibiting the penetration of liquor into the yarn core. In case of fabrics, swelling is further restricted by the yarn crossing points. In addition, at such concentration, the viscosity of sodium hydroxide solution is also high (Wagaw & Chavan, 2012). Dimensional stability of fabrics increases by increase in concentration of alkali solution from 20% to 25% when bath temperature C (Moghassem & Valipour, 2016).

2.3 Effects of Mercerization

Fabric tensile strength, fabric shrinkage (fibre swelling), absorbance and dye exhaustion are basic indicators of the extent of mercerization. Tensile strength of the fabric increases with mercerization as shown in Table 2.2 (Zahid et al., 2017). This strength increase is attributed to; removal of convolutions (removal of weak spots at the reversal points), the fibrils are arranged parallel along the fibre axis, more fibre uniformity, circular and smoother cross section after mercerization (Kafle et al., 2014). In the case of Rotor yarn (Hymes, 2005) observed that maximum increase in yarn tenacity obtained by slack mercerization was 46%, at the lowest twist level. Mercerization influences the initial portion of the breaking load frequency curve of a fabric by strengthening the weak fibres. As a result, the frequency curve becomes symmetric, the mode shifts to higher load values, and a higher mean and a lower coefficient of variation are obtained for breaking load (Hymes, 2005).

Table 1.2: Tensile strength for un-mercerized and mercerized cotton fabrics (Zahid et al., 2017)

Fabric Treatment	Tensile strength (Ibf)	
	Warp	Weft
Un-mercerized	78	40
Mercerized (20%)	85	54

Cotton fibre has a kidney-type cross-sectional view and a ribbon-like twist longitudinal view. As a result of swelling during mercerization process, the fibre cross-section changes from kidney shape to round and longitudinally enlarges to circular form (Gemci & Cebicci, 2011; Hymes, 2005). Mercerization induces a decrease in the volume of crystalline region. It increases the amorphous content of the fibre and it is estimated that the number of available hydroxyl groups are increased by about 25%. This treatment modifies principally their accessibility in an aqueous medium. Consequently, this increase in the proportion of amorphous part and increased availability of hydroxyl groups is directly related to the increase in moisture sorption, reactivity and dye absorption of mercerized cotton (Ammayappan et al., 2016). Cotton fabric becomes more reactive to aqueous chemical reagents, and are more accessible to dye molecules. Mercerization increases the dye absorption (dye pickup), the rate of dyeing, and the visual colour yield. The mercerized material show darker shade than the un-mercerized material when dyed with dye baths of same composition, under the same conditions (Hymes, 2005). Slack Mercerization with 150-190 grams per litre sodium hydroxide solution is capable of decreasing dyeing unevenness resulting from differences in cotton maturity (Hymes, 2005)

2.4 Types of Mercerization

There are two types of mercerization which include tension and slack state mercerization. The purpose of tension mercerization is to increase luster of cotton fibres. In this mercerizing process, the fibre untwists and swells, lumen becomes

rounder in cross-section and it gains luster. Dye affinity and chemical reactivity increase. Fabric becomes stronger and smoother. Yarn and fibre strength in tension mercerization are respectively, 60% and 53% higher than those in slack treatment (Akhbari et al., 2012)

On the other hand, slack mercerization at swelling of the cotton fibre. Cotton fabric is treated with cold sodium hydroxide solution. Other names for slack mercerization are mercerized loose and mercerization without tension. There is complete shrinkage of cotton fibres or textile structures in sodium hydroxide solutions of sufficiently high concentrations. Hence the maximum effect of sodium hydroxide would be obtained on fibres where no restrictions on swelling or shrinkage would be present. The fabric is slacked and treated with NaOH solution by this process of mercerizing with the main aim of increasing fabric absorption. Slack mercerization is not as lustrous as tension mercerization. The sorption capacity of mercerized cotton is greater when the fabric is mercerized without tension (slack mercerizing) to give stretch properties to the fabric. Elongation and recovery properties improve and thus have been used to produce comfort stretch garments and fabric bandages, which need to conform to body shapes. Moisture absorption, fibre and yarn extension, swelling and shrinkage in slack mercerization are higher than when the yarns are treated under tension (Akhbari et al., 2012; Ammayappan et al., 2016).

2.5 Pretreatment of Grey Cotton Fabric Prior to Mercerization

Cotton fibre is composed of about 90–96% cellulose of weight of the fibres. The cotton fibre impurities range from 4% to 10% (Choudhury, 2011; Rahmatinejad et al., 2016). The non-cellulosic components are mainly found in the fibre cuticle layer and primary wall, which are the outermost layers of the cotton fibres. The components are pectin

(0.4 - 1.2%), waxes (0.4 - 1.2%), protein (1.0 - 1.9%), seed coat fragments (0.5–1.0%), inorganic salts (0.7 -1.6%) and pigments, and hemi-cellulose (0.5 - 0.8%) (Joshi et al., 2013a; Ma et al., 2017; Sojka-ledakowicz et al., 2015). In addition, some other impurities such as sizing agent and lubricants are added to the textile during the subsequent manufacturing process (Rahmatinejad et al., 2016). The cotton fibre yellowish colouration of the cotton fibres is due to the protoplasmic residues of protein and the flavones pigments of cotton flower (Abdul & Narendra, 2013).

Cotton woven fabric pretreatment before mercerization includes desizing of the sizing elements (starch, polyvinyl alcohol etc.) which are usually applied on warp yarns to avoid breakages during weaving process, alkali scouring to take out the natural impurities such as fats and waxes, pectin and proteins followed by a hypochlorite or hydrogen peroxide bleaching process which imparts whiteness by destroying the natural colouring matters. Basically fabric is made shipshape, hydrophilic, chemical penetrable and comparatively whitened through desizing, scouring and bleaching processes during the pretreatment (El-naggar et al., 2017; Nur et al., 2016)

2.5.1 Desizing

Desizing is the first and one of the most important steps in cotton fabric wet processing of a cotton fabric. Desizing is the treatment process of removing the size from the warp yarns in woven fabrics to facilitate the penetration of dyes and chemicals in the subsequent wet processing operations (El-naggar et al., 2017). Sizing agents are selected depending on the type of fabric, eco-friendliness and ease of removal, cost considerations and effluent treatment. Starch and its derivatives are the most common sizing material for cotton. Desizing involves impregnation of the fabric with the desizing agent, allowing the desizing agent to degrade or solubilize the size material,

and finally to wash out the degradation products (Teli & Adere, 2016). The major desizing processes include; Enzymatic desizing of starches on cotton fabrics, oxidative desizing, acid desizing and removal of water soluble sizes (Chand et al., 2012). Starch sizes that are extremely difficult to remove by enzymatic desizing due to the fat content, non-degradable tapioca starch or to the fungicides that added to prevent the size becoming mouldy. In these cases enzymes are ineffective and an oxidative desizing treatments must be used (Ammayappan et al., 2016).

2.5.1.1 Oxidative desizing

The most important aspects of oxidizing agents are that they can be applicable to a wide range of fabrics, the size content of which is often not known. Table 2.3 summarizes the necessary conditions for desizing starch in the presence of some important oxidizing agents. For continuous desizing using hydrogen peroxide (H_2O_2), the cotton fabric is impregnated with a 0.8% solution of H_2O_2 at 90^0C at near neutral pH; without intermediate rinsing, the fabric passes into the second bath which contains 0.5% sodium hydroxide before final wash-off at minimum temperature of 70^0C (Rahmatinejad et al., 2016). In continuous processes, sodium bromite treatment can be carried out hot using a dwell time of 20 min. Persulphates are recommended for ambient temperature desizing containing 0.5% persulphate, 0.5% tetra sodium pyrophosphate and 0.5-3% sodium hydroxide with 4-8 h treatment time (Teli & Adere, 2016).

Table 2.1: Desizing conditions with oxidizing agents (Hashem, 2006)

Oxidizing agent	Process	Additives	pH	Time (min)	Temp (°C)
Hydrogen peroxide	Pad-steam	1-2 vol. H_2O_2 7-15g/l NaOH	8-9	1-5	90
Sodium bromite	Pad-batch (cold)	1-3g/l active Br_2, 20-30g/l sodium hydroxide, 5-10g/l Wetting agent	7.5-8.5	15	20-40
Persulphate	Pad-steam	3-6g/l Na-persulphate, 5-10g/l Sodium hydroxide	10-10.5	1-3	95-100
Persulphate+ H_2O_2	Cold batch	40ml/l H_2O_2 (25%) 10g/l Persulphate 10ml/l Water glass 10ml/l NaOH 5g/l Stabilizer 5g/l Wetting agent	10-10.5	6-20	20-40

2.5.1.2 Enzymatic desizing

The enzymes' application in the textile industry is increasingly becoming popular because of the mild conditions of pH and temperature that are required and the capability of enzymes of replacing harsh inorganic and organic chemicals. Also wastewater from enzymatic treatments is readily biodegradable and does not pose any environmental hazard (Wang et al., 2012)

Malt alpha-amylase (α-amylase) enzymes are used in hydrolyzing of starch molecules present in the sizing preparation, transform starch to dextrins and breaking them down to soluble sugars thus helping in desizing (Chand et al., 2012; Imran et al., 2015). The enzymatic desizing process is very easy to use and is adaptable to any type of equipment. In practice the grey fabric is first passed through hot water to have an

approximate of 100% pick-up and then padded with the enzyme desizing mixture containing 0.5-2% malt extract and non-ionic wetting agent at 60-70^{0}C and neutral to acidic pH range (Hardin, 2010).

Although there is a common use of amylase enzymes in desizing with its specific reaction on starch and minimum effect on cotton in textile industry, there are some drawbacks associated with it which include; limited shelf life, very sensitive to application condition such as temperature and pH and being denatured in the presence of some metal ions. The marginal cost of production of amylase enzyme is also high (Rahmatinejad et al., 2016).

2.5.1.3 Acid desizing

In acid desizing, the cotton fabric is treated with dilute sulfuric/hydrochloric acid with a concentration of 5-10 g/1 at a temperature of 40^{0}C for 3-4 hours. This method is particularly suitable for cotton varieties containing large metal contents as the mineral acid converts the metals to their corresponding sulfate which are water soluble. The degraded starch is removed from the fabric by normal washing treatment. The used acids have some disadvantages such as the release of toxic gases during the reactions. Many of them are also corrosive (Rahmatinejad et al., 2016).

2.5.1.4 Evaluation of desizing

i. Conventional Method

In this method, the weight (W_1) of the sized fabric is taken. The fabric is desized using the selected desizing method, dried and the weight (W_2) is taken. Another sized fabric sample is treated with 3g/l (35%) hydrochloric acid (*HCl*) at 70^0 C for 30 minutes, dried

and the weight (W_3) of the fabric is taken. Desizing efficiency can be calculated as shown in Equation 2.1;

$$Desizing\ Efficiency = \left(\frac{Total\ size - Residual\ size}{Total\ size}\right) \times 100\% \qquad \text{Equation 2.1}$$

Where; Total size = $W_1 - W_3$; Residual size = $W_2 - W_3$.

ii. Weight loss

The samples are washed after desizing, dried at 105^0C for 1 hour and weighed after cooling. The desizing performance is evaluated by calculating the weight loss percentage (W.L%) as shown in Equation 2.2 (Chand, Shams, et al., 2012; Rahmatinejad et al., 2016):

$$W.L\% = \left(\frac{W_1 - W_2}{W_1}\right) \times 100\% \qquad \text{Equation 2.2}$$

Where W1 and W2 are the weights of the fabric before and after desizing, respectively.

iii. Iodine staining (TEGEWA Rating)

TEGEWA (TExtilhilfsmittel (textile auxiliaries), GErbstoffe (tanning agents) and WAschrohstoffe (detergent raw materials)) rating reflects the degree of desizing of the fabric, which is represented on scale range of 1-9. A higher TEGEWA rating indicates a high degree of removal of the starch sizing agent from the fabric (Rahmatinejad et al., 2016). Then scale mark of 9 represents complete starch removal, whereas the scale mark of 1 indicates completely inadequate starch removal (Chand, Shams, et al., 2012; Imran et al., 2015). The reagents and methods applied in this technique are as follows;

a) Reagent

10 g potassium iodide (KI,100%) is dissolved in 100 ml of water. To the solution, 0.6358 g of iodine (100%) is added. The mixture is stirred well until iodine is completely dissolved in the KI solution. To the solution, 800 ml of ethanol is added. The volume is made up to 1000 ml by adding water.

b) Method

Two drops of the iodine solution are put on the desized fabric sample and rubbed gently. The fabric is cold and free from any residual alkalinity. The change in colour in the spotted area is assessed with TEGEWA scale visually. No change of colour indicates no starch size present; Pale blue to bluish indicates presence of starch size or blend; and Violet indicates starch size with synthetic size. For a desized fabric, Pale blue to bluish violet refer to violet scale TEGEWA which indicates residual Starch content.

2.5.2 Scouring

Scouring is done with the purpose of removing non-cellulosic natural impurities as well as added impurities from the surface of the cotton fibre to give the cotton fabric adequate water absorbance (hydrophilicity) for subsequent dyeing and finishing. This requires removal of the cuticle waxes and the pectin and proteins attached to the primary wall cellulose. Other introduced impurities that require removal before chemical processing are dirt, oils and even defoliants applied to the cotton plant before harvesting (Hardin, 2010).

Conventionally, scouring process is carried out by use of sodium hydroxide solution at high temperature to achieve uniform colouration and finishing. The sodium hydroxide scouring treatment emulsifies the waxes and breaks down proteins and pectin into water-soluble or water-emulsifiable products that are then washed off from the cotton

substrates. This process effectively removes all impurities that exist in the raw cotton substrate (Joshi et al., 2013b). Scouring can also be done using hydrolytic enzymes, a process called bio-scouring. The enzymes include; cellulases, pectinases, proteases, xylanases and lipases (Joshi et al., 2013b). The conventional scouring is done using 3% o.w.f (of weight of fabric) NaOH, 2.5% soda ash (Na_2CO_3), 1% detergent, 3hrs time and MLR of 1:20 at 90^0 C temperature (Daberao et al., 2016).

2.5.2.1 Evaluation of scouring

(a) Wettability (Drop test)

The water absorbance of the fabric is performed according to AATCC Test Method 79-2010 (Moghassem & Valipour, 2016). According to this method, the time required for absorbing a drop of distilled water applied from a distance of 2 cm from the surface of the fabric is measured. The results are recorded as the average wettability time of 10 different points on a fabric sample. The number 0 means extremely fast wettable sample (less than one second) and wettability for samples whose time is larger than 1 minutes, the result is recorded as 60+ (Rahmatinejad et al., 2016).

(b) Sinking time (Immersion test)

Currently, sinking time test AATCC 17-2005 is used as an indicative test for evaluating absorbance (Joshi et al., 2013b).

2.5.3 Bleaching

Bleaching process is the removal of unwanted (yellowness for the case of cotton fibre) colour from the textile fibres (Abdul & Narendra, 2013). Bleaching is done using four major bleaching chemicals which include; Sodium hypochlorite, calcium hypochlorite, sodium chlorite and hydrogen peroxide. However, chlorine based bleaching agents are

non-ecofriendly in nature because they generate more adsorbed organic chlorine compounds (AOX 17.2–18.3 mg/L) in the effluents and hence they belong to the banned chemicals category. They also consume more water (45–80 L/ kg of yarn/cloth). On the other hand, bleaching with hydrogen peroxide hardly generates the toxic substances in the effluents thus it is environmentally friendly (degradable into water and oxygen)and the water consumption is also comparatively less (40 L/ kg of yarn/cloth) (Mamun et al., 2017). The textile industries mostly use the oxidation process for elimination of the non-cellulosic characteristic yellowish colour material present in raw cotton (Oliveira et al., 2015). Therefore, the hydrogen peroxide bleaching is the most common bleaching method (Mamun et al., 2017)

Bleaching with hydrogen peroxide is carried out under near boiling temperature to remove coloured impurities from fabrics that may produce an undesirable appearance and hinder dyeing performance (Teli & Adere, 2016). Measuring weight loss and wetting time assesses the effect of bleaching treatments. Whiteness index can be measured from the reflectance (%) at 470µm with a spectrophotometer using magnesium carbonate ($MgCO_3$) as standard (Teli & Adere, 2016). Bleaching using hydrogen peroxide has the following advantages (Ammayappan et al., 2016);

i. Complete removal of the seed husks.
ii. Extraction of coloured impurities of indeterminate type caused by the growing conditions.
iii. Hydrolysis, oxidation and removal of residual size.
iv. Achievement of the requisite degree of white with the least possible damages to the fibre.
v. Improved absorbance of the fabric to a uniform standard.

The mostly used hydrogen peroxide bleaching recipe includes 3% hydrogen peroxide, 1.5% NaOH, 1 % soap, 1% detergent, 90 minutes' time, 1% Sodium Carbonate, drop HCl and MLR of 1:20 at 120^0C temperature (Daberao et al., 2016).

2.5.4 Integrated (combined) desizing, scouring and bleaching

It is possible to combine the three preparatory processes namely desizing, scouring and bleaching into a single stage preparatory process by using hydrogen peroxide as a desizing as well as bleaching agent and sodium hydroxide as a scouring agent (Ammayappan et al., 2016). The three processes can be accomplished concurrently using one process called integrated pre-treatment that could also be named as combined process, one-step process, or single bath process (Nur et al., 2016).

On account of the continually increasing cost of energy, chemicals and process time reports on the conventional pretreatment processes, the development of a commercially viable single stage preparatory process combining desizing, scouring and bleaching also appeared (Ammayappan et al., 2016). Many processes have recently been reported for combined desizing, scouring and bleaching of cotton fabrics. One-bath pre-treatment process brings remarkable conservations in water usage (35%), steam (30%), chemical usage/cost (25%), electricity consumption (25%) and the process time (40%) in woven fabric pre-treatment process (Imran et al., 2015; Nur et al., 2016).

Rahmatinejad (2016) carried out combined scouring and bleaching of the desized cotton fabric samples using 5g/L hydrogen peroxide (35%), 0.4 g/L sodium hydroxide, 0.4 g/L sodium carbonate and 1.4 g/L sodium silicate, material to liquor ratio being 1:40 and boiling for 2 hours. After the washing process (hot, warm and finally cold washing), the fabric was neutralized by a solution of 0.1% acetic acid (Rahmatinejad et al., 2016).

Hardin (2010) carried out combined desizing, scouring and bleaching using sodium hydroxide (4.0% o.w.f NaOH) and hydrogen peroxide (2% o.w.f H_2O_2) in one-bath pretreatment process. Acceptable absorbability of the fabric was produced, which is due to better removal of starch through its hydrolysis by hydrogen peroxide and on the other hand sodium hydroxide results in better removal of the saponifiable oils, fats and waxes present in cotton (Hardin, 2010; Nur et al., 2016).

2.6 Cotton Fabric Dyeing

Dyeing is a method which adds beauty to the textile substrate by applying different colours and their shades on to textile substrate. Dyeing can be done at any stage of the textile manufacturing. The textile substrates are fibre, yarn, fabric or a finished textile product including garments and apparels. In the dyeing process, the objective is to transfer or diffuse dye molecules into the fibre from the dye liquor (Daberao et al., 2016). Dyeing processes go through three fundamental stages. The first stage consists of the dissolution or dispersion of the dye to be readily absorbed by the substrate. The second dyeing stage consists of the adsorption on the surface of the substrate. Finally, the dyeing process is achieved by the penetration and diffusion of the dye molecules into the substrate. It would be very easy to control these three stages when the dyeing bath contains a single dye. The cotton affinity for dye depends on a number of factors exercising an influence on the cotton dyeing process. It varies according to the cotton history, the dye category, the dyeing process (continuous dyeing or exhaust method) and the dyeing conditions (liquor ratio, temperature, auxiliary, pH, water quality, among others) (Hamdaoui, et al., 2013).

2.6.1 Dyeing with reactive dyes

There are five classes of dyes that can be applied to cotton and other cellulosic materials using immersion dyeing processes. The dyes include direct dyes, sulphur dyes, vat dyes, azoic colourants and reactive dyes (Burkinshaw & Salihu, 2017b). Reactive dye name is derived from the fact that it possess a reactive system, containing one or more electrophilic groups, which enable the reactive dyes to form a covalent bond with nucleophilic hydroxyl groups in the cellulosic substrates (Burkinshaw & Salihu, 2017c).

Reactive dyes are most commonly used to dye cellulosic materials (Demir et al. 2008) because they produce a complete gamut of bright colours with a high degree of colour fastness properties to washing and versatile for different dye application methods (Khatri et al., 2011; Lee et al., 2018). Furthermore they are cheap and available (Irfan et al., 2018). The high degree of colour fastness to washing of reactive dyes is attributed to the unique nature of reactive groups, which form covalent bonds with the cotton cellulose hydroxyl groups under alkaline pH conditions adjusted using sodium hydroxide and sodium carbonate (Khatri et al., 2015; Siddiqua et al., 2017).

Significant levels of inorganic electrolyte are added to the dye liquor to promote the uptake of reactive dyes onto cotton materials through suppression of negative charge build-up at the cotton fibre surface (Xiao et al., 2017). These electrolytes are sodium sulphate (Na_2SO_4) or sodium chloride (NaCl). The exhaust reactive dye application to cotton materials is carried out in the presence of 20-100g/L NaCl or Na_2SO_4 depending on the dye substantivity and shade. For example, 80 g/L for low substantivity vinylsulfone dyes and 100 g/L for dark shades (Burkinshaw & Salihu, 2017a, 2017b). Addition of electrolyte to a reactive dye bath and reducing the MLR used for immersion

dyeing have the same impact, which reduces the solubility of reactive dyes in the dye bath and thus increases dye uptake (Burkinshaw & Salihu, 2017c).

2.6.1.1 Dyeing with reactive HE (highly exhaustive) dyes

These dyes are superior to other reactive dyes as these are: suitable for exhaust dyeing with higher exhaustion rate, higher substantivity, higher tinctorial value, possess excellent compatibility within group, good build-up of shade, insensitivity to liquor ratio, freedom from listing' and 'ending' in jig dyeing, economy in use because of high tinctorial yield, consistently high fixation, reliability – excellent reproducibility owing to insensitivity to probable variations in liquor ratio, dyeing time, salt concentration, temperature, etc., complete shade range, higher molecular weight to provide good light and excellent wash fastness, very good fastness-resistant to acid and alkaline hydrolysis and to attack by detergents containing mild oxidizing agents and too low waste-water load (Khatri et al., 2015)

2.6.2 Dyeing with Natural dyes

Natural dyes include all the dyes obtained from natural resources that is from animal, plant mineral, and microbial sources of origin (Chirila et al., 2017; Daberao et al., 2016). Natural colourants (dyes) have been classified in a number of ways. The majority of natural dyes are vegetable dyes from plant sources which include flowers/petals (e.g. Marigold, Flames of the forest etc.), fruits/seeds (e.g. Myrobolan, Beetle nut etc.), leaves (e.g. Indigo, Eucalyptus, Lemon Grass,), barks/branches (e.g. Jackfruit, Rik acasia, Purple bark, Sandal wood etc.), and roots/bulbs (e.g. Allium, Turmeric, Beet root etc.) (Yusuf et al., 2017). Mineral natural dyes are produced from purified natural organic compounds which include chrome yellow, iron buff, nankin yellow, and manganese brown. Natural dyes from animals are extracted from the dried

body of the insects (e.g. lac and cochineal) (Kumar & Agarwal, 2009; Yusuf et al., 2017).

The natural dyeing operation is generally carried out by exhaustion dyeing technique using MLR of 1:17-40 (the mostly used being 1:20) with 20% dye (w/v). Addition of a suitable mordant using a suitable mordanting technique is required. Dyeing is done at boil (temperature of 90-100^{0}C) for 45-60 minutes, the dye bath temperature then is reduced to 50-70^{0}C and the dyeing operation continues for another 15 minutes. Dyed fabrics are rinsed with hot and cold water, soaped and then successively rinsed with hot water and cold water, respectively, squeezed and air dried (Ameuru et al., 2018). From the research conducted by (Daberao et al., 2016), it was found out that the natural dyes along with mordant give better result on 100% cotton substrates.

2.6.3 Dyeing evaluation

2.6.3.1 Colour fastness

Colour fastness by definition means the resistance of the colour of textile materials to different agents to which these textiles may be exposed during manufacture and their subsequent use (Ameuru et al., 2018). In another context described by (Daberao et al., 2016) the resistance of a textile material to change its colour characteristics or extent of transfer of its colour to adjacent white materials in contact is called colour fastness. The colour fastness property depends upon two factors that is selection of proper dye according to the textile substrate to be dyed and selection of the method for dyeing the fibre, yarn or fabric (Daberao et al., 2016). The colour fastness is rated by loss of depth of colour in original sample and staining of the accompanying white material expressed by staining scale due to tints or stains transferred by the colour of the original fabric. However, among all types of colour fastness, light fastness, wash fastness and rub

fastness are the general considered colour fastness tests for any textile (Samanta & Agarwal, 2009).

2.6.3.2 Dye exhaustion

Hymes (2005) studied the effect of Sodium Hydroxide causticization and Mercerization on the dyeing behaviour of Rotor spun and Ring spun cotton yarns for different dyes and improved dye uptake was showed. Testing parameters included absorbance values for dye bath exhaustion. For all the dyes, slack mercerized samples exhibit optimum values for dye bath exhaustion. When dyed, mercerized yarns showed higher rates of dye uptake than un-mercerized yarns (Hymes, 2005). This implies that mercerization increases dye exhaustion.

In his research, Hymes, 2005 used ultraviolet-visible (UV-Vis) spectrophotometer in testing absorbance values for dye bath exhaustion. This spectrophotometric method is mostly based on calculating colour differences from visible spectra (Lopez et al., 2018). UV-Vis measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I/I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, *A*, is based on the transmittance according to Equation 2.3.

$$A = -log\left(\frac{\%T}{100\%}\right) \qquad \text{Equation 2.3}$$

The absorbance of the dye liquor is taken both before and after dyeing. This is determined using a UV/Visible-spectrophotometer in the region of 200–800 nm. The percentage exhaustion of the dyebath, %E, is calculated using Equation 2.4 where A_0 and A_1 represent the absorbance of the dye solution before and after dyeing, respectively (Burkinshaw & Salihu, 2017c).

$$\%E = 100 \times \left(1 - \frac{A_1}{A_O}\right)$$ Equation 2.4

2.6.3.3 Colour measurements

For the colour measurements a Spectroflash spectrophotometer is used with a defined light source. The obtained values for the parameters of the attributes of colour difference represent the average of three to five determinations carried out in different points on dyed samples (Chirila et al., 2017). To assess the colour strength of dyed samples the K/S parameter is calculated at dominant wavelength based on Equation 2.5 derived from the Kubelka –Munk theory (Demir et al., 2008). The colour yield has been defined by Kubelka and Munk as a function of the reflectance (R) of dyed material in terms of the ratio between a light absorption factor (K)and a light-scattering factor(S), the factor (C) being in linear connection with the amount of absorbed dye.

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$ Equation 2.5

An increase in colour yield is especially connected to a decrease in the light- scattering factor. This is related to the change in cotton morphology. More rounded form of the mercerized fibres is accompanied by a lower amount of internal scattering of the incident light.

2.7 Optimization Using Response Surface Methodology

The response surface methodology (RSM) is a statistical and mathematical method for modeling and evaluating the effects of multiple factors (independent variables) and their interactions on one or more responses (dependent variables) (Imran et al., 2015). The RSM investigates an appropriate relationship between factors and responses (Akhbari & Zahiri, 2012), and identifies the optimal operating conditions for a system

under study or a region of the factor field that satisfies the operating requirements (Aydar, 2018). Response surface is a method based on surface placement, therefore, the main goals of RSM studies are to understand the topography of the response surface including the local maximum, local minimum and ridge lines, and find the region where the most appropriate response occurs. A response surface is a geometric representation obtained when a response is plotted as a function of one or more quantitative factors. The results are graphed in two dimensions as contour plots or three dimensions as surface plots, showing the response as a function of factors of interest (Bhatti et al., 2012). Linear methods such as linear programming reveal main effects and interactions but cannot find quadratic or cubic effects. However, when nonlinearities are included in the experimental design, the results give an idea of the shape of the response surface under investigations (Leivisk, 2013). RSM is based on the fit of a polynomial equation to the experimental data, which must describe the behavior of a data set with the objective of making statistical previsions.

Traditionally, optimization has been carried out by monitoring the influence of one factor at a time on an experimental response (Murray et al., 2016). While only one parameter is changed, others are kept at a constant level. This optimization technique is called one-factor optimization. Its major drawback is that it does not include the interactive effects among the variables studied. Consequently, this technique does not depict the complete effects of the factors on the studied response (Bezerra et al., 2008). In RSM, the real problem is identified and the predicted responses are validated as shown in Figure 2.4 which highlighted the steps that must be followed in order to apply this method correctly.

Box-Behnken designs (BBD) and central composite design (CCD) are two main experimental designs used in response surface methodology. In Box-Behnken Design, The Box-Behnken design is an independent quadratic design which does not contain an embedded factorial or fractional factorial design. In this design the treatment combination are at the midpoints of edges of the process space and at the centre. These designs are rotatable (or near rotatable) and require three level of each factor. The minimum number of factors (continuous or numerical) which can be accommodated is three at three levels.

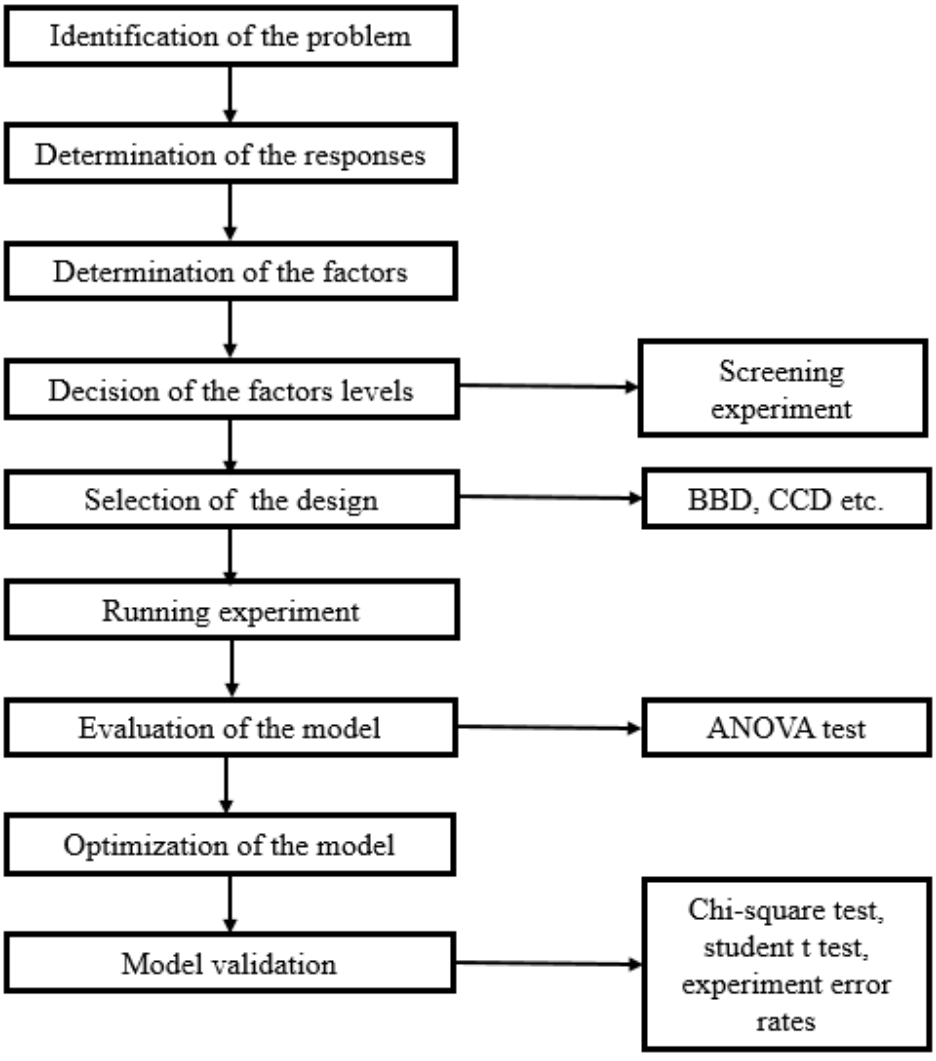

Figure 2.4: Steps for response surface methodology (Aydar, 2018)

On the other hand, CCD is a response surface design which has axial or star points in addition to the three-levels of the respective factors. Three variants of CCD exist: circumscribed, inscribed and face centred. However, circumscribed CCD is the original CCD and it does testing at five levels which provide high quality predictions over the entire design space. The axial or star point usually denoted as (α) increases the number of levels from three to five thereby giving the experimental design flexibility. The minimum numbers of factors that CCD can accommodate is two. Its advantages over Box-Behnken is that it allows the experimental designer to know what effect the factors had on response since the experimental designer goes beyond or below the chosen levels of factors (Olawoye, 2016). It is for this reason that CCD was used in the study analysis and optimization of the mercerization process conditions.

2.8 Summary of Key Research Gaps

Studies have been conducted to improve dye absorption properties of cotton fabrics but the results have shown that there is still need for more research to achieve that. A study done by (Akhbari et al., 2012) investigated the effect and optimization of mercerizing parameters on the tensile strength of mercerized yarn. The parameters included tensioning time in NaOH, concentration of NaOH and concentration of wetting agent. In this particular study, one response of tensile strength of mercerized yarn was studied. Another study by (Alam, 2016) analyzed and compared the colour strengths of mercerized and unmercerized fabric among different fabric structures but the conditions of mercerization were not varied. El-Sayed & Saleh, 2015, investigated the effect of spinning systems on properties of dyed Egyptian cotton yarns after mercerization treatment. The target response was yarn tensile strength which necessitates further investigations of mercerization on other yarn and fabric properties. An investigation by (Karim-nejad et al., 2015), attempted to resolve high flammability of mercerized cotton through cross-linking with citric acid and ZnO

nanoparticles optimized by RSM models. The nanoparticles were successfully utilized on the mercerized cotton surface but dyeing behaviour was not discussed. In a bid to enhance dye uptake ability of cellulosic fabrics and improving colour strength and colour fastness, a study was conducted by (Chirila et al., 2017) to modify cotton cellulose using the gamma irradiation of cotton fabrics in preliminary treatment phase. In this investigation, attention was not given to mercerization. A study by (Aboalasaad et al., 2017) established optimum conditions of mercerization and resin finishing treatments and obtained cross-linked cotton fabrics having good wrinkle resistance properties without severe strength loss. The study highlighted that performing optimum mercerization followed by cross-linking retained enhancement in strength properties of cotton fabrics. In this study also, one response of tensile strength was studied. Another research by (Gemci & Cebicci, 2011) examined the effect of mercerization process applied under different conditions on the degree of whiteness. In this study, degree of whiteness was the response and dye absorption properties were not attended to.

The studies have been focusing on the effect of mercerization on basically one response at a time. However, the effect and optimization of mercerization on a set of responses for example absorbance, dye exhaustion and colour fastness at the same time is inadequate. Statistical analysis and optimization are therefore, important to create models and optimize mercerization following a number of responses simultaneously to precisely establish the processing conditions. The present work intended to evaluate the effect and optimization of mercerization variables (sodium hydroxide concentration and treatment time) on the three main outputs (absorbance dye exhaustion and colour fastness) as well as other outputs of shrinkage, tensile strength and weight loss using RSM.

CHAPTER 3: RESEARCH METHODOLOGY

This chapter gives the research design, procedure and materials which were used in pretreatment (desizing, scouring and bleaching), mercerization and dyeing of woven cotton fabric. Dyeability (exhaustion, absorbance and colour fastness) testing methods of dyed mercerized fabric and optimization procedure is given in this chapter.

3.1 Research Design

There are several factors which influence mercerization which include sodium hydroxide concentration, time and temperature of treatment, type of cellulose, degree of polymerization, tension and additives. The dyeing properties vary only slightly with the treatment temperature (5 to 55 ^{0}C.) and largely with the sodium hydroxide concentration and time of treatment (Akhbari & Zahiri, 2012). Therefore, a constant RT of 19^{0}C was used in this study. Slack mercerization as used which does not necessitate tension requirement. One fabric type was used to ensure that cellulose type and degree of polymerization are constant factors. This was made by using one fabric from which all samples were prepared. Pure sodium hydroxide pellets and pretreated fabric were used in the study which made the factor of additives to be constant.

Experimental design was used in this study. This is because an experiment supports or refutes a hypothesis using statistical analysis. An experiment is also thought to be the only experimental design that can establish cause and effect relationships. The control sample was pretreated un-mercerized cotton fabric. The experimental samples were subjected to varying mercerizing conditions of sodium hydroxide concentration and treatment time. All samples were dyed at the same conditions.

Design of experiment (DoE) was used to explore the effect of concentration and time at constant (room) temperature on the fabric dyeability and colour fastness properties.

A wide- range for each factor was selected which enabled the design to explore a sufficiently large area of the reaction space (Murray et al., 2016). In this experiment a two-factor circumscribed rotatable central composite design (CCCD) was used to identify the relationship existing between the response functions and the process variables as well as to determine those conditions that optimized the responses. The circumscribed central composite design (CCCD) of experiments is a response surface method that uses a combination of statistical and mathematical methods to choose the best experimental methods to maximally reduce the number of experiments (Karim-nejad et al., 2015)

In CCCD, the factors are tested at a minimum of three levels, that is, minimum, middle and maximum and are coded as – 1, 0 and 1. For a rotatable design, each experimental factor must be represented at the five levels of coded units, that is, lowest (-α), low (-1), centre (0), high (+1), highest (+α) as shown in Table 3.1. This property ensures constant variance at points that are equidistant from the centre point and therefore provides equal precision of response estimation in any direction of the design (Imran et al., 2015). nThe value of α is calculated as shown in Equation 3.1.

$$\alpha = (2^k)^{0.25} = (2^2)^{0.25} = 1.4142 \qquad \text{Equation 3.1}$$

Where, *k* is the number of factors

The number of factors (k) is 2 hence an alpha (α) value of 1.4142 was obtained. The independent variables were sodium hydroxide concentration and treatment time. Mercerization of fabrics is performed using NaOH with the concentration normally being in a range of 18-25% (Zahid et al., 2017). Studies have however showed that below 18% causticization takes place (Min & Huang, 1999). In this study, a range of

13-27% concentration was used. The range of sodium hydroxide concentration was first selected at three levels with an interval of 5% that is; 15%, 20% and 25%. Using CCCD, axial points were established as 13 and 27 % which made a total of five levels as shown in table 3.1. Previous research has shown that the effect of slack mercerization time is significant at times of between 2 to 8 minutes (Moghassem & Valipour, 2016), thereafter the results did not show a significant change. This time range was therefore used in this study. The impregnation time was selected at three levels that is; 3, 5 and 7 minutes from which in CCCD, the axial points of 2 and 8 minutes were determined to make five levels as shown in Table 3.1. The responses of the design were weight loss, absorbance, dye exhaustion, tensile strength, shrinkage and colour fastness.

Table 3.1: Actual DoE levels of the factors

Factors (x_i)	*Levels*				
	- α	-1	0	+1	+ α
x_1 : *NaOH concentration (% w/v)*	13	15	20	25	27
x_2 : *Time (minutes)*	2	3	5	7	8

3.2 Materials

3.2.1 Fabric

The fabric with specification in Table 3.2 was sourced from grey room section, processing department, Rivatex East Africa Limited, Eldoret, Kenya.

Table 3.2: Fabric specifications

Fabric composition	Cotton
Fabric type	Woven
Fabric structure	Plain
Fabric GSM	126
Ends per inch	54
Picks per inch	37
Warp count	Nm 34/1
Weft count	Nm 34/1

3.2.2 Chemicals

The chemicals and auxiliaries used in this research included; sodium hydroxide (pellets form), hydrogen peroxide (liquid form/35%), commercial reactive red HE3B powder, sodium carbonate powder, sodium sulphate crystals, wetting agent (non-cresylic) and liquid soap.

3.3 Procedure of Data Collection

3.3.1 Pretreatment

In this research, work was developed to combine the three preparatory process that is; desizing, scouring and bleaching into a single stage in which effective removal of size, natural impurities and colouring matter could be achieved in the shortest possible time. In the process, hydrogen peroxide was used as desizing as well as bleaching agent and sodium hydroxide as conventional scouring agent.

Pretreatment was carried out in a stainless-steel container as illustrated in Figure 3.1. The fabric samples were soaked in the treatment bath containing 5% o.w.f (of weight of the fabric) sodium hydroxide, 3% o.w.f hydrogen peroxide, 1ml/l wetting agent and 1ml/l detergent using a material to liquor ratio of 1:20. 14 fabric samples each with dimension of 60cm × 30cm with an average weight of 20.0g were used. The pretreatment proceeded at a temperature of 80^0C for 2 hours. Cold wash with liquid soap was done on the treated fabric samples at room temperature for 5 minutes and then finally dried in oven at a temperature of 70^0C.

Pretreatment process Gray fabric Pretreated fabric

Figure 3.1: Pretreatment process

3.3.2 Control fabric

The control fabric was pretreated fabric without mercerization. The control fabric sample (un-mercerized) was tested upon all the responses as the experimental (mercerized) fabric samples. The un-mercerized fabric sample was dyed using the same conditions as mercerized samples.

3.3.3 Mercerization

Mercerization proceeded with slack mercerization process. The mercerizing baths containing strong sodium hydroxide of varying concentration were prepared in 1000cm^3 (1 litre) respective beakers as shown in Figure 3.2. The respective pretreated fabric samples were impregnated with strong solution of 13-27 % w/v sodium hydroxide containing 5g/l (0.5% w/v) wetting agent (mercerizing oil) at room temperature of 19^{0}C for 2-8 minutes using a material to liquor ratio of 1:20. Therefore, 400cm^3 of water was used for each experiment. The range of process parameters was taken in five different levels that is; 13 %, 15%, 20%, 25% and 27% and impregnation (dwell) time that is; 2, 3, 5, 7, and 8 minutes. Then the fabric samples were rinsed with hot water (70^{0}C) and then cold water. The remaining sodium hydroxide after hot and cold washing was neutralized by dipping the respective mercerized samples in 1% w/v

acetic acid solution for 1 minute, followed by washing with cold water. Then fabrics were air dried.

Figure 3.2: Mercerization process

3.3.4 Dyeing

Un-mercerized and mercerized fabric samples were dyed with similar conditions. The samples were dyed with a reactive red HE 3B dye using 3% shade (o.w.f), 20g/L sodium carbonate, 55g/L sodium sulphate, 0.5g/L sodium hydroxide and 2ml/l wetting agent. The dye solution was initially prepared in the Rotawash testing pots with all the auxiliary chemicals added at room temperature. The fabric sample was put into the dye solution using M: L of 1:20. Dyeing was carried out for 1 hour at 80^0C using M228 Rotawash. After dyeing the fabric samples were rinsed in cold water, soap solution, rinsed in cold water again and then dried.

3.4 Characterisation of Treated Fabric Samples

Prior to the testing, samples were conditioned for 24 hours. For grey fabric state; the average weight and tensile properties (strength and elongation) of 60cm × 30 cm fabric samples were determined. Mercerized and control fabric samples were tested upon weight loss, absorbance, shrinkage properties and tensile strength. Dyed samples were tested upon dye exhaustion and colour fastness to light, washing and crocking. The

appropriate tests were carried out in Moi University Textile laboratory, School of biological and physical sciences and Rivatex East Africa Limited Textile testing laboratory.

3.4.1 Weight loss and desizing efficiency

Pretreatment of cotton fabric results in a remarkable loss of weight. This is attributed to removal of impurities such as oil, fats, wax, salts etc. The pretreatment effect, thus, can be evaluated based on this weight loss of fabric. Weight loss percentage of treated samples was determined by finding the differences in weight of sample before and after treatment and always after conditioning. The weight loss is of the order of 5-10% for sufficient removal of impurities (Aly et al., 2010). In this method, the weight (W_1) of the 60 × 30 cm grey fabric was taken. The fabric was pretreated (combined desizing, scouring and bleaching), dried and the weight (W_2) after drying was taken. Another sample of the gray fabric was treated with 3g/l hydrochloric acid (HCl) at 70^0 C for 30 minutes, dried and the weight (W_3) of the fabric was taken. Desizing efficiency and weight loss were then determined using equations 3.2 and 3.3 respectively (Asaduzzaman et al., 2016).

$$Desizing\ Efficiency = \left(\frac{Total\ size - Residual\ size}{Total\ size}\right) \times 100\%$$

Equation 3.2

$$Weight\ loss\ \% = \left(\frac{W_1 - W_2}{W_1}\right) \times 100\%$$

Equation 3.3

Where; Total size = W_1-W_3; Residual size = W_2-W_3.

3.4.2 Absorbance

There are two facets to the absorption of water that's the total amount that can be absorbed regardless of time (absorption capacity) and the other is the speed of uptake of the water (Asaduzzaman et al., 2016). In this research, speed of water uptake was used to evaluate the fabric absorbance. The following tests were done to measure the absorbance of cotton fabric samples.

3.4.2.1 Drop test (wetting time)

Wettability is defined as the time in seconds for a drop of water or 50% sugar solution to sink into a fabric. Fabrics that give times exceeding 3 minutes are considered to be unwettable. The dried samples were tested at room RT by the absorbance test standard AATCC-79-2000 (Moghassem & Valipour, 2016). The time period (in seconds) between the contact of the water drop with the fabric and the disappearance of the water drop into the fabric was counted as the wetting time. The time of drop disappearance was averaged from measurements at different points of the fabric sample. Wetting times equal or less than 5s were considered as an indication of the adequate absorbency of the cotton fabrics (Aly et al., 2010). The fabric sample was placed flat on a table and creases removed. A burette was placed at a height of 10 mm from the fabric surface (Teli & Adere, 2016). A drop of water was allowed to fall from a fixed height of 10 mm on to taut fabric sample and the time required for specular reflection of the water drop to disappear was read and recorded using a stopwatch as wetting time. An assembly of burette clamped on a retort stand was used to provide the drops. All measurements were performed three times and the average was calculated.

3.4.2.2 Immersion test (sinking time)

Sinking time is the time (seconds) taken by the fabric samples to sink under their own weight. Absorbance was also assessed in another method called sinking time test using AATCC 17-1994 (Asaduzzaman et al., 2016; Clark, 2011). Test specimens of 1 cm × 1 cm was cut at random and placed on the surface of 500ml of water contained in 1000ml beaker at a temperature of 19^0C from a height of 25mm. Slowly the fabric samples were wetted and entrapped air was removed. Using a phone stopwatch, the time taken by the fabric samples to go inside water from floating state and sank in completely was noted down. 3 areas on every fabric sample was tested and the average sinking time was calculated. The shorter the time taken by the specimen to sink in water completely, the greater is its absorbance. Samples which didn't sink in 2 minutes was considered as floating samples.

3.4.3 Fibre swelling (fabric shrinkage)

Fibre swelling is attributed and proportional to fabric shrinkage. Swelling shrinkage results from the swelling of the constituent fibres of a fabric due to the absorption of strong sodium hydroxide solution. The fabric dimensions at the respective treatment stages that is after combined pretreatment and mercerization and compared to the original fabric dimension of 60cm × 30cm. Fabric shrinkage was then determined by using the equation 3.4.

$$Shrinkage\ \% = \left(\frac{l_b - l_a}{l_b}\right) \times 100 \qquad \text{Equation 3.4}$$

Where; l_b = length before treatment and l_a = Length after treatment

3.4.4 Tensile strength

The tensile test was carried out using a universal tensile tester available in Rivatex Textile laboratory. The test was carried out according to standard ASTM D751. The sample was aligned into the grips and then loaded and secured into a pair of clamps. The speed of the testing was set at 100mm/min. The machine was then started with the fabric sample extended to break. The test was stopped as soon as the specimen broke. After the breaking of the specimen the results were saved on the computer and the machine returned to the starting position as shown in Figure 3.3. The breaking force was then recorded.

Figure 3.3: Tensile testing

3.4.5 Dye exhaustion

The percentage of dye exhaustion (E) were determined spectrophotometerically using UV-Vis spectrophotometer by measuring dye concentrations in the bath before and after dyeing using the equation below. The dye concentration was measured by the peak absorbance of the dye solution at wave length range of 200 to 600nm. The dye

exhaustion (E) was determined using equation 3.5 where A_1 and A_2 are the absorbances of the dye solutions before and after dyeing, respectively.

$$E = \frac{A_1 - A_2}{A_1} \times 100\% \qquad \text{Equation 3.5}$$

3.4.6 Colour fastness

Prior to testing, samples were conditioned as per AATCC Standards. The test specimens were kept in the laboratory conditions of 65% ±5 relative humidity and a temperature of 22^0C for 24 hours. The dyed fabrics were evaluated using a standard procedure that is, fastness to rubbing according to AATCC Test Method 169-2016, fastness to light according to AATCC Test Method 16.3-2014 and fastness to washing according to AATCC Test Method 61-2013. Gray scales were used to evaluate colour fastness. Gray scale of 1(poor) to 5(excellent) was used to assess colour fastness to rubbing and washing where as a gray scale of 1(poor) to 8(excellent).

3.5 Statistical Analysis

All statistical analyzes of data were done using MINTAB version 17 software. Response surface methodology (RSM) was used in the optimization procedure because the objective of RSM is to simultaneously optimize the levels of variables to attain the best process performance. Statistical model was derived to predict the response (weight loss, absorbance, shrinkage, tensile strength, dye exhaustion and colour fastness) of the fabric samples based on the mercerization conditions of sodium hydroxide concentration and treatment time. In this study, a non-linear regression model including main, interaction and quadratic effects of the independent parameters were examined. Response surface and contour plots were generated by using the model described by the equation 3.6

$$Y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2$$ Equation 3.6

Where *Y* is the response, *x* is a variable, and β is a regression coefficient. Significant effects remain in the model and non-significant ones are removed. If the significance is less than 0.05 (P-value < 0.05), which is in the area of the hypothesis rejection, the effect of the parameter considered was significant and remain in the model. On the other hand, when the significance is greater than 0.05 (P-value > 0.05), the effect of the parameter considered is not significant; hence it is excluded from the model.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Effect of Combined Pretreatment on Fabric Properties

The desized, scoured and bleached fabric was tested upon the weight loss, shrinkage, absorbance and tensile strength. Table 4.1 shows the test results.

Table 4.1: Combined pretreatment results

Fabric property		Test result
Weight loss (%)		5.1
Shrinkage (%)	Warp	8.2
	weft	4.7
Absorbance (seconds)	Wetting time	78
	Sinking time	108
Tensile strength (N)	Warp	283
	Weft	124

The fabric samples exhibited an average weight loss of 5.1%. This is because starch and non-starch polysaccharides (e.g. pectin, hemicelluloses, lignin, dirt, etc.) as well as the natural fats and waxes were broken down and saponified and hence they go out of the fibre pores and the fibre surfaces leading to a remarkable reduction in fabric weight (Zahran, 2006)

Shrinkage in the warp direction (8.2%) was greater than that in the weft direction (4.7%) because of higher yarn density in warp direction than weft direction. Fabric shrinkage is a consequence of increased fibre diameter and decreased fibre length and was characterized by dimensional change on warp and weft direction. During the aqueous pre-treatment, fabric shrinks because of the relaxation and release of yarn tensions incorporated during the spinning and weavings processes, a similar observation made by (Imran et al., 2015). Due to fabric shrinkage the number of yarns per unit area increases, resulting in an increase in fabric density.

Scouring imparts sufficient absorbance apart from enhancing the cleanliness of the material, bleaching further enhances the absorption and imparts whiteness to the material. For complete sinking (immersion test) of fabric, it required 108 seconds for pretreated fabric whereas gray fabric required 13 minutes. So low sinking time of the fabric indicates the improved absorbance resulted because of good pretreatment. The absorbance of the samples was also assessed through drop test (wetting time) and it was observed that there was a tremendous improvement in the wettability fabric. It is seen in table 4.1 that the fabric required 78 seconds for the water drop to disappear whereas for the gray fabrics it required more than 18 minutes. So rapid disappearance of water drop indicated the good pretreatment of fabric and improved absorbance as also observed by (Asaduzzaman et al., 2016).

Tensile strength is one of the most key indicators of degradation of mechanical properties of the fabric during pre-treatment. The warp and weft tensile strength of the cotton fabric under investigation before and after combined pretreatment was examined. The gray fabric strength in warp and weft was 304N and 136 N respectively and the pretreated fabric strength was 283 N and 124 N in warp and weft directions respectively. The results signify that there was deterioration in the warp (6.9%) and weft (8.8%) tensile strength which is attributed to oxidative degradation of cellulosic chains, a similar observation made by (Nur et al., 2016). When the rate of decomposition of hydrogen peroxide in the presence of sodium hydroxide is greater than that of its consumption in the bleaching action, the excess formation of perhydroxyl ions can lead to formation of oxycellulose, which is lower in strength than the native cellulose as also observed by (Imran et al., 2015).

4.2 Independent Effects of Sodium Hydroxide Concentration and Treatment Time on Fabric Properties

The mercerization process is the treatment of cotton goods with concentrated solutions of sodium hydroxide at a temperature of 15 to 20°C. For this study, the process was carried out at 19^0C. Cellulose undergoes chemical, physico-chemical and structural modifications on treatment with sodium hydroxide solution of mercerizing strength under an appropriate treatment time. This results in improvement of various physical and chemical properties of cotton.

4.2.1 Weight loss

The main effects plot for percent loss in fabric weight when cotton fabric was mercerized with varied conditions [NaOH] and treatment time. A second order regression models were formulated to predict the independent effects of contributing factors of sodium hydroxide concentration (x_1) and treatment time (x_2) on weight loss (Y_{wl}). Equation 4.1 and 4.2 give the fitted regression models

$$Y_{wl} = 0.40 + 0.57x_1 - 0.01x_1^2 \quad \text{Equation 4.1}$$

$$Y_{wl} = 7.04 + 0.05x_2 \quad \text{Equation 4.2}$$

The independent effects of sodium hydroxide concentration and treatment time onto weight loss was also represented graphically in Figure 4.1. The coefficient of determination (R-sq) was 89.6% and 71.2% for sodium hydroxide concentration and treatment time respectively with the P value of 0.002 and 0.01 which was less than 0.05 hence the models were statistically significant. The coefficient of determination (R-sq) of the model represents the percentage of the response (dependent) variable variation that is explained by the predictor variables which are included in the regression equation. The higher the R-sq, the better the regression equation fits data set. The value

of R-sq ranges between 0 to 100%. If R-sq is 100, the variance in the response could be explained by the predictor terms of the regression equation, and results predicted by the regression equation would always be equal to the experimental results, which if usually rare because there are always some errors associated with experimentation due to noise variables. High values of R-sq (89.6 and 71.2%) for Eqn. 4.1 and 4.2 respectively implies that 89.6% and 71.2% of variation in the fabric weight loss can be explained by the indepenent predictor terms included of [NaOH] and treatment time. Results of Figure 4.1 reveal that the fabric exhibits a relatively lower percent loss in its weight at lower concentartion of sodium hydroxide but higher percent loss at higher concentrations. Additionally, longer duration of treatment results in increments in loss in fabric weight. Treatment time of the process increases from 2 to 8 minutes with a gradual increase of weightloss (Figure 4.1). This is attributed to removal of residual wax and impurities not completely removed from the substrate during the pretreatment process.

From the regression Eqn. 4.1, linear effect of concentration substantially increased weight loss while square effect decreased the weight loss by 1%. From Figure 4.1, a rapid increase in the weight loss was observed only up to 20% concentration, thereafter a gradual increase occurred up-to 24% and above 24% concentration, a negligible decrease of weight loss results. This decrease is attributed to incraese in the viscosity of sodium hdroxide solution due to increased concentration,so the penetration of sodium hydroxide solution into the fabric and fibres becomes less rapid thus the less starch and wax can be removed from fabric. Therfore weight loss tends to decrease.

From the regression Eqn. 4.2, linear effect of treatment time gradually increased weight loss while square effect was insignificant. An increase in sodium hydroxide concentration increases the interaction of sodium ions with the constituent fibres that is the penetration of sodium hydroxide into the fibres becomes more significant thus the more starch and wax can be removed from fabric. Increase treatment time increases the interacting time of sodium hydroxide solution with the constituent fibres. Therefore weight loss increases up to the maximum where all the natural and added impurities have been removed and further increase in concentration results in a nearly constant change in weight loss. In other words, increasing loss in fabric weight as the treatment increases is due to the favorable effect of concentration on swellability of the starch-size and natural impurities, swellability of the sized cotton fabric degradation of the starch macromolecules to shorter ones and prolonging duration of treatment may enhance these effects.

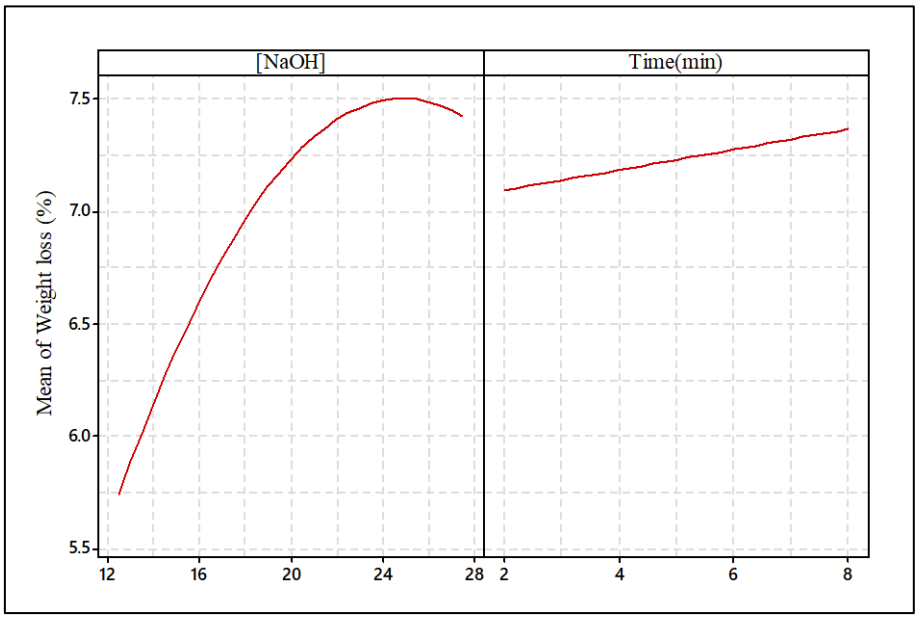

Figure 4.1: Main effects plots for Weight loss

4.2.2 Absorbance

Absorbance of a fabric can influence the uniformity and completeness of textile processing by the ability to take in water into fibre, yarn or fabric structure.

Mercerization imparts consistent and sufficient absorbency Absorbance was measured with respect to sinking and wetting times. The smaller the time the higher the absorbance. Two second order models were formulated to predict the effect of sodium hydroxide concentration on fabric sinking time. Equations 4.3 and 4.4 give the fitted regression models that described the relationship between sinking time (Y_{st}) and sodium hydroxide concentration (x_1) and between sinking time and treatment time (x_2). The R-sq was 85.9% and 70.3% with the P values of 0.003 and 0.007 respectively hence the model for sinking time was significant.

$$Y_{st} = 300.7 - 26.41x_1 + 0.60x_1^2 \qquad \text{Equation 4.3}$$

$$Y_{st} = 34.9 - 6.5x_2 + 0.72x_2^2 \qquad \text{Equation 4.4}$$

From the regression Eqn. 4.3, a rapid decrease in the sinking time from 60seconds to 15 seconds was observed from 13 to 20% concentration, thereafter a gradual decrease occurred up-to 21% with the minimum being 7.5 seconds registered at 22% and above 22% concentration, a gradual increase in sinking time results as shown in Figure 4.2. From Eqn. 4.4, treatment time variation had a small change in the snking time with the minimum sinking time being obtained at 4.5 minutes.

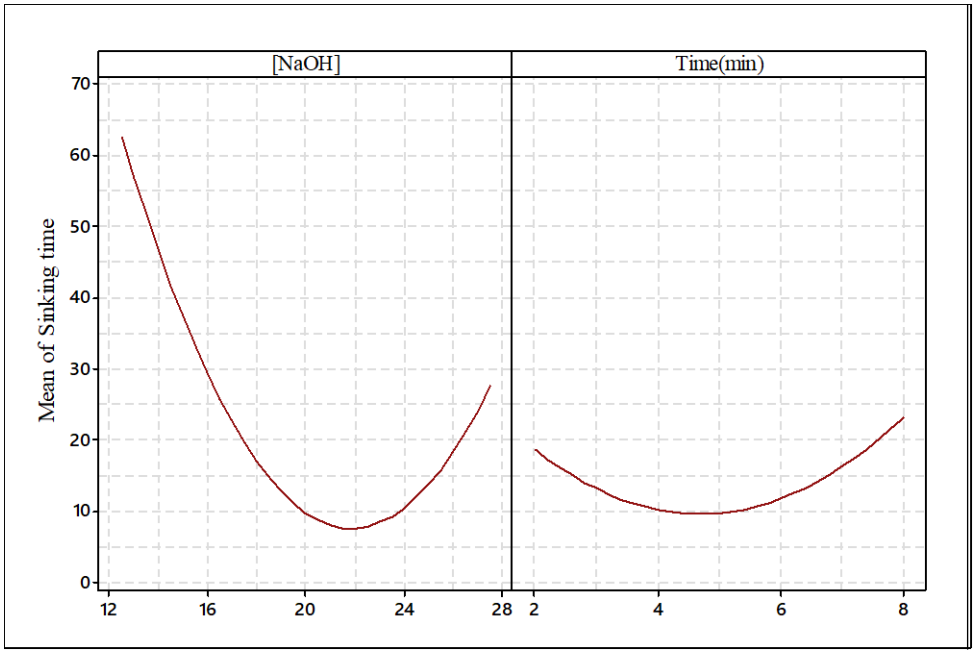

Figure 4.2: Main effects plots for sinking time

On the other hand, for wetting time, the R-sq was 76.6% and 72.6% with the P value of 0.001 and 0.004 for sodium hydroxide concentration and treatment time respectively. Equations 4.5 and 4.6 are the fitted regression models for sodium hydroxide concentration and treatment time

$$Y_{wt} = 126.3 - 11.05x_1 + 0.2524x_1^2 \qquad \text{Equation 4.5}$$

$$Y_{wt} = 21.70 - 5.53x_2 + 0.58x_2^2 \qquad \text{Equation 4.6}$$

From the regression Eqn. 4.5, a rapid decrease in the wetting time from 26 seconds to 15 seconds was observed from 13 to 20% concentration, thereafter a gradual decrease occurred up-to 22% with the minimum being 3 seconds registered at 22% and above 22% concentration, a gradual increase in wetting time results as illustrated in Figure 4.3. The treatment time lightly affected the wetting time with the minimum being 4 seconds at 4.8 minutes as illustrated in Figure 4.3

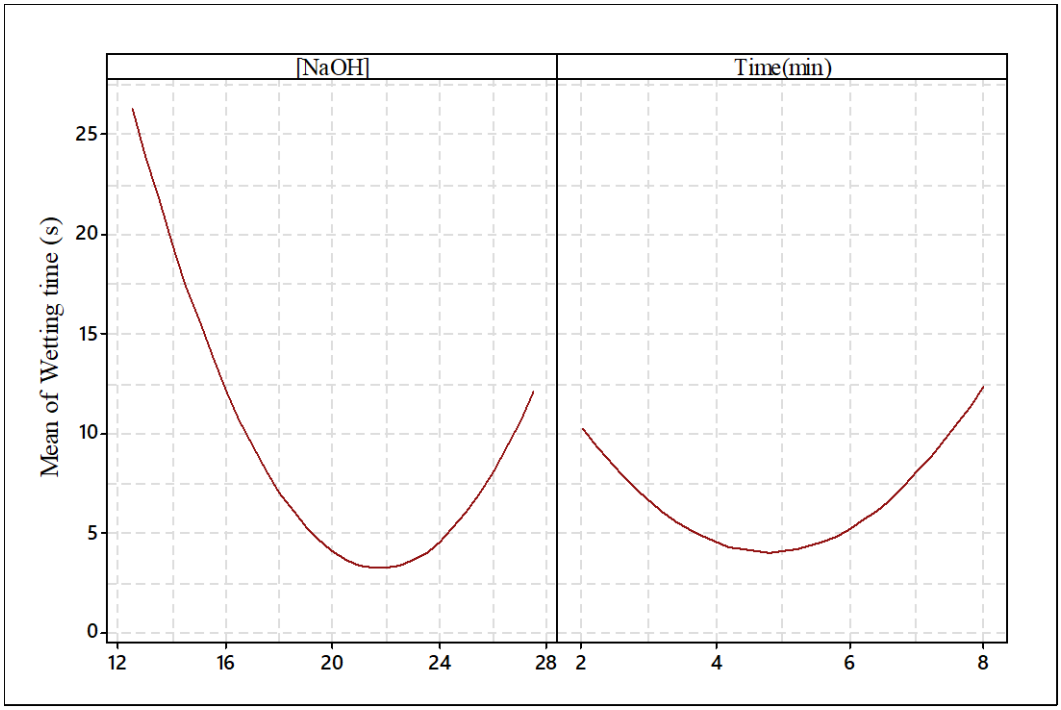

Figure 4.3: Main effects plots for wetting time

The absorbance of the fabrics increases probably due to additional removal of the residual starch, saponifiable oils, fats and waxes present in cotton through hydrolysis by strong NaOH concentration. The absorbance of slack mercerized samples at 20 to 24% was greater than that of unmercerized. This could be due to uncontrolled swelling of fibres in slack state. When cellulosic fibres are treated in sodium hydroxide solution, the cellulosic crystalline structure is altered and the percentage of less ordered or amorphous regions increases. Therefore, as the capacity of cellulose fibres for water absorption depends basically on the availability of free hydroxyl groups, it is generally considered that water absorption occurs almost entirely in the less ordered regions of cellulose. Therefore, these amorphous or non-crystalline regions are also termed as accessible regions of cellulose. It has been shown that crystalline areas of cellulose absorb only small amounts of water. The extent of less ordered regions in a fibre or fabric may be estimated by evaluating water absorption. Cellulose fibres with greater amorphous content absorb a greater quantity of water. The fibre becomes more

absorbent and this is attributed to the change of the cellulose crystal unit cell from cellulose I to cellulose II and an increase in openness of the amorphous area. Therefore, mercerized cotton fibre absorbs more water and consequently more dye than unmercerized cotton.

4.2.3 Shrinkage (swelling)

Mercerization is based on the swelling action of the concentrated aqueous solutions of sodium hydroxide on cotton. Fabric shrinkage is a consequence of increased fibre diameter and decreased fibre length and was characterized by dimensional change on warp and weft (fill) direction. This swelling action depends on the concentration of sodium hydroxide. As the concentration of sodium hydroxide increases, the extent of swelling passes through a maximum and then decreases. An increase in sodium hydroxide solution concentration determined the increase in shrinkage. The results indicated that increase in average percentage fabric shrinkage in warp direction was rapid up to 22% sodium hydroxide concentration, gradual rise in shrinkage observed between 22-24 % sodium hydroxide concentrations with a maximum warp shrinkage being 21%. Beyond 24% sodium hydroxide concentration, a negligible change in warp shrinkage was observed. A second order regression model was formulated to predict the effect of sodium hydroxide concentration and treatment time on warp shrinkage. Equations 4.7 and 4.8 give the fitted regression model that described the relationship between warp shrinkage (Y_{wps}) and sodium hydroxide concentration (x_1) and between warp shrinkage (Y_{wps}) and treatment time (x_2).

$$Y_{wps} = -48.22 + 5.57x_1 - 0.11x_1^2 \qquad \text{Equation 4.7}$$

$$Y_{wps} = 20.55 - 2.21x_2 + 0.25x_2^2 \qquad \text{Equation 4.8}$$

The effect of sodium hydroxide concentration and treatment time onto fabrics warp shrinkage was also represented graphically in Figure 4.4. The R-sq was 72.7% and 70.1% with P value of 0.000 and 0.03 for sodium hydroxide concentration and treatment time respectively.

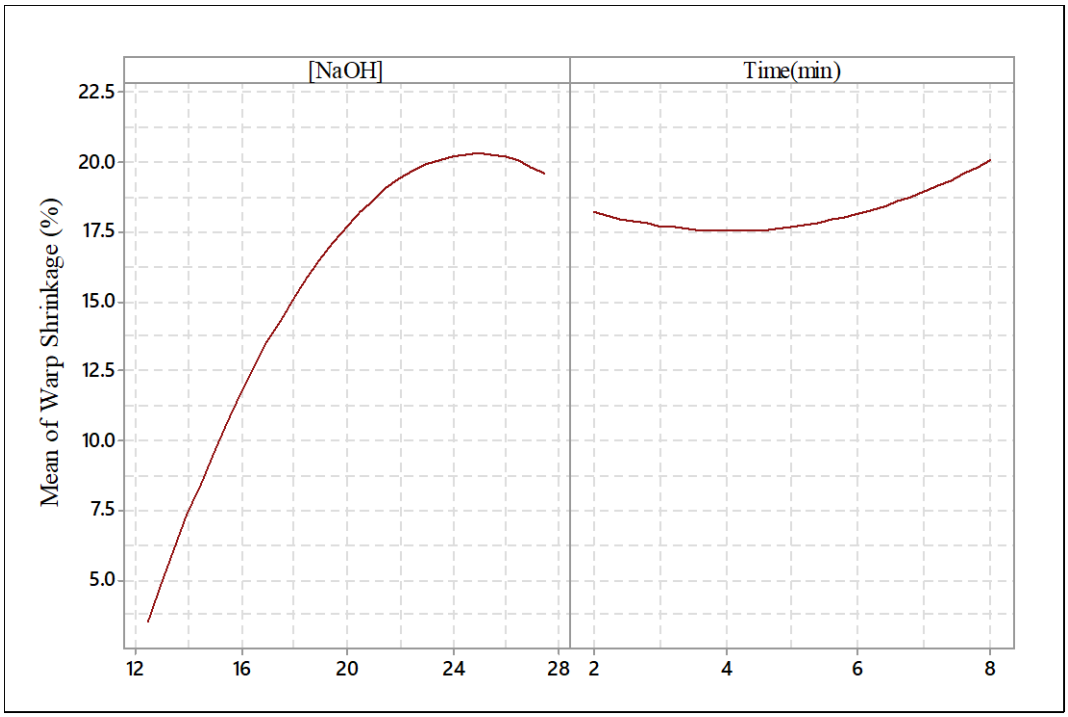

Figure 4.4: Main effects plots for warp shrinkage (%)

The results also indicated that increase in average percentage fabric shrinkage in the weft direction was rapid up to 25% sodium hydroxide concentration, gradual rise in shrinkage observed thereafter. A second order models were formulated to predict the effect of sodium hydroxide concentration and treatment time on warp shrinkage. Equations 4.9 and 4.10 give the fitted regression model that described the relationship between weft shrinkage (Y_{wts}) and sodium hydroxide concentration (x_1), and weft shrinkage (Y_{wts}) and treatment time (x_2).

$$Y_{wt} = -30.40 + 3.40x_1 - 0.06x_1^2 \qquad \text{Equation 4.9}$$

$$Y_{wt} = 20.46 - 3.9x_2 + 0.42x_2^2 \qquad \text{Equation 4.10}$$

The effect of sodium hydroxide concentration and treatment time onto fabric weft shrinkage was a represented graphically in Figure 4.5. The R-sq was 80.9% and 71.2% with P value of 0.006 and 0.02 for sodium hydroxide concentration and treatment time respectively.

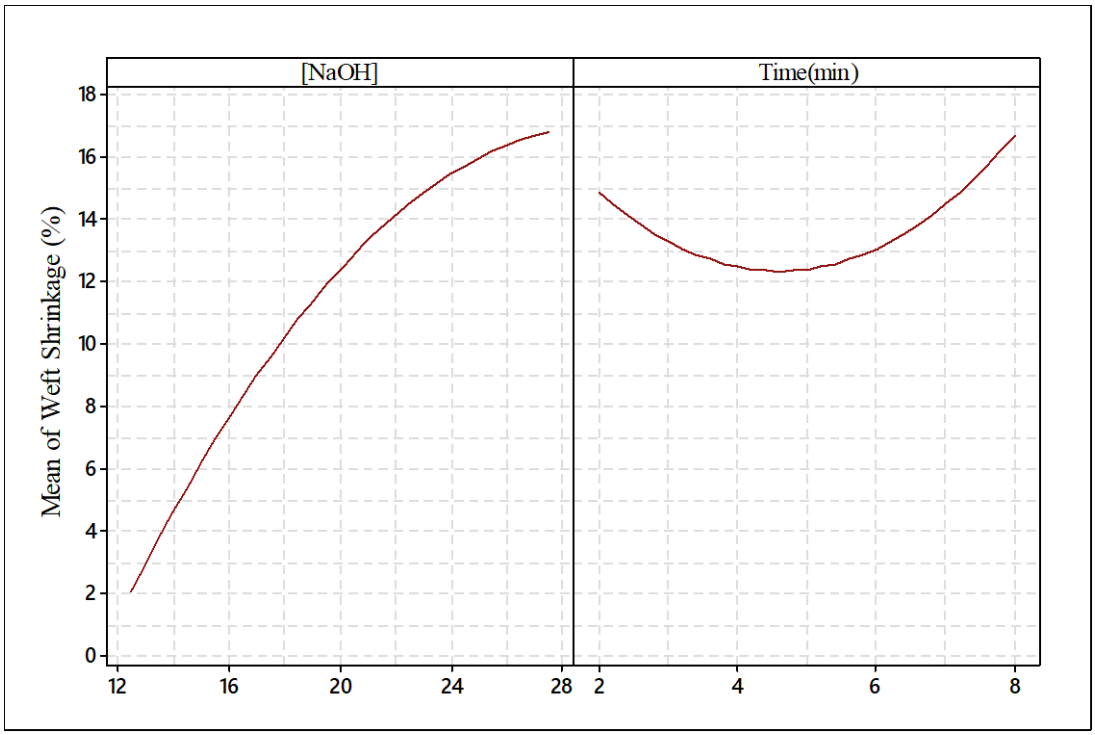

Figure 4.5: Main effects plots for weft shrinkage (%)

During mercerization treatment, fabric shrinks because of the relaxation and release of yarn tensions incorporated during the spinning and weavings processes. Increase in sodium hydroxide concentration increases shrinkage as illustrated in Figures 4.4 and 4.5. The increase in warp direction was higher as compared to that in weft direction. This is associated with the higher thread density in warp as compared to weft direction. The shrinkage is attributed to the extent of conversion of cellulose I to cellulose II thereby indicating the effectiveness of the mercerization. Sodium hydroxide solution contains dissolved sodium hydroxide as sodium ions and hydroxide ions. When cotton fabric is entered into the solution, sodium ions and hydroxide ions can easily diffuse

into the amorphous region of the fibre and get hydrogen bonded with the accessible hydroxyl groups of cellulose. Because of the presence of these ions in the amorphous region, the chain molecules try to vibrate with longer amplitude, when some of the hydrogen bonds and other weaker bonds between the adjacent chain molecules on the fringe of the crystalline region are ruptured and the unbound molecular fragments vibrate with still longer amplitude and further sodium hydroxide molecules diffuse and get bound to the liberated hydroxyl groups. In other word, cellulose chain molecules acquire greater degree of movement. As a result, the fibre swells laterally and shrinks longitudinally.

4.2.4 Tensile strength

Tensile strength is one of the most important indicators of improvement in mechanical properties of the fabric during mercerization. The warp and weft tensile strength of the cotton fabric under investigation after the varied mercerizing conditions were examined. Results related to this set of examinations are given in Equations 4.11, 4.12, 4.13 and 4.14 and Figures 4.6 and 4.7. Generally, as the sodium hydroxide concentration increases, the tensile strength also increases, reaches a maximum value and then decreases with further increase in sodium concentration. The tensile strength increases in both warp and weft direction with the increase of concentration of NaOH. The increase reached a maximum value of 405N at concentration of 22-23% in warp direction and a maximum value of 185N at 22-24% in weft direction. Two second regression models were formulated to predict the effect of sodium hydroxide concentration on warp and weft tensile strength. Equations 4.11 and 4.12 give the fitted regression model that described the relationship between warp tensile strength (Y_{wpt}) and sodium hydroxide concentration (x_1) and between warp tensile strength (Y_{wpt}) and treatment time (x_2)

$$Y_{wpt} = 25.68 + 33.94x_1 - 0.75x_1^2$$ Equation 4.11

$$Y_{wpt} = 326.50 + 27.30x_2 - 2.64x_2^2$$ Equation 4.12

The effect of sodium hydroxide concentration and treatment time on fabric warp tensile strength was represented graphically in Figure 4.6. The R-sq was 75.7% and 71.6% with P value of 0.000 and 0.002 for sodium hydroxide concentration and treatment time.

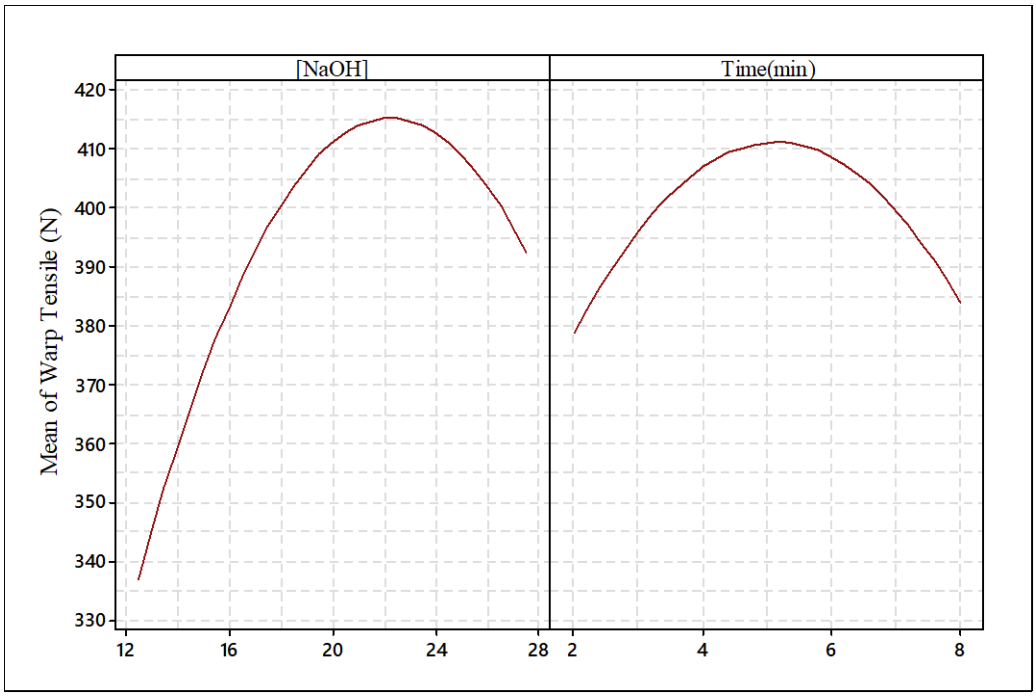

Figure 4.6: Main effect plots for warp tensile strength

On the other hand, Equations 4.13 and 4.14 give the fitted regression model that described the relationship between weft tensile strength (Y_{wtt}) and sodium hydroxide concentration (x_1) weft tensile strength (Y_{wtt}) and treatment time (x_2).

$$Y_{wtt} = -44.83 + 20.20x_1 - 0.44x_1^2$$ Equation 4.13

$$Y_{wtt} = 133.60 + 16.5x_2 - 1.5x_2^2$$ Equation 4.14

The effect of sodium hydroxide concentration and treatment time on fabric weft tensile strength was represented graphically in Figure 4.7. The R-sq was 74.5% and 72.7%

with P value of 0.002 and 0.03 for sodium hydroxide concentration and treatment time respectively.

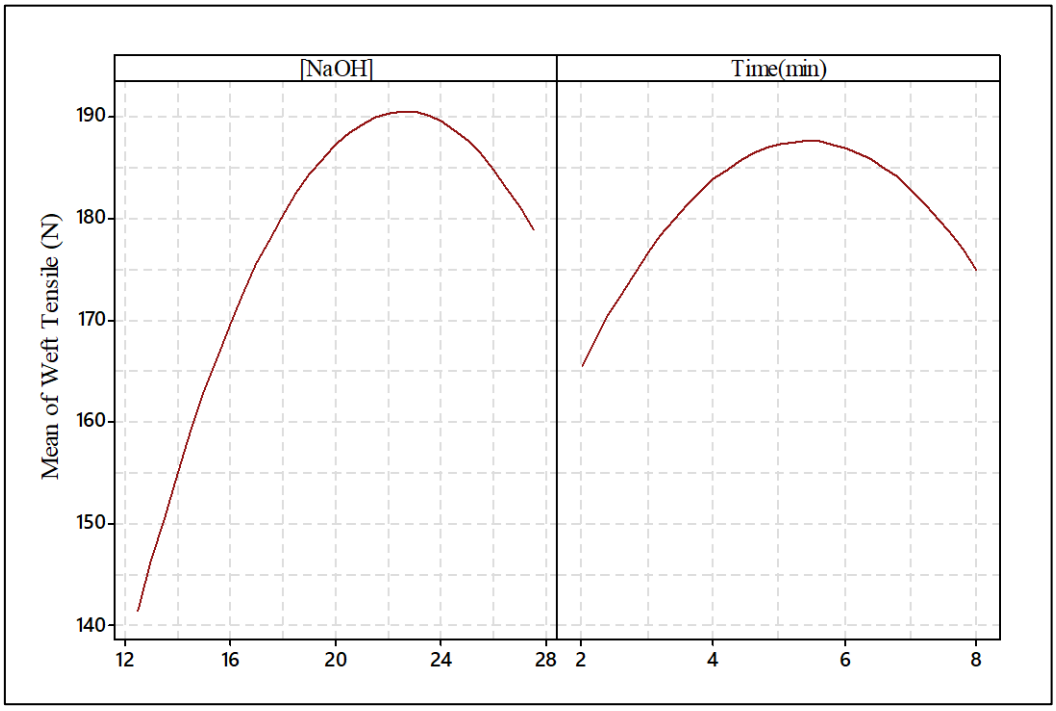

Figure 4.7: Main effects plots for of weft tensile strength

The results signify that lower warp and weft tensile strengths were brought about at lower concentrations of sodium hydroxide and shorter treatment time as well as at higher concentrations and prolonged duration of treatment. Lower concentration may not be sufficient to align the cellulosic chains which is ought to increase crystallinity responsible for increased tensile strength. Shorter duration of treatments further emphasizes the fact of lower tensile strength since shorter time of interaction of the solution with the cellulosic chains is permitted. On the other hand, lower tensile strength results at higher concentrations and prolonged duration of treatment due to oxidative degradation. This brought about by very high pH of the solution which is sought to induce oxidative degradation reactions upon the cellulosic chains. Additionally, high viscosity of sodium hydroxide solution at high concentration leads to less penetration of the solution into the cellulose chains. It is understandable that oxidation degradation

reactions may intensify by increasing time thus at prolonged duration of treatment, lower tensile strength results. The effects have been more pronounced in warp direction than in weft direction as shown in Fig. 4.6 and 4.7. This is attributed to higher density of ends than picks in the fabric. Due to fabric shrinkage, the number of yarns per unit area increases, resulting in increase in fabric density and the thus fabric strength. As the concentration of NaOH increases, more swelling takes place which results molecular alignment in more regular way leading to an increase in hydrogen bond formation (Bhatti et al., 2012). This is due to two different conformations of the hydroxymethyl group that causes variations in intra-molecular hydrogen bonding Furthermore, the increase in tensile strength can also be attributed to a strengthening of the weak points along the fibre for effectiveness weak points are consolidated. Other important factors of strengthening are the crystalline length, crystal size and degree of crystallinity as well as the removal of fractions of cellulose of very low degree of polymerization (Hymes, 2005). During mercerization of cotton fibres, swelling occurs to a much greater extent and its molecular structure become decrystallized and the canals within the cellulosic structure become more uniform. Cotton fibres align themselves in a regular way leading to an increase in the hydrogen bond formation. The major reason can be an alleviation of internal stresses and the deconvoluting of the fibres in the fabric during swelling process (Patil et al., 2019). Tensile strength increases with the increase in swelling. Mercerization increases cohesion between individual cotton hairs and this closer embedding of the hair in the yarn not only increase the strength but makes it more uniform in strength. Because of the longitudinal shrinkage and lateral swelling of yarn, fabric shrunk and the yarn appeared closer together with an increased thickness, polymer chain minimizes the weak link in the fibre which helps to increase strength. Therefore, tensile strength increases with the sodium hydroxide concentration.

4.2.5 Dye exhaustion

In this study it was noted that sodium hydroxide concentration directly affected dye exhaustion of the dye molecules into the cotton fabric in such a way that its increment beyond 24% NaOH led to a reduction in dye exhaustion. A regression model was formulated to predict the effect of sodium hydroxide concentration and treatment time on dye exhaustion. Equations 4.15 and 4.16 give the fitted regression model that described the relationship between dye exhaustion (Y_{DE}) and sodium hydroxide concentration (x_1) and between dye exhaustion (Y_{DE}) and treatment time (x_2)

$$Y_{DE} = 9.6 + 5.20x_1 - 0.104x_1^2 \qquad \text{Equation 4.15}$$

$$Y_{DE} = 68.25 + 0.12x_2 \qquad \text{Equation 4.16}$$

The effect of sodium hydroxide concentration and treatment time on dye exhaustion was represented graphically in Figure 4.8. The R-sq was 74.1% and 72.4% with P value of 0.001 and 0.04 for sodium hydroxide concentration and treatment time respectively. The square effect of treatment time was statistically insignificant.

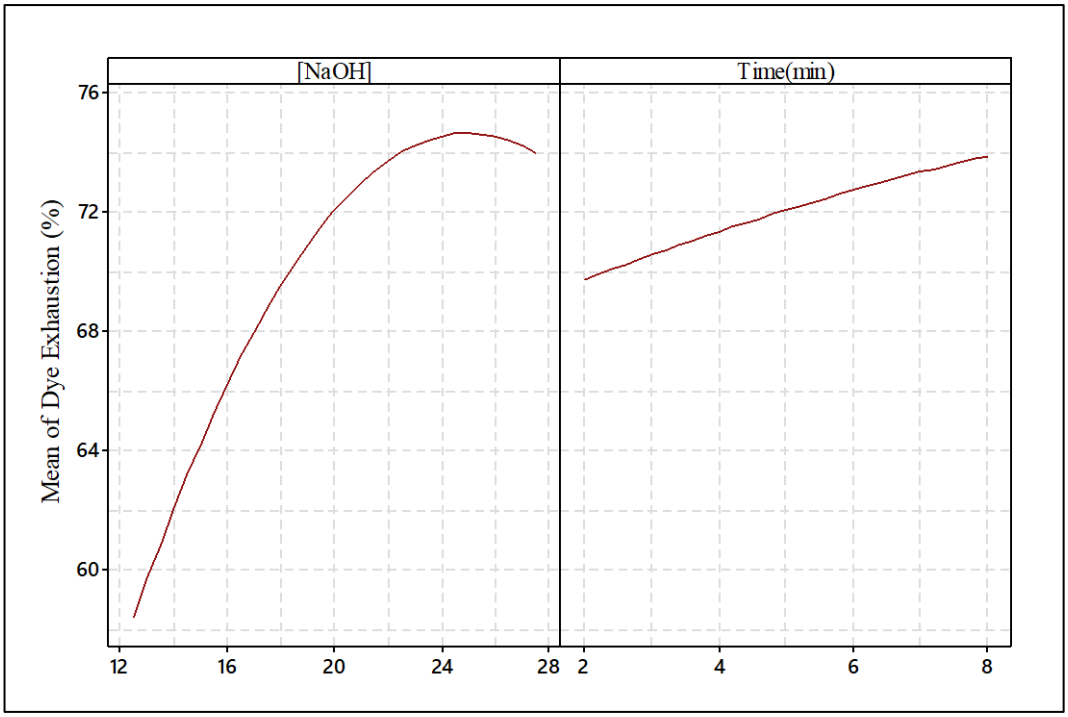

Figure 4.8: Main effect plots for dye exhaustion

During mercerization with sodium hydroxide solution cotton fibres swell so that the secondary wall thickness is increased. The swelling process increases the accessibility of cotton fibres to dyestuff ions, resulting in substantial increase in the dye uptake and hence the exhaustion of the dye bath increases. The fibre surface appearance and the internal structure of the fibre are modified. This improves the uniformity of fabric appearance after dyeing, and there is an apparent increase in colour depth after mercerization. Due to this increased colour depth, (Holme, 2016) found out that cost savings of up to 30% on pale colours (e.g. 1–2% o.w.f) and even 50–70% on heavy depths when using some reactive dyes. Mercerized cotton shows increased rate of dyeing and decreased the irregularities. The increased depth of shade of mercerized cotton has been attributed due to increased amorphous part of the fibre. However, cotton fibres with little or no secondary wall are not improved after mercerization.

4.3 Combined Effect of Sodium Hydroxide Concentration and Treatment Time on Fabric Properties

For all interactions, the three main factor levels for time were considered and these are 3(-1), 5(0) and 7(+1) minutes. They were considered at all design levels of sodium hydroxide concentration.

4.3.1 Weight loss

The numerical terms obtained were statistically fitted into to generate regression Eqn.4.17 that modeled the relationship between weight loss (Y_{wl}) and sodium hydroxide (x_1) and treatment time (x_2). The square effect of treatment time was insignificant. From Eqn. 4.17, it can be noted that the combination of time and sodium hydroxide concentration reduced the weight loss by 2% .

$$Y_{wl} = -1.32 + 0.65x_1 + 0.34x_2 - 0.01x_1^2 - 0.02x_1x_2 \qquad \text{Equation 4.17}$$

The interaction effect of sodium hydroxide concentration and treatment time on weight loss was represented graphically in Figure 4.9. The R-sq was 91.25% with P value of 0.001 hence the model was statistically significant. The combined effect of [NaOH] and treatment time showed that as the [NaOH] and the treatment time are increased, there was an increase in the mean weight loss as shown in Figure 4.9.

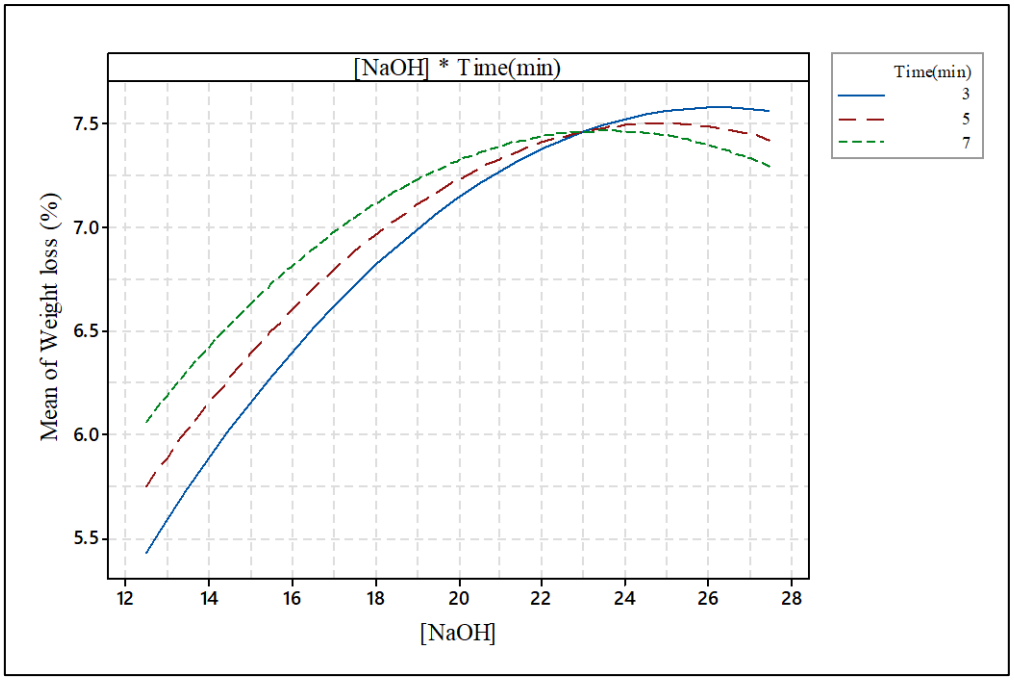

Figure 4.1: Interaction Plot for Weight loss (%)

4.3.2 Absorbance

A second order regression Eqn.4.18 was generated and modeled the relationship between sinking time (Y_{st}) , sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.18, it can be noted that the combination of time and sodium hydroxide concentration reduced the sinking time by 3.8%.

$$Y_{st} = 330.8 - 27.26x_1 - 10.83x_2 + 0.63x_1^2 + 1.236x_2^2 - 0.038x_1x_2 \quad \text{Equation 4.18}$$

The interaction effect of sodium hydroxide concentration and treatment time on sinking time was represented graphically in Figure 4.10. The R-sq was 85.33% with P value of 0.002 hence the model was statistically significant.

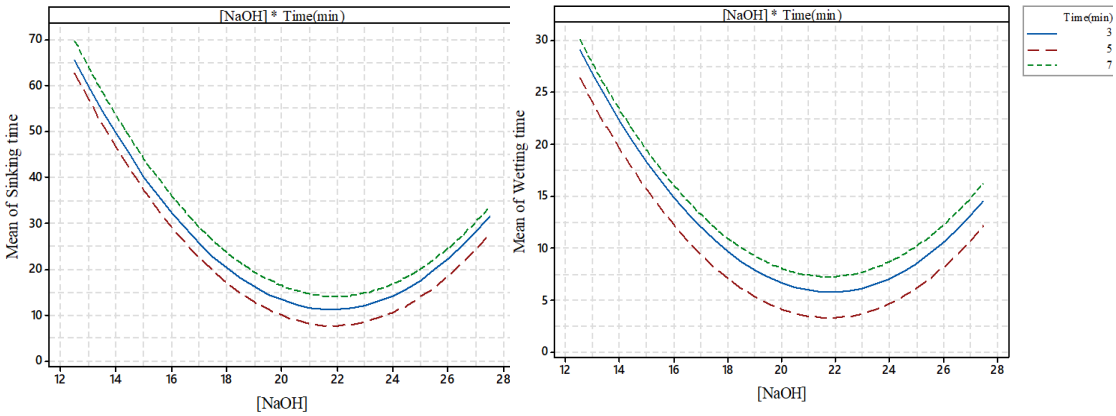

Figure 4.2: Interaction plots for sinking and wetting time

A second order regression Eqn.4.19 was generated and modeled the relationship between wetting time (Y_{wt}) , sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.19, it can be noted that the combination of time and sodium hydroxide concentration reduced the wetting time by 1%.

$$Y_{wt} = 150.5 - 11.78x_1 - 7.98x_2 + 0.2693x_1^2 + 0.81x_2^2 - 0.01x_1x_2 \quad \text{Equation 4.19}$$

The interaction effect of sodium hydroxide concentration and treatment time on wetting time was represented graphically in Figure 4.10. The R-sq was 89.37% with P value of 0.002 hence the model was statistically significant.

4.3.3 Fabric shrinkage (fibre swelling)

A second order regression Eqn.4.20 was generated and modeled the relationship between warp shrinkage (Y_{wps}), sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.20, it can be noted that the combination of time and sodium hydroxide concentration reduced the warp shrinkage by 13.7%.

$$Y_{wps} = -58.54 + 6.12x_1 + 1.43x_2 - 0.20x_1^2 + 0.16x_2^2 - 0.137x_1x_2 \quad \text{Equation 4.20}$$

The interaction effect of sodium hydroxide concentration and treatment time on warp shrinkage was represented graphically in Figure 4.11. The R-sq was 90.58% with P value of 0.0007 hence the model was statistically significant.

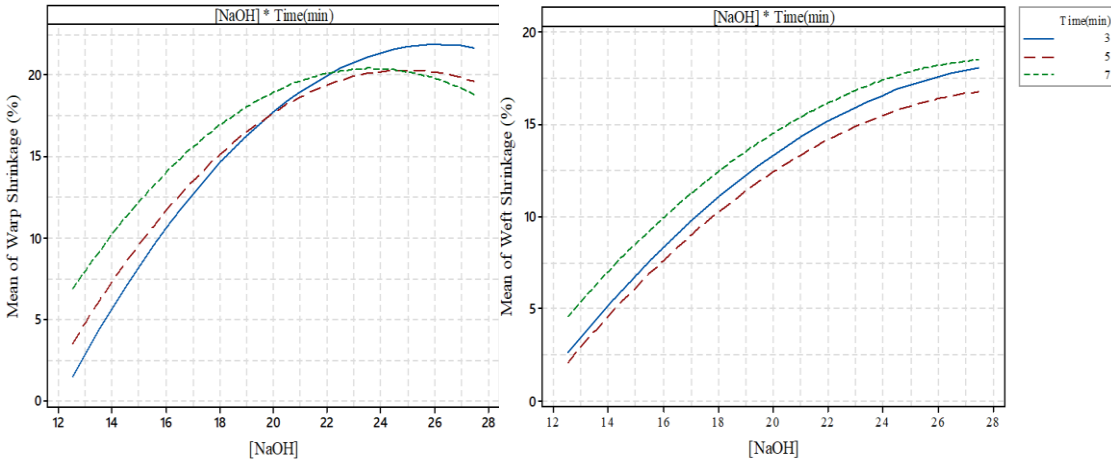

Figure 4.11: Interaction plots for warp and weft shrinkage

A second order regression Eqn.4.21 was generated and modeled the relationship between weft shrinkage (Y_{wts}), sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.21, it can be noted that the combination of time and sodium hydroxide concentration reduced the weft shrinkage by 2.5%.

$$Y_{wps} = -22.9 + 3.21x_1 - 2.96x_2 - 0.05x_1^2 + 0.38x_2^2 - 0.025x_1x_2 \qquad \text{Equation 4.21}$$

The interaction effect of sodium hydroxide concentration and treatment time on weft shrinkage was represented graphically in Figure 4.11. The R-sq was 88.26% with P value of 0.0003 hence the model was statistically significant.

4.3.4 Tensile strength

A second order regression Eqn.4.22 was generated which modeled the relationship between weft tensile strength (Y_{wtt}), sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.22, it can be noted that the combination of time and sodium hydroxide concentration reduced the weft tensile strength by 28.7%.

$$Y_{wtt} = -139.2 + 23.21x_1 + 26.22x_2 - 0.48x_1^2 - 1.89x_2^2 - 0.287x_1 \quad \text{Equation 4.22}$$

The interaction effect of sodium hydroxide concentration and treatment time on weft tensile strength was represented graphically in Figure 4.12. The R-sq was 87.54% with P value of 0.0001 hence the model was statistically significant.

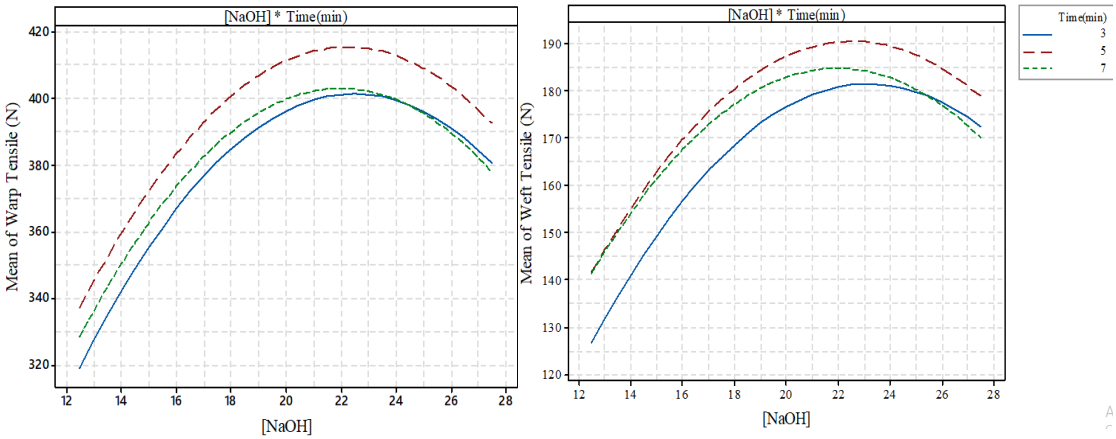

Figure 4.12: Interaction plots for warp and weft tensile strength

A second order regression Eqn.4.23 was generated which modeled the relationship between warp tensile strength (Y_{wpt}), sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.23, it can be noted that the combination of time and sodium hydroxide concentration reduced the warp tensile strength by 20.0%.

$$Y_{wpt} = -99.9 + 37.70x_1 + 38.00x_2 - 0.83x_1^2 - 3.31x_2^2 - 0.200x_1x_2 \quad \text{Equation 4.23}$$

The interaction effect of sodium hydroxide concentration and treatment time on warp tensile strength was represented graphically in Figure 4.12. The R-sq was 87.63% with P value of 0.004 hence the model was statistically significant.

4.3.5 Dye exhaustion

A second order regression Eqn.4.24 was generated which modeled the relationship between dye exhaustion (Y_{DE}), sodium hydroxide (x_1) and treatment time (x_2). From Eqn. 4.24, it can be noted that the combination of time and sodium hydroxide

concentration reduced the dye exhaustion strength by 15.0%. The regression analysis showed that the square effect of time had no significant effect thus it is not captured in the model.

$$Y_{DE} = -9.7 + 5.97x_1 + 3.97x_2 - 0.10x_1^2 - 0.15x_1x_2 \qquad \text{Equation 4.24}$$

The interaction effect of sodium hydroxide concentration and treatment time on dye exhaustion was represented graphically in Figure 4.16. The R-sq was 76.72% with P value of 0.001 hence the model was statistically significant.

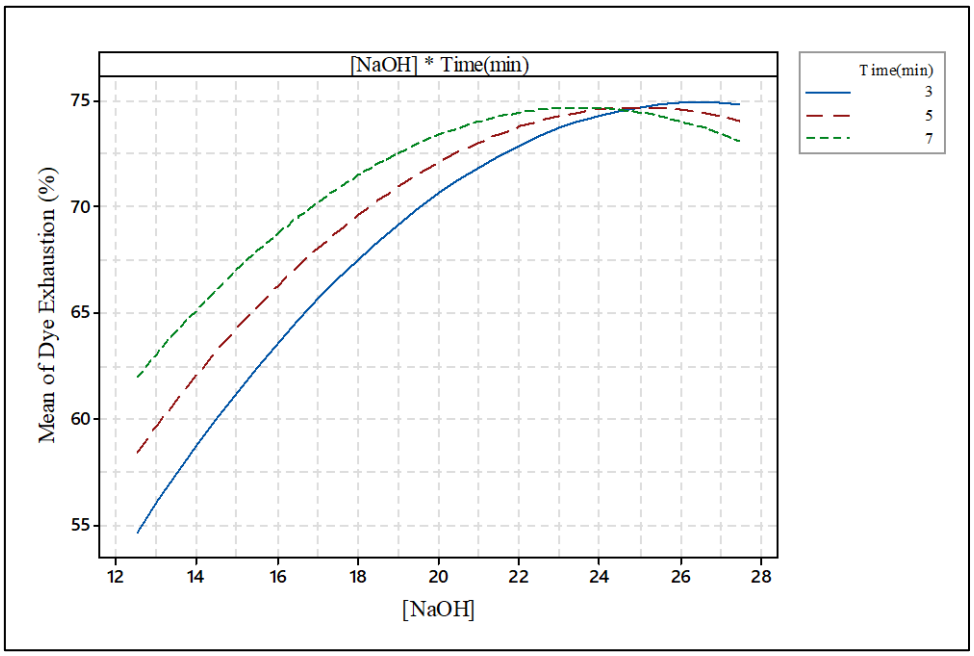

Figure 4.13: Interaction plots for dye exhaustion.

The interaction effect as shown in figure 4.13 illustrates that 24.5% [NaOH] at a minimal time of 3 minutes gave an improved dye exhaustion of 74.2% as compared to the 34% of the unmercerized fabric. Mercerization process not only resulted in increased accessibility of fibre to dye molecules but also introduced disorder in the crystallites. The highly ordered structure of cotton was assumed to play an important role in the dyeability changes occurring with improved fabric absorbance. A similar observation was also reported by (Haga & Takagishi, 2001).

The ANOVA test was carried out as shown in the Table 4.2. The P values for the estimated coefficients, curvilinear and interaction effects were less than 0.05 and were therefore significant in the model. From the table it is noticed that [NaOH] and treatment time have a significant influence on dye exhaustion of the woven fabrics at 0.05 significance level. The factor that has the highest F value is determined as the most effective, influencing process parameter performance. Consequently, [NaOH] with the F-Value of 34.82 has the highest contribution to the model.

Table 4.1: ANOVA for dye exhaustion

Source	DF	Adj SS	Adj MS	F-Value	P-Value	
Model	5	577.549	115.510	9.29	0.001	Significant
Linear	2	463.853	231.926	18.64	0.000	Significant
[NaOH]	1	433.210	433.210	34.82	0.000	Significant
Time(min)	1	30.642	30.642	2.46	0.019	Significant
Square	2	95.696	47.848	3.85	0.002	Significant
[NaOH]*[NaOH]	1	94.959	94.959	7.63	0.001	Significant
Time(min)*Time(min)	1	0.176	0.176	0.01	0.906	Not significant
2-Way interaction	1	18.000	18.000	1.45	0.007	Significant
[NaOH]*Time(min)	1	18.000	18.000	1.45	0.007	Significant
Error	20	248.797	12.440			
Lack-of-Fit	3	5.897	1.966	1.11	0.372	Not significant
Pure Error	17	242.900	14.288			
Total	25	826.346				

Analysis of variance (ANOVA) was used to determine the adequacy of the model as seen in Table 4.2. Using F-value and P-value, the significance of the model was determined by evaluating the F-value expressed as the square to residual error ratio of the mean model. The model F-value is the ratio of mean square for the individual term to the mean square for the residual. If the determined F-value is found to be greater than that of the tabulated F-value, then the model is a strong experimental data predictor. The F-value obtained in the present study was 9.29 (Table 3.2) which suggested the fitness of the response surface model. More so, the significance of each of the model

terms was evaluated using the probability of error value (P values). In Table 3.2, the p-values of 0.0001 was less than the significance level of 0.050 thus the model best suits the dataset.

4.3.6 Colour fastness

Colour fastness of any fabric is of considerable importance to the consumer as it directly affects the serviceability of the fabric. The best fastness rates for each fastness test were recorded with 20% concentration of sodium hydroxide. It was good to excellent for dry rubbing fastness (4/5-5), good to very good (4-4/5) for wet rubbing fastness good to very good (4-4/5) for wash fastness and very good to excellent (6-7) for light fastness. It can be noted from Table 4.3 that the wash fastness rates for both colour change (WCC) and colour staining (WCS) of the fabric were relatively good ranging from 3 to 4/5. Dry rubbing fastness to colour change (DRCC) was good as most fabrics indicated acceptable rates of 4 (good) to 5 (excellent). In this particular study, fabrics treated with 20% sodium hydroxide presented the best results (4 to 5) followed by 15%, 25 % and 27% (3/4 to 4) and lastly 15% with 3. Dry rubbing fastness to colour staining (DRCS) was also good as most fabrics indicated acceptable rates of 4 to 5. Wet rubbing fastness to colour change (WRCC) demonstrated in Table 4.3 was good as most fabrics indicated acceptable rates of 3 (fair) to 4/5 (very good). Wet rubbing fastness to colour staining (WRCS) was good as most fabrics indicated acceptable rates of 3 to 4. In this particular, fabrics treated with 20% sodium hydroxide presented the best results (3/4 to 4) followed by 15%, 25 % and 27% (3 to 3/4) and lastly 15% with 3. Light colour fastness (LCF) for all the samples ranged from appreciable fading (4) to very slight fading (7). Fabrics treated with above 20% sodium hydroxide presented the best results (6 to 7) followed by 15% (5) and lastly by 13% with 4. In contrast, un-mercerized fabric (UM) presented a poor fastness of 2/3 for colour staining and colour change for both

wash and wet rubbing fastness, fair fastness of 3 for colour staining and colour change for dry rubbing and fair/significant fading (3) for light fastness as shown in Table 4.3 and Figure 4.17. The good colour fastness of mercerized fabric samples implies that the dye had substantivity and affinity for the fabric which enable the auxochromes to properly diffuse and desorb into the fabric. The highest staining of cotton fabrics is because during washing, the unfixed dyes were remove thus causing a lot of staining.

Table 4.2: Effect of mercerization on colour fastness

[NaOH] (%) w/v	Time (min)	Colour fastness						
		Wash fastness to colour change	Wash fastness to colour staining	Dry rub fastness to colour change	Dry rub fastness to colour staining	Wet rub fastness to colour change	Wet rub fastness to colour staining	Light colour fastness
13	5	3/4	3	3	3	3	2/3	4
15	3	4	3/4	3/4	3/4	3	2/3	4
	7	4/5	4	4	3	3/4	3	5
20	2	4	4	4	4	4	3/4	6
	5	4/5	4	4	4	3/4	4	7
	5	4	4	4/5	5	4	3/4	7
	5	4	3/4	4/5	4/5	4	4	6
	5	4	3/4	4	5	4	3/4	6
	5	4/5	3/4	5	4	4	3/4	7
	8	4/5	4	4/5	4	3/4	4	7
25	3	4/5	4	4	3	3	2/3	7
	7	4	3/4	4	3	3/4	3	6
27	5	4	3/4	3/4	4	3/4	3	6
UM		2/3	2/3	3	3	2/3	2/3	3

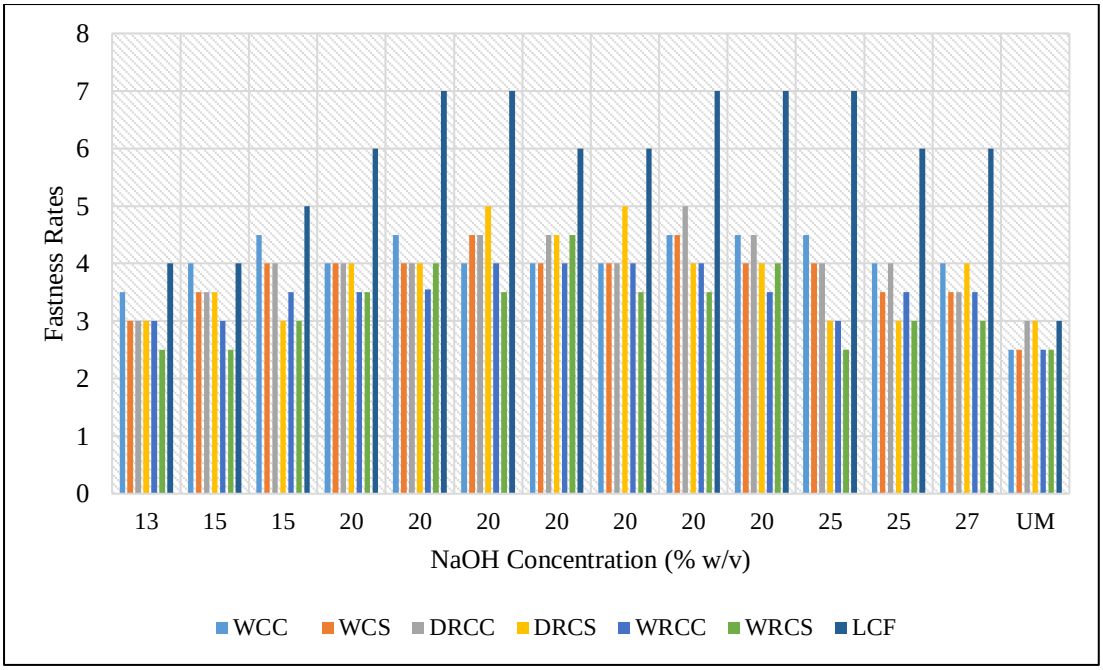

Figure 4.14: Illustration of fastness rates against [NaOH]

4.4 Optimization of Mercerizing Conditions

For the overview of effects of independent variables, 3D response surfaces and 2D contour plots are the graphical representations, which were constructed by taking two different variables in different combination at a time. In RSM, 3D response surfaces and 2D contour plots are helpful in understanding the relation of a response with the two selected factor levels. Three statistical tools were used in the optimization process. These are response surface plots, contour plots and response optimizer which generated plots from which the optimal response values were derived. One response was being optimized at a time using surface and contour plots separately. The surface plots suggest that the linear and interaction terms plus the quadratic term explain just about all of the variability in the responses (Y). The need for a quadratic term in each factor was mandatory as dictated from the fold in the surface (Figure 4.18) on each factor. Thereafter, all responses were analyzed using response optimizer to obtain the overall optimum conditions.

The fabric properties (absorbance, dye exhaustion, shrinkage, tensile strength and weight loss and colour fastness) were taken as the responses of the system while the two mercerizing process parameters (sodium hydroxide concentration and treatment time) were taken as input independent variables. The effects of sodium hydroxide concentration (X_1) and treatment time (X_2) on absorbance (wetting time (Y_{wt}) and sinking time (Y_{st})) dye exhaustion (Y_{DE}), shrinkage (warp (Y_{wps}) and weft e (Y_{wts})), tensile strength (warp (Y_{wpt}) and weft (Y_{wtt})), weight loss (Y_W) and colour fastness were determined. These factors were monitored for the optimization of the fabric properties. The result from the study indicated that all the regression models were statistically significant with a P value of <0.05.

The optimal response values for as outputs of response surface plots and response contour plots are illustrated in 4.18 and 4.19 respectively. The faint (light) green region in surface plots represents region of optimum points as illustrated in Figure 4.18. The region of darkest green for contour plots (Figure 4.19) also represents region of optimum points if the response goal is to maximize however, darkest blue region represents optimum points if the response goal is to minimize.

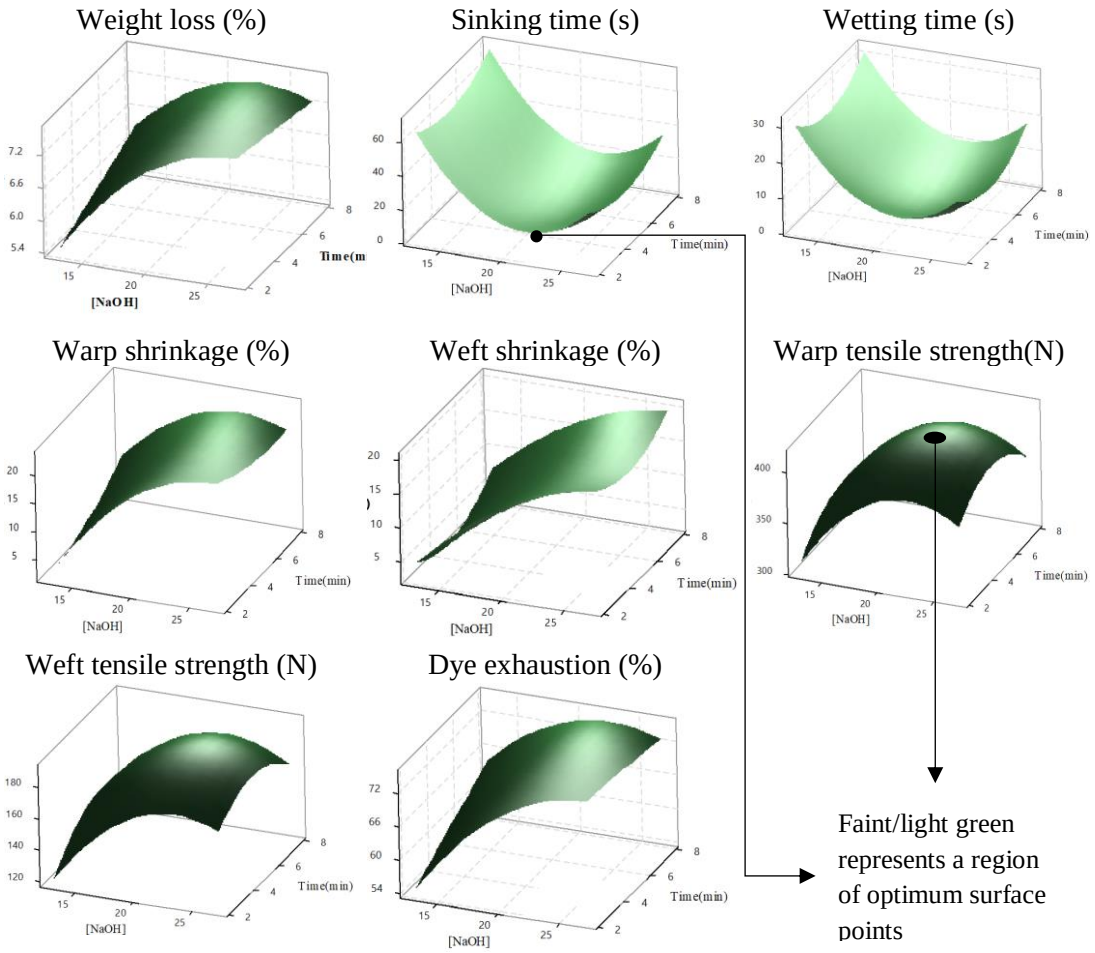

Figure 4.15: Response surface plots

From the surface and contour plots, weight loss was statistically found to be 7.5% being obtained by 23.4% [NaOH] and treatment time of 3.88minutes. The optimal response values for sinking time was statistically found to be 7.6 seconds being obtained by 22.1% [NaOH] and treatment time of 4.2 minutes, wetting time was statistically found to be 3.4 seconds being at 23.4% [NaOH] and treatment time of 5 minutes, weft shrinkage of 15.7% at 24.6% [NaOH] and treatment time of 5.1 minutes, warp tensile strength of 410.3N at 22.5% [NaOH] and treatment time of 5 minutes, weft tensile strength of 185.4N being at 23.1% [NaOH] and treatment time of 5.2 minutes and dye exhaustion of 75.3% at 24.7% [NaOH] and treatment time of 5 minutes.

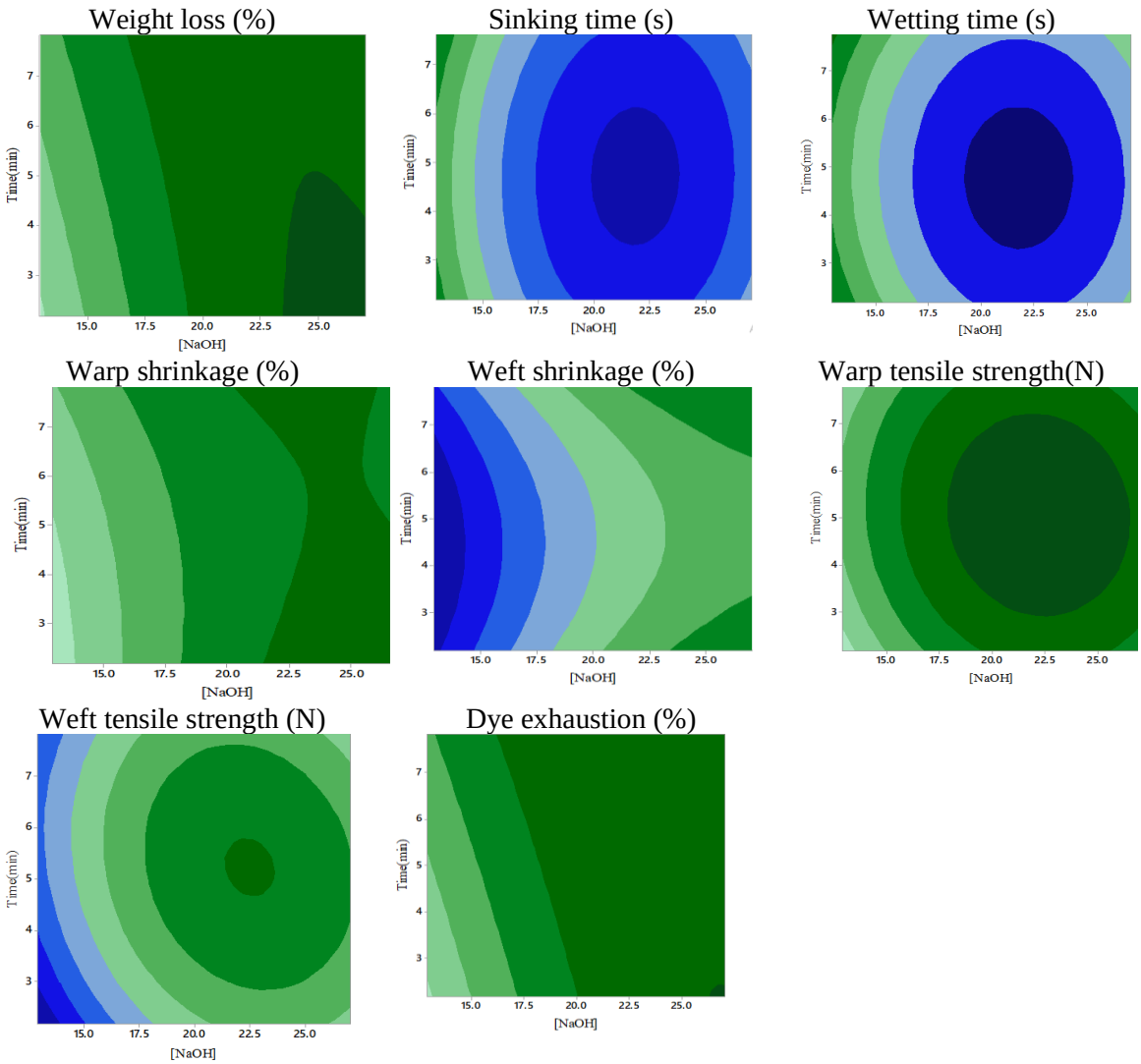

Figure 4.16: Contour plots for the responses

The optimum conditions as output by the response surface optimizer were 23.36% sodium hydroxide and 4.97minutes treatment time with a composite desirability of 0.89817. The optimal values of the responses as displayed by response surface optimizer are shown in the Table 4.4.

Table 4.1: Optimized response values

Response		Goal	Optimized value
Absorbance (seconds)	Wetting time	Minimize	3.9
	Sinking time	Minimize	5.1
Dye Exhaustion (%)		Maximize	74.4
Shrinkage (%)	Warp	Maximize	20.1
	Weft	Maximize	15.1
Tensile strength (N)	Warp	Maximize	414.3
	Weft	Maximize	190.2
Weight loss (%)		Maximize	7.5
Colour fastness	WCC	Maximize	4.2
	WCS	Maximize	4.3
	DRCC	Maximize	4.6
	DRCS	Maximize	4.4
	WRCC	Maximize	4.0
	WRCS	Maximize	4.1
	LCF	Maximize	6.8

4.5 Comparative Effects on Dye Exhaustion and Colour Fastness of Mercerized and Un-Mercerized Fabric

Comparative effects on mercerized and un-mercerized fabric are shown in the Table 4.4. The effect of sodium hydroxide concentration with its interaction with treatment time on dye exhaustion was represented in Figure 4.8. The R-sq was 76.72% with P value of 0.001 hence the model was statistically significant. An increase of 8% - 37 % (42-78%) in dye exhaustion was observed in all mercerized fabric samples as compared to un-mercerized which had 34% dye exhaustion fabric with the maximum increase being obtained at 25 % NaOH and a treatment time of 5 minutes. The pretreated but un-mercerized dyed samples gave poor colour fastness rates of 2/3 to 3 as compared to the mercerized dyed samples gave acceptable colour fastness results of 4 to 4/5 to washing and rubbing and 7 light colour fastness. After mercerization, the structure of native cotton fibres, cellulose I, is converted into cellulose II, which is the stable fibre form after drying. The best colour fastness properties were obtained at 20% NaOH and a treatment time of 5 minutes. This is attributed to the maximum adsorption and

diffusion of dye molecules into the fibre as a result of the increased absorbance and affinity of the cotton fabric which is brought about by the modification of the fibre surface appearance and the internal structure. These results therefore affirm that mercerization is a good preparatory process in order to come up with a fault-free dyeing process. For dyed mercerized samples, samples mercerized using 13% NaOH presented the highest measure of fading following by those mercerized using 15% NaOH. In contrast, dyed samples mercerized using 20-27% NaOH showed better colour fastness rates.

Table 4.1: Comparative effects on dye exhaustion of mercerized and un-mercerized fabric

[NaOH] (%) w/v	Time (min)	Dye Exhaustion (%)	Colour fastness						
			Wash fastness to colour change	Wash fastness to colour staining	Dry rub fastness to colour change	Dry rub fastness to colour staining	Wet rub fastness to colour change	Wet rub fastness to colour staining	Light colour fastness
13	5	52	3/4	3	3	3	3	2/3	4
15	3	56	4	3/4	3/4	3/4	3	2/3	4
	7	57	4/5	4	4	3	3/4	3	5
20	2	70	4	4	4	4	4	3/4	6
	5	76	4/5	4	4	4	4/5	4	7
	5	78	4	4	4/5	5	4	3/4	7
	5	71	4	3/4	4/5	4/5	4	4	6
	5	78	4	3/4	4	5	4	3/4	6
	5	76	4/5	3/4	5	4	4	3/4	7
	8	73	4/5	4	4/5	4	3/4	4	7
25	3	68	4/5	4	4	3	3	2/3	7
	7	70	4	3/4	4	3	3/4	3	6
27	5	70	4	3/4	3/4	4	3/4	3	6
UM		34	2/3	2/3	3	3	2/3	2/3	3

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, the effect and optimization of mercerization on dye exhaustion, absorbance, colour fastness, weight loss, shrinkage and tensile strength was investigated. Reference to results and discussions in chapter 4, which refers various parameters in mercerization process, the following general variables are considered to be important while drawing the reliable conclusions from the study. In this study, the dyeability of a cotton fabric has been successfully demonstrated by clearly establishing the optimum mercerizing conditions of sodium hydroxide concentration and treatment time using the model generated by RSM in MINITAB software.

The pretreatment process was combined desizing, scouring and bleaching using 5% o.w.f sodium hydroxide and 3% o.w.f hydrogen peroxide in one-bath pretreatment process. Acceptable absorbability of the fabric was produced that is wetting time of 78seconds and sinking time of 108 seconds, which is due to better removal of starch through its hydrolysis by hydrogen peroxide and on the other hand sodium hydroxide results in better removal of the saponifiable oils, fats and waxes present in cotton. It is of importance to establish the ideal concentration of sodium hydroxide during mercerizing process in dyeing industry. Less concentration of sodium hydroxide gives poor colour fastness properties and dye exhaustion while more concentration is a big threat to fibre damage which reduces the absorbance properties of textile product. The experimental results obtained in this work proved that the samples mercerized with 20-25% showed the best performance in terms of absorbance, dye exhaustion colour fastness, shrinkage (swelling), weight loss, and tensile strength at the expense of the maximum amounts of fabric shrinkage and weight loss. Below 20% NaOH a slight improvement in colour fastness and dye exhaustion was observed. In contrast, the un-

mercerized samples yielded poor colour fastness and dye exhaustion. The generated model established the optimum conditions as output by using the response optimizer. The study revealed that there is an interaction between NaOH concentration and time of treatment. Therefore, less value of NaOH solution is required to complete mercerization treatment when long time is applied. The conditions were 23.36% sodium hydroxide and 4.97minutes treatment time. ANOVA test confirmed significant effects of each parameter itself and their interactions on the properties of the fabric samples.

5.2 Recommendations

In this present study, there are areas for improvement. To maximize the full research potential, there is a need for further investigation of the effect of mercerization on the surface morphology and crystallinity of the fibres using scanning electron microscope (SEM) and XRD. X-ray diffraction studies for the determination of the fine structure of cellulose and mercerized cellulose will certainly throw a great deal of light about the original structure as well as the changes occurring in the structure during the process of chemical modification at Mercerization. Further research can also be carried out in the dyeing process such as using natural dyes to study the effect of mercerization on natural dyeing. In this study, 100% cotton fabric was used therefore, a cotton blended fabric is recommended. The mercerizing temperature was constant in this study. Therefore, a study which involve variation of mercerizing temperature is also recommended.

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