SURVEY ON OCCUPATIONAL VAT DYEING IN KANO METROPOLIS, ITS ENVIRONMENTAL IMPACTS AND IMPROVEMENT ON THE DYEING PROCESSES USING DESIGN OF EXPERIMENT

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DECLARATION

I declare that the work in this Thesis entitled **"Survey on occupational vat dyeing, its environmental impacts and improvements on the dyeing processes using design of experiment"** has been performed by me in the Department of Polymer and Textile Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.





Sani Abdullahi Signature Date

CERTIFICATION

This Thesis entitled "SURVEY ON OCCUPATIONAL VAT DYEING, ITS ENVIRONMENTAL IMPACTS AND IMPROVEMENT ON THE DYEING PROCESSES USING DESIGN OF EXPERIMENT" by SANI ABDULLAHI meets the regulations governing the award of the degree of Doctor of Philosophy in Colour Chemistry and Technology of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This Thesis is dedicated to my father, late Abdullahi Muhammad Danbatta of blessed memory who ensured that I attended one of the best Science Secondary Schools in Kano State despite the fact that he only had Qur'anic education and very limited financial resources. May Allah forgive his sins and may his gentle soul rests in peace.

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ABSTRACT

Due to continuing decline of traditional indigo dyeing and availability of synthetic dyes, most occupational dyeing in Kano Metropolis today is done with vat dyes. The dyeing activities are scarcely documented to have an incline on who are the dyers and what they actually do. If dyeing/mercerizing wastewater is poorly managed, it may contaminate groundwater in the neighbourhood. If proper dyeing conditions are not employed, quality characteristics of the dyed material may be inferior. The aim of this study is to survey the occupational dyers, assess the environmental impacts of the dyeing activities, and improve on the dyeing processes. Baseline information was obtained using a structured questionnaire from 226 dyers selected by convenience sampling and the data was complimented with information from focus group discussions. It was found that majority of the dyers were male, of youthful age, natives, and educated. Their work experience ranged from 5 to 31 years (mean = 11.11± 5.01) where about one half of them earn more than the minimum wage of civil servants in the country. The dyers work as informal groups with synthetic vat dye, caustic soda, hydros, and woven fabrics (all imported from China). The dyers face numerous challenges which are rendering them jobless. Samples of caustic soda, hydros and dye powders were selected by purposive sampling from local markets and tested for heavy metals using Agilent 4210 MP-AES. Results show that the concentrations of heavy metals detected in caustic soda and hydros may not be of immediate environmental concern. Metal content of all the dyes investigated were found to be within ecological and toxicological association of dyers and organic pigment manufacturers (ETAD) heavy metal limits for dyes and are therefore safe to use. Effluent and groundwater samples were collected and characterized according to procedures described by American public health association (APHA). Based on the physico-chemical parameters and heavy metals investigated in dye effluent and groundwater samples, the former was found to be non-

biodegradable while the latter was found to be unsuitable for drinking and irrigation. Occupational vat dyeing parameters were determined in selected dyehouses. Results showed that the dyers use an average of 21.43±3.46 g/l caustic soda and 18.99±2.05 g/l hydros which can be considered adequate based on previously reported vat dye formulations. An average temperature of 76±4 ^{o}C used by the dyers may aid in over-reduction of the dye. Mercerization experiment was carried out with different levels of input variables viz. temperature, time, caustic soda concentration, and fabric type and with shrinkage, tensile strength, and elongation as responses according to central composite design (CCD) by response surface methodology (RSM) using design expert® software version 7 (DX7) software. Multi response optimization of mercerization parameters were carried out using desirability function. The optimal conditions indicated mercerization using 250 g/l caustic soda at 85 ^{o}C for 3 min. Five sets of experiments conducted at the optimized conditions resulted in 6.9±0.4 and 9.7±3.6 % average shrinkage, respectively, for blend and cotton fabrics. The elongation of blend and cotton fabrics were 51.6 and 120.85 % higher than those of the original untreated samples. Dyeing experiment was carried out at 60 ^{o}C for 10 min. in a liquor ratio of 100:1 with different levels of input variables viz. caustic soda and hydros concentration, fabric type, and dyeing methods and with appearance rating (levelness) as the response. Optimization of dyeing parameters indicated that the use of 10g/l caustic soda and 20 g/l hydros is more desirable. Under the same dyeing conditions, the dry dyeing method was found to be the best for cotton fabric with an appearance rating of more than 98.8 %. It is suggested for the mercerized samples to be washed before wet-on-wet dyeing to avoid unlevelness. All finished fabrics (dyed and beaten locally) were found to have inferior strength compared to untreated and unmercerized samples. It is suggested for the finishing (beating) operation to be avoided. Fastness ratings of samples from the dyeing experiments are much better than those obtained

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry
AATCC	American Association of Textile Chemists and Colourists
Adj.	Adjusted
ADMI	American Dyestuff Manufacturers Institute
ANOVA	Analysis of Variance
APHA	American Public Health Association
As	Arsenic
AWWA	American Water Works Association
BAN	Barium Activity Number
BF	Cotton/polyester Blend Fabric
BFCWE	Blend Fabric Cotton Weft
BFPWA	Blend Fabric Polyester Warp
BOD	Biological Oxygen Demand
Ca	Calcium
CCD	Central Composite Design
Cd	Cadmium
CF	100 % Cotton Fabric
CFWA	Cotton Fabric Warp
CFWE	Cotton Fabric Weft
Cm	Centimetre
Co	Cobalt
Co.	Company

COD	Chemical Oxygen Demand
conc.	Concentration/Concentrated
cond.	Conductivity
Cr	Chromium
Cu	Copper
DO	Dissolved Oxygen
DOE	Design of Experiment
DX7	Design Expert® Software Version 7
e.g.,	For example,
Et.	Ethanol
ETAD	Ecological and Toxicological Association of Dyers and Organic Pigment Manufacturers
etc.	And so forth
F	Finished
Fe	Iron
FEPA	Federal Environmental Protection Agency
g	Gramme
g/l	Gramme per litre
GDP	Growth Domestic Product
GIS	Geographical Information System
Hg	Mercury
hr.	Hour
i.e.,	That is
ICI	International Commission on Illuminants

ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IK	Indanthrene cold
ILO	International Labour Organization
IN	Indanthrene normal
ISO	International Standards Organization
IW	Indanthrene warm
KAD	Kano Amalgamated Dyers
kg	Kilogramme
Km	Kilometre
KSMCI	Kano State Ministry of Commerce and Industry
KSME	Kano State Ministry of Education
KSMEN	Kano State Ministry of Environment
l	Litre
l/min	Litres per minute
Lat.	Latitude
Long.	Longitude
LR	Liquor ratio
ltd.	Limited
m	Metre
M	Molar
mg	Milligramme

Mg	Magnesium
mg/kg	Milligramme per kilogramme
mg/l	Milligramme per litre
min.	Minute
mm	Millimetre
mm/min.	Millimetre per minute
Mn	Manganese
MP-AES	Microwave Plasma Atomic Emission Spectrometry
MSME	Micro, Small and Medium Enterprises
MSW	Municipal Solid Waste
mv	Millivolt
N	Newton
Na	Sodium
NaOH	Caustic soda
NBCI	Nigerian Bank of Commerce and Industry
NBTX	Ningbo Tong Xi
NDE	National Directorate of Employment
NESREA	National Environmental Standard and Regulations Enforcement Agency
NEXIM	Nigerian Export-Import Bank
Ni	Nickel
NIDB	Nigerian International Development Bank
NIR	Near Infrared Region
nm	Nanometre

pa	Paschal
Pb	Lead
PET	Poly (ethylene terephthalate)
Pred.	Predicted
pt-co	Platinum cobalt
PVC	Poly (vinyl chloride)
rpm.	Revolution per minute
RSM	Response Surface Methodology
RSN	C.I. Vat Blue 4
SAP	Structural Adjustment Program
Sec.	Seconds
SME	Small and Medium Enterprises
SMEDAN	Small and Medium Enterprise Development Association of Nigeria
SON	Standards Organization of Nigeria
SPSS	Statistical Package for the Social Sciences
TDS	Total Dissolved Solids
temp.	Temperature
UF	Unfinished
UMBF	Unmercerized Blend Fabric
UMCF	Unmercerized Cotton Fabric
UMD	Unmercerized Dyed
UMUD	Unmercerized Undyed
UNEP	United Nations Environmental Programme

UNESCO	United Nations Educational, Scientific, and Cultural Organization
UNICEF	United Nations International Children Emergency Fund
UV	Ultraviolet
viz.	Namely
VR1	C.I. Vat Red 1
VRR	C.I. Vat Violet 1
vs.	Versus
WEF	Water Environment Association
WHO	World Health Organization
WSSCC	Water Supply and Sanitation Collaboration Council
WUP	Water Utility Project
ZDHC	Zero Discharge of Hazardous Chemicals Programme

CHAPTER ONE

1.0 INTRODUCTION

1.1 **General Background**

Dyeing has accompanied the development of human culture since the early beginnings where different cultures, in many aspects totally unrelated and unconnected have developed similar dyeing techniques using dyes from available natural colourants (Dagani *et al*., 2015). The art of dyeing is very common among Africans where occupational dyers can be found in Mali, Zaire, Cote-de-Ivoire, Senegal, Gambia, Morocco as well as Nigeria (Amubode, 2009). Dyeing textiles with natural indigo dye is a popular traditional craft among many Nigerians particularly Hausa and Nupe in the north, Tiv in the Middle Belt and Yoruba in the west (Amubode, 2009). The ancient city of Kano has attracted historical prominence since the 14th century with its fine indigo dyed cloth (Ezeanya-Esiobu, 2019) where dye pits are located at various locations in Kano Metropolis including the ones in Kofar Mata, which is the most organized, and in Zage, Dala, and Karofin Gangamau (Barau, 2007) among others.

Production of synthetic indigo in 1880 led to the industrial synthesis of the dye in 1887 resulting in rapid decline of traditional dyeing with natural indigo globally (Meksi and Mhenni, 2015). In the case of Nigeria, the situation was worsened by indiscriminate importation of white undyed woven fabrics and coloured textiles from China (Renne, 2015). Synthetic dyes offer advantages such as lower production cost, better resistance towards environmental factors, ease of application, etc. (Nidheesh *et al*., 2013). Since the 1930s, Yoruba began incorporating synthetic vat dyes (including indigo) and chemicals and most dyeing in the major dyeing centres of Abeokuta, Lagos and Ibadan today is done with

synthetic dyes (Byfield, 1994). Traditional indigo dyers in Kano Metropolis have also followed the modern trend (Dutsenwai, 2010).

The incorporation of synthetic blue vat dye and its derivatives in Nigeria reflected significant development within the dyeing industry where the dyers had to acquire skills and the technical know-how in the use of the new line of ingredient. As such, it is important to know what the occupational dyers do by conducting a survey and then to improve on the quality characteristics of the dyed materials by design of experiment (DOE). Large percentage of synthetic dyes do not bind but are lost to the waste stream making the effluent highly coloured, aesthetically unpleasant (Ratna and Padhi, 2012), and the auxiliary chemicals are unreactive. Kano river basin, which serves as a source of water for drinking and irrigation, is receiving considerable pollution from Sharada and Challawa industrial estates (Bichi and Anyata, 1999) and this may also apply to groundwaters in the neighbourhood of where the occupational dyers operate.

A lot of work has been done to study occupational vat (including indigo) dyers in Abeokuta, Nigeria, namely the history of the dyeing occupation (Rice, 2015), demographic (Awogbade-Mabel, 2010) and socio-economic characteristics (Saheed, 2013) of the dyers, geography of the dyeing centres (Areo and Kalilu, 2013), the role of women in indigo dyeing (Byfield, 1997), environmental impacts (Bankole *et al.,* 2017), and toxicity of the dyes in humans (Soyinka *et al.*, 2007) etc. Until now, little work has been done to study occupational vat dyers in Kano Metropolis. Previous studies were mainly on toxicity of vat dye powders used (Abdullahi *et al*., 2016; Sani *et al*., 2018). This work comprises of a survey on occupational

vat dyers in Kano Metropolis, assessment of the environmental impacts of the dyeing occupation, and improvements on the dyeing processes by design of experiments.

1.2 Statement of the Research Problem

Despite the huge vat dyeing practices in urban Kano including the use of natural indigo in the past and synthetic vat dyes at present, there is scarcity of literature on the web regarding the dyeing occupation. The effluent discharged may seep into the ground and affect groundwater quality. Vat dye effluent was classified in some countries as the most toxic class of waters which is extremely toxic to aquatic organisms (Bozic and Kokol, 2008).

The dyeing occupation is threatened by indiscriminate importation of Chinese textiles to "Kantin Kwari" market in the Kano Metropolitan area which are similar to the ones produced locally (Renne, 2015) and this may render the dyers jobless. The dyers produce a deep, lustrous, dyed material on mercerized fabrics which in some instances the dyed article have inferior tensile strength coupled with excessive shrinkage, poor fastness properties and unlevelness. The dyers may not be able to compete with the Chinese since they lack modern equipment and chemistry background among other challenges.

Questionnaire survey together with focus group discussions could provide adequate information on the dyers/dyeing venture. Evaluation of environmental impacts of the dyeing operations through determination of some physico-chemical parameters and heavy metals in dye effluent and groundwater samples may result in hands-on campaign for stakeholders to

take practical actions. Improvement on the mercerizing/dyeing processes by optimizing important process parameters could make the Kano dyers credible competitors.

1.3 Justification

The modern vat dyers may have the same fate as traditional indigo dyers because of competition and the fact that their handcraft and ability to employ huge labour are scarcely documented to campaign for government support. This could render over 30,000 dyers and traders jobless (Muhammed, 2015) who have dependents and could earn more than ₦2,000 ($5.52) for dyeing 5 garments (Flynn, 2007) in a country where 60 % of the people live on less than $1 per day (Thurston, 2016). Questionnaire survey could provide a baseline information which may possibly help in creating awareness for government intervention and/or private partnership.

Textile effluents are complex waste products containing dyes, sizing agents and dyeing aids that are characterized by high concentration of environmental pollutants namely physico-chemical parameters and heavy metals (Manu and Chaudhari, 2003). Heavy metals in dyes affect human health by dermal contact and by drinking contaminated water (Abel-Ghany, 2013). In Nigeria, industrial byproducts are discharged as untreated wastes and effluents directly into rivers and lagoons (Adedeji and Ako, 2009) which will find their way to groundwater through hydrological cycle.

Due to surface water contamination, groundwater is the major source of fresh water worldwide (Raji and Abdulkadir, 2020) where approximately one third of global population depend on this water source for drinking (Li *et al.,* 2021). Aquifers are experiencing serious

threat of pollution where about 3.4 million people die every year from water related diseases (Temilola *et al.,* 2011) and nearly 1.8 billion people all over the world may face absolute water scarcity by 2025 (Hasan *et al.,* 2020) hence there is need to assess the quality of groundwater in the neighbourhood of the dyeing units.

In vat dyeing, too little sodium dithionite (hydros) results in oxidation which removes the dye from solution resulting in poor fastness to washing and addition of too much hydros can lead to destruction of the dye chromophore resulting in loss of colour yield (Teli *et al.,* 2001). Improper temperature control results in increase in dyeing cost for unutilized expensive vat dyes (Patra *et al.,* 2018). Optimization of mercerizing and dyeing parameters could help improve the dyeing processes.

1.4 Aim and Objectives

1.4.1 Aim

The aim of the research is to evaluate occupational vat dyeing in Kano Metropolis, assess its environmental impacts and improve on the dyeing processes using design of experiments.

1.4.2 Objectives

The specific objectives of the research are to:

1. carry out a structured questionnaire survey to determine the demographic/socioeconomic characteristics of the dyers, the management of the dyeing enterprises, operations, challenges/prospects as well as waste management and potential environmental impacts of the dyeing wastewaters.

2. find out the distribution of the major dyeing units using geographical information system (GIS).
3. determine the concentrations of some heavy metals in caustic soda, hydros and vat dye powders.
4. determine some physico-chemical parameters and heavy metals content in dye effluent and groundwater samples.
5. investigate the dyeing conditions used by the artisans and examine the light, wash and perspiration fastness ratings of the resultant dyed fabrics both from the dyers and from the dyeing experiments.
6. optimize mercerizing and dyeing conditions to produce a dyed material with improved tensile strength and fastness properties as well as good levelness and minimal shrinkage.

1.5 Scope, Limitations and Delimitations of the Study

The study involved the use of questionnaire along with focus group discussion, field exercise, and laboratory analysis. The study is to focus on collecting qualitative data related to the dyers from structured questionnaire and focus group discussion between the researcher and the dyers as well as with cloth vendors to provide baseline information on the occupational dyers. The field exercise involves taking geograpHical coordinates of the dyeing units; sampling of dyes, caustic soda and hydros in colour shops, and fabrics in cloth market; collecting dyebath effluent and groundwater samples, respectively, from the dyeing units and wells within 100 m radius in the neighbourhood; determining the dyeing conditions used by the occupational dyers; and collecting the resultant dyed samples.

The laboratory work covers geospatial analysis of the dyeing units; determination of heavy metal content in dyes, caustic soda, hydros, effluent, and groundwater samples; determination of physico-chemical parameters in effluent and groundwater samples; fabric characterization; determination of shrinkage, tensile strength and elongation of mercerized samples; assessment of appearance rating, tensile strength, and fastness properties of dyed samples; and optimization of mercerization and dyeing parameters. Data from questionnaire survey, heavy metal content, and physico-chemical parameters were analyzed by descriptive statistics (frequency, average and range). The study is limited to a sample size of 226 due to reluctance on the part of the dyers to participate in the survey and financial constraint. Due to unavailability of reagents, mercury and arsenic could not be determined among the heavy metals investigated. The colour strength (k/s value) of the dyed materials could also not be determined due to lack of accessibility to Colour-Eye UV-Visible spectrophotometer and limited financial resources to test the samples abroad.

The study is delimited to the use of convenience sampling technique in questionnaire administration, purposive sampling in the selection of dyes and fabrics, and random sampling of dye effluent which is considered more suitable to achieve the objectives of the study. The study does not cover the collection of effluent and groundwater samples in dry season as well as the effect of fibre/yarn characteristics on the shrinkage, tensile strength, and elongation of mercerized fabrics. The study excludes wet-on-wet dyeing of mercerized samples after washing to neutral pH. The study is limited to the determination of only 5 heavy metals in effluent and groundwater samples and does not cover other statistical techniques in the analysis of data from questionnaire survey, metal content and physico-chemical parameters.

Financial constraint could not allow the determination of tensile strength of all the dyed materials. Toxicity of the dyes and chemicals on humans has been excluded from the study.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Textile Dyes

Dyeing was an art in prehistoric times (Leube and Ruttiger, 2016) where natural colourants derived from plants, insects or animals were the only dyes used for textile colouration until 1856 when William Henry Perkin accidently invented the first synthetic dye from aniline (Zerin *et al.*, 2020). It is estimated that currently only 1 % of the total world textiles are dyed with natural colourants (Zerin *et al.*, 2020). Nearly 8×10^5 tonnes of synthetic dyes are produced annually and the textile industry account for approximately 75 % of the global dyestuff market with around 10,000 different dyes being used for dyeing and printing. Synthetic dyes are mostly derived from petrochemical compounds and are commercialised in liquid, powder, pastes or granular forms (Slama *et al.*, 2021).

Dyes are organic compounds capable of absorbing light radiation in the visible region of the spectrum and of reflecting or diffusing complementary radiation on the one hand, and dyeing a substrate in a sustainable manner on the other hand (Berradi *et al.*, 2019). They differ in terms of chemical structure, dyeing process, chemical/physical properties, and application fields (Croce *et al.*, 2017). Dyes can firmly attach to the fibres by virtue of chemical or physical bonding between the groups in the dye and groups on the fibre and to be of commercial importance, a dye should be fast to light, rubbing and washing (Nidheesh *et al.*, 2013). Generally, in addition to textile fibres, dyes are used for colouration of several other materials such as paper, cosmetics, leather, food, and pharmaceutical products (Slama *et al.*, 2021).

Chemical classification of dyes is based on the chemical structure and more particularly on the nature of their chromophore grouping which include azo, anthraquinone, indigo, xanthene, phthalocyanine, nitrated and nitrosated, diphenyl methane and triphenyl methane as well as polymeric dyes (Berradi *et al.,* 2019). Dyes are also classified into different application classes namely disperse, acid, basic, direct, fibre reactive, pre-metallized, mordant, solubilized, sulphur, azoic, and vat dyes (Wardman, 2018). Natural indigo, woad and Tyrian purple belong to the vat class (Yusuf *et al.,* 2017) among which indigo is considered as one of the most important industrial dyes due to continuing popularity of blue jeans and other blue denims (Park *et al.,* 2012).

2.1.1 Vat dyes

Vat dyes are amongst the oldest colourants used in textiles, dating back over to 2,000 years. They have excellent all-around fastness to washing, light, and chlorine bleaching which is uncommon in other dye classes but tend to have poor rubbing fastness which can be mitigated with particular treatments of the dyed fabric (Shi, 2014). In their coloured form vat dyes are insoluble pigments and therefore their application requires them to be rendered soluble. In the dyebath, the pigment is converted into a water-soluble form using a strong alkaline solution of a reducing agent, usually sodium dithionite also called hydros (Wardman, 2018; Sabnis, 2017).

In the colouration of cellulose fibres, vat (including indigo) and sulphur dyes represent a relatively large part (about 31%) of the dyestuff market as shown in Figure 2.1 (Ahmed and El-shishtawy, 2010). Unlike reactive and direct dyeing, vat dyeing is a difficult task due to involvement of oxidation and reduction processes during its application (Adeel *et al.,* 2018).

The dyes are commercially available in the form of liquids, granules, or dedusted powders. They are also available as pastes and in pre-reduced or solubilized leuco sulphuric ester forms (Xu *et al.*, 2000).

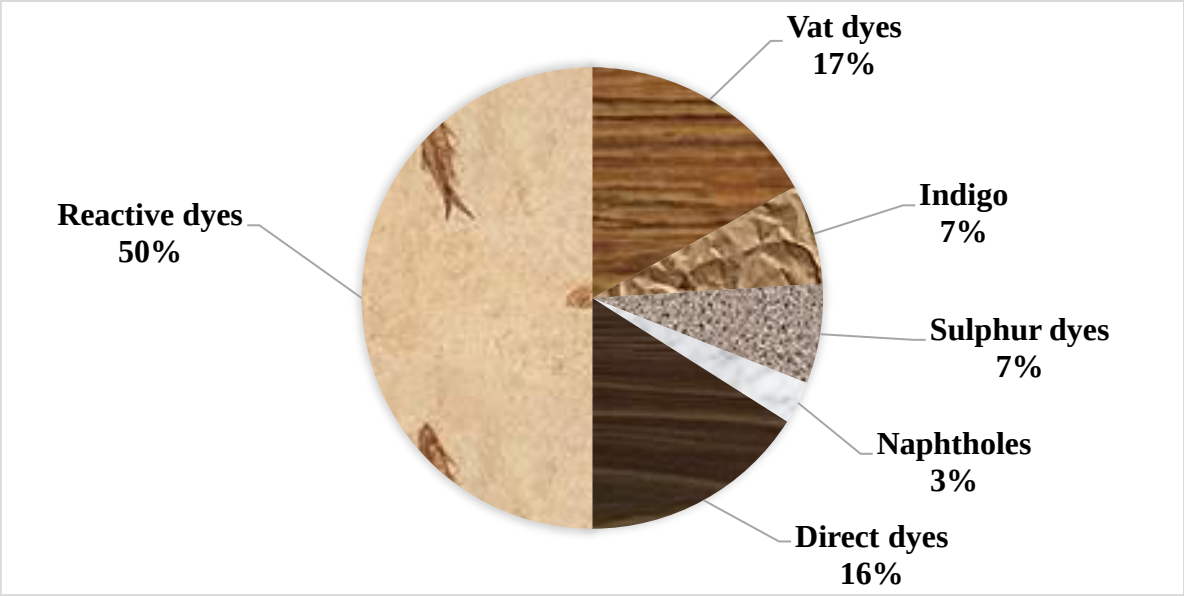


Figure 2.1: Consumption of dyes for cellulosic fibres (Ahmed and El-shishtawy, 2010)

2.1.1.1 Classification of vat dyes

Based on leuco compound substantivity and the required dyeing conditions (shown in Table 2.1) to give the best overall dyeing results, vat dyes are classified into three groups or classes, namely, IN, IW, and IK dyes (Shi, 2014):

IN dyes: the dyes require a high amount of sodium hydroxide at relatively high temperatures (around 60 °C) during the dyeing process. No salt is needed because of the high substantivity of the leuco dyes for cotton and more levelling agent is required for those dyes. Examples include C.I Vat Violet 1 and C.I Vat Blue 6.

IW dyes: the dyes require a medium amount of sodium hydroxide and medium temperature where 50 °C gives maximum affinity. Some addition of salt is required to aid exhaustion during dyeing since the leuco dyes have moderate substantivity for cotton. Some levelling agent is needed for better levelling when those dyes are applied. Examples are C.I Vat Red 10 and C.I Vat Blue 4.

IK dyes: for those dyes, only low amounts of sodium hydroxide and low temperatures are necessary and the temperature of maximum affinity is as low as 20 °C. These dyes have low substantivity for cotton and need high amount of salt for good dyebath exhaustion. The dyes have good levelling properties and thus no levelling agent is required. Example of this group is C.I Vat Blue 1.

Table 2.1: Dyeing conditions for different groups of vat dyes (Chakraborty, 2010)

Parameters	Groups		
	IK	IW	IN
Vatting temperature (°C)	35–50	45–50	55–60
Dyeing temperature (°C)	35	40-45	50–55
Hydros (g/l)	8	10	12
Caustic soda (g/l)	8	10	12
Sodium chloride (g/l)	20	15	10

2.1.1.2 Chemistry of vat dyes

The vast majority of modern vat dyes are based on the anthraquinone or the indigo (or thioindigo) chromophores. Several of the anthraquinone dyes are complex polycyclic quinones and all possess two carbonyl (C═O) groups linked by alternate single and double bonds in a conjugated chain (Wardman, 2018). Vat dye is one of the well-known carbonyl class of dyes having coplanar and multiring system where those rings contribute in strengthening the van-der-Waals forces between the dye and the substrate which is the main reason why vat dyes offer better colour fastness than reactive dyes (Khatri *et al.,* 2017).

Carbonyl groups in vat dyes affect the substantivity, dye stability, dyeing processes, degree of adsorption, diffusion of the dye into the fibre, and colour uniformity (Sutlovic *et al.,* 2021). Other functional groups in the vat dye molecule are usually absent because such groups can be sensitive to the reduction and oxidation reactions. Halogen substituents are occasionally found in the structure. Pyranthrones and flavanthrones are typical examples of carboxylic and heterocyclic anthraquinone vat dyes (Christie, 2015). Carbonyl groups in anthraquinone dye act as chromophore and groups such as hydroxyl (OH), alkylamino (NHR, NR), benzamide (NH-CO-RH), alkoxy (-OR) etc. are auxochromes (Chakraborty, 2010).

The replacement of natural indigo by synthetic indigo at the end of 19th century gave impetus to research on other syntheses and many vat dyes followed (Wardman, 2018). There are around 200 different anthraquinone vat dyes in use commercially with widely different structural types and covering the entire spectrum from yellow through blue to black belonging to both carboxylic and heterocyclic types (Christie, 2015). Some chemical classification of vat dyes includes Indanthrones (Figure 2.2) e.g., C.I. Vat Blue 4, Flavanthrones (Figure 2.3)

e.g., C.I. Vat Yellow 1, Benzanthrone acridone (Figure 2.4) e.g., C.I. Vat Green 3 (Wardman, 2018), Violanthrones (Figure 2.5) e.g., C.I. Vat Blue 20, and Pyranthrones (Figure 2.6) e.g., C.I Vat Orange 9 (Christie, 2015).

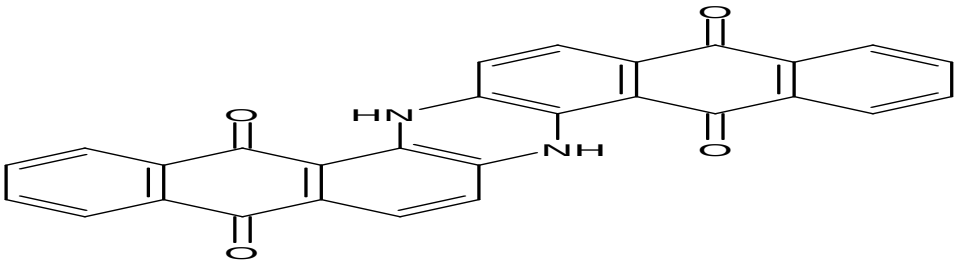


Figure 2.2: Indanthrone

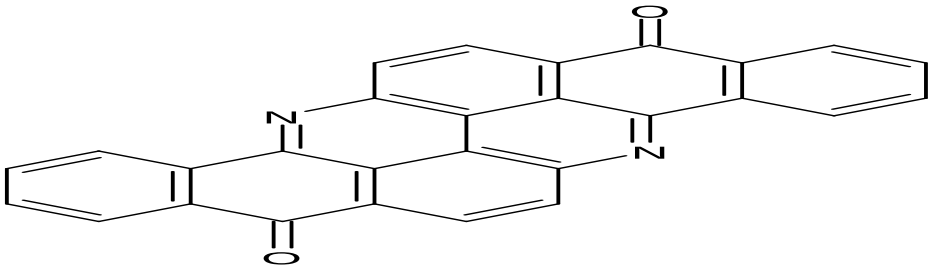


Figure 2.3: Flavanthrone

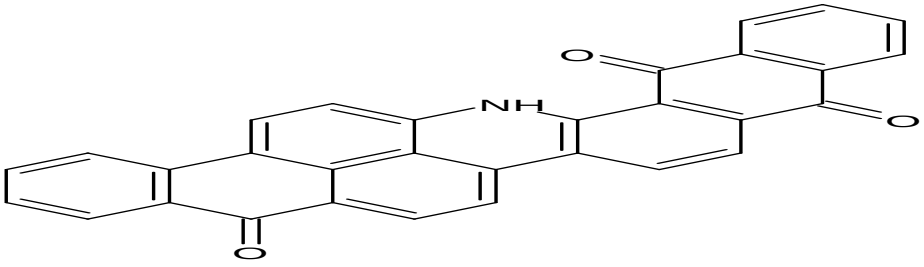


Figure 2.4: Benzanthrone acridone

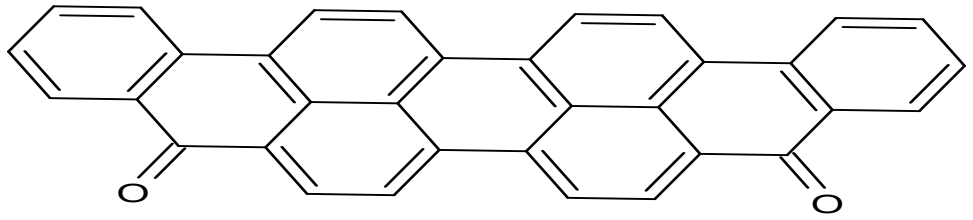


Figure 2.5: Violanthrone

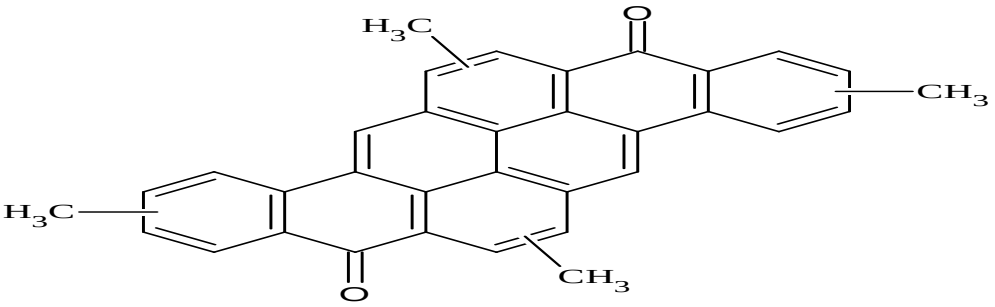


Figure 2.6: Pyranthrone

The starting materials for the synthesis of vat dyes include naphthalene, benzene, toluene, etc., to form anthraquinone which further reacts through sulphonation, ammonia treatment, or addition of an aromatic ring to modify the end properties of the synthesized dye. Modification of those starting materials and the addition of various groups through multiple synthetic steps lead to a plethora of available vat dye formulations (Baptista, 2009).

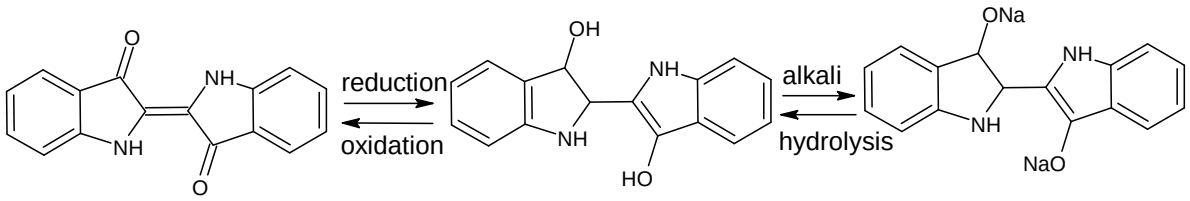
2.1.1.3 Vat dyeing processes

Vat dye colouration may be carried out at any stage in the manufacture of goods where dyeing machines are available for dyeing textiles in the form of loose stock, tow, sliver, yarn, garment and woven fabric (Wardman, 2018) either in rope form or open width. Vat dyeing process for cotton knit fabric has also been developed (Wakoh *et al.*, 2015). There are at least 5 processes used in vat dyeing namely vatting (leuco dyeing), semi-pigmentation, pre-pigmentation, use of acid leuco compounds (vat-acid method), and dyeing with 'solubilized' leuco ester vat dyes

(Giles, 1974). There is no standard process for vat and sulphur dyeing since the procedure will depend on the available equipment, material, amount of material, and the actual dye (s) (Xu *et al.,* 2000).

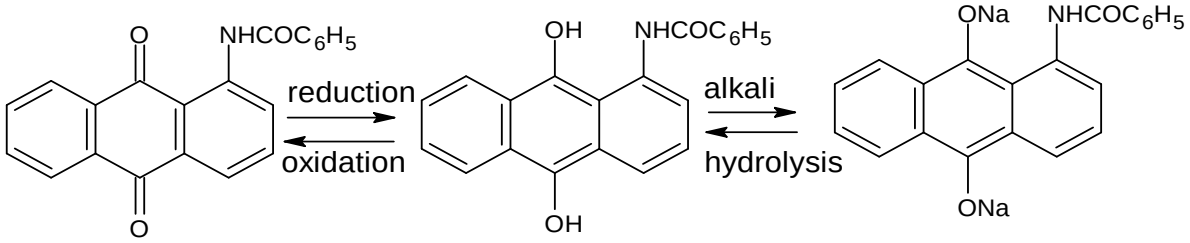
In vat dyeing, a reduction stage (vatting) is required to convert the oxidized form of the dyes into water soluble form (leuco enolate form) in alkaline solution of a reducing agent which will then be absorbed into the fibres and then re-oxidized into the original water insoluble keto form *in-situ* in the fibres to redevelop the crystal structure (Sabnis, 2017). Reduction of indigo and anthraquinone vat dyes are shown in Equations 2.1 and 2.2 respectively. The amount of reducing agent is determined by the chemical structure and nature of a particular dye (number of reducible groups), relative molecular weight, and pure dye content (Sutlovic *et al.,* 2021).

The conversion of vat dye into the leuco form is a heterogeneous reaction that comprises of the following stages: diffusion of molecules of the reducing agent to the surface of dye particles, sorption of the reducing agent, chemical reaction between the dye and reducing agent with the formation of a leuco compound (Bozic and Kokol, 2008). Indigo requires a reduction potential of around (-700 to -750 mV) and anthraquinonoid dyes require around (-800 to -1000 mV) for complete reduction depending on the class of vat dye (Chakraborty, 2010) and therefore the reducing agent to be employed should have a reduction potential in the same range or even more negative (Bozic and Kokol, 2008).



Indigo insoluble form soluble form

Equation 2.1: Reduction of indigo dye (Bozic and Kokol, 2008)



Anthraquinone dye insoluble form soluble form

Equation 2.2: Reduction of anthraquinone dye (Ahmed and El-shishtawy, 2010)

In modern dyeing processes, reduction of vat dyes is usually carried out with powerful reducing agents among which hydros is of major importance (Wardman, 2018). Hydros, with reduction potential of approximately 1000 mV, is the reducing agent of choice because its alkali solution meets those requirements. It is used with all vat dyes at temperatures starting from 30 ^{o}C, permits swift reduction, and enables short fixing times in various dyeing methods (Vuorema, 2008). The stability of alkaline solution of hydros decreases with increase in temperature, an increase in surface area exposed to air, and a decrease in agitation of the bath where the ultimate result is that nearly three times the amounts of hydros and caustic soda over the stoichiometric requirement are needed for efficient dyeing (Kulandinathan *et al.*, 2007).

Despite the different basic chemistry, application methods/dyeing processes for both indigoid and anthraquinoid groups are the same but in general the former gives brighter shades than the latter but with inferior light and wash fastness (Sanchez, 2015). Vat dyes are characterised by a change in hue during reduction and oxidation processes due to the transition of the chromogen from one resonance structure to another and depends on the degree of oxidation and reduction (Sutlovic *et al.,* 2021). Many vat dyes have rapid strike where the dyebath may be 80–90 % exhausted within 10 min. of dyeing. As in the dyeing of cellulosic fibres with some direct dyes, the rate of dyeing with leuco vat dyes is higher at higher temperature, lower liquor ratio, and lower dye concentration (Broadbent, 2001).

Two kinds of auxiliary chemicals which may be used in leuco-vat dyeing are levelling and stripping agents. They are essentially similar in their action as both interact with the leuco-vat anions in solution to form complexes. Those complexes lower the effective concentration of dye anions in the dye bath and hence lower the rate of dyeing, and increases the rate of stripping (Aspland, 1997). After vat dyeing, oxidation, and removal of excess alkali and reducing agents by rinsing, vat dyed material is usually soaped (Aspland, 1992a). The function of soaping is thus three folds: It removes loosely attached superficial dyes, it develops right tone of shade placing dye crystals perpendicular to fibre axis and it helps in the formation of large dye crystals to offer superior fastness (Chakraborty, 2010).

2.1.1.4 Vat dye application fields

Vat dyes are used in the dyeing of all types of cellulosic fibres as well as their blends with polyester (Wardman, 2018). In addition to cellulosic fibres, vat dyes have been applied on Poly (ethylene terephthalate) (Baig, 2012), Poly (lactic acid) (Sawada and Ueda, 2007),

Polypropylene (Gupta *et al.,* 2010). acrylic and lycra (Baig, 2012), viscose rayon (Shim *et al.,* 2004), and nylon (Burkinshaw and Son, 2010) using the vat acid process. Vat dyes also exhibit substantial substantivity towards protein fibres such as wool and silk (Bechtold, 2013; Sabnis, 2017). The insolubility and generally good fastness properties of vat dyes stimulated considerable effort into the selection of suitable examples of the colourants for use as pigments even though of the known vat dyes only few have been fully converted into pigment use (Christie, 2015).

Vat dyes are widely used in the colouration of quality shirts, table cloths, towels, sports wears, and high-quality overalls. They are also very useful in the dyeing of fabric for awnings, curtains, upholstery, military and naval uniforms (Wardman, 2018). Vat dyes are used to obtain camouflage fabric with absorption near infrared region (NIR) and reflectance of green leaf (Goudarzi *et al.,* 2014; Wendel, 2015). NIR camouflage uniforms conceal the human body both in the visible and NIR ranges against NIR detection devices by mimicking natural or artificial backgrounds (Kim *et al.,* 2013) and almost all vat dyes have the same or similar reflectance at relatively longer wavelength such as above 900 nm where the patterns appearing on military uniforms typically consists of three to eight colours chosen specifically to blend in a particular environment e.g., desert, jungle, lake, woodland, etc. (Wendel, 2015).

2.1.1.5 Problems in vat dyeing

Despite their advantages, vat dyes have limitations such as high cost and difficulty of application (Sabnis, 2017). A number of chemical problems arise with some quinone vat dyes which include: multiple reduction steps (over-reduction) for polyquinones such as indanthrone; isomerism of leuco compounds to oxanthrones; hydrolysis of amide groups;

over-oxidation after dyeing; dehalogenation of some dyes. Over-reduction is the reduction of more than one pair of conjugated carbonyl groups in a polyquinone and often results in poor colour yields and off-shade dyeings. To minimise these types of problems, the supplier's recommendations for vatting and dyeing must be followed (Broadbent, 2001).

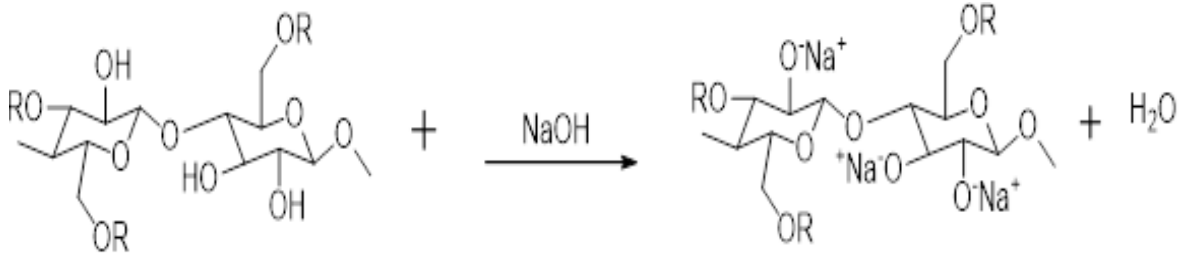
Some combinations of yellow and blue or green vat dyes show anomalous behaviour in which the blue or green component is lost more readily on exposure to light than expected. This is often referred to as catalytic fading which is not very predictable. Another occasional problem is photo-tendering in which some few vat dyes such as C.I Vat Orange 2 are partly reduced under the influence of light. In the dark, in the presence of atmospheric oxygen, they are regenerated but with oxidative tendering of the fibre by peroxides formed as by-products (Aspland, 1997).

2.2 Pretreatment Processes for Cellulose Fibres

Cellulose fibres, whether natural or regenerated, require pretreatment to remove natural or added impurities and can be carried out on loose fibres, yarns or fabrics (Hickman, 1995). The conventional pretreatment processes consist of desizing, scouring, bleaching and mercerization (Hauser, 2015). Desizing removes previously added size or starchy material; scouring remove oils, fats and waxes; bleaching uses oxidising agents to improve the whiteness of the fabric (Harane and Adivarekar, 2016); and mercerization improves cotton's weak characteristics such as low lustre, dye uptake, tensile strength, dimensional stability, etc. (Ayetollahi *et al.*, 2013).

2.2.1 Mercerization of cellulose

Mercerization, a process named after its inventor, John Mercer, is the swelling of cellulose fibres by immersion in highly concentrated caustic soda solution, washed with water, and then dried (Tatsumi *et al.,* 2022). It is believed that Na+ breaks the intermolecular hydrogen bonds and that the most probable location of the Na^+ is at carbon 2 where as carbon 3 seems to be the most resistant to complexation with caustic soda (Budtova and Navard, 2016). Reaction between cellulose and caustic soda is shown in Equation 2.3.



Cellulose mercerized cellulose

Equation 2.3: Chemical reaction during mercerization process (Merkel *et al.,* 2017)

Mercerization can be carried out on raw fibre, yarn, or knitted and woven fabrics (100 % cellulose, blend, or alkaline treatment of polyester) and can be done without tension to effect mainly an increase in strength and dye affinity or under tension to bring about an increase in lustre (Patil *et al.,* 2019) as shown in Table 2.2. Mercerization can also be performed using a wide range of operating conditions, for instance, reaction time can be as short as min. or as long as hours or days, temperature can range from ambient to 150 ^oC, and caustic soda concentration may vary from 150 to 300 g/l (Table 2.3). The properties of mercerized samples usually studied include degree of mercerization (BAN), dimensional stability (shrinkage), breaking load, elongation at break, etc. as shown in Table 2.4.

Table 2.2: Alkali treatment of different samples and different sample conditions reported in the literature

Sample type	References	Sample condition	References
Fibre	Jiao and Xiong, 2014	Slack	Khajavi *et al.* 2015; Paul and Teli, 2011
Yarn	Khajavi *et al.* 2015: Khalifa, 2017	Under tension	Aboalasaad *et al.* 2017; Sutlovic *et al.* 2021
100 % cellulosic fabric	Aboalasaad *et al*. 2017: Lin *et al.* 2022		
Cotton/polyester blend fabric	Borisova and Reihmane, 2013: Nazir *et al.* 2014		
100 % polyester fabric	Carrera-Gallissa *et al.* 2017		

Table 2.3: Some typical mercerizing parameters quoted from selected publications

NaOH conc. (g/l)	References	Temperature (^oC)	References	Time (min.)	References
150	Khajavi *et al.* 2015	Ambient	Marzouki *et al.* 2019	2	Tarbuk *et al.* 2014
200	Marzouki *et al.* 2019	18	Tarbuk *et al.* 2014	3	Lin *et al.* 2022
0-240	Goswani *et al.* 2008	30	El-Oudani *et al.* 2011	5-10	Khajavi *et al.* 2015
240	Zeronian *et al.* 1990	65	Patil *et al.* 2019	10	Bhatti *et al.* 2012
250	Lin *et al.* 2022	95	Nazir *et al.* 2014	40	Zlenko *et al.* 2021
Up to 300	Aboalasaad *et al.* 2017,	100	Jiao and Xiong, 2014	60	Paul and Teli, 2010

Table 2.4: Characterization of mercerized samples reported in previous studies

Sample characteristics	References
Dimensional change	Aboalasaad *et al.* 2017: Moghassem and Valipour, 2013
Breaking load and elongation at break	Khajavi *et al.* 2015
Structural modification	Khajavi *et al.* 2015: Marzouki *et al.* 2019
Barium activity number (degree of mercerization)	Khajavi *et al.* 2015: Khalifa, 2017
Surface properties	Khajavi *et al.* 2015: Marzouki *et al.* 2019:
Thermal stability	Marzouki *et al.* 2019
Electrical properties	Marzouki *et al.* 2019
Dyeability	Khalifa, 2017; Lin *et al.* 2022

Mercerization is one of the most important wet processes of cotton textiles. It is necessary to modify the structure of cotton to achieve enhanced physical (dye uptake and lustre) and mechanical (tenacity, elongation and work of rupture) properties (Khajavi *et al.,* 2015). It is possible to impart similar superior properties of synthetic fibres to cotton fibres with mercerization processes (Elrys *et al.,* 2015). Through mercerization, the crystallinity of the cotton fibre decreases and the amorphous characteristics increases, providing more pores and effective hydroxyl groups in the fibre (Lin *et al.,* 2022). The crystallinity of mercerized cellulose is lower than that of natural cellulose commonly of the order of 60 % (Tatsumi *et al.,* 2022). It is estimated that the number of available hydroxyl groups are increased by about 25 % where this increase is directly related to the increase in moisture absorption, reactivity, and dye absorption of mercerized cotton (Wagaw and Chavan, 2012).

At alkali concentration greater than 6 %, many structural and morphological changes begin to occur in cellulose. As concentration increases, crystalline structures (highly ordered polymer chains) and amorphous regions begin to swell where the swelling starts first in the latter followed by the former. Degree of polymerisation and the degree of crystallinity also decreases with increasing alkali concentration (Modenbach and Nokes, 2014). As such, the crystalline structure is transformed from cellulose I (a natural cellulose in which its chains are parallel) to cellulose II (a form of regenerated cellulose in which its chains lie antiparallel to one another with alternating reducing ends) while retaining its solid phase (Tatsumi *et al.,* 2022; Zlenko *et al.,* 2021).

There are difficulties in carrying out normal mercerization because cotton exhibits hydrophobic behaviour in the loom state due to its greasy impurities hardly allowing high viscosity caustic soda solution at low temperature to penetrate into the fibres' internal structure (Sameii *et al.,* 2008). At high concentration of sodium hydroxide, swelling of the outermost fibres forms a barrier, inhibiting the penetration of liquor into the yarn core and crossing points which results in poor mercerizing of the core and lack of uniformity. In the case of fabric, swelling is further restricted by the yarn crossing points (Wagaw and Chavan, 2012). Hot mercerization, in which caustic soda is applied at about 60 ^{o}C, affords better penetration of the alkali into the fibres (Tarbuk *et al.*, 2014).

Mercerization parameters have been extensively studied and reported in the literature. Akhbari *et al.* (2012) mercerized different counts of carded and combed yarns made of cotton fibres from different origins in two different machines and different settings of the machine parameters and concluded that technical characteristics of the untreated yarn has a

considerable effect on the strength of the mercerized yarn. Wagaw and Chavan (2012) optimized the causticization of 100 % cotton fabric using single factor completely randomized experimental design and recommended 14-16 % sodium hydroxide concentration to get the advantage of increase in colour yield. Gemci (2010) studied mercerization process on cotton fabrics with plain, twill, and dobby weave to examine its effects on dimensional stability and suggested that the shrinkage values on warp direction were greater than those of weft. Khajavi *et al.* (2015) carried out conventional and ultrasound assisted mercerization of cotton fabric where they optimized caustic concentration, temperature, and time of treatment to obtain mercerized samples with maximum strength/elongation and minimum shrinkage using response surface methodology.

2.2.2 Caustic treatment of polyester and cotton/polyester blend

It is common to give poly (ethylene terephthalate) (PET) fibres a finishing treatment with alkaline solution to improve its handle and soil resistance (Tavanai, 2009). Caustic treatment gives a silk-like finishing to 100 % polyester fabrics mimicking natural silk in drape and hand. Just like in mercerization of cotton, the important treatment variables in caustic treatment of polyester include caustic concentration, temperature and time. Studies suggest that temperature has stronger effect on the reaction rate than caustic concentration (Carrera-Gallissa *et al.,* 2017). The process is referred to as weight reduction or hydrolysis. In the process, the electron deficient carbonyl carbons of PET are attacked by hydroxyl ions of aqueous caustic soda resulting in chain scission and formation of carboxylate and hydroxyl end groups (Tavanai, 2009).

The synergistic action of alkali media on blended textiles has been recognized. Caustic treatment of cotton/polyester blend changes the fine structure, morphology, and conformation of cellulose chains component (Borisova and Reihmane, 2013) and gives a silky handle, lustre, soil repellency and anti-static properties to the polyester component reducing its stiffness, tenacity and elongation (Haji *et al.*, 2011). Hot alkali treatment of cotton/polyester fabric improves water and dye absorption of both fibres in the fabric. Hydros is normally used during alkali treatment of polyester or cotton/polyester blend to reduce fabric yellowing and also to act as oxygen scavenger (Montazer and Sadighi, 2006).

2.3 Waste Management, Environmental Impacts of Vat Dyeing, and Heavy Metals

2.3.1 Waste management

Waste management is one of the greatest challenges facing humanity in modern times and its principle is saddled with the mandate of protecting the environment by reducing, reusing, recycling, and proper disposal of waste (Yalcin-Enis *et al.*, 2019; Balogun *et al.*, 2021). Waste management is all the activities and actions required to manage waste from its inception to its final disposal which include collection, transport, treatment, disposal, as well as monitoring and regulation. The best practice available for waste management is zero waste which is an approach to eliminate waste rather than manage it (Islam and Islam, 2021). Recently, environmental legislation states that dyehouses have to ensure that the wastewater they release abide by the international dye industry wastewater discharge quality standards that were adopted from the Zero Discharge of Hazardous Chemicals Programme (ZDHC) (Rapo and Tonk, 2021).

Textile industries produce liquid waste containing dyes and finishing agents, a significant amount of solid waste, and greenhouse gases (Islam and Islam, 2021). Dye manufacturing industries and dyehouses constitute about 28 % of effluent generated worldwide as shown in Figure 2.7 (Rapo and Tonk, 2021). During colouration process, a large proportion of the dyes are not absorbed where approximately 10-15 % are lost in the wastewater (Arcanjo *et al.*, 2018). The composition of textile industry wastewater varies from mill to mill and from country to country, depending on the process, the equipment used in the factory, type of fabric produced, chemicals applied, etc. (Yaseen and Scholz, 2019). Textile effluents are characterized by high values in terms of several physico-chemical and biological parameters including colour, temperature, pH, salinity, biological oxygen demand (BOD), total dissolved solids (TDS), chemical oxygen demand (COD), total nitrogen, total phosphorous, and non-biodegradable organic compounds (Berradi *et al.*, 2019).

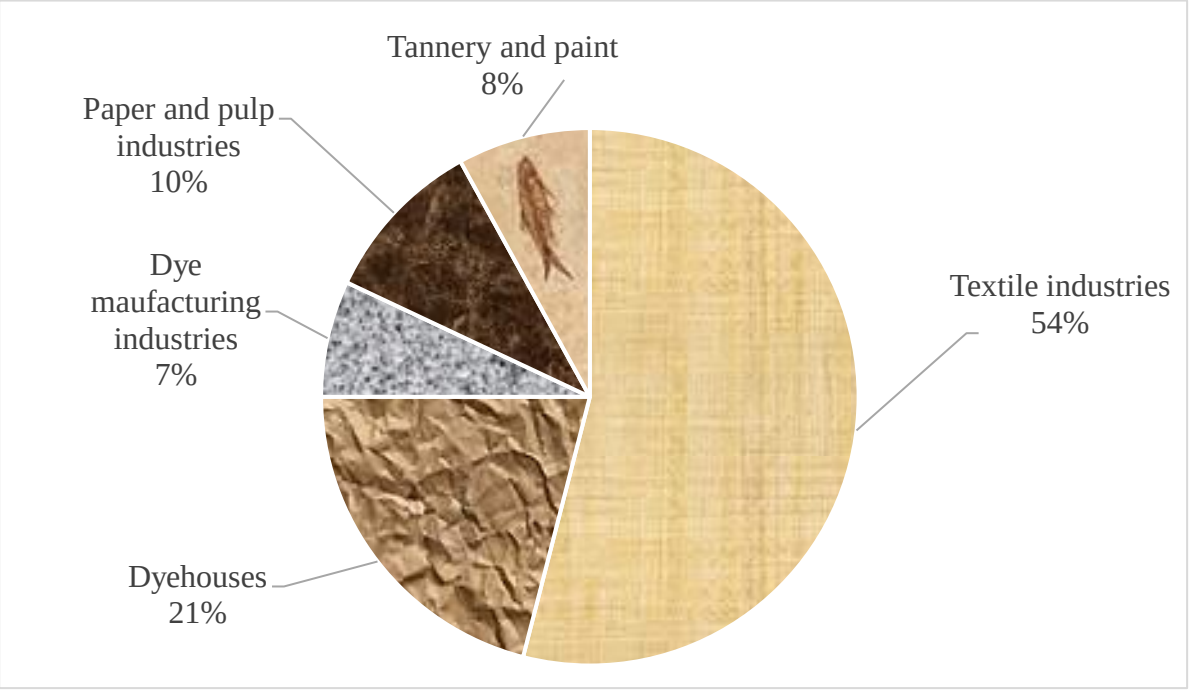


Figure 2.7: Share of dye effluent from various industries (Velusamy *et al.*, 2021)

Effluent components can be classified in four ways of sustainability: colour and colourless, dissolved or not dissolved, biodegradable or non-biodegradable, and toxic or non-toxic (Khatri *et al.,* 2015). As the quantity of wastewater increases and its characteristics become more complex, the carrying capacity of the receiving environment eventually decrease to a level where natural treatments are insufficient and environmental problems begin to arise (Amare *et al.,* 2018). Environmental pollution due to dyeing is mainly related to water pollution as emissions to air are generally not significant due to the low vapour pressure of the substances in the dyebath (Chavan, 2011). Contamination of aquatic systems is a universal phenomenon that greatly affects developing countries as a consequence of the dumping of untreated or partially treated wastewater (Barrios-Ziolo *et al.,* 2016). After their breakdown, dyes and auxiliary chemicals contaminate the nearby soil, sediment, and surface water becoming a major global environmental pollution challenge (Yaseen and Scholz, 2019).

Several environmental protection agencies worldwide have imposed rules governing the protection of human health and guarding the environment from pollution caused by the textile industry where these agencies set certain limits on the disposal of effluents into the environment (Ghaly *et al.,* 2014). For example, the National Environmental Standards and Regulations Enforcement Agency (NESREA), an agency under the Federal Ministry of Environment, is responsible for the management and enforcement of national environmental standards in Nigeria. The agency recently warned manufacturers in Kano Metropolis to desist from degrading the environment and disregard for human lives and also urged industrialists to treat effluent at least to primary levels before discharge into the public drain (Essen, 2017).

Several studies investigated waste management strategies and environmental impacts of effluent generated by small scale dyeing industries. Sulthonuddin and Herdiansyah (2021) suggested the strategies for sustainable batik wastewater management in Paoman village, Indonesia. Rahman *et al.* (2020) assessed public perception and the impact of loom-dye effluent contaminated irrigation water on the growth of rice in Belkuchi, Bangladesh. Selase *et al.* (2021) conducted a survey on waste management among batik and tie-dye workers in Ho Municipality, Ghana. Oguntade *et al.* (2018) investigated the impact of dye-laden effluent contaminated irrigation water on growth, yield, and metal uptake of plants produced in Abeokuta, Nigeria. Bioremediation of "Adire" tie-dye effluent in Ibadan, Nigeria (Okareh *et al.*, 2017), and Abeokuta, Nigeria (Bankole *et al.*, 2017) has been reported.

2.3.2 Environmental impacts of vat dyeing

The anthraquinone based vat dyes require more synthetic steps than the acid, basic, direct, disperse and reactive dye classes. The multiple chemical reactions increase the consumption of raw-materials, resulting in vat dyes having the highest ratio of raw-materials to finished dye and this high ratio makes vat dyes the leading generator of wastewater and hazardous waste compared to other dye classes (Baptista, 2009). Low chemical yields and use of hazardous raw-materials, catalysts, and solvents made vat dyes the most highly polluting class of dyes manufactured (Baptista, 2009). Common solvents used in vat dye synthesis are nitrobenzene, naphthalene, 1,2-dichlorobenzene etc. and all of these solvents are hazardous chemicals with the potential of severe environmental contamination (Baptista, 2009).

Vat dyes in the non-soluble form do not represent an environmental risk as regards to their toxicity (Bozic and Kokol, 2008) but are the main causes of pollution in the wastewaters of

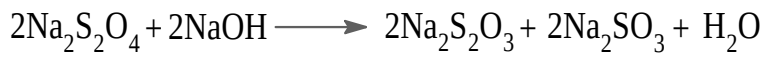
textile and other industrial effluents (Rapo and Tonk, 2021) which some countries classify as the most toxic class of wastewaters (Bozic and Kokol, 2008). Typically, released vat dyebath contains spent caustic soda, reducing agent, dispersing agents, auxiliaries such as levelling and sequestering agents (Bechtold and Turcanu, 2009) and heavy metals (Baptista, 2009).

Use of hydros as reducing agent in vat dyeing is being criticised for the formation of environmental unfriendly oxidation by-products such as sulphite $(SO_3)^{2-}$, sulphate $(SO_4)^{2-}$, thiosulphate ions $(S_2O_3)^{2-}$ and toxic sulphur (Shi, 2014). The sulphide ions released from hydros and sodium sulphide decompositions affect the environment detrimentally by noxious odours, toxicity and high COD of the wastewater (Bozic and Kokol, 2008). Equation 2.4 to 2.6 show different reactions leading to decomposition of hydros. Salts of sulphur in the form of sulphates and sulphites contaminate sewage, lower its pH and show corrosive action where sewage comes in contact with concrete works, iron structures etc. (Kulandainathan *et al.*, 2007).

As most vat dyes are exhausted up to 95 %, a little is left in the bath and consequently the effluent load from this unused dye is negligible but the residual dye solution becomes oxidised and deposited increasing the percentage of suspended solids (Chakraborty, 1992). In order to reduce these pollutants, several processes have been used for the reduction of indigo including fermentation and bacterial reduction, chemical reduction, electrochemical reduction, catalytic hydrogenation, and electrocatalytic hydrogenation. Yet, there is no reducing agent available today that can replace hydros in vat dye application (Chavan, 2015).



Equation 2.4: Decomposition of hydros under oxidative condition



Equation 2.5: Decomposition of hydros under thermal condition



Equation 2.6: Decomposition of hydros under hydrolytic condition

Some vat dyes have tendency to biodegrade and produce intermediate products more toxic than the original dye (Arcanjo *et al.,* 2018). Aquatic toxicity of some vat dyes has been reported. De-Luna *et al.* (2014) investigated acute and chronic ecotoxicity of vat, reactive, acid and food dyes and showed that among the textile dyes used, vat dye was the most toxic where after 30 mins. of treatment the generated products were more toxic than the original dyes. Mounteer *et al.* (2018) evaluated the influence of different dyes classes on ADMI colour, COD, and acute toxicity and showed that COD removal was higher when vat dyes were absent and that vat dyes exhibited greater recalcitrance to treatment with no ADMI colour removal and COD removal was less than 30 %. De Oliveira *et al.* (2016) investigated the toxicity of direct, reactive, and vat dyes to the embryonic and larval development of zebra fish and suggested that all the dyes exhibited developmental toxicity to the fish embryo which could decrease survival.

2.3.3 Heavy metals

Heavy metals are naturally occurring substances often present in the environment at low concentration but augmented by anthropogenic activities (Ocheri *et al.,* 2014). Raw textile

materials e.g., cotton, flax, hemp etc. may contain different elements where their metal content varies significantly between seasons and between climate growth areas. Those fibres adsorb very large amounts of elements from the environment and contribute to problems in textile industry namely yarn manufacture, dyeing, chemical processing etc. (Rezic *et al.,* 2011). Heavy metal catalysts used in key intermediate steps in dye synthesis such as mercury, arsenic, copper, and chromium may be released in dyebath wastewaters contaminating soil and groundwater if improperly treated or disposed of (Baptista, 2009).

Common heavy metals known to be toxic to humans include arsenic, cadmium, chromium, copper, lead, zinc where chromium, copper, and zinc are essential micronutrients required by the human body for growth and their toxicity depends upon enhanced dose (Walker *et al.*, 2019). Non-essential heavy metals such as cadmium, mercury, and lead can damage biological structures and cause health problems even at very low concentrations through inhalation, ingestion, and by skin exposure (Ozbek, 2018). Toxic effects of heavy metals on human health are well known and include damage of organs, disorders in the respiratory tract and long diseases, dysfunction of the heart, disorders in nervous system, skin diseases, abnormality in fertility and pregnancy, etc. (Rezic and Steffan, 2007).

Heavy metals have been determined in dye powders (Abel-Ghany, 2013; Abdullahi *et al.*, 2016; Sani *et al.,* 2018) and in different fibres (Rezic and Steffan, 2007; Rezic *et al.,* 2011). To regulate the use of heavy metals, different standards are now used globally which includes the European product guarantee, OKO Tex standard, Ecological and Toxicological Association of Dyers and Organic Pigment Manufacturers (ETAD), and clean fashion,

stellman, commitextile (Rezic and Steffan, 2007). Heavy metal content of some dyes is shown in Table 2.5.

Table 2.5: Heavy metal content of dyes (Chavan, 2011; Barclay and Buckley, 2000)

Metal	Typical concentration (ppm)	Dye type with highest metal content
Arsenic	<1-1.4	Reactive
Cadmium	<1	All types
Chromium	3-83	Vat
Cobalt	<1-3.2	Acid
Cupper	33-110	Vat
Lead	6-52	Reactive
Mercury	0.5-1	Vat
Zinc	3-32	Basic

Different analytical methods can be used for quantitative and qualitative determination of heavy metals such as thin layer chromatography, UV-visible photometry, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), microwave plasma atomic emission spectrometry (MP-AES), and atomic absorption spectrometry (Zeiner *et al.,* 2007). MP-AES represents a completely new elemental analytical technique that has been designed to improve analytical performance and productivity while decreasing operating costs by elimination of the flammable and/or expensive gas requirements used in typical elemental analytical techniques (Sungur and Gülmez, 2015). Unlike other methods where there is question of safety, long analysis time and cost, MP-AES has a possibility of multielement analysis, convenience/safety of nitrogen plasma, and more affordability compared to argon plasma (Smirnova *et al.*, 2018).

2.4 Groundwater Quality and Pollution

Groundwater is a necessary substitute to surface water in every society. It is a hidden, replenishable resource whose occurrence and distribution greatly varies according to the local as well as regional geology, hydrogeological setting, and to an extent the nature of human activities (Ismail and Yola, 2012). Due to surface water contamination, groundwater is the major source of fresh water worldwide (Raji and Abdulkadir, 2020; Aghazadeh *et al.,* 2017) where approximately one third of global population depend on this water source for drinking (Li *et al.,* 2021). The number of individuals living in water scarce areas will increase to around 3.9 billion by 2030 as assessed by world water council (Velusamy *et al.,* 2021).

Groundwater occurs below the water table and its quality depends on chemical constituents and their concentration which are mostly derived from the geological data of the particular region. The traditional way of extracting groundwater is by drilling boreholes and shallow wells through the existing water table to form a well point (Yahaya *et al.,* 2017). Increased population growth usually results in the dumping of high heaps of municipal solid waste into open water bodies resulting in contamination of streams and groundwater especially shallow wells (Butu and Mshelia, 2014).

In addition to geological data, groundwater quality also depends on a number of factors such as the degree of chemical weathering of rocks, quality of recharge water, and water-rock interactions (Aghazadeh *et al.,* 2017). Water-rock interactions is one of the main processes driving the concentration of chemical constituents in groundwater. The relative proportions of various dissolved ion concentration in groundwater depends to a large extent on the solubility

of rocks in aquifers (Feng *et al.,* 2020). An Aquifer is a body of the earth that contain sufficient permeable material to yield significant quantity of water (Raji and Abdulkadir, 2020).

Anthropogenic sources of water contamination include industrial effluent, underground storage tanks, landfills, sewage, contaminated surface water, and fertilizers/pesticides used for agriculture (Brindha *et al.,* 2020). Few years ago, there were about 270 factories in the 4 industrial estates of Kano Metropolis where tanneries and textiles are dominant and generate more than 90 % of liquid and solid waste mostly discharged into open drains and eventually onto land surfaces and into natural waters in the vicinity (Nabegu, 2016). Increased population in Kano Metropolis results in the generation of high heaps of municipal solid waste which are dumped at available open spaces and in open water bodies which are good contaminants of streams and groundwater especially shallow wells (Butu and Mshelia, 2014).

Water pollution has been attributed to the ability of water to dissolve more substances than any other liquid where this characteristic makes it easily polluted (Velusamy *et al.,* 2021). Groundwater is generally less susceptible to contamination than surface water and is usually highly mineralized in its natural state. The water moves slowly through the subsurface and can remain for extended periods of time in contact with minerals present in soil and bedrock until chemical equilibrium is reached between the water and minerals (Kumar *et al.,* 2016). Once groundwater is polluted, natural purification processes can take decades or even hundreds of years even if the source of contamination is cut off (Li *et al.,* 2021).

Polluted water is the major cause for the spread of many epidemics and some serious diseases like cholera, tuberculosis, typhoid, and diarrhea among others (Shawai *et al.,* 2019). Water

related diseases caused by insufficient safe water supplies coupled with poor sanitation and hygiene caused 3.4 million deaths a year, mostly among children (UNICEF, 2008). Because of the negative public health impacts of unsafe water, government agencies have established drinking water quality standards that public sources must meet or exceed. Guidelines for drinking water quality provides guidance in setting health-based targets for three classes of contaminants viz microbiological, chemical, and radiological (UNICEF, 2008).

The threat of absolute water scarcity in the near future has necessitated the need for an extensive study on the quality of groundwater used for drinking and irrigation. Groundwater quality parameters have been evaluated in many places worldwide e.g., China (Zhang *et al.*, 2020), India (Brindha *et al.*, 2020), Iran (Aghazadeh *et al.*, 2017), and in Nigeria such as in Ogun (Zacchaeus *et al.,* 2020), Lagos (Popoola *et al.*, 2019), Gombe (Yusuf *et al.,* 2018), Jigawa (Tukur *et al.,* 2020), and Kano Metropolis (Balogun *et al.,* 2020; Suleiman *et al.,* 2020; Shawai *et al.,* 2018; Yahaya *et al.,* 2017).

2.5 Design of Experiment

Design of experiment (DOE) was invented by Ronald A. Fisher in the 1920s at Rothamsted experimental station, new London, England (Montgomery, 2001; Telford, 2007). Although the experimental design method was first used in an agricultural context, the method has been applied successfully in the military and in industry since the 1940s (Telford, 2007). Applications of statistical design in industrial settings began since in the 1930s and this was catalyzed by the development of response surface methodology (RSM) by Box and Wilson in 1951. The work of Genichi Taguchi which began in the late 1970s ushered another era of

statistical design as it had a significant impact on expanding interest in quality improvement (Montgomery, 2001).

DOE is an action or series of actions in which input variables of a process or system are changed on purpose so that the reasons for changes in the output response can be identified and observed. After the response is measured, data is obtained and analyzed using Analysis of Variance (ANOVA) leading to the determination of significant factors that affected the response variable. A model is then generated to represent the response variable as a function of the significant factors (Ledari *et al.*, 2014). Good DOE helps to protect real effects from being obscured by experimental error which is different from errors due to variations in raw-material, sampling, and in setting of experimental factors (Box *et al.*, 2005).

The objectives of DOE include determine which variables are most influential on the response, identify where to set the influential factors so that the response is always near the desired nominal value, determine where to set the influential factors so that the effects of uncontrollable variables are minimized, determine where to set the influential factors so that variability in the response will be minimal (Montgomery, 2001). One of the fundamental principles of DOE is randomisation which protects an unknown bias, e.g., instrument drift and satisfies the statistical requirement that observations should be independently distributed random variables (Montgomery, 2001).

Other principles of DOE include replication which increases the sample size and precision of the experiment allowing the experimenter to obtain an estimate of the experimental error (Telford, 2007), blocking which is a restriction of complete randomization to remove batch to

batch variation from the experimental error, and factorial experiment where in each complete trial or replicate of the experiment all possible combinations of the levels of the factors are investigated and for a new system/process, screening experiments are carried out to reduce the number of runs of 4-5 factor combinations by fractional factorial design (Montgomery, 2001).

Approaches used in DOE involves best guess approach used frequently by scientists and engineers where if the initial best guess does not produce the desired results the experimenter has to take another guess at the correct combination of factor levels; one factor at a time which involves selecting a starting point (baseline) for each factor, successively vary each factor over its range with the other factors being held constant, and then construct a graph showing how the response is affected by varying each factor; methods based on statistical approach to design (factorial experiment) in which factors are varied together to determine individual factor (main) effects as well as interaction among factors (Montgomery, 2001).

It is very important to have a first-hand knowledge of the system/process being studied. Stages in experimental design involve stating the objective of the study, choosing the factors, their levels and ranges, selecting the response variable, choosing the experimental design to be used, and then statistical analysis of data. Factors may be potential design factors which are the factors that the experimenter wish to vary in the experiment or nuisance factors which may have large effects that must be accompanied for. Potential design factors can be either the design factor selected for study in the experiment, held constant factor that may exert some effect on the response but not of interest and held at constant level, or allowed to vary factor which are either experimental units or “materials” to which design factors are applied and are usually nonhomogeneous. Nuisance factors may be controllable, such as different batches of

raw-materials or different days the experiment is conducted, or uncontrollable e.g., relative humidity.

Controllable factor may be time, temperature, concentration of a chemical, etc., which can be measured while uncontrollable factors cannot be measured e.g., type of chemical used, the experimenter, equipment used, production rate, environmental condition, etc. (Montgomery, 2001). Factor levels are normally kept low with 2 levels being adequate and factor ranges over which factors are varied should be broad. Response variable is the average or/and standard deviation of the measured characteristics. Factors and responses can either be nominal or categorical. Number of replicates required determines the choice of experimental design, for example, RSM suits well with central composite design (CCD). Statistical analysis of data, e.g., analysis of variance (ANOVA), residual analysis, model adequacy checking etc. provides objective results of an experiment in terms of empirical model (Montgomery, 2001).

Optimizing refers to improving the performance of a system, a process, or a product in order to obtain the maximum benefit from it. The term optimization has been commonly used in analytical chemistry as a means of discovering conditions at which to apply a procedure that produces the best possible response (Bezerra *et al.,* 2008). An approach for solving the problem of the optimization of several responses is the use of a multicriteria methodology. This methodology is applied when various responses have to be considered at the same time and it is necessary to find optimal compromises between the total numbers of responses taken into account. The Derringer function or desirability function is the most important and most currently used multicriteria methodology in the optimization of analytical procedures (Bezerra *et al.,* 2008).

2.5.1 Response surface methodology

RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes (Myers *et al.*, 2009). RSM offer DOE tools that lead to peak process performance. It produces precise maps based on mathematical models. This methodology facilitates putting all responses together via sophisticated optimization approaches which ultimately lead to the discovery of sweet spot to meet all specifications at minimal cost. The optimal response may be a surface such as simple maximum, rising ridge, or a saddle (Anderson and Whitcomb, 2017).

Some stages in the application of RSM as an optimization technique are the selection of independent variables of major effects on the system through screening studies and the delimitation of the experimental region, according to the objective of the study and the experience of the researcher; the choice of the experimental design and carrying out the experiments according to the selected experimental matrix; the mathematic–statistical treatment of the obtained experimental data through the fit of a polynomial function; the evaluation of the model's fitness; the verification of the necessity and possibility of performing a displacement in direction to the optimal region; and obtaining the optimum values for each studied variable (Bezerra *et al.,* 2008).

2.6 Small and Medium Enterprises

It is widely recognised that Small and Medium Enterprises (SMEs) play dynamic role in enabling economic growth, poverty alleviation, employment and wealth creation for equitable distribution of income and increased productivity (Igwe *et al.,* 2018). In most countries including developed nations such as Japan, USA, UK, etc., SMEs account for more than half

of the total share of employment, contribution to growth domestic product (GDP), and sales (Ogbo and Nwachukwu, 2012). According to International Labour Organisation (2014a), SMEs have the potential to contribute significantly to the social and economic progress of workers and communities.

In the developing regions, self-employment which constitutes a greater share of informal employment (non-agricultural) represents nearly one third of total non-agricultural employment in sub-Saharan Africa (ILO, 2014b). The manufacturing sector in Sub-Saharan Africa is dominated by very small and informal enterprises and majority of them grow only when they are young and because of this lack of growth, the job creation falls short of what they are expected to achieve (Sonobe *et al.,* 2011). Business environment in Africa is affected by some institutional barriers, such as, ineffective credit and finance system; corruption, political instability and inefficient legal system; lack of quality education; poor infrastructure; religion; tradition and customs (Igwe *et al.,* 2018).

Studies have shown that micro, small and medium enterprises (MSMEs) have the propensity to drive the Nigerian economy where over 17 million MSMEs employed about 31 million Nigerians and also accounted for more than 80 % of all enterprises (Afolabi, 2015). Most SMEs in Nigeria die within the first 5 years of existence, a few go into extinction between the 6th and 10th year while only about 5-10 % survive, thrive and grow (Agwu and Emeti, 2014). Factors responsible for premature death of SMEs in Nigeria include insufficient capital, infrastructural inadequacies, lack of proper book keeping, lack of proper records or no records at all, inability to separate business and family or personal finances, inability to distinguish

between revenue and profits (Agwu and Emeti, 2014), lack of focus, lack of succession plan, inexperience, and lack of business strategy (Aremu and Adeyemi, 2011).

Since the mid-1980s there has been an increased commitment of government to entrepreneurship development especially after the introduction of structural adjustment programme (SAP) in 1986, and the establishment of National Directorate of Employment (NDE), the Small and Medium Enterprise Development Association of Nigeria (SMEDAN) (Afolabi, 2015), Nigerian International Development Bank (NIDB), Nigerian Export-Import Bank (NEXIM), Nigerian Bank of Commerce and Industry (NBCI), among others (Ogbo and Nwachukwu, 2012). In classifying SMEs, three parameters are generally applied by most countries singly or in combination, namely, capital investment on plant and machinery, number of workers employed, and volume of production or turnover of business. Within the Nigerian context, roadside artisans, petty traders, pure/bottled water producers, bakers, local fabricators (regarded as micro enterprises) constitute part of SMEs (Aremu and Adeyemi, 2011).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals/reagents and substrates

Commercial grade of sodium hydroxide (99 %, UN No. 1823, Tianya chemicals, China) and hydros (85 %, UN No. 1384, Jinhe hydrosulphite Factory Co. Ltd., China), as well as analytical grades of potassium chloride, ferrous ammonium sulphate, synthetic detergent, sodium carbonate, hydrochloric acid, acetic acid, disodium hydrogen orthophosphate, 1-histidine mono hydrochloric monohydrate, magnesium chloride hexahydrate, sodium acetate, barium chloride, sodium sulphate, sulphamic acid, hydrogen peroxide, perchloric acid, ferroin indicator solution, potassium hydrogen phthalate, anhydrous potassium dichromate, sulphuric acid, and nitric acid were purchased and used without purification.

C. I Vat Blue 4 (lot No. 101-196, Hangzhou Tiankun Chemical Co. Ltd., China), C. I Vat red 1 (lot No. 261-308, Hangzhou Tiankun Chemical Co. Ltd., China), and C. I. Vat Violet 1 (lot No. 1-40, Shaoxing Shangyu Haohua Chemical Industrial Co. Ltd., China) were selected by purposive sampling and purchased from Al-Ameen Chemicals, a colour shop located at No. 11, Hausawa Sabon Titi, Tarauni Local Government Area, Kano. They were selected based on the fact that they are more frequently used than other colours and are, respectively, of anthraquinone, indigoid, and polycyclic types. Structures of the dyes used and their application and chemical classes are shown in Table 3.1. Two types of white un-dyed fabrics, 100 % cotton (CF) and cotton/polyester blend (BF) were selected purposively and purchased from “Kantin Kwari” market, the biggest cloth market in Kano, which provides the materials usually dyed in the Metropolis. Specifications of the fabrics used are shown in Table 3.2. Wool

fabric used as undyed adjacent fabric in staining tests was kindly supplied by the Department of Textile Engineering, Leads University, United Kingdom.

Table 3.1: Dyes used in the study

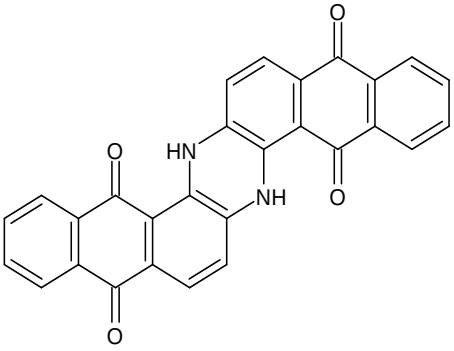
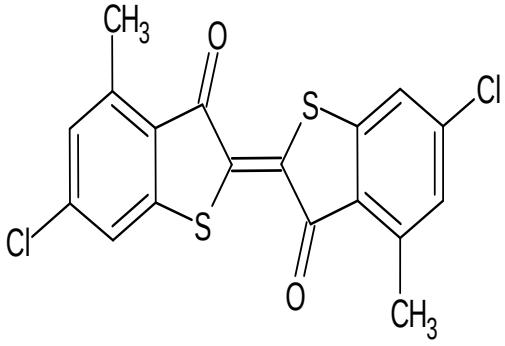
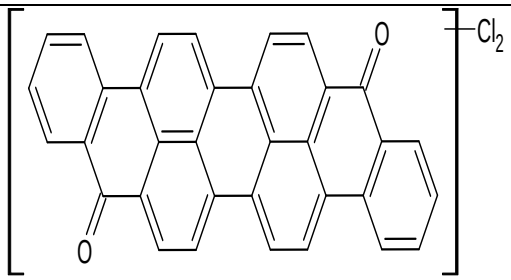
Sample Code	Name	Structure	Application class	Chemical class
A	C. I. Vat Blue 4 (RSN)		IW	Indanthrone
B	C. I. Vat Red 1 (VR1)		IK	indigoid
C	C. I. Vat Violet 1 (VRR)		IN	Violanthrone

Table 3.2: Specifications of fabrics used in the study

Sample	Composition	Weave	Warp density (ends/cm)	Weft density (picks/cm)	Warp yarn count (Tex)	Weft yarn count (Tex)
BF	43/57 % cotton/polyester blend	Plain weave	38 polyester yarns	44 cotton yarns	8.15	10.1
CF	100 % cotton	Derivative of plain weave	44 Cotton yarns	28 Cotton yarns	14.25	14.5

3.1.2 Analytical equipment

The equipment used in the study include UV-Visible spectrophotometer (Spectrumlab 752S, U.S.A), Microwave Plasma Atomic Emission Spectrophotometer (Agilent Technologies 4210, U.S.A), pH meter (Jenway 3310, UK), conductivity meter (Jenway 4520, U.S.A), handheld GPS equipment (Garmin 78SC, China), multifunction electronic fabric strength tester (model YG0260, Chang Y, Fang Yi, China), light fastness tester (Microscal LFT 225, U.S.A), and dissolve oxygen meter (HANA, HI9143, USA).

3.2 Methods

3.2.1 Study area

Kano Metropolis is among Nigeria's four largest urban areas and it is also the largest in the northern part of the country (Garba, 1997). By the beginning of the 20th Century Kano City was the largest urban settlement in Hausa land and comprised of the space within the wall and the adjoining Fagge settlement just outside it. It later translated in space as Nassarawa and Bompai (for the Europeans) and Sabon-Gari (for non-Europeans and non-natives). Later,

Tudun Wada, Gwagwarwa and Brigade (for natives) came into existence where all together these residential units with the old Kano City were known as Kano township which formed what is referred to as Urban Kano (Umar *et al.*, 2019). The oil boom era developments have incorporated adjoining villages such as Gama, Dawakin Dakata, Hotoro, Kawo, Giginyu, Unguwa Uku, Na'ibawa, Sharada, and Dorayi into the Urban Kano and transformed into a Metropolis (Liman, 2015).

Kano Metropolis is boarded by Madobi and Tofa Local Government Areas to the South West, Gezawa to the East, Dawakin Kudu to the South East, and Minjibir on the North East. The Metropolitan Area comprises six core Local Governments (Dala, Fagge, Kano Municipal, Nassarawa, Gwale, and Tarauni) and two peri-urban Local Governments including Kumbotso and Ungogo (Balogun *et al.*, 2020). Its population is 1.6 million in 2000, 2.3 million as at 2003, 2.8 million in 2006 (Balogun *et al*., 2020), about 3.5 million as at 2014 (Weber *et al*., 2017) and is projected to reach about 5.7 million by 2025 (Abdullahi *et al*., 2019). It has a population density of about 1000 inhabitants per km^2 compared to the national average of 267 per km^2. It lies between Lat. 10^o and 12^oN and Long. 8^o and 9^oE (Figure 3.1) with an area of 600 km^2, an altitude of 488 m above sea level (Suleiman *et al.*, 2020) and predominantly comprised of Hausa and Fulani ethnic groups who are mostly Muslims (Iliyas, 2000).

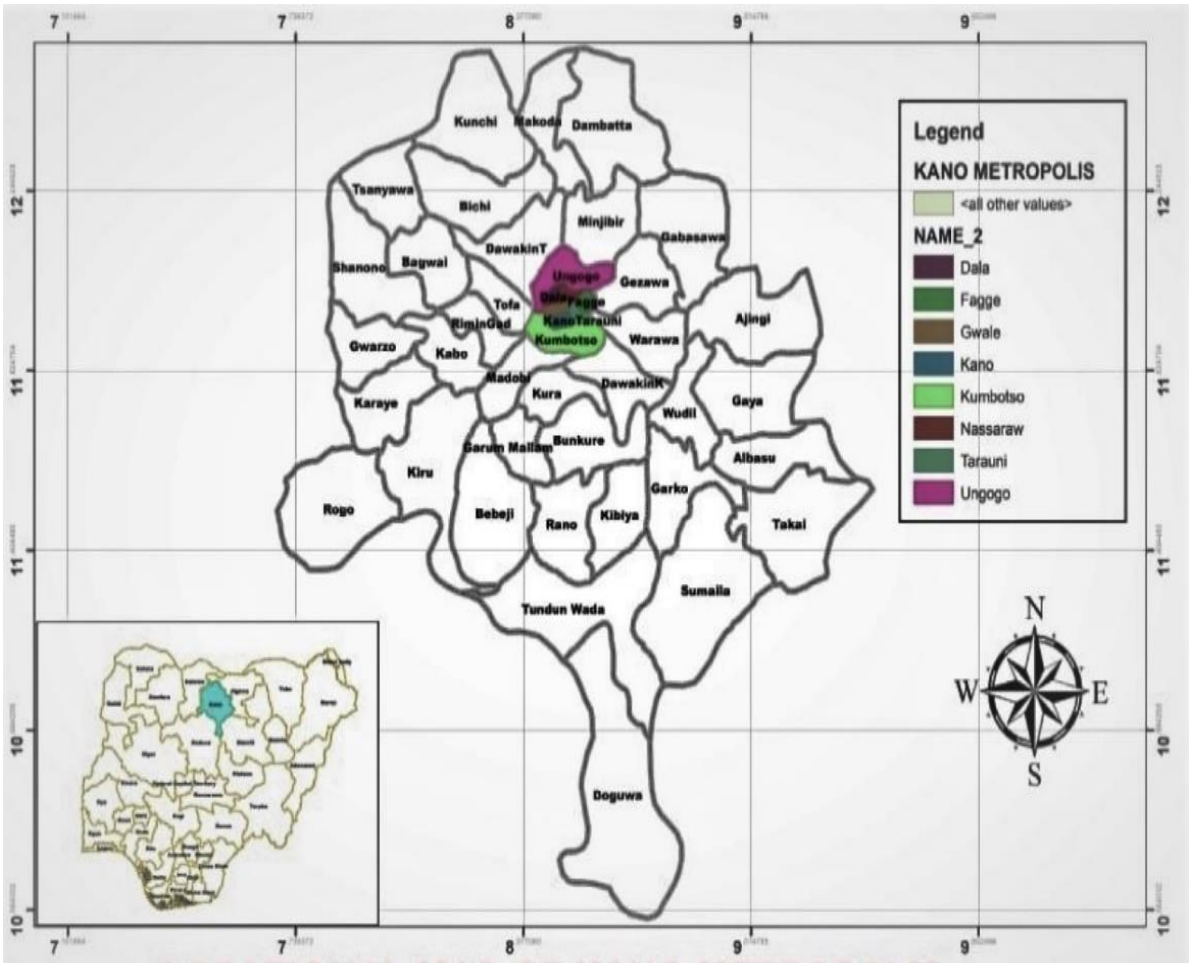


Figure 3.1: Location map of Kano Metropolis (GIS Laboratory, Ahmadu Bello University, Zaria)

The Kano Metropolitan Area was selected for this study because the ancient city has attracted historical prominence since the 14th Century with its fine indigo dyed cloth (Ezeanya-Esiobu, 2019) and currently there are many secondary dyeing units in the area that are engaged in hand dyeing using synthetic vat dyes. Large population and abundant markets could enable huge patronage of the services offered by the dyers. For the purpose of this study, the non-industrial dyeing units are referred to as dyehouses and traders in 'Kantin-Kwari' cloth market and colour shops are called cloth and colour vendors, respectively.

3.2.1.1 Geology and hydrogeology of the study area

Fundamental to the study of groundwater in any place is the geology of the environment because geology is the main controlling factor in groundwater hydrology (Ocheri *et al*., 2014). The Kano region extends over two major geological structures separated by an interphase known as hydrological divide. The southern and western parts of the divide are underlain by the basement-complex rocks and the northern parts by the sedimentary chard formation (Tukur *et al*., 2018). Kano Metropolis lies on the basement complex which is known as the high plains of Hausa land.

Pre-Cambrian rock of the basement complex comprises of gneisses, amphibolite, marbles and the older granites which underlie large part of Nigeria including 80% of the Kano region. Jakara River is underlain by crystalline basement complex of pre-Cambrian origin which losses its density by disappearing into the Chad formation. The basement complex consists of granite rocks extending up to Yadai towards the North and Gabasawa towards the East. The granites are generally gneissic and commonly developed in a mixture of pegmatite of schist granite, Gneiss and irregular mass of pegmatite (Olofin, 1987).

In urban Kano, groundwater occurs within the weathered mantle or in the joint and fractured systems. The aquifer types in the study area include weathered layer aquifer, weathered/fractured or partly weathered aquifer and fractured aquifer (Tahir *et al*., 2015). Water table in the study area is usually found at depth of less than 20 m where in some places it can be found even around 8.4 m and boreholes hardly go beyond 60 m. The hydraulic

conductivity of the aquifer ranges from 0.039 to 0.778 m/d and permeability differs from 3.756 to 36.600 m^2/d (Bello and Tuna, 2014).

The Challawa, Jakara, Kano and Watari River systems provide water for human consumption, irrigation and industrial activities in Kano Metropolis (Liman, 2015). Water resource in the study area is faced with several challenges including migration of water from the areas underlain by the basement complex to those underlain by the Chad formation, rising demand of water by an ever-increasing population and climate variability (Abdulhamid, 2013).

3.2.1.2 Water demand and drainage in the study area

About a decade ago, water supply was just 36 % of the total demand of the Metropolitan Area by water treatment plants of Challawa, Tamburawa and Watari. In order to satisfy the demand, community, private individuals and philanthropists supplement government effort in water supply (Bello and Abdullahi, 2014). The low-income community meet their water demand requirements through various means including dug wells in houses, community lined concrete wells, boreholes with hand pumps, public stand posts, privately owned boreholes-based systems, and hawkers/vendors (Iliyas, 2000). Boreholes and hand-dug wells get recharged during rainy season but get exhausted in dry season (Bello and Abdullahi, 2014).

Hadejia river system constitutes the main drainage in the study area which contributes about 80 % of the historic flow of the river system. The remaining 20 % of the river discharge comes through the Jakara system which disappears underground in the Chad formation (Abdulhamid, 2013). There has been a recent outcry regarding lack of drainage system on the streets of Kano

Metropolis because drainages were not constructed by the government along road networks and some house owners normally built structures without constructing drainages (Murtala, 2018).

3.2.1.3 Commerce and industry in the study area

Kano City has, for centuries, been the most important commercial nerve centre of northern Nigeria attracting millions from all parts of the country and beyond. Far back as 13th to 18th century, seven markets (1st generation markets) were established in Kano Metropolis among which only Kurmi market retained its historic and international status (Ibrahim, 2014). Currently, there are numerous markets in the area and the business landscape is characterised with the proliferation of super stores, shopping malls and other trading centres along major roads and streets which form another kind of market. "Kantin Kwari", a 2nd generation international cloth market established in 1934 (Ibrahim, 2015), provides a significant demand for locally dyed materials.

In pre-colonial time, Kano City exported leather, dyed cloth, and plain-woven fabric because the people were astute entrepreneurs who managed workers with skills in tanning, dyeing, weaving, and metal work which is highly developed (Afolabi, 2015). In contemporary northern Nigeria, Kano provides a stable continuous market for both manufactured and semi-processed goods. There are many privately owned SMEs in the Metropolitan Area producing textile, tanned leather, foot wears, plastics, cosmetics, foods, beverages etc. located in Bompai, Sharada (phases I, II and III), Challawa, or Tokarawa industrial estates (Tanko and Idris, 2013). "Kofar Mata", established in 1498 (Plate I), is a local industry for traditional indigo

dyeing even though most of the dyers now use synthetic vat dyes and chemicals (Dutsenwai, 2010).



Plate I: "Kofar Mata" dyeing facility located in Kano Municipal Local Government (Fieldwork, 2018)

3.2.2 Data collection for the survey

The survey relied on data gathered through a structured questionnaire, focus group discussion, observation, and records. A structured questionnaire was developed according to standard protocol for questionnaire design and testing as described by Geer *et al.* (2006) and questions were developed as a result of insight from UNESCO (1999) and information from Aspland (1992a) and Chakraborty (2010). The validity of the coverage of the questions included in the questionnaire (content validity) was gained through experts in the field, colleagues as well as

members of the target population. Reconnaissance visits were made in June, 2018 to locate the dyehouses as well as colour and cloth vendors.

The developed questionnaire was pretested among the dyers that did not participate in the study and during the reconnaissance visits. Variability in dyers response and the understanding of question content (face validity) were evaluated and this information was used to produce a revised final version of the questionnaire, specifically questions were added where content coverage was lacking and questions were rephrased where understanding was vague. The questionnaire was prepared in English but was communicated to the dyers in their local dialect (Hausa).

As shown in Appendix A, the questionnaire consists of seven parts, A to G. Part A of the questionnaire covered thirteen questions which dealt with demographic and socio-economic characteristics of the dyers (e.g., age, level of education, state of origin, monthly income, etc.). Part B comprised of five questions with regards to the management of the dyeing enterprises (e.g., type of the enterprise, number of dyers per location, location of the enterprises, etc.). Part C has eleven questions related to the operations of the dyeing enterprises (e.g., services offered, tools/equipment used for dyeing, water/power source, raw-materials used, etc.). Part D consisted of seven questions on the step-by-step dyeing processes (e.g., dyeing sequence, treatments carried out before and after dyeing, vatting and dyeing time, etc.).

Part E of the questionnaire comprised of twelve questions regarding the challenges and prospects of the dyeing occupation (e.g., challenges faced by the enterprises, quantity of

material dyed in the past and present time, consequences of the dyeing occupation continuing to decline, etc.). Part F dealt with perception of the dyers on the toxicity associated to the occupation and comprised of ten questions (e.g., protective behaviour employed, encounter with public health worker, symptoms experienced due to the occupation etc.) but the data has not been used since toxicity is not part of the research objectives. Part G has five questions on the dyer's perception on the environmental impacts of dyeing (e.g., distance of the next available house from the location of the enterprise, wastewater management, and potential environmental impacts).

The research population is the total number of occupational vat dyers in Kano Metropolis and participating dyers were chosen as a purposive sample. A total of two hundred and twenty-six questionnaires were administered in twenty dyehouses where willingness to participate in the study was confirmed through completed consent form. Dyers who are at least eighteen years of age and had worked for at least five years in the dyehouses were eligible to participate in the study. Data was collected from June to August, 2018, with the dyers working, through self-completed questionnaire by the researcher and 3 enumerators over a duration of 25-30 min. with each dyer being asked the same question in the same order.

A monetary incentive of ₦3,000 ($8.28) was provided for participation due to initial reluctance to participate because, according to the dyers, the Chinese used similar approach to learn their techniques. Dollar exchange rate has fluctuated considerably from 2018 till February, 2023 (Exchange rate of ₦362.12 per US$ as at 30 August, 2018 was used where dollar equivalent is given in the text). Before initial data screening, all the completed

questionnaires were coded and entered in Excel software after which the data were analysed by descriptive statistics (frequency, percentage and average) using SPSS version 26.

Other data sources included observations while the dyers are on the job and records from Kano State Ministry of Commerce and Industry (KSMCI) and Kano Amalgamated Dyers (KAD), a non-formal association of the dyers. Additional information was obtained from focus group discussion with the researcher, assistant researcher and seven dyers, one from a dyehouse in each of seven Local Government Areas (Nassarawa was not represented) and with five cloth vendors from different shops separately in September, 2018 at Senior Secondary School Rumfa College, Kano and "Kantin Kwari" cloth market respectively.

Focus group discussion with the dyers centred on a shortlist of thirteen open-ended questions related to how they start the dyeing occupation, the nature and composition of the dyehouses, whether the enterprises are formal or informal, type of services rendered and type of customers, cost of services, type (s) of material (s) normally dyed, availability and cost of dye and chemicals, frequency/peak periods of operation, dyeing methods employed, treatments carried out before and after dyeing, challenges of the dyeing occupation, current state of the occupation, and prospects of the dyeing job.

Focus group discussion with cloth vendors centred on shortlist of six open-ended questions related to who dye the materials in the shops, how frequent is the service of the dyers needed, who are the customers of the dyed cloth, what are the sources and cost of white undyed cloth, how the dyers are paid for services, and customers preference to imported and locally dyed

materials. Discussions were audiotape-recorded so that reference could be made to the remarks of the participants in order to ascertain common themes. Discussion with both the dyers and cloth vendors lasted for 2 hours and was recorded using paper and pencil.

Two key informants were used in the study. Aliyu Umar, a wholesale colour vendor, whose nature of business permits him to know the major dyers in Kano Metropolis as well as cloth vendors in the market, and Mallam Haruna Baffa who has valuable information being the Secretary of Kofar Mata dyers Association coupled with his exposure having attended numerous exhibitions of Africa by Design namely Ghana (2016 and 2019), Dubai (2017), and London (2018).

3.2.3 Geographical locations of the dyehouses

Hand-held Gamine78SC GPS receiver was used to obtain the coordinates of the 20 dyehouses visited i.e., dyehouse A to dyehouse T (DA-DT) which are located within the 8 Local Government Areas of the Metropolis. The data was recorded, converted to appropriate units, and input into google earth to get the actual geographical locations of the dyehouses.

3.2.4 Determination of heavy metals

3.2.4.1 Metal content in caustic soda, hydros, and dyes

Samples of caustic soda grains, hydros powder as well as powders of RSN, VR1, and VRR dyes were prepared in similar manner according to a programme suggested by the equipment software (EHOS EASY). A topwave microwave-assisted digestion system equipped with pressure-controlled Teflon vessels (50 ml) was used for the sample digestion. Each sample was weighed 0.2 g and digested using 10 ml mixture of 15.9 Normal trace metal grade nitric

acid, hydrogen peroxide, and perchloric acid (7:2:1). The digestion system uses a ramp temperature from ambient to 200 ^{o}C over 2 min. and then held at 200 ^{o}C for 20 min. The digested samples were allowed to cool to about 50 ^{o}C and then transferred to 50 ml volumetric flask with the solution volume adjusted to 50 ml with distilled water and filtered for analysis.

All measurements were performed using Agilent 4210 MP-AES. The sample introduction system consisted of poly (vinyl chloride) (PVC) peristatic pump tubing, a single pass cyclonic spray chamber, and a oneNeb nebulizer. The Agilent MP Expert® software was used to automatically subtract the background signal from the analytical signal. A background spectrum from a blank solution was recorded and automatically subtracted from each standard and sample solution analysed. The software also optimizes the nebulization pressure and viewing position for each wavelength selected to maximize sensitivity. Heavy metal content was determined sequentially by the equipment under optimized conditions except for the determination of sodium which was carried out separately. The MP-AES operating conditions are shown in Table 3.3 while the wavelength of each metal at which concentration was determined is shown in Table 3.4.

3.2.4.2 Metal content in effluent and groundwater samples

Unfiltered effluent and water samples, acidified at the time of collection, were acid digested using the procedure: 0.5 ml of conc. hydrochloric acid and 0.2 ml of conc. nitric acid were added to 10 ml sample aliquots in 16 by 125 mm polypropylene tubes and digested at 90-100 ^{o}C in a sand bath on a hot plate until the final digested volume was 10 ml. If the sample volume was less than 10 ml, distilled water was added to make up the sample volume to 10 ml mark.

An Agilent 4210 MP-AES was also used to determine heavy metal content as described previously but manual sample introduction mode was used in this case.

Table 3.3: MP-AES operating conditions

Parameter	Setting
Replicates	3 (except for Na, 4)
Background correction	Auto
Read time (s)	3
Viewing position	0
Nebulizer flow (l/min.)	0.45-0.95 (depending on the element)
Pump speed (rpm)	15
Uptake time (s)	60 (Et/H_2O) (except for Na, 15 s)
Stabilization time (s)	15 (Et/H_2O)
Calibration fit	Linear weighted
Rinse time (s)	30 (Et/H_2O)
Calibration correlation coefficient limit	0.999

Uptake time:80 s, rinse time:40 s and calibration fit:0.995 (for dye powders), Replicates:4, uptake time:25 s, rinse time:25 s, stabilization time:10 s, calibration fit:0.995 (for hydros and caustic soda), Instrument type: MY17380004, Current software: version 1.6.0.9255

Table 3.4: Wavelengths at which concentrations of heavy metals are determined

Analyte	Wavelength (nm)
Chromium	425.433
Lead	405.781
Sodium	588.995
Zinc	213.857
Manganese	403.076
Iron	373.713
Cupper	324.754
Nickel	352.454
Cadmium	361.051

3.2.5 Determination of physico-chemical parameters in effluent and water samples

Each of eighteen dyehouses was presented with 20 g of desized CF, 2 g of either RSN, VR1, or VRR and large amounts of caustic soda and hydros. The dyers were asked to dye the fabric in a 2 l-beaker for 10 min. using liquor to goods ratio (LR) of 100:1. After dyeing, dyebath wastewaters, 2 l each, containing spent caustic soda and hydros, and residual VR1 (6 samples, DA to DF), RSN (6 samples, DG to DL), and VRR (6 samples, DM to DR) were collected in triplicates (a total of fifty-four samples) before disposal. The dyehouses where the effluent is collected were selected by convenience sampling technique and the colour of the effluent from each dyehouse was randomly selected. Water samples from hand-dug wells, 2 l each, were collected within 100 m radius of some of the dyehouses.

The water samples were collected within 100 m radius of each of twelve dyehouses using the same material that is used to fetch water from each well which is usually a 2-l paint rubber tied to a long rope or a rubber container made from motorbike and car wheel tube attached to a long chord. Groundwater in wells was agitated to obtain a homogeneous and representative sample. The collection and handling of effluent and water samples were carried out as described in the standard methods for the examination of water and wastewater by American Public Health Association (APHA, 1985).

Specifically, samples were collected in triplicate using clean plastic containers which were covered with black polyethene bags to prevent growth of algae. One set of the samples for heavy metal analysis were acidified with few drops of nitric acid to prevent adsorption of ions on the wall of the containers and to prevent bacterial activity. The samples were labelled (DA to DR for effluent samples and WA to WL for water samples) and transported to the laboratory

in a cooler with ice packs within few hrs. of collection and samples that were not analysed immediately were stored in a refrigerator at 4 ^{o}C. Sampling was conducted between 24 and 28 August, 2018.

3.2.5.1 pH and temperature of water samples

The pH and temperature of water samples were determined *in-situ* at the point of sample collection. pH was measured using pH metre (Jenway 3310, UK) after the metre had been calibrated using buffers at pH 7.0. The electrode was then immersed into the samples and the reading was recorded. Temperature was determined using a thermometer.

3.2.5.2 Colour in effluent

The colour of the dye containing effluent was measured at wavelength of maximum absorption value using a UV-Visible spectrophotometer and according to American Dye Manufacturers Institute (ADMI) method as per the procedure outlined in standard methods (APHA, 1998). Sample transmittance was measured from 400 to 700 nm and the transmittance values were calculated to give a single number for the colour value. The ADMI uses the pt-co standard from APHA and 1 unit of ADMI is equivalent to 1 mg/l pt-co units.

3.2.5.3 Dissolved oxygen and biological oxygen demand in effluent and water samples

Sample, 50 ml, was poured into a beaker. The electrode of dissolved oxygen (DO) meter (HANA model HI9143) was rinsed with the sample water or effluent and then dipped into the beaker containing the sample. The DO value was recorded as DO_1. The sample was saturated with seed solution of bacteria, nutrient, and buffer according to standard methods and then kept in a 300 ml biological oxygen demand (BOD) bottle in a dark incubator at 20 ^{o}C for 5

days after which the DO was recorded as DO_5. BOD was obtained by deducting the value of DO_5 from DO_1 and multiplying the value with the dilution factor (APHA, 1998).

3.2.5.4 Chemical oxygen demand of effluent

Chemical oxygen demand (COD) was determined by titrimetric method according to standard methods (APHA, AWWA, WEF, 1997). Specifically, 1.25 ml sample, 3.5 ml standard potassium dichromate digestion solution, and 3.5 ml sulphuric acid was placed in previously washed standard 10 ml tubes. The tubes were tightly capped and the mixture was thoroughly shaken. The tubes were then placed in block digester preheated to 150 ^{o}C and refluxed for over 2 hrs. before cooling to room temperature.

The excess potassium dichromate was titrated with standard 0.1 M ferrous ammonium sulphate using few drops of ferroin indicator where a sharp change from blue green to reddish brown was the end point. The procedure was repeated twice for each sample and COD was calculated using Equation 3.1.

$$COD\ \left(mg\frac{oxygen}{l}\right) = \frac{(A-B)(M*8000)}{ml\ sample} \ldots\ldots\ldots.. 3.1$$

where A = ml ferrous ammonium sulphate used for blank, B = ml ferrous ammonium sulphate used for sample, M = molarity of ferrous ammonium sulphate, and 8000 = milliequivalent weight of oxygen multiplied by 1000 ml/l.

3.2.5.5 Conductivity and total dissolved solids

Electrical conductivity was measured using digital conductivity meter where the meter was switched on, standardised using 0.1 Normal potassium chloride at 25 ^{o}C, immersed into the effluent/water samples, and the conductivity reading recorded (APHA, 1992). Total dissolved solid (TDS) was determined using the same meter used for determination of conductivity where the programme menu of the meter was switched to TDS option. The electrode was standardized using distilled water and immersed into the effluent/water sample and the TDS recorded (APHA, 1992).

3.2.5.6 Sulphate

Sulphate concentration in effluent and groundwater samples was determined by turbidimetric method as described by APHA (1985). Sample, 100 ml, was placed into a 250 ml Erlenmeyer flask and mixed with 20 ml buffer solution by stirring. Spoonful barium chloride crystals was added and immediately stirred for 1 min. at constant speed. The solution was then poured into cuvette of a spectrophotometer and absorbance reading measured at 420 nm. Five known concentrations of standard sulphate solutions were prepared to construct a calibration curve. Sulphate concentration in samples was estimated by comparing turbidity reading with calibration curve.

3.2.6 Determination of vat dyeing parameters used by the dyers

Fabrics sold in Kano cloth market are usually starched from where they are produced and therefore the starch has to be removed by desizing to enhance the absorbency of the fibre towards the dye. Desizing was carried out by preparing 0.5 % hydrogen peroxide (50 %

solution) and 2 % sodium hydroxide and then treating the material for 5 min. after which it was washed and rinsed with distilled water (Nkeonye, 1993).

Each selected dyehouse was presented with 20 g of desized CF, 2 g of RSN, and large amounts of caustic soda and hydros. The dyers were asked to estimate the quantities of caustic soda and hydros to be used in dyeing the fabric. The quantities estimated were collected in separate polyethene bags in triplicates, measured on a weighting balance, recorded, and then the average was calculated. The average quantities of caustic soda and hydros were measured and given to the dyers to carry out the dyeing of the fabric to 10 % shade for 10 min. in a 2-l beaker using a LR of 100:1. After preparing each dye bath, just before a fabric is immersed, the solution temperature was measured. The 18 dyed materials, samples from dyehouse A to dyehouse R (DA to DR) were collected after dyeing, oxidation, and drying.

3.2.7 Mercerization experiments

3.2.7.1 Procedure for mercerization

A perforated stainless-steel cylinder (with holes about 1 cm apart) which is 20 cm in length with a circumference of 30 cm was constructed to hold the fabric samples during the experiments. A 30 by 30 cm sample was placed round the cylinder starting at 5 cm from its top, without tension, by means of polyester threads knotted at the 2 upper edges of the fabric. The lower end of the fabric, which is about 15 cm in excess of the cylinder length, was carefully tucked in to the lower end of the cylinder. The cylinder was suspended just above the bottom of a 2-l beaker (to allow the movement of a magnetic stirrer) by two copper wires attached to two tripod stands at opposite ends which are placed at 90^{o} to the base as shown in Plate II.

Mercerization was carried out in a 2-l glass beaker with continuous stirring of the solution by a magnetic stirrer similar to a procedure described by Kokot and Stewart (1995). The fabric, round the cylinder, was immersed in caustic soda solution in a LR of 100:1 and the mercerization carried out at specified caustic soda concentration, solution temperature, time of treatment, with different fabric samples according to the conditions shown in Table 3.5. The experiments were designed with the aid of RSM using CCD which generated 40 runs in random order. The mercerized fabrics were rinsed in water for 10 min. and then in 2 % acetic acid for 15 min. to neutralise the alkali. A final rinse in water for 5 mins. was followed by drying in open air for 6 hrs. The data was analyzed using Design Expert® Software version 7 (DX7). After statistical analysis and optimization of mercerization parameters using Desirability function, five sets of experiments were carried out at the optimized conditions to validate the results.



Plate II: Setup for mercerization experiment

Table 3.5: Central composite design of mercerization experiments

Variable	Unit	Level	
		Low (-1)	High (+1)
NaOH conc.	g/l	150	400
Temp.	^{o}C	32	100
Time	min.	1	10
Fabric type	-	CF	BF

3.2.7.2 Determination of shrinkage

An area was marked from the centre, having 4 small squares measuring 10 by 10 cm (0.1 m by 0.1 m), with the aid of a ruler and permanent marker, two squares in the direction of warp and two squares weft way in each of forty samples of 2 different fabrics measuring 30 cm by 30 cm (0.3 by 0.3 m). The use of permanent marker is for the benchmarks to still remain during and after mercerization. The changes in the dimensions of the marked areas were recorded in terms of warp and weft shrinkages by taking the average from 3 measurements for both warp and weft and the average % shrinkage was calculated according to AATCC TM135-2018 standard and using Equation 3.2.

$$Average\ shrinkage\ (\%) = \frac{B - A}{A}\ (100) \ldots\ldots\ldots\ldots\ldots 3.2$$

where A = initial measurement and B = average measurements from 6 observations per sample.

3.2.7.3 Determination of tensile strength and elongation

All treated fabric samples were conditioned at a standard atmosphere of 27±2 ºC and 65 % relative humidity for over twenty-four hrs. before testing and the evaluations were performed in the same conditions according to NIS 43:1980. The tensile properties of the mercerized fabrics were tested using a multifunctional electronic tensile strength tester at a tensile speed of 350 mm/min., a gauge length of 100 mm (0.1 m), a clamping distance of 200 mm (0.2 m), and a pretention of 1 N to acquire breaking strength. Before characterization, all samples were cut to 50 mm (0.05 m) and 150 mm (0.15 m) in warp and weft directions. The tensile test was conducted in both warp and weft directions. Each test was run five times and the standard deviation was determined.

3.2.8 Dyeing experiments

3.2.8.1 Dyeing procedure

Before the dyeing process, each fabric, 20 g (about 30 by 30 cm), was treated with caustic soda solution using the same conc., the same temp. and time of treatment as previously optimized under the mercerization experiment but the mercerization conditions used has reduced it significantly. Shrinkage is unavoidable as the fabric samples are in slack state. Some of the mercerized samples were neutralized to remove the alkali and dried before dyeing while others were passed through a pad mangle (Werner Mathis AG, Switzerland) with a loading pressure of 0-120 pa and adjustable squeeze rollers to remove excess caustic soda. The pressure was adjusted using loading arm while the distance between squeeze rollers was set using German 13 Blatt feelers gauge set at 0.005 to 1 mm (Fabric thickness=0.31 mm for BF and 0.33 mm for CF). In each case, dyeing was carried using the same setup described under the mercerization experiment (Plate III). Dyeing was carried out according to the experimental

design shown in Table 3.6 where the software generated 56 runs in random order. The dyebath was prepared by stirring the dye and caustic soda for one min. while adjusting the temp. to 60 ^{o}C and then adding hydros and stirring for another one min. before immersing the fabric. The material was entered at 60 ^{o}C and dyed at the same temp. for ten mins. using LR of 100:1



Plate III: Setup for dyeing experiment

Table 3.6: Central composite design of dyeing experiments

Variable	Unit	Level	
		Low (-1)	High (+1)
NaOH conc.	g/l	8	22
Hydros conc.	g/l	8	22
Fabric type	-	CF	BF
Dyeing method	-	Wet-on-wet	Dry

3.2.8.2 Visual assessment of levelness

Two reference samples were prepared by dyeing mercerized CF and BF (previously neutralized and dried) using 10 g/l of caustic soda (Chakraborty, 2010) and 20 g/l hydros (to compensate for oxidative decomposition in large liquor ratio and open bath) at 60 ^{o}C for 45 min. (Giles, 1974), in a goods to liquor ratio of 1:100 to produce visually uniform-coloured standard samples. Depending on the conc. of caustic soda and/or hydros used in the dyeing experiment and whether mercerized samples are neutralized and dried or embedded with caustic soda prior to dyeing (wet-on-wet), different degrees of levelness are produced compared to the reference samples. The procedure employed was similar to that reported by Solymanian *et al.* (2015) where the authors produced different degrees of unlevelness on cotton fabric dyed with a direct dye Solophenyl Blue AB, navy blue colour (which approximated the colour of indigo vat dye), by tying the material with polyester yarn prior to dyeing or by using non-standard dyeing conditions.

Solymanian *et al.* (2015) graded the reference material (uniformly coloured specimen) "0"and a team of observers was allowed to rate 12 unlevelled samples at an interval of 1 compared to the reference sample. In this study, the reference samples are graded "9" and the evaluators rated 28 samples each of cotton and blend fabrics compared to the standard CF and BF respectively in order of decreasing levelness at an interval of 1 with the most uneven sample rated "1". A 9-point scale was selected for ease of statistical analysis using DX7 software and due to the fact that there are 8 factorial points (each for CF and BF) with different factor combinations in the central composite design which can produce different degrees of levelness. There are many similar samples as some experimental runs are replicated (the same fabric type and dyeing conditions) to increase precision and allow determination of

experimental error. For this reason, samples that are similar in terms of levelness are rated the same. Samples that are perceived to have the same levelness with the standard samples are rated “9”.

A panel of sixty observers was selected by convenience sampling which constituted of experienced occupational dyers who are regularly engaged in the dyeing activity and whom are 100 % male and 80 % educated with an average age of 33±6.26 years. All the assessors that participated in the visual evaluation of the fabrics with different degrees of levelness were tested for normal colour vision as described by Ishihara colour test. The observers were asked to arrange samples on the basis of the perceived colour levelness while standing by the windows of a classroom during the daytime from morning to noon as the light is similar to CIE (International Commission on Illuminants) standard illuminant D65 as shown in Plate IV.

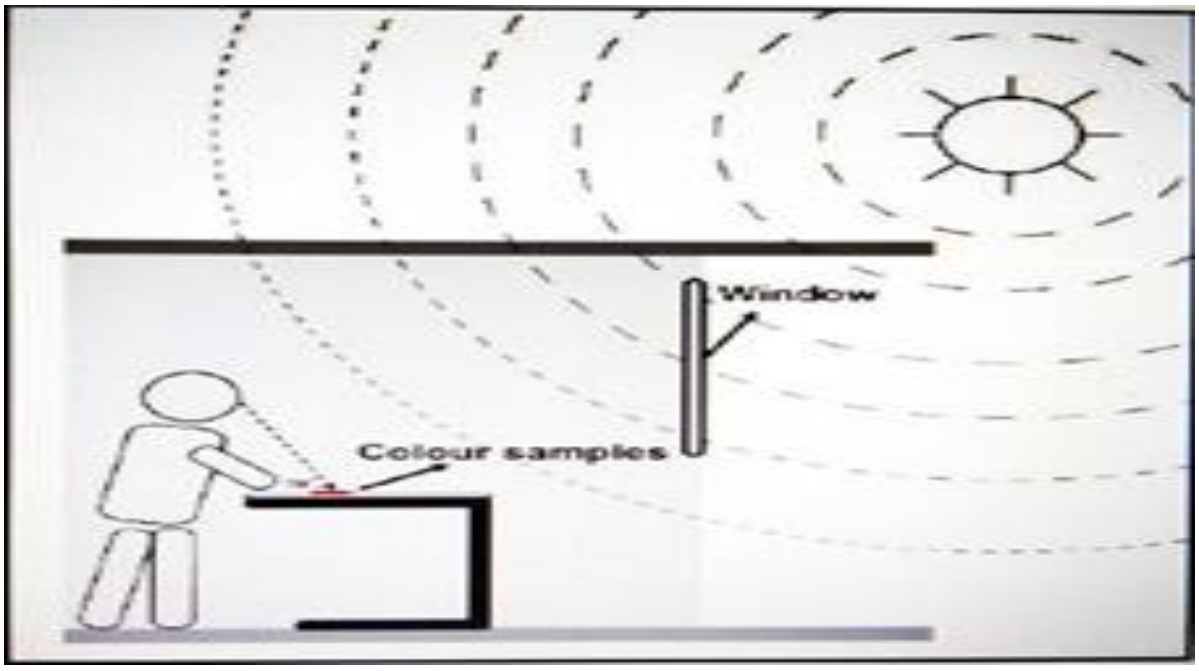


Plate IV: Fabric viewing position (Lai and Chang, 2021; Gong and Lee, 2017))

The fully evenly dyed standard fabrics were presented to the observers as a reference uniform sample. To avoid any possible impression, samples with different degrees of uniformity were randomly presented to each observer and they were asked to grade each sample among CF or BF as compared to the reference specimens. Fabrics were arranged by the observers from most levelled (9) to the least (1) based on the apparent distances from reference samples as well as their position in relation to other samples. The ratings were averaged and multiplied by 10 as a linear "transformation" which eliminates decimal point to make data entry and analysis easier and this does not affect the relative results. The evaluation experiment was repeated 3 times for some randomly selected observers to determine the inter- and intrasubject variability. The observers were allowed to change the initial ranks before their responses were recorded in all visual evaluations.

3.2.8.3 Determination of tensile strength of dyed fabrics

Samples of CF were selected from the dyeing experiments based on the dyeing method employed and conc. of caustic soda and hydros used for dyeing. The four selected samples were divided into two equal halves with one half of each subjected to a beating operation (local calendering) shown in Plate V. The material was placed on a wooden base and beaten twice at nine different spots with 6.85 kg wooden pestle (about 58 cm circumference) raised to the height of 80 cm which takes 0.32 secs. to reach the fabric surface. The dyed and finished fabric samples were conditioned at a standard atmosphere of 27±2 ^{o}C and 65 % relative humidity for over 24 hours before testing and the evaluations were performed in the same conditions according to NIS 43:1980. The tensile properties of the mercerized fabrics were tested using

a multifunctional electronic tensile strength tester according to a procedure described in section 3.2.7.3.



Plate V: Beating operation (Field work, 2022)

3.2.8.4 Fastness tests

Light fastness*:* Eight blue wool standards and specimen (1 cm×4.5 cm) each were placed side by side on a hinged opaque cover and the central one third of each covered with a black cover. The assembly was placed in the test chamber at 40 ^{o}C and 85 % relative humidity until the contrast between the unexposed and exposed portions of the target blue wool reference is equal to a grey scale grade 4. The samples were compared with the original unexposed samples. The change in colour was assessed using the Blue wool standards. Light fastness test was carried out according to ISO 105-B02:2013 (E).

Wash fastness: The specimen (10 cm×4 cm) was covered on both sides with two pieces of undyed outer-lining white cotton and wool fabrics (5 cm×4 cm) and the three pieces stitched round the edges leaving 5 cm×4 cm exposed. Wash fastness test was carried out using the ISO-3 test under the following conditions: washing with 5 g/l soap and 2 g/l sodium carbonate in a LR of 50:1 at 60±2 ^{o}C for 30 mins. The composites specimen was removed, rinsed and the components separated and dried. The change in colour of the dyed specimen and the staining of the adjacent cloths were assessed using the appropriate grey scale. wash fastness test was carried out according to ISO 105-C10:2006 (E).

Fastness to perspiration: Samples were prepared as described in wash fastness test and then treated in alkaline and acidic artificial perspiration solutions using the following conditions: thoroughly wetting the composite samples with 0.5 g/l l-histidine monohydrochloride monohydrate, 5 g/l sodium chloride, 2.5 g/l disodium hydrogen orthophosphate dihydrate and adjusting the pH to 8 or 5.5 using 0.1 Normal sodium hydroxide or acetic acid, respectively, in a LR of 50:1 for 30 mins. at room temp. The treated samples were placed between 2 glass plates under a weight of 4.5 kg for 4 hours at 37±2 ^{o}C (body temperature), removed, dried at 60 ^{o}C and then the change in colour and degree of staining of under-lining fabrics assessed as in wash fastness. Fastness to perspiration was carried out according to ISO 105-E04:2013.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Survey Results

4.1.1 Demographic /socio-economic characteristics of the dyers

All the two hundred and twenty-six (100 %) administered questionnaires (see Appendix A) were adequately self-completed and the results of the demographic and socio-economic characteristics of the dyers are shown in Appendix B. The ages of the dyers ranged from 18 to 65 years (mean= 31.27± 7.59) where majority were aged 21 to 40 years indicating that they are predominantly of youthful age. In contrast, a study of local dyers in Ghana indicated that only about 40 % were aged 17-40 years (Asmah and Sherifatu, 2016). Majority of the dyers were male which may be because of the tradition and religious beliefs of the people in the study area (mostly Hausa-Muslims). According to Barau (2007), majority of the population in Kano Metropolis is Hausa/Fulani with Hausa language being the vernacular and more than 90 % of the people are Muslims.

The dominance of male dyers can also be due to the strenuous nature of the job, long working hours and inconvenient worksite. The latter reasons were given for male domination in dyeing and printing occupation (Paramasivam *et al.,* 2010). Traditionally, indigo vat dyeing in most west African communities is a female task (Acquaye, 2018) and even recently, studies have shown that there were more female dyers in Abeokuta (Saheed, 2013; Acquah and Oduro, 2012). A little above one half of the dyers were single which may be due to the fact that civilisation and economic realities have changed the concept of early marriage in the region.

Most of the dyers schooled above primary education while only a few (4.9 %) lack western education. The dyers revealed that some of them used dividends from the dyeing occupation to sponsor their education and as a result, there are currently teachers, lawyers and other civil servants in the dyeing business. Similarly, dyers in Abeokuta were found to have higher percentage of those that attended secondary school (Adekunle *et al.*, 2017). According to an annual education sector performance report, the gross intake rate into first grade of primary education is 118 % indicating an adequate access to primary education in the state where the metropolitan area has a good share of both public and private primary and secondary schools (KSME, 2010).

The dyehouses are spread across the 8 metropolitan local government areas of the state where more dyers were found in Gwale followed by Fagge with very few in Nassarawa (2.7 %). Vast majority of the dyers (95.1 %) are natives with very few foreigners from Mali and Gambia. Similarly, the presence of dyers from other African countries working with local dyers in Lagos, Nigeria, has been reported (Areo and Kalilu, 2013). Dominance of dyers in Gwale and Fagge could be due to the fact that a woman that started the art of tie-dye using synthetic vat dyes and trained many people in Gwale for the past 35 years, and also many Malians and Gambians have relocated to Kano to establish the venture thereby training a lot of youths in Fagge. Decline in the dyeing venture among other reasons forced most of the foreigners back home while some of them have changed line of business.

Job specifications among the occupational dyers include colour mixing, dyeing, starching/rinsing/drying and marketing where more individuals were involved in the actual dyeing job. The marketers have some level of capital and are hardly involved in the actual

dyeing but are frequently involved in colour mixing and some of them own stalls along the streets of Kantin Kwari cloth market where they sell dyed cloth. It is the marketer's responsibility to find customers, provide the site, tools and raw-materials needed for dyeing and to assign job specifications. Some individuals engaged in rinsing/starching/drying can also partake in dyeing depending on job availability and quality requirement.

About three fifth of the dyers have learnt the art of dyeing by apprenticeship which is contrary to traditional indigo dyeing in Kano where the craft is passed on to many generations as inheritance. Nowadays, dyeing with synthetic dyes in Kano Metropolis has become a highly specialised art where apprentices have to spend years to learn from their master before establishing their own dyehouse. In contrast, Saheed (2013) has reported that 56.25 % of dyers studied in Abeokuta, who use synthetic dye and chemicals, have learnt the art of dyeing through long standing tradition in the family usually inherited by birth and the heritage passed onto many generations.

Work experience ranged from 5 to 31 years (mean = 11.11± 5.01) where a little more than one half of the dyers have worked for 1-10 years, and nearly one half have been working for more than 10 years. Similarly, Adekunle *et al.* (2017) reported that 40 % of the dyers investigated in Abeokuta had more than 10 years' work experience. About two fifth of the dyers survive solely on the dyeing occupation while the rest are additionally involved in other activities namely trading, calendering, tailoring, civil service and others among which trading is more prevalent. This is in line with the finding of Acquah and Oduro (2012) that 27.5 % of local dyers investigated in Ghana were involved in trading in addition to the dyeing occupation.

According to the dyers, the art of dyeing, cloth vending, calendering and tailoring are related such that every dyed cloth is finished by calendering and finished goods are usually tailored according to customer specification. This suits well with a situation in Abeokuta where the textile producers comprised of adire makers, traders, dyers, weavers, dress makers and tailors (Byfield, 1997). In another study, Areo and Kalilu (2013) reported that textile production in Abeokuta comprised of designers, dyers, beaters (calendering) and cloth vendors.

Close to one half of the dyers earn more than ₦20,000 ($55.23) per month which is a good wage in a country where over 60 % of the people live on less than $1 per day (Thurston, 2016) and also a good income as the amount earned is more than the minimum wage of ₦18,000 ($49.7) proscribed by the Nigerian government for civil servants as at the time of the study. According to Sonobe *et al.* (2011), even though workers in the informal economy face higher risks, some occupations offer reasonable livelihood and incomes as in this case. Some of the dyers investigated (19 %) could earn more than ₦60,000 ($165.69) per month. Similarly, Saheed (2013) and Adekunle *et al*. (2017) reported that nearly the same proportion of resist dyers in Abeokuta earn ₦50,000 ($138.08) per month.

4.1.2 Management of the dyeing enterprises

The dyers belong to either informal enterprise various owners or an informal enterprise sole owner as shown in Figure 4.1. Limited space suitable for the dyeing activity is the result of various owners/group of dyers sharing the same facility and, in some cases, sharing the same equipment depending on mutual understanding and agreed work schedule. According to the dyers, they are comfortable with their setup and do not want to be formal in order not to be disturbed by government officials. Imposition of heavy taxation by Kano State Government

on shop owners and business enterprises in the last few years may have contributed to the reluctance of the dyers to become formal.

It was gathered that the enterprises are not regulated by any organization and majority do not pay for rent to anybody or tax to the government. Similarly, it has been reported that small and informal enterprises are usually reluctant to become large because being large requires being formal and, thus, being subject to excessive regulations (Sonobe *et al.,* 2011). Similarly, informal sectors are usually neither recognized nor regulated or protected under labour and social protection legislation (ILO, 2014b). Findings of this study corroborate well with the fact that small and micro business in Africa are mostly informal, unregistered, unlicensed and typically do not pay taxes (Igwe *et al.*, 2018).

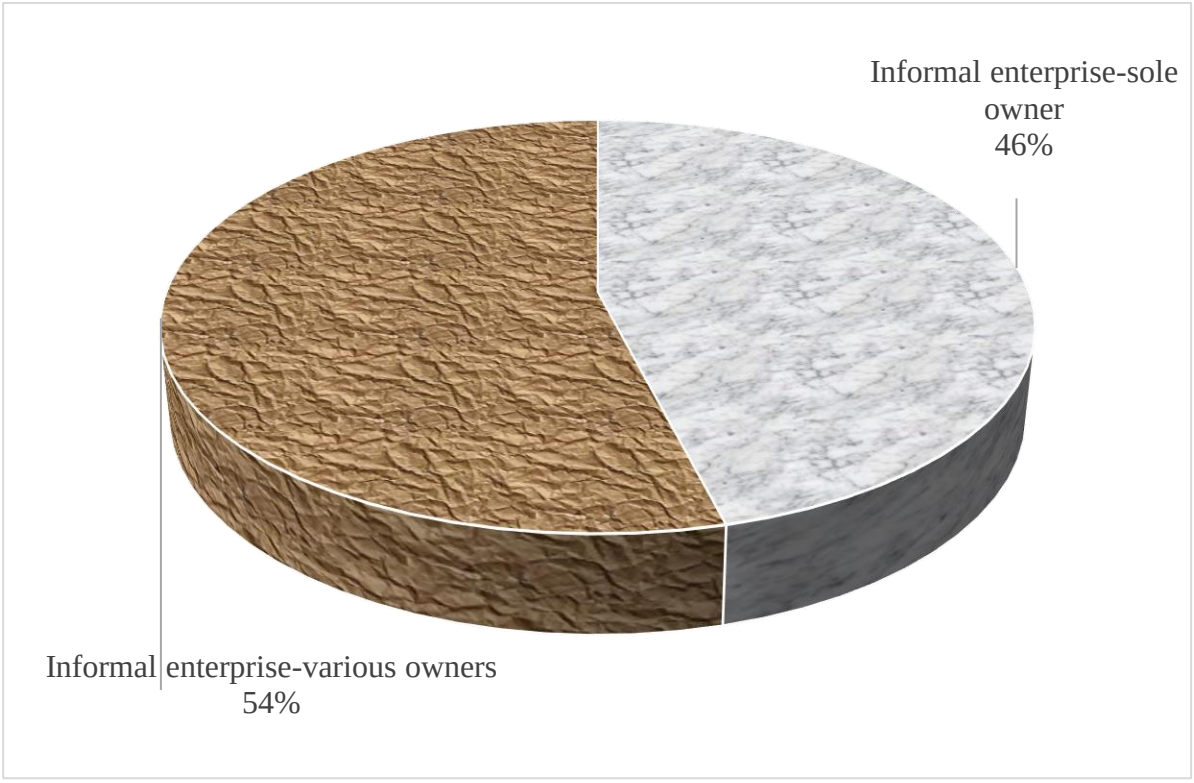


Figure 4.1: Types of the dyeing enterprises

Figure 4.2 shows that most of the dyers work in the neighbourhood of residential houses. The dyers disclosed that working in the vicinity of residential houses is manageable since the choice of a spot suitable for dyeing only depends on availability of water, drainage and adequate space to dry the dyed materials. Dyeing in the house of owner/group member usually involves female dyers who by virtue of culture and religion cannot work amidst male dyers in the neighbourhood. Dyeing in the house is possible for small lot/order and only where the house is large enough. The setup of the dyehouses vary and some of them are similar to those described in an area in India where dyeing is carried out in the courtyard of residential houses and then dried in an open space in the neighbourhood (Singhi *et al.*, 2005).

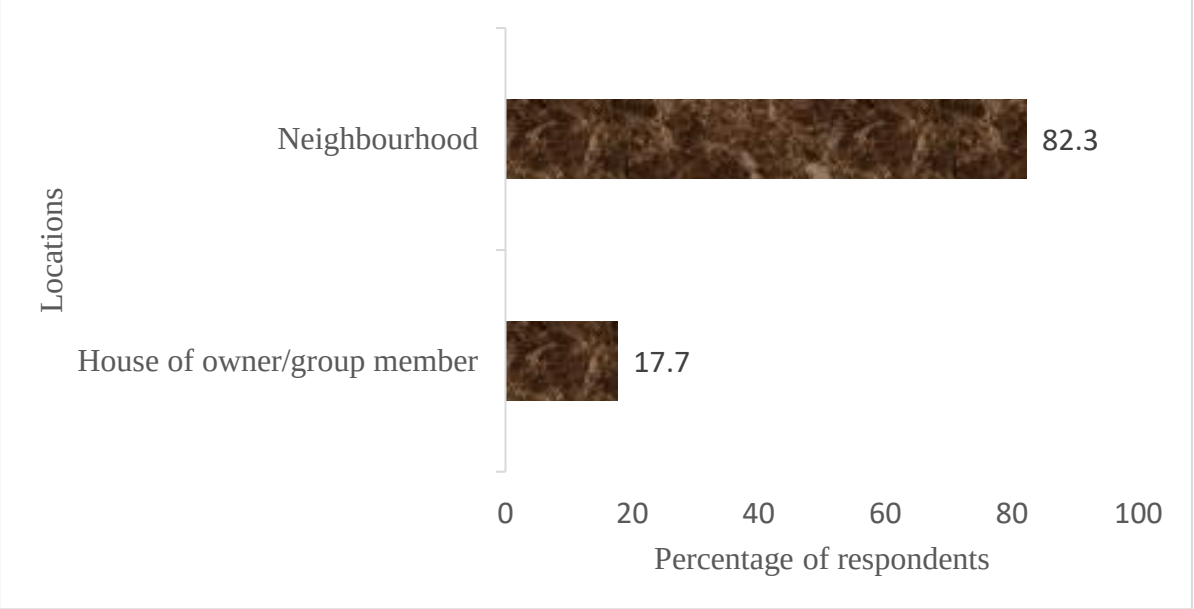


Figure 4.2: Locations of the dyeing enterprises

Majority of the dyers work in a group of more than 10 persons per dyehouse as shown in Figure 4.3. The result indicated that the occupation is an employer of labour. According to Junne (2018), there were about 480 million youth in Africa with 10-13 million entering the

job market every year and only 3 million getting wage employment and government cannot provide those jobs. Due to scarcity of jobs, people were forced to be creative resulting in a large number of necessity entrepreneurs. Additionally, small and medium enterprises (SMEs) are believed to be responsible for more than 50 % of the new jobs created globally and in developing countries they employ more people than large scale enterprises (ILO, 2014a).

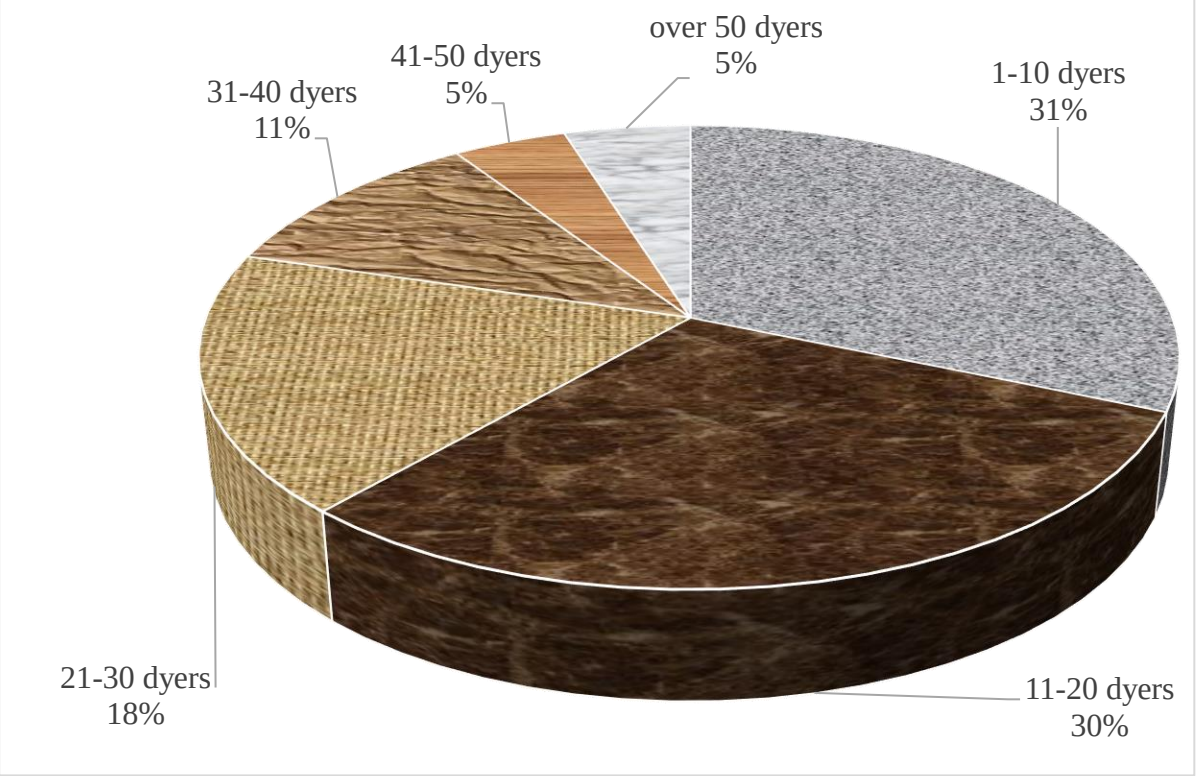


Figure 4.3: Number of dyers per location

4.1.3 Operations of the dyers/dyeing enterprises in relation to industrial practices

4.1.3.1 Services

As shown in Table 4.1, plain dyeing and redyeing of faded garment are more prevalent. Plain dyeing, which involves dyeing the whole fabric uniformly, is easier and faster compared to tie-dye and batik work since it does not require additional work before the dyeing process.

Discussion with the dyers revealed that both plain dyeing, tie-dye and batik work are normally carried out on 5 yards (4.57 m) of undyed or light-coloured woven CF or BF predominantly imported from China. According to them, such fabrics are cheaper, lighter and easier to manipulate than locally woven cloth used traditionally. The fabrics are also more available in larger quantities. The dyers refer to BF as "mix" or "Me-roba" (in Hausa). Artisans in Ghana also dye BF using similar dyes and chemicals (Aboagyewa-Nitri and Mintah, 2016).

Table 4.1: Services offered by the dyers

Services	Yes N=226 (%)	No N=226 (%)
Plain dyeing of cotton fabric	226 (100)	0 (0)
Plain dyeing of cotton blend fabric	226 (100)	0 (0)
Redyeing of faded garment	226 (100)	0 (0)
Tie-dye	174 (77)	52 (23)
Batik work	13 (5.8)	213 (94.2)

According to the dyers, redyeing of faded garment is popular because used cloth usually fades due to contact with sweat by the arm fit and around the chest and back. According to them, faded denim and stained garments are oftenly redyed. Due to the fact that most sewing threads are made of polyester which they cannot sufficiently dye, the articles have to be redyed to the same shade as the colour of the thread otherwise the thread will show. Another approach is to carefully remove the sewing thread with the aid of razor blade, redye the material, and sew it back with a matching thread. Embroidery threads are usually cellulosic and therefore do not have this problem only that they appear deeper in colour than other parts of the garment which some customers find desirable.

The dyers also revealed that dyeing of garment is cheaper and more uniform but requires higher dyeing temperature compared to fabric dyeing and that the former takes longer time to dry than the latter. Similarly, Chakraborty *et al*. (2005) reported that garment dyeing has advantages over fabric dyeing such as reduced fabric waste, no shrinkage, low water and labour costs and production of uniformly dyed garments with no variation in shade at different parts of the garment while the disadvantages include longer drying of goods resulting in waste of time, excessive heating and inaccurate production and cost figures.

The tie-dye/batik techniques usually employed by the dyers include knotting, binding, folding, sewing, application of molten wax to the fabric, tying, pinching, and pleating which are similar to the techniques described by Mayusoh (2015). The dyers that offer tie-dye/batik normally give the material to women at home to make the pattern after which they carry out the dyeing processes themselves. This is in line with the practice of local dyers in Abeokuta (Eicher and Eicher, 2014). Dyers engaged in batik work were few may be because it is not an everyday attire in the community and therefore customers rarely demand for such service.

Products from finished plain dyed materials, plain dyed material sewn to 'Kaftan', and tie-dyed fabric sewn to 'Bubu' are shown in Plates VI to VIII respectively. The dyers revealed that white or light-coloured household items and fashion accessories such as towels, shoes, bags, table cloth etc. are difficult to maintain especially when limited in number and frequently used hence such items are usually dyed to enhance their aesthetic appeal and prolong duration of use. Similarly, dyeing of fashion accessories in a small-scale dyeing unit in Ghana has been reported by Selase *et al* (2019).



Plate VI: Plain dyed fabrics in a shop at Kantin-Kwari cloth market (Field work, 2018)



Plate VII: Plain dyed fabric sewn to ‘Kaftan’ (Field work, 2018)



Plate VIII: Tie-dyed fabric sewn to 'Bubu' (Field work, 2018)

4.1.3.2 Tools/equipment

Table 4.2 shows that all the dyers (100 %) use similar equipment for batch dyeing. Observation and measurement revealed that 50-100 L iron drum for heating water, open plastic bowl (average diameter= 9.7±0.38 m, average depth= 4.6±0.11 m, and average capacity= 24.3±0.41 L) as the dyebath, stirrer for mixing the chemicals, and bucket as rinsing vessel. Plate IX and X show equipment type at work site and typical dyebath respectively while Figure 4.4 shows stirrer type. Similarly, the use of open plastic bowl for dyeing in a small-scale vat dyeing unit has been reported by Frimpong (2009). Dyers in Kano Metropolis lack access to expensive industrial machinery as in the case of local artisans studied by Shuvo II (2018) and therefore practice hand-dyeing.

There is no standard process in vat dyeing and the procedure depends on the available equipment and the dyeing may be batchwise, semi-continuous or continuous (Xu *et al.*, 2000). According to Yusuf *et al.* (2017), vat dyeing takes place in a bucket or vat which is in line with the finding of this study. Baumann and Fletcher (1966) suggested for the use of dyeing machines made of stainless steel in order for the equipment to be able to withstand the chemical and physical conditions used in the dyeing operation. For this reason, use of plastic bowl may not give the best overall result.

Table 4.2: Tools/equipment used by the dyers

Tool/Equipment	Yes N=226 (%)	No N=226 (%)
Plastic bowl	226 (100)	0 (0)
Drum	226 (100)	0 (0)
Stirrer	226 (100)	0 (0)
Washing vessel	226 (100)	0 (0)



Plate IX: Equipment type at work site (Field work, 2018)



Plate X: Typical dyebath (Field work, 2018)

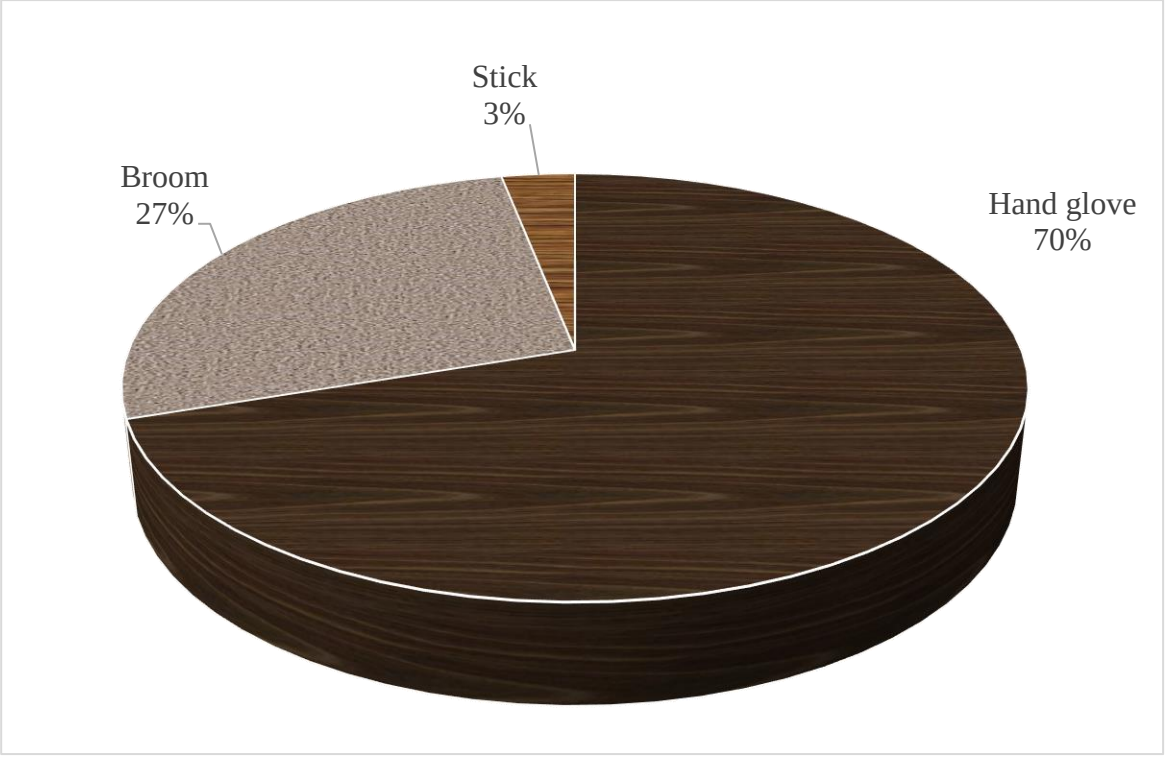


Figure 4.4: Stirrer type

4.1.3.3 Sources of power

Firewood is majorly used as fuel (Figure 4.5) may be due to the fact that most of the dyers work in the neighbourhood with no electrical installations to use electric heater and which will not allow efficient use of cooking gas in the open. Plate XI show typical fuel used by the occupational dyers. Coal is also another power source used to a limited extent. Basically, the enterprises using electric heater and cooking gas are those that are located in the house of owner/group member and is usually applicable when dyeing small lot/order where just a small quantity of hot water is needed. Similarly, the use of firewood as fuel in local dyeing industry has been reported by Singhi *et al.* (2005).

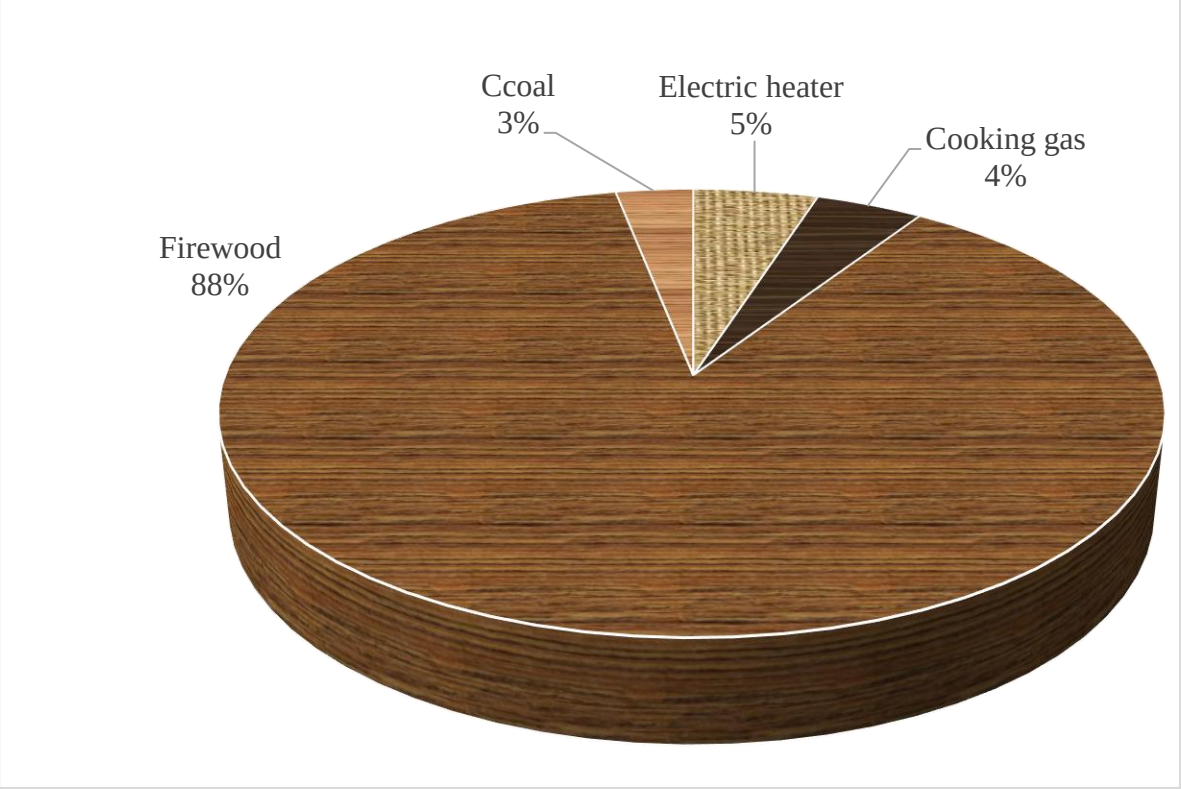


Figure 4.5: Sources of power



Plate XI: Typical power source (Field work, 2018)

4.1.3.4 Sources of water

Dyeing is characterized by high water consumption (Rosa *et al*., 2014; Wardman, 2018) and, for example, dyeing of 1 kg of cotton with reactive dye demand an average of 70-150 litres of water (Allegre and Charbit, 2006). Challawa, Tokarawa, Kano, and Watari River systems provide water for human consumption, irrigation and industrial activities in Kano Metropolis (Liman, 2015) but water supplied by the treatment plants is far less than the demand of the area (Bello and Abdullahi, 2014) and this can explain why only 7.1 % of the dyehouses use tap water (Figure 4.6).

High proportion of dyers purchasing water from vendors and making use of borehole may be attributable to the fact that low-income communities in Kano Metropolis meet their water demands through dug wells in households, community lined concrete wells, boreholes with hand pumps, public stand posts, privately owned borehole-based systems and hawkers. Water

vendors (hawkers), who normally operate hand-dug wells, provide alternative supply (Iliyas, 2000). Cost of water increases significantly over the years where 25 l is sold at about ₦14 ($0.039) and ₦20 ($0.06) respectively as at 2016 (Ahmad, 2016) and as at the time of this study water from borehole cost ₦30 ($0.08) whereas tap water cost ₦50 ($0.138).

The use of generator to pump water from nearby boreholes in order to save the cost of dyeing is shown in Plate XII. Water from hand-dug well may be a hard water and the use of soft water is essential in vat dyeing because the dyes are sensitive to some degree to aluminium, calcium, magnesium and other salts which could lead to increased dyeing cost (Baumann and Fletcher, 1966).

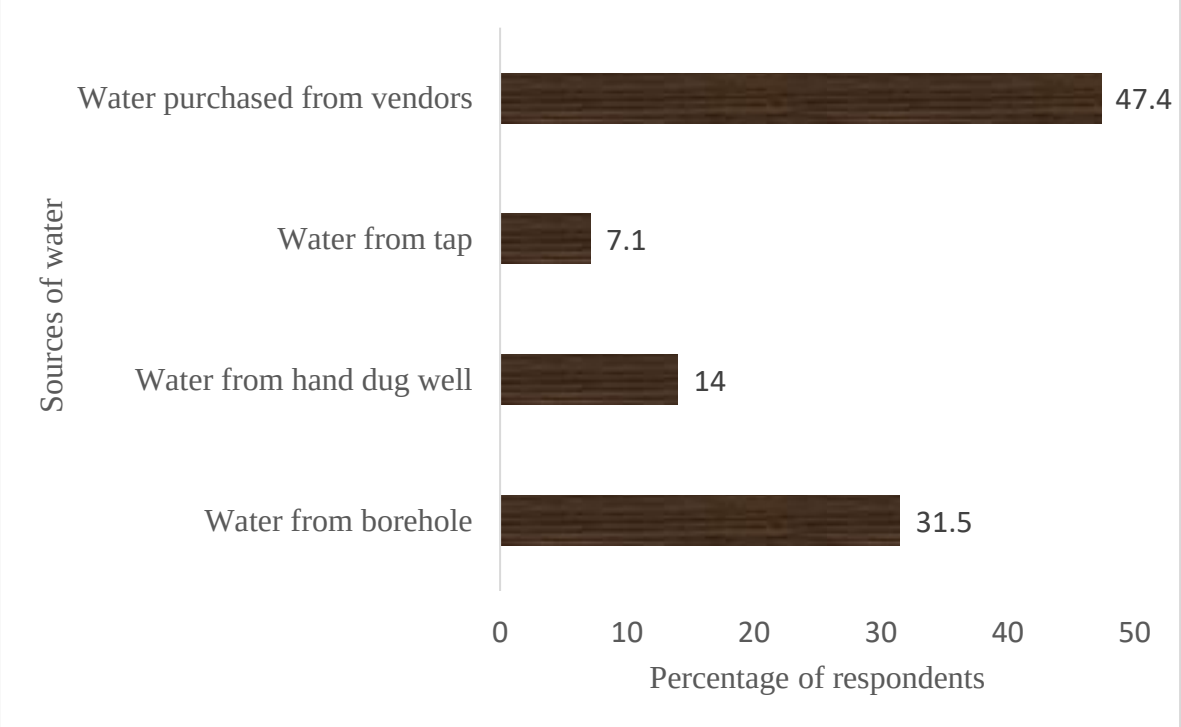


Table 4.6: Water sources



Plate XII: Use of generator to pump water from borehole (Field work, 2018)

4.1.3.5 Input/raw-materials, their sources, and costs

As shown in Table 4.3, all the dyers use similar inputs/rawmaterials. Vat dyes are commonly available in the form of liquids, granules, de-dusted powders and in pre-reduced or solubilized leuco sulphuric ester forms (Xu *et al.*, 2000). Practical dyeing does not begin until the vat pigment is dissolved in caustic soda and hydros solution (Aspland, 1992a). Hydros is readily available, inexpensive and capable of reducing a variety of functional groups (Gassman *et al*., 1981). Caustic soda is a popular solubilizing agent for leuco vat dyeing where it serves to dissolve leuco vat dye to its sodium salt, develop affinity of the dye for the fibre and neutralize acidic by-products of hydros to maintain pH (Chakraborty, 1992). The dyers use cassava starch to stiffen the dyed material in preparation for calendering.

Table 4.3: Inputs/raw-materials for the work of the dyers

Input/raw-materials	Yes N=226 (100)	No N=226 (100)
Dye	226 (100)	0 (0)
Hydros	226 (100)	0 (0)
Caustic Soda	226 (100)	0 (0)
Starch	226 (100)	0 (0)
Sodium chloride	0 (0)	226 (100)

According to Aspland (1997) sodium chloride and/or sodium sulphate may be added to vat dyebath towards the end of dyeing in order to improve exhaustion. According to the dyers, sodium sulphate is useful when dyeing with black colours as it enhances dye absorption and shine and they refer to it as “flex”. Figure 4.7 shows that more than one half of the dyers purchase inputs/raw-materials from retailers. Dye powders and chemicals at work site are shown in Plate XIII. There are many small colour shops in the proximity of the dyehouses where the dyers purchase chemicals either when dyeing small lots/order or in situations where certain chemical gets exhausted while on the job. Plate XIV shows dyes and chemicals in a colour shop. Wholesale shops are situated in “Kasuwar Kurmi”, “Kofar-Mata”, “Hausawa-Sabontiti” and “Rijiyar-Lemo”. Dyes and chemicals in the colour shops are mostly imported from China.

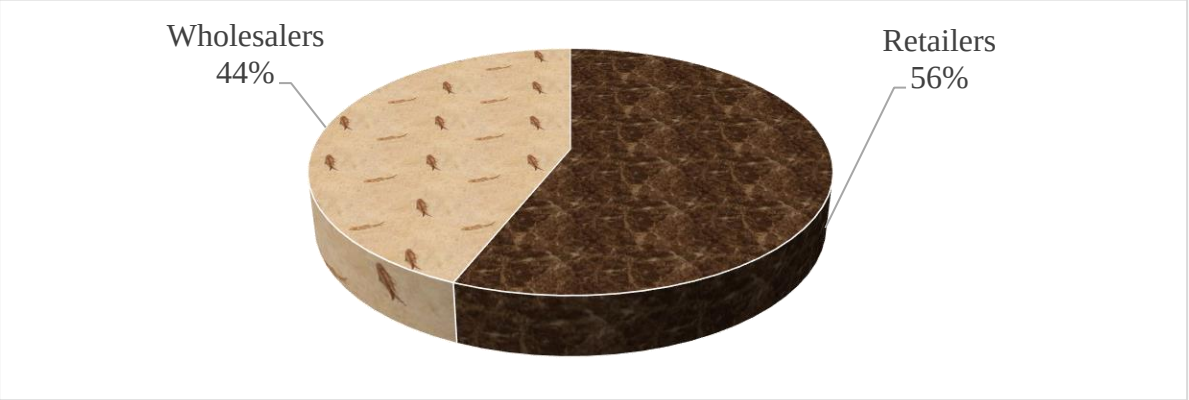


Figure 4.7: Source of inputs/raw-materials



Plate XIII: Dye powders and auxiliaries at work site (Field work, 2018)



Plate XIV: Dyes and auxiliaries in a colour shop (Field work, 2018)

Caustic soda and hydros are respectively sold at ₦400 ($1.1) and ₦800 ($2.2) per kilogram where the former is usually from Tianye chemicals and the latter is mostly produced by Jinhe hydrosulphite factory. Colours that are more commonly available include RSN, VR1 and VRR which are sold at about ₦10,000-₦12,000 ($27.62-$33.14) per kilogram depending on the prevailing market. Other colours such as yellow, green, brown, black, orange, red etc. are also available and are sold within the same price range. India and Germany also supply dyestuff to a limited extent and are more expensive according to the dyers. According to them, dyes and chemicals are readily available but their cost has increased almost 5 times from 2013 to the time that this study was conducted.

Cloth vendors revealed that some of them have visited Ningbo Tong Xi (NBTX), a textile manufacturing company in China, which is the major supplier of white undyed materials to 'Kantin-Kwari' cloth market. According to them, Blue Sky and King Peam, also in China, are among the leading textile suppliers. Similarly, wholesale textile buyers who have long standing trade relationship with Chinese companies have been invited to visit the industries as a reward for loyalty (Renne, 2015). Some of the textile suppliers do not own textile industry but place order from other factories in China and then import to the Kano market.

The cloth vendors also disclosed that a small bale called 'dealer' contains 200 yards (182.88 m) cut into 10 yards (9.144 m) each and usually cost between ₦90,000 ($248.5) to ₦200,000 ($552.30) per dealer depending on the material quality. According to them, there is another type of material called 'Wagambari' (Plate XV) that has been accepted for several years especially by the people of Borno State, Nigeria and is usually sold at ₦120,000 ($331.38) to ₦140,000 ($386.61) per dealer.



Plate XV: White, undyed ‘Wagambari’ fabric (Field work, 2018)

According to the vendors, since 2013, designs of choice of white undyed materials suitable for dyeing became scarce and very expensive when available. Designs appealing to customers are only available in coloured form and entirely imported from China. Both the dyers and cloth vendors revealed that at the peak of the dyeing business in 2013, the Chinese started bringing similar dyed cloth to ‘Kantin-Kwari’ which are sold at the outskirt of the market. Similarly, Renne (2015) has reported the same situation.

4.1.3.6 Peak periods of dyeing, type of customers, and cost of services

The dyers were found to be more engaged during Eid Al-Fitr ‘Karamar Sallah’, Eid Al-Adha ‘Babbar Sallah’, Mawlud al-Nabi ‘Birth of Prophet Muhammad’ and Christmas period as shown in Figure 4.8. During these festive periods, people in the northern part of the country wear new clothes for the celebrations which are mostly from dyed materials thereby making

the dyers busy. There are also significant number of Christians in Kano Metropolis that celebrate Christmas with native clothing and therefore require the services of the dyers.

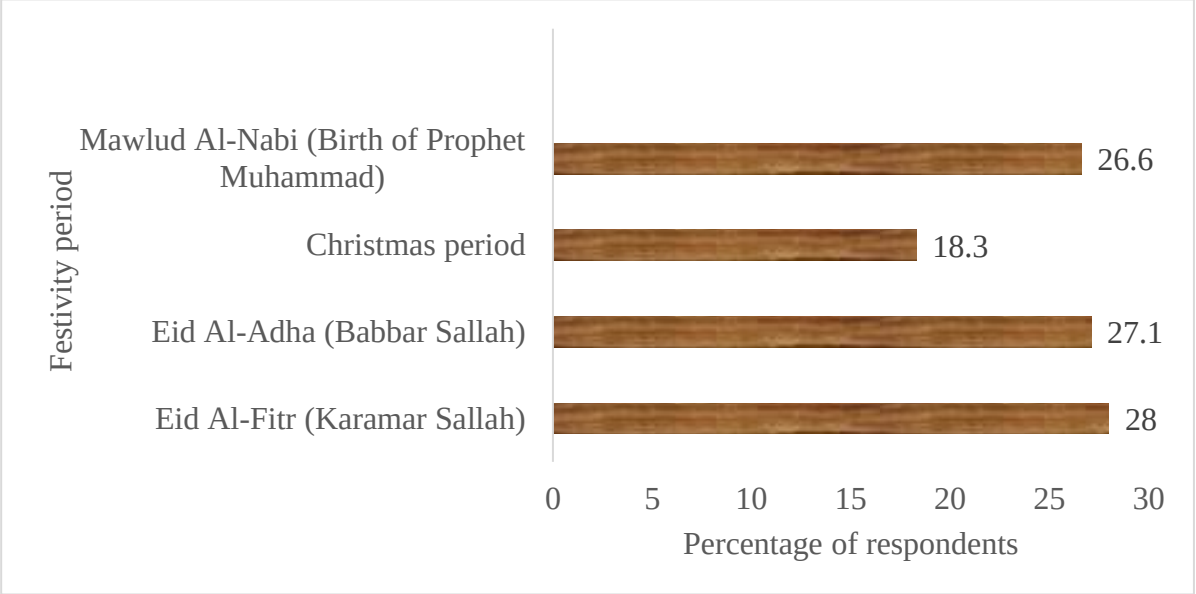


Figure 4.8: Peak periods of the dyeing activities

The dyers disclosed that they offer more services to customers in the neighbourhood (Figure 4.9) due to rampant cases of faded garment, dyeing of household items/fashion accessories, and frequent wedding ceremonies, where dyed uniforms ("Anko" in Hausa) are used. Some of the dyers have customers from neighbouring states as well as from Niger, Chad and Cameroun. Cloth vendors revealed that they regularly give out cloth for dyeing which are kept in the shops and that they also have customers coming from other places that could make a large order of dyed materials where the quantity needed may not be available.

It was learnt from the dyers that they charge an individual a minimum of ₦1,500 ($4.14) for plain dyeing of 5 yards (4.57 m) of material to any colour and ₦1,000 ($2.76) for redyeing of

faded garment while they charge cloth vendors ₦35,000 ($96.65) for dyeing 1 ‘dealer’ (200 yards or 182.8 m) which is equivalent to ₦875 ($2.42) per 5 yards (4.57 m). Tie-dye and batik work are more expensive and cost ₦2000 to ₦4000 ($5.52-$11.04) per 5 yards (4.57 m) depending on the complexity of the pattern to be made. Cost of dyeing of household items such as towels and fashion accessories such as shoes, bags, handkerchiefs etc. range from ₦200 to ₦1,000 ($0.55-$2.76) depending on the size of the article.

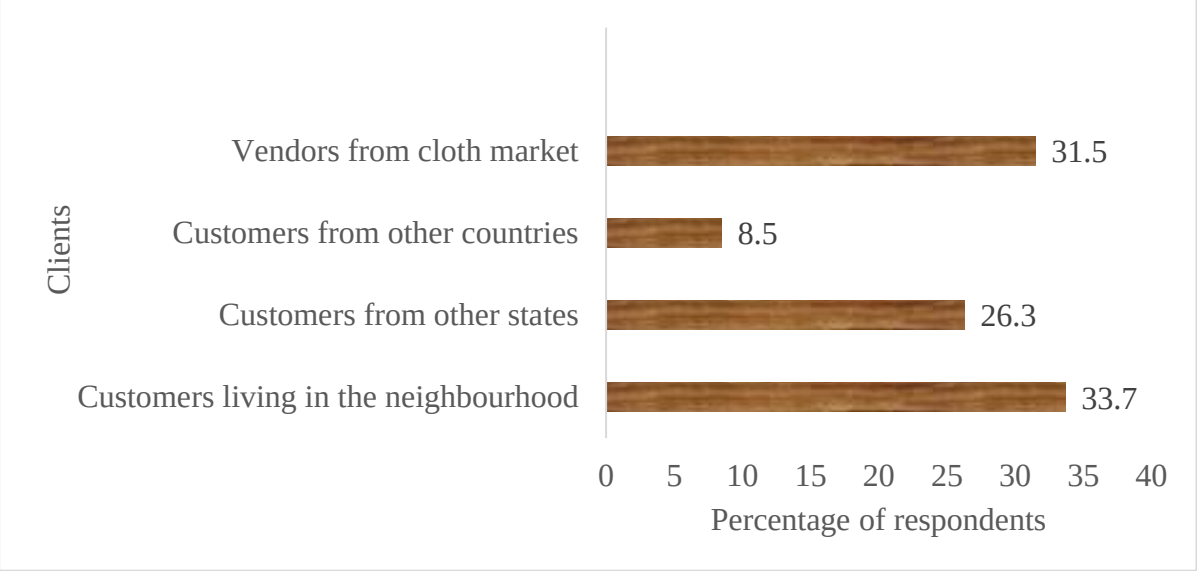


Figure 4.9: Clients of the services offered by the dyers

4.1.3.7 Means of measurement

The dyers mostly measure dyes/chemicals using uncalibrated stainless-steel spoon and none of the dyers use weighing balance for measurement as shown in Figure 4.10. This can be a disadvantage as, for example, addition of too little hydros results in oxidation which removes the dye from solution, incorrect heavy colour selvedge and poor fastness to washing while too much hydros can lead to destruction of the dye chromophore which leads to loss of colour yield (Teli *et al.*, 2001).

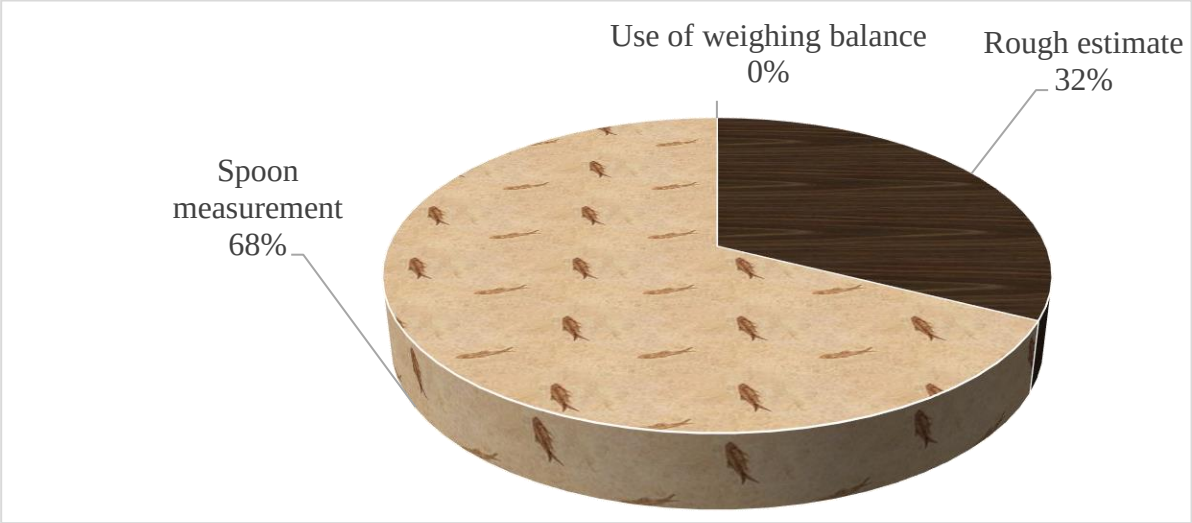


Figure 4.10: Weighing system

4.1.4 Step by step dyeing processes in relation to industrial practices

4.1.4.1 Treatments carried out before dyeing

As shown in Table 4.4, all the dyers carry out partial desizing and most of them conduct mercerization process. Fabrics sold at “Kantin Kwari” cloth market are mostly finished by the manufacturers with light starch and according to the dyers soaking the material in water and squeezing after a few minutes removes most of the starch, the remaining being washed up during dyeing. This mimics rot steeping (Harane and Adivarekar, 2016) but with much shorter treatment time. This can be a disadvantage since the nature of the starch is unknown and some types are difficult to remove (Hickman, 1995) impeding dye penetration. According to Sameii (2018), in hot mercerization, the desizing stage can be eliminated whether the sizing material is starch-based, a modified starch, carboxy methyl cellulose, or a synthetic size such as poly (vinyl) alcohol.

Those that carry out mercerization do that for the purpose of increasing dye absorption to produce a deep shade while those that do not are of the opinion that excess caustic soda reduces the strength of the material resulting in tear and customer complain. Amubode (2009) reported a situation in Abeokuta where the use of caustic soda in preparation of vat dyebath was banned in the past due to complaints from traders and customers that the dyed material rots.

Table 4.4: Treatments carried out before dyeing

Treatments	Yes N=226 (%)	No N=226 (%)
Partial desizing	226 (100)	0 (0)
Scouring	0 (0)	226 (100)
Bleaching	0 (0)	226 (100)
Mercerization	198 (87.6)	28 (12.4)

4.1.4.2 Dyeing methods

The dyers are involved in hand dyeing making use of batchwise method in an open plastic bowl and moving the fabric/garment relative to the dye liquor as shown in Plate XVI. Application of colour can be achieved by exhaust dyeing (batch), continuous (padding) and printing where in exhaust dyeing the dye is transferred to the fibre surface by motion of the dye liquor or by motion of the substrate being dyed (Clark, 2011). Dyeing machines are designed to move the material or the liquor or both relative to each other (Holme, 2016; Wardman, 2018; Baumann and Fletcher, 1966). The use of open bath may be a problem because oxygen from air combats with the reduction action of hydros and that is why machines are designed to either exclude air or to apply hydros only at crucial moment during the dyeing process (Baumann and Fletcher, 1966).



Plate XVI: Dyebath and dyeing position (Field work, 2018)

Sequences A and B shown in Figure 4.11 are referred to as leuco vat dyeing where the material to be dyed is entered into a prepared liquor that contain the fully vatted dye, caustic soda and hydros with various amounts of auxiliaries (Latham, 1995). According to the dyers, leuco vat dyeing is referred to as "Danbusununu" (in Hausa) meaning a duller dyeing in which the design of the dyed material is not quite visible. Sequences C and D mimic pre-pigmentation which is a process where dispersions of vat pigments with no substantivity are circulated and uniformly distributed at the fibre surface before alkali and reducing agent are added (Aspland, 1997).

In practice, for methods C and D, the dyers prepare a dyebath containing the dye and caustic soda, circulate the material and then add hydros to initiate reduction and absorption of the dye. The proportion of dyers employing starching prior to full oxidation (sequences B and D) are

higher irrespective of whether it is a leuco or modified pre-pigmentation process. The dyers revealed that oxidation process is always almost completed during rinsing and that starching before full oxidation is advantageous since there will be saving in time speeding up the dyeing process. Starching immediately after rinsing can also be a disadvantage.

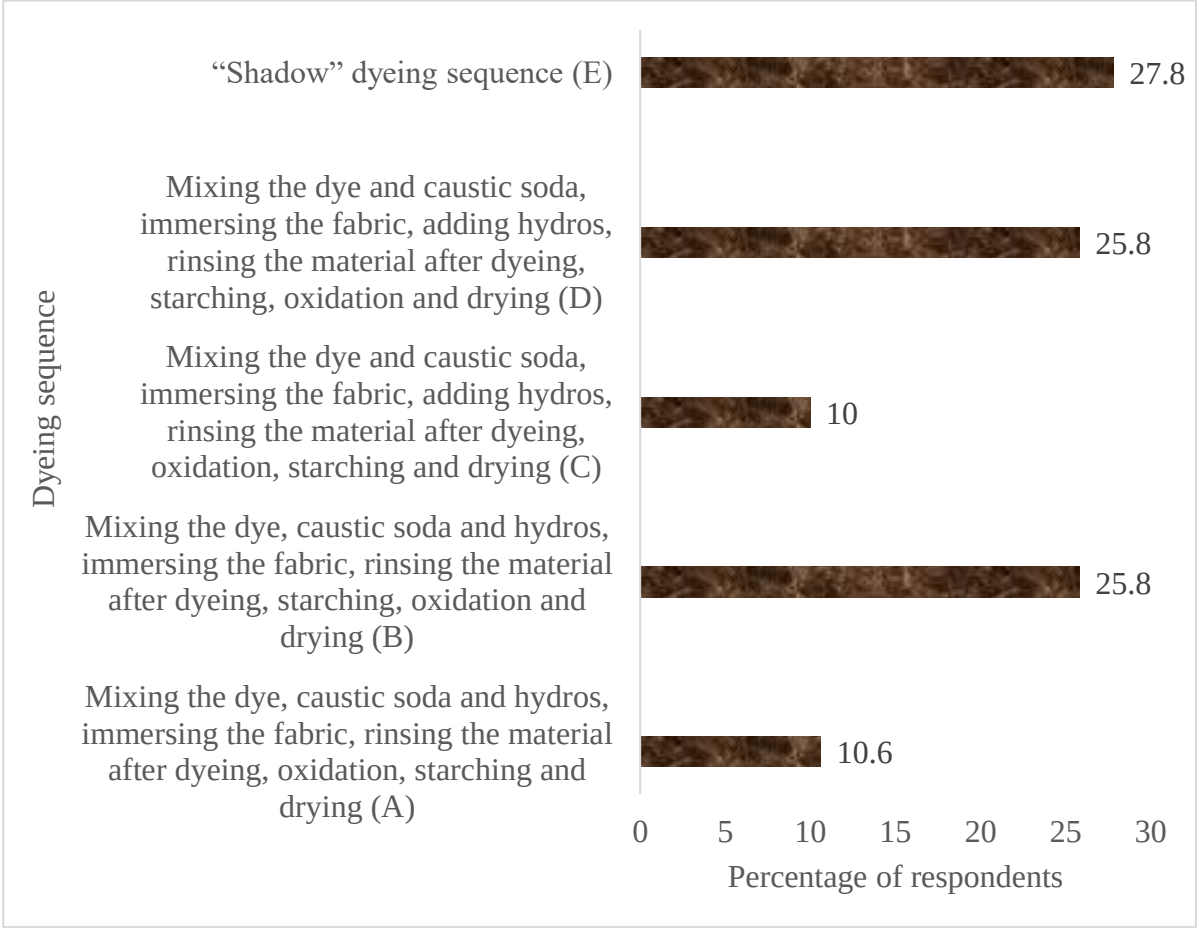


Figure 4.11: Dyeing methods

According to the dyers, sequence E is called "Rinin kwalba" or "Dan Sokoto" (in Hausa). They also refer to it as "shadow" which is a word used to describe irregular shadow dyeing (Eltz and Maier, 1973). It was revealed that the "shadow" effect is more pronounced on cotton blend fabric due to selective dye absorption. The method involves treating the material with

very high conc. of caustic soda (mercerization) without tension at elevated temperature for a few min. and dyeing to a very deep shade using any of the dyeing sequences described above and without the intermittent washing and drying step after the caustic treatment (wet-on-wet process). Samples of mercerized and unmercerized fabrics are shown in Plate XVII.

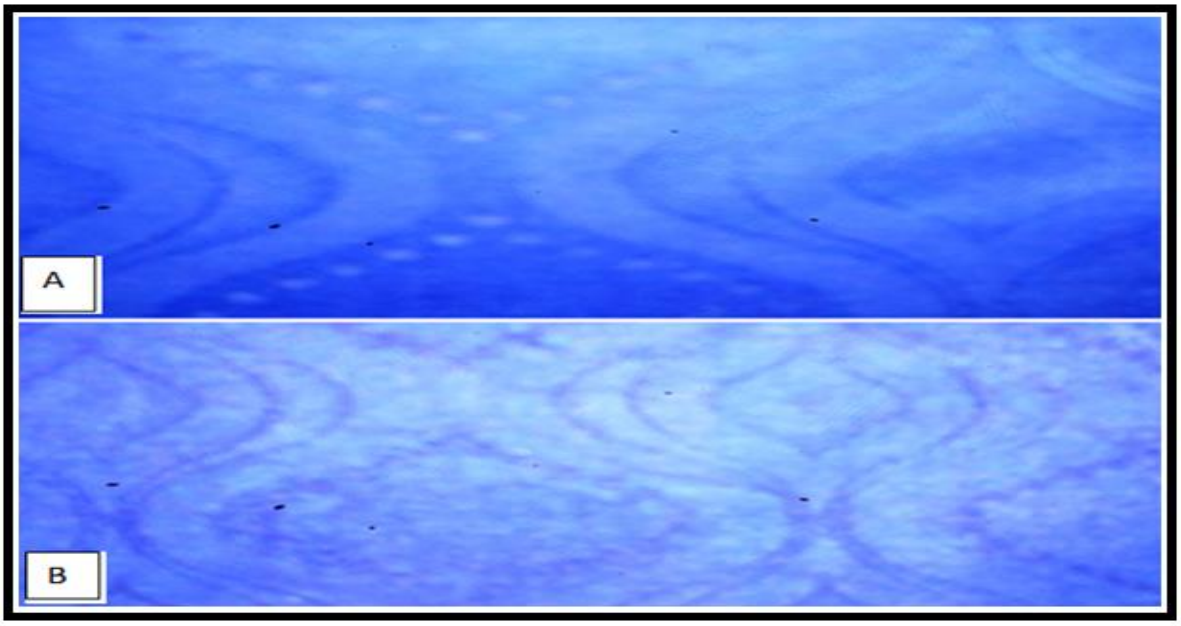


Plate XVII: Dyed samples of un-mercerized (A) and mercerized (B) materials

The dyers also produce cheaper, low quality, dyeings by reusing spent dyebath after addition of caustic soda and hydros and they refer to this as “Kanbakare” or “Tsome” (in Hausa). Similarly, the possibility of reuse of spent dyebath has been suggested by Chakraborty (1992). The dyers also continuously add dye and hydros in the course of dyeing as shown in Plate XVIII and this could compensate for hydros lost due to oxidative degradation. Similarly, Chakraborty (1992) reported that in vatting and dyeing, hydros must be compensated by supplying extra amount to continue the reduced state throughout dyeing. Metered addition of hydros has advantages such as better levelling by slower vatting, no need of levelling agent, protection from over-reduction, control of initial dyeing rate (strike), possibility of warm pre-pigmentation and good reproducibility (Shamey and Hussein, 2005).



Plate XVIII: Metered addition of chemicals (Field work, 2018)

According to the dyers, they normally work in the early hours of the morning to minimize the effect of heat which could otherwise be intense under the sun and to avoid levelling problems associated with yellow and orange dyes. Giles (1974) described phototendering common with red, yellow, and orange dyes as a chemical attack on cellulose fibre causing severe weakening 'tendering' when the dyed fibre is exposed to light during the actual dyeing process or in use in the normal finished state. In the dark, in the presence of oxygen, the original colour is restored (Aspland, 1992a).

4.1.4.3 Vatting and dyeing time

As shown in Figure 4.12, the vatting time employed by the dyers in not more than 2 min. The duration of vatting may be too short because normally, vatting is carried out for about 10 min. prior to dyeing (Aspland, 1992a; Aspland, 1997; Giles, 1974). It is possible that the dyers normally start the dyeing process before the vat pigment is completely converted into soluble dye anions in order to avoid rapid strike common with vat dyes. The dyeing time employed

by most of the dyers (Figure 4.13) is 4-6 min. and majorly accomplished dyeing in less than 10 min. Industrially, dyeing time at the maximum temp. can vary from about 45 min. at 60 ^{o}C (Giles, 1974) to about 20 min. at 100 ^{o}C (Aspland, 1992a; Aspland, 1997). It may be assumed that the dyers take advantage of the rapid strike of var dyes where 80-90 % may be exhausted within 10 minutes of dyeing (Broadbent, 2001).

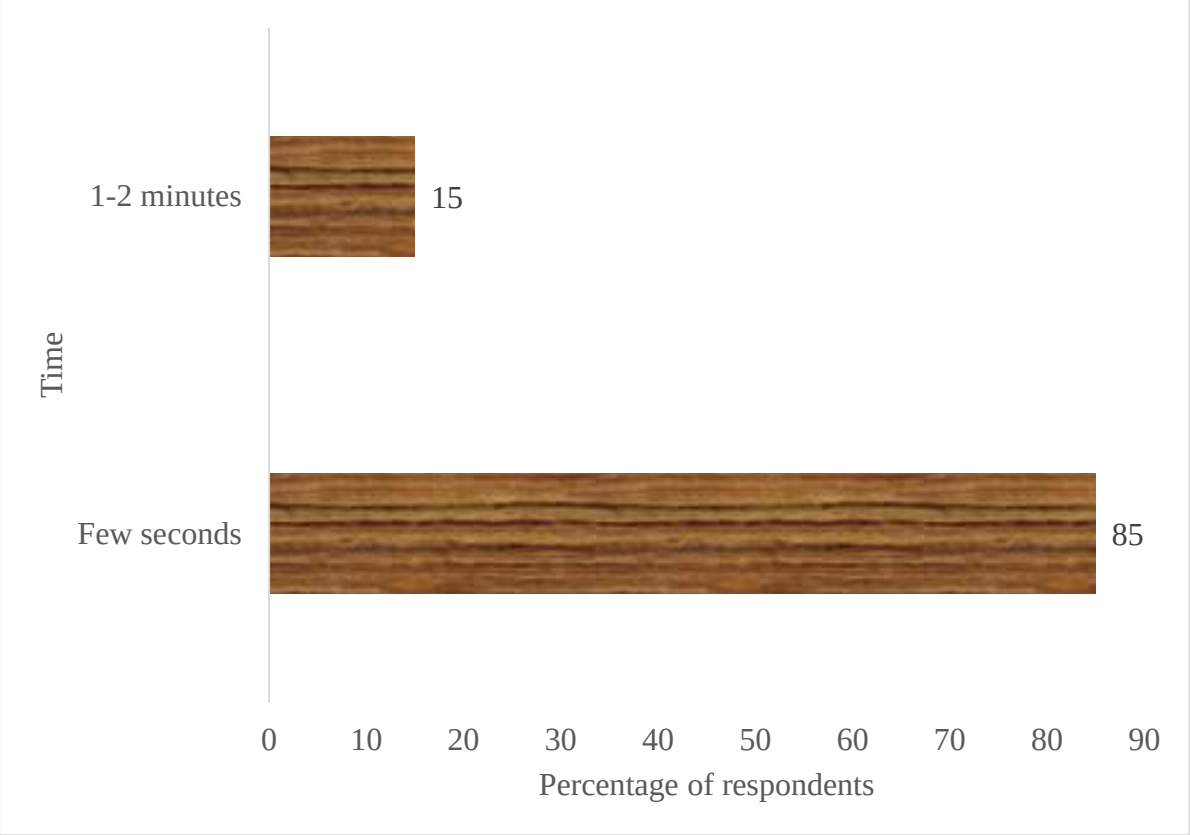


Figure 4.12: Vatting time

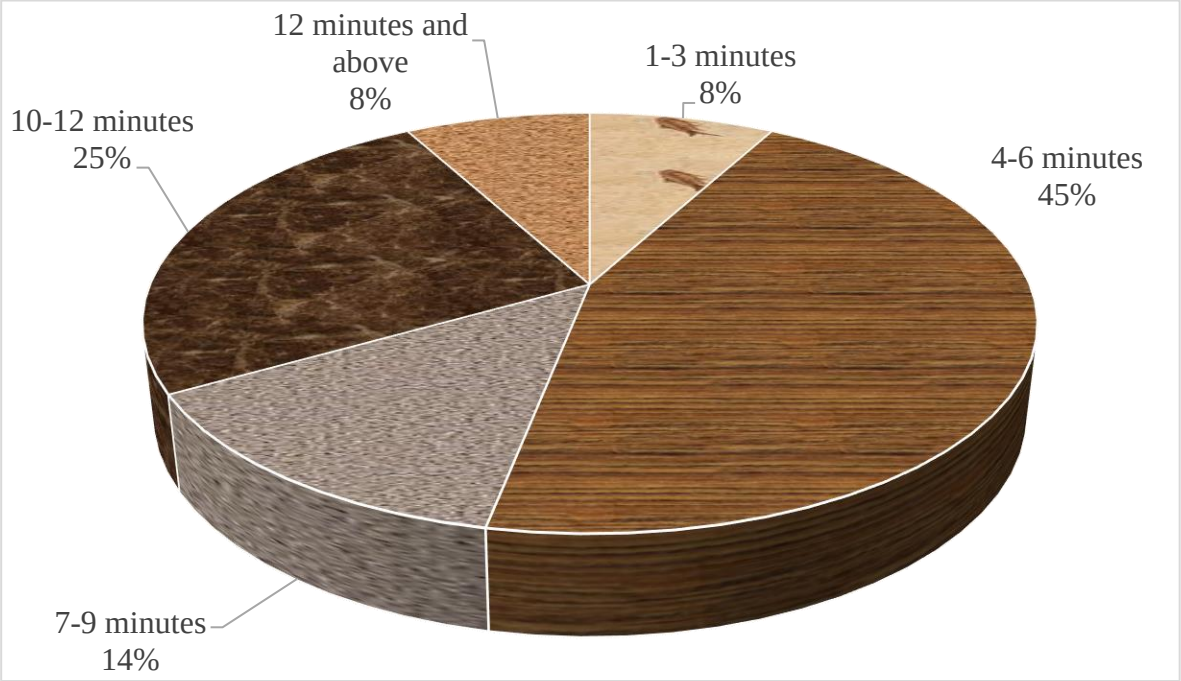


Figure 4.13: Dyeing time

4.1.4.4 Liquor ratio and levelness of shade

Liquor ratio (LR) is the amount of water required in relation to the mass of textile expressed in a ratio. The dyers use an average of 20 L of water to prepare a dyebath for dyeing 5 yards (4.57 m) of material which is in the range of 710 to 814 g (LR of ≈ 40:1). LR for various batch dyeing machines range from 5:1 to 30:1 or even more (Wardman, 2018). It has been reported that majority of some local vat dyers in Ghana use a LR of 40:1 (Frimpong, 2009). Use of too large LR is disadvantageous because water causes oxidative decomposition of hydros and when in excess, due to the presence of more dissolved oxygen, the decomposition rate will be accelerated (Chakraborty, 1992).

As shown in Figure 4.14, the dyers achieve level dyeing through various means. Because the chemicals necessary for vatting process make the leuco vat dye anions in solution highly substantive, there is always the possibility of unlevelness if circulation of the dye liquor is

inadequate (Aspland, 1997). Level dyeing is attained through the migration of dye by desorption from inside the fibre into the dye liquor and subsequent adsorption and diffusion in another part of the fibre, the levelling process being aided by the relative motion of fibre and the dye liquor (Holme, 2016).

Some of the dyers reported that they hardly achieve levelled dyeing and this may be because they are unaware that the levelling properties of different group of vat dyes are not the same and therefore maximum overall result may not be achieved. For example, in general, the IK group levels very well, the IW group levels well, and the IN-group levels badly. Industrially, the problem of levelness has been addressed through the following: control of dyebath assistants, time, and temperature; application of the dye in the form of a non-substantive dispersion and reduction and oxidation of the dye in-situ; and use of auxiliary compounds designed to slow down the rapid rate of exhaustion characteristics of most vat dyes (Fox, 1948).

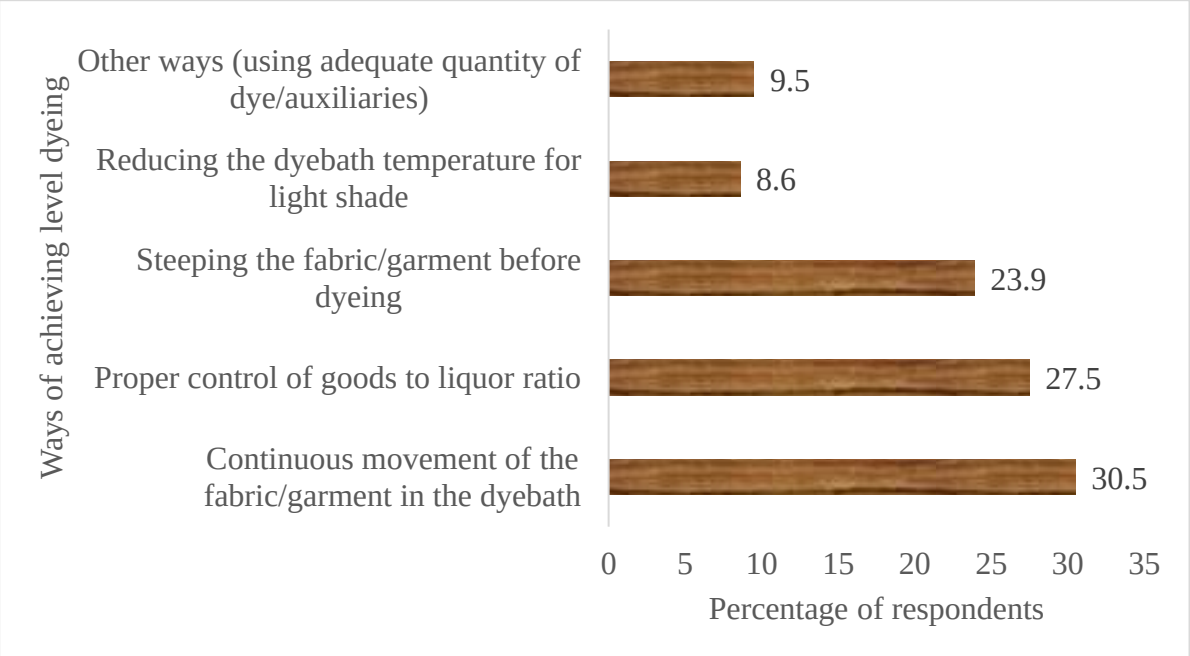


Figure 4.14: Ways of achieving level dyeing

4.1.4.5 Colour and shade

Different techniques are being used by the dyers to achieve desired colour and shade as shown in Figure 4.15. According to the dyers, the ability to obtain an exact colour and shade from a sample provided by a customer is the most tasking in the dyeing occupation and requires several years of experience. Similarly, Saikhao *et al.* (2018) reported that dyeing process of natural indigo vat dye requires a high level of expertise and experience to achieve the desired colour and shade. The fact that the dyers do not measure dye/chemicals analytically and cannot control temperature precisely which makes it very difficult for them to reproduce an exact shade.

Additionally, when large lot/order is to be dyed to the same shade, variation is hardly avoidable since the dyers can only dye 20 yards (18.29 m) of fabric at a time in a single dyebath. Industrially, colour matching system is used which works on the principle that colour is measurable and so is reproducible. The system allows the identification of colour since the human mind is deficient in remembering specific shades and no single person can recall the exact differences in a hue without a sample/recipe as a guide (Frimpong, 2009). For these reasons, obtaining desired colour and shade can be a setback for the occupational dyers.

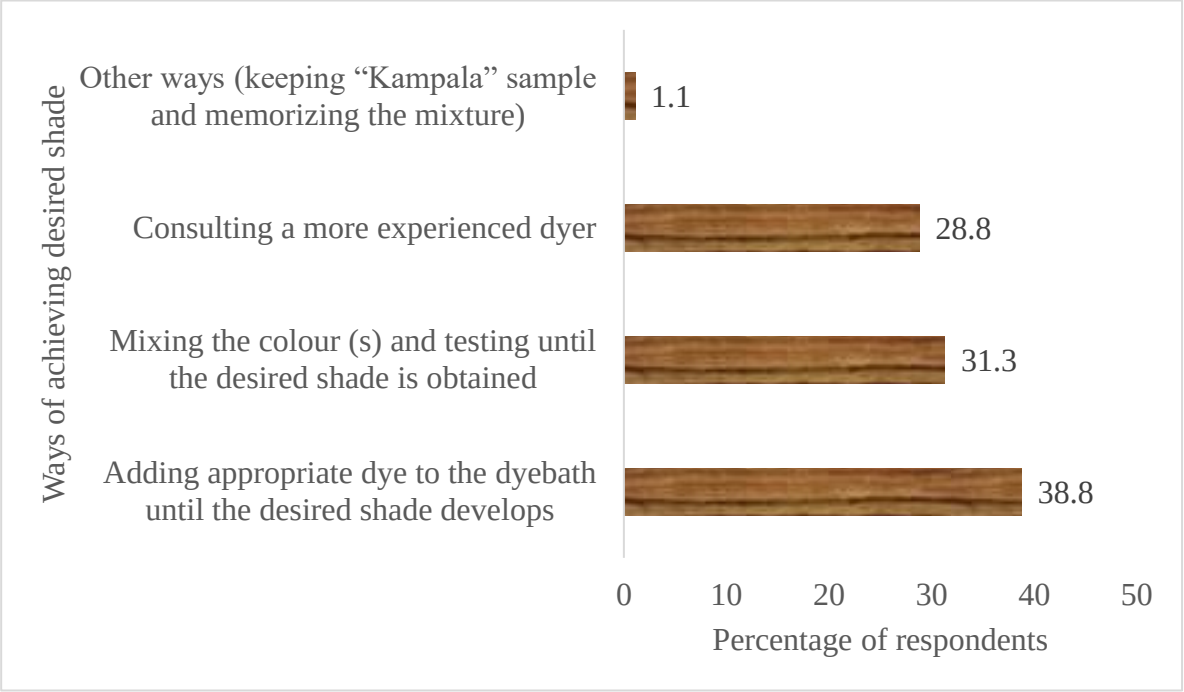


Figure 4.15: Manner in which the dyers achieve desired colour and shade

4.1.4.6 Treatments carried out after dyeing

All the dyers (100 %) subject the dyed materials to air oxidation usually during rinsing as shown in Table 4.5. Similarly, according to Shuvo II (2018), local artisans lack technical chemistry background required for aftertreatment. Industrially, after-treatments namely oxidation, soaping and neutralization/acidification are carried out as vat dyebath is dropped (Aspland, 1992b). Soaping is the final stage in vat dyeing which involves treatment in a boiling solution of soap/other detergent and has the double purpose of removing from the fibres loosely attached surface dye thus achieving the full degree of fastness to washing and rubbing and of effecting a colour change to final shade (Summer *et al.*, 1953; Shamey and Hussein, 2005). Neutralization/acidification removes any residual alkali in the material.

Table 4.5: Treatments carried out after dyeing

Treatments	Yes N=226 (%)	No N=226 (%)
Oxidation	226 (100)	0 (0)
Soaping	0 (0)	226 (100)
Acidification	0 (0)	226 (100)

4.1.5 Challenges and prospects of the dyeing occupation

4.1.5.1 Challenges

Figure 4.16 shows that the dyeing occupation is threatened by numerous challenges which are presented in order of proportion, from more significant to the least.

Limited capital: Limited capital is a major challenge confronting the dyers even though the venture requires low capital investment. Similarly, Selase *et al.* (2019) reported that lack of capital is the major reason for the decline of batik and tie-dye centres in Ghana. Also, according to Agwu and Emeti (2014), poor financing constitutes a big problem in the performance of majority of SMEs in Nigeria. The dyers revealed that they need to improve on the business as majority of them spend as they earn without savings. According to them, they do not have access to credit due to lack of collateral neither do they get financial support from Government or any other organization. According to ILO (2014b), informal economy does not enjoy secure property rights which deprives them of access to both capital and credit.

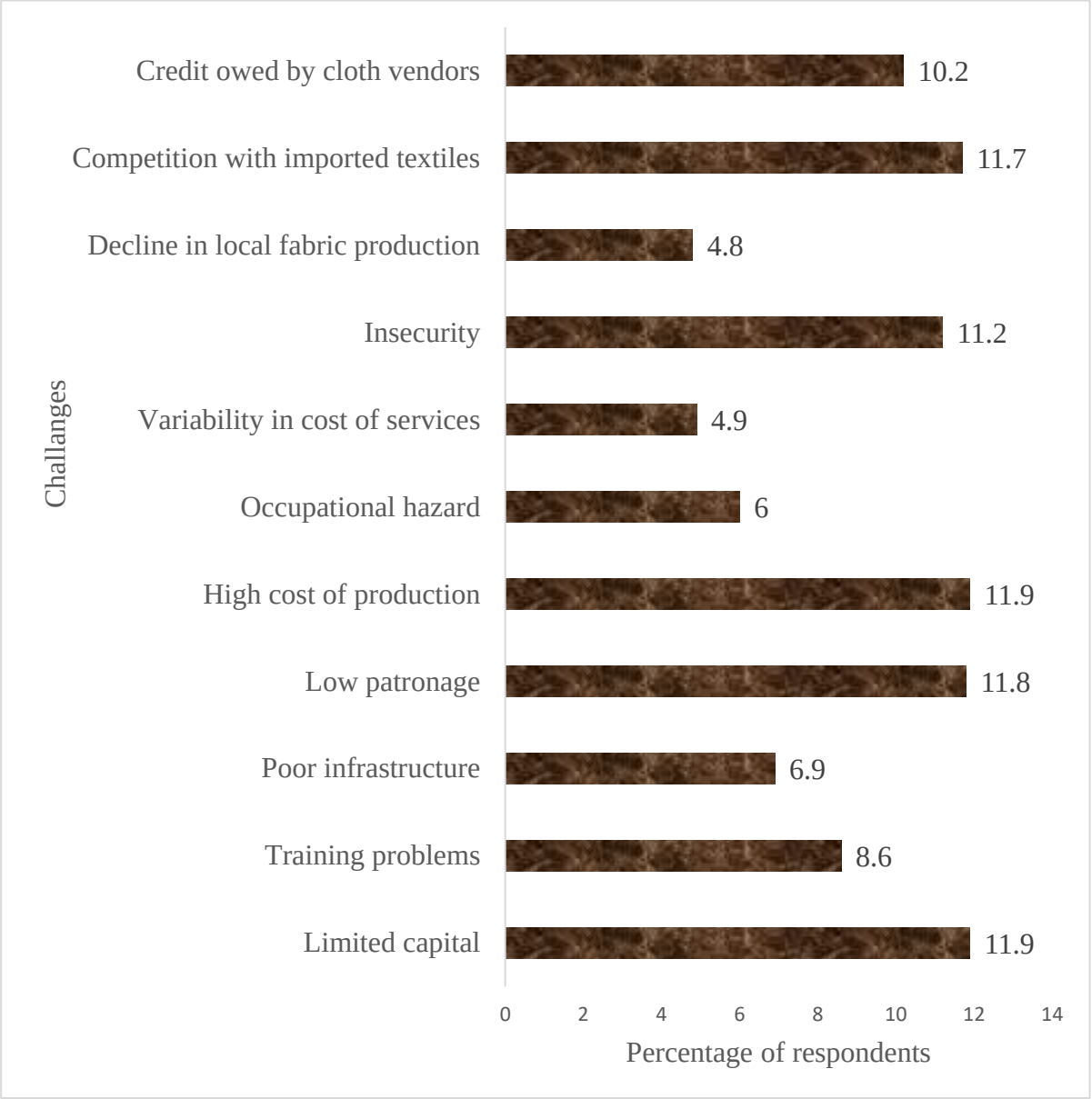


Figure 4.16: Challenges faced by the occupational dyers

High cost of production: This is also a major challenge to the dyeing occupation. Costs of dyes and chemicals, being majorly imported, have increased about 5 times from 2013 to date. Cost of water has also increased which will invariably add to the cost of dyeing considerably due to high water consumption. The dyers revealed that cost of fuel, calendering, and stipend paid as labour have increased significantly. This makes it very difficult for the dyers to break

even especially due to the fact that there is very little corresponding increase in cost of services. Similarly, according to Afolabi (2015) and Ogbo and Nwachukwu (2012), over dependence on imported rawmaterials is a problem to SMEs. High cost of production was also found to be a challenge to batik and tie-dye centres in Ghana (Selase *et al.,* 2019).

Low patronage: The dyers disclosed that poor economy has resulted in many customers not being able to afford their services. According to them, presently, many people change their mode of dressing to western style. Similarly, decline in local dyeing in Ghana has been attributed to low patronage (Asmah and Sherifatu, 2016; Selase *et al.,* 2019). Change in fashion trend where people see anything western as modern is one of the reasons for low patronage hence the decline in indigo dyeing in Africa (Mayusoh, 2015) and nowadays, most Nigerians have developed a high propensity for the consumption of foreign goods as against their locally made substitutes (Agwu and Emeti, 2014).

Competition with imported textiles: On May 14, 2015, thousands of local fabric dyers staged a demonstration against the importation of Chinese textiles and engagement of the expatriates in retail sale of dyed fabrics in the Kano market (Muhammed, 2015). This also appears to be the case in Egypt where an influx of Chinese goods has swamped local production, and in Zambia and Zimbabwe where there has been riots against Chinese merchants and products (Eisenman, 2012). This is also in line with the findings of Ringuede (2016) that Chinese manufacture synthetic textiles reproducing a variety of traditional designs and keeping the counterfeit for sale in the region where they are usually produced, directly competing with the local cloth dyers. Nigeria was China's second largest trading partner in Africa, after South Africa, and importation of manufactured textiles from China have undermined both hand and

mechanized textile production in the country which endangers the self-sufficiency of the people (Eneji *et al.*, 2012). Similarly, influx of Chinese textiles threatened local textile dyeing industries in Abeokuta, Nigeria, making it difficult for the industry to compete favourably in the local market (Amubode, 2009).

Insecurity: The dyers disclosed that insecurity threatens the dyeing occupation because the number of foreign customers buying the dyed materials in the market has drastically reduced thus the demand for their services has declined. According to them, Ethnoreligious violence and Boko Haram insurgency are the causes of the problem. It is known that there has been many outbreaks of bloody violence between communities since the return of democracy in 1999 such as the riots in the urban centres of Kaduna and Kano (Walker, 2012). Boko Haram insurgency has been a major security challenge in northern Nigeria. It is a Hausa language nickname given by outsiders meaning "western education is forbidden by Islam". The jihadi group pledged allegiance to the Islamic State in March, 2015 and has killed many people in Nigeria, Niger, Chad and Cameroun (Thurston, 2016) resulting in the loss of significant number of trading partners in the dyeing business. Currently, banditry is also a mitigating factor in the dyeing venture.

Credit owed by cloth vendors: The dyers disclosed that cloth vendors pay only 40-50 % of the charges as advance payment and due to increasing cost of rawmaterials, calendering etc. the payment is usually inadequate for the dyers to complete the job and have to owe for either dyes and chemicals or calendering or labour. According to the dyers, cloth vendors, in most cases, feel reluctant to pay the balance when the job is completed where some offer clothes equivalent to the money they owed. This default in payment will naturally affect business

relationship between the dyers, jobbers, colour vendors etc. which may cripple the dyeing venture. Similarly, default in payment by clients has been reported as a challenge to Ntonso local dyers in Ghana (Acquah and Oduro, 2012).

Training problems: The dyers disclosed that in the past, politicians have organized several training sessions involving various entrepreneurial skills (including dyeing) among selected individuals as a reward for loyalty. According to them, the training usually last for few days after which money is shared as capital to set up business related to the skill acquired. It was also revealed that none of the beneficiaries has ever opened a dyeing venture and that no occupational dyer has ever been recruited. In contrast, government and non-governmental organizations have trained and continue to train people in the making of batik and tie-dye in Ghana in an attempt to create employment and alleviate poverty (Selase *et al.*, 2019). In Kano metropolitan area the dyers lack technical chemistry background and will therefore require training to improve on the technical know-how of vat dyeing processes. Similarly, lack of technical know-how and training were reported as challenges facing Daboya local dyeing industry in Ghana (Asmah and Sherifatu, 2016).

Poor infrastructure: The dyers revealed that their infrastructural challenge includes wastewater disposal problem due to lack of proper drainage, lack of water, and inadequate space for the dyeing job. Informal enterprises have limited or no access to public infrastructure (ILO, 2014b) and infrastructural inadequacies such as water. are serious problems to SMEs (Agwu and Emeti, 2014).

Occupational hazard: Hazard due to dye and chemicals is of great concern in dyeing industries hence several safety measures including the use of personal protective equipment are put in place. The dyers revealed that occupational hazard is not a serious problem to them because they tend to become resistant to inhalation of chemicals and believe that eating meat and drinking milk immediately after the dyeing process suppresses the effects. However, this claim cannot be scientifically justified. According to them, some have suffered work related symptoms such as coughing, chest pain, shortness of breath, nausea etc. due to inhalation of hydros and fumes from the dyeing liquor as well as chemical burns due to spills and splashes. Typically vat dyes have been found to cause all the symptoms stated above (Lakshmi *et al.*, 2009). It has been reported that annually, occupational accidents and work-related diseases caused over 2.3 million fatalities, out of which over 350,000 are caused by occupational accidents and close to 2 million by work related diseases (ILO, 2014a).

Variability in cost of services: The dyers reported that, nowadays, it is typical of youths to start working as apprentice and suddenly decide to start their own business without completing the training. According to them, apprentices just stay for a few months learning the job and running errands either to buy chemicals, collect materials from or deliver finished goods to cloth vendors. Such apprentices quit the job that is supposed to last for at least 3 years and open their own dyehouse competing directly with the local market and delivering poor quality services. The cloth vendors use this opportunity to reduce cost of dyeing in their favour and this ultimately brings about variation in cost of services which affects the profit that could be made after a good quality job. For this reason, dyers may accept a meagre amount as cost of services and reduce the dyeing quality.

Decline in local fabric production: Cloth vendors revealed that due to limited number of textile manufacturing companies hence limited availability of locally produced fabric, currently, both availability and cost of white undyed fabric is determined by the Chinese. Similarly, according to Renne (2015), by 2012, most of the textiles sold in "Kantin Kwari", are imported from China. Formally, Nigerian textile industry was the third largest in Africa after Egypt and South Africa and was the largest employer of labour in the manufacturing sector where it accounted for about 25 % of total manufacturing employment (Eneji *et al*., 2012). At present, there is serious decline in local fabric production which gave the Chinese a competitive advantage. In a typical textile industry studied, production figures per meter from a weaving department has shown that about 9.6 million meters were produced in 2000 which fell to about two third and then one third in 2009 and 2013 respectively (Muhammad *et al.*, 2017) and since then the figures continue to decline.

4.1.5.2 Prospects

Occupational vat dyeing before 2013: Most of the dyers believe that the dyeing occupation has declined significantly with majority of the opinion that it was more profitable over 5 years ago i.e., before the 3rd quarter of 2013 (Figure 4.17). The result shows that during the period that the business was more lucrative, most of the dyers can process over 20,000 yards (>18,288 m) weekly as shown in Figure 4.18. Among the reasons why the business excelled in the past, better economy was found to be of greater importance as shown in Figure 4.19. The dyers reported that the Chinese import only white, undyed, fabric as at the time.

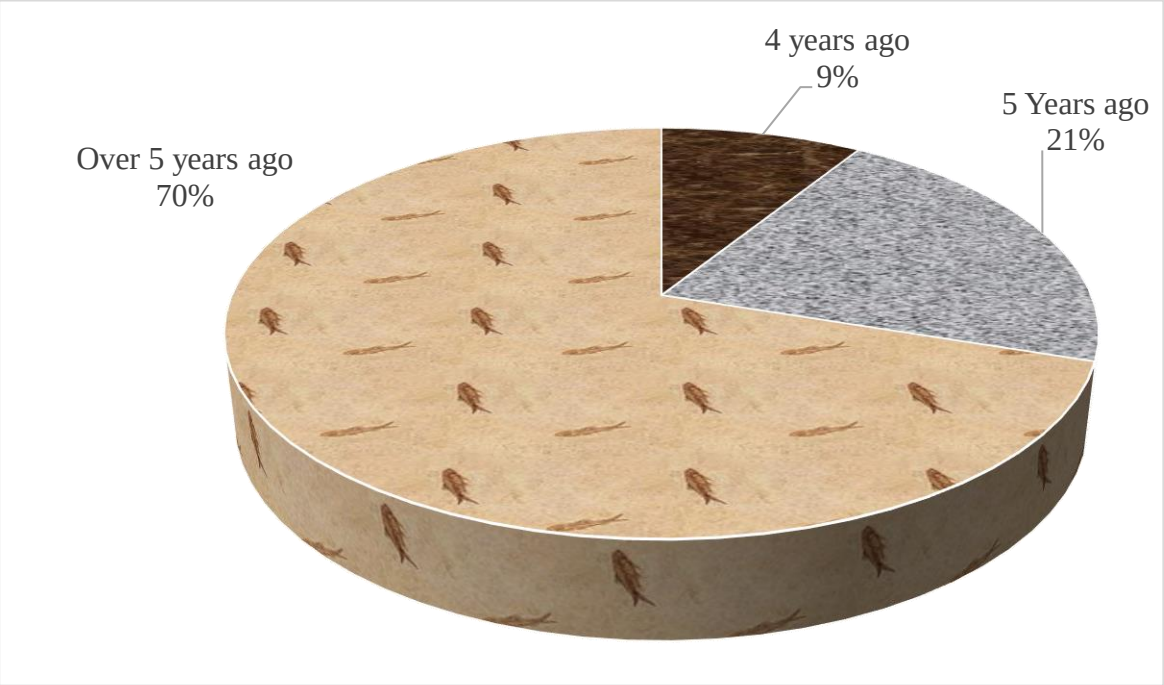


Figure 4.17: Period that the dyeing occupation flourished

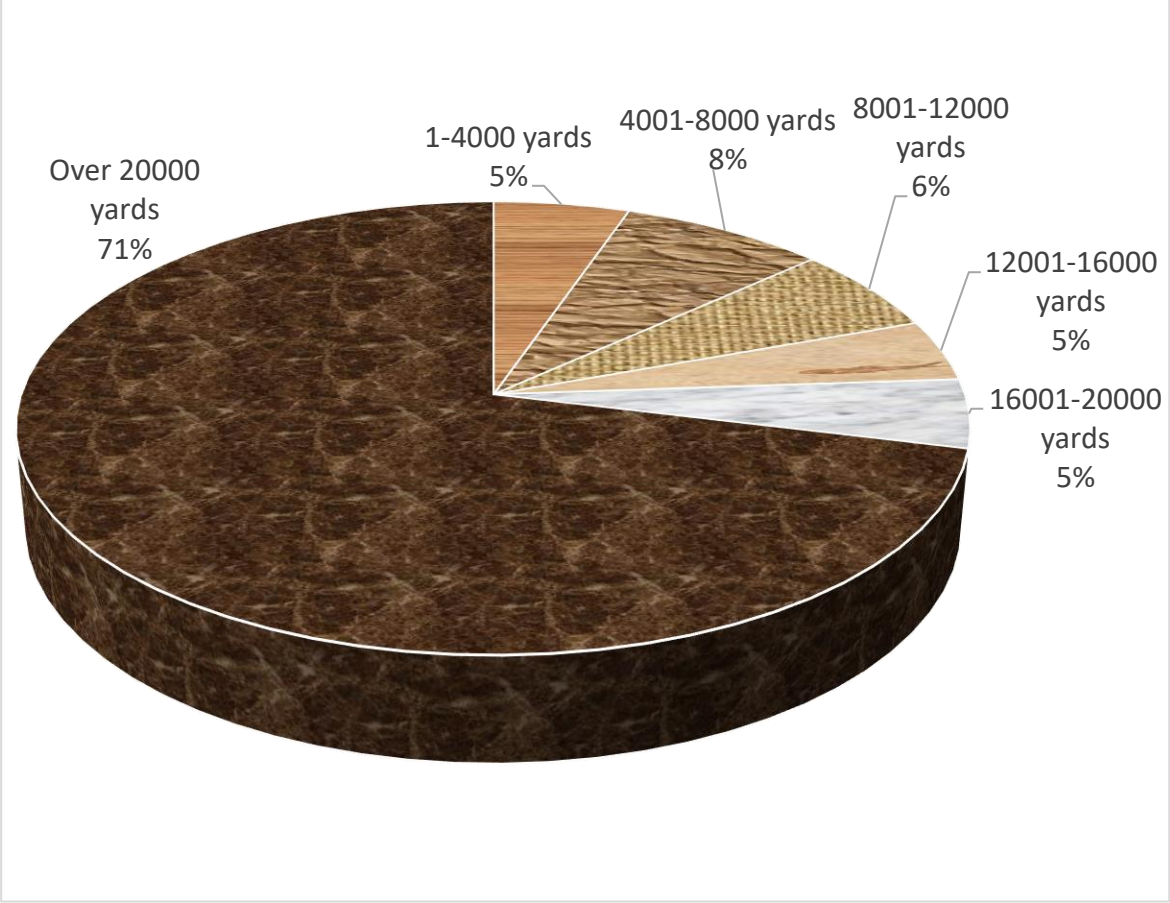


Figure 4.18: Weekly dyeing rate as at 2013

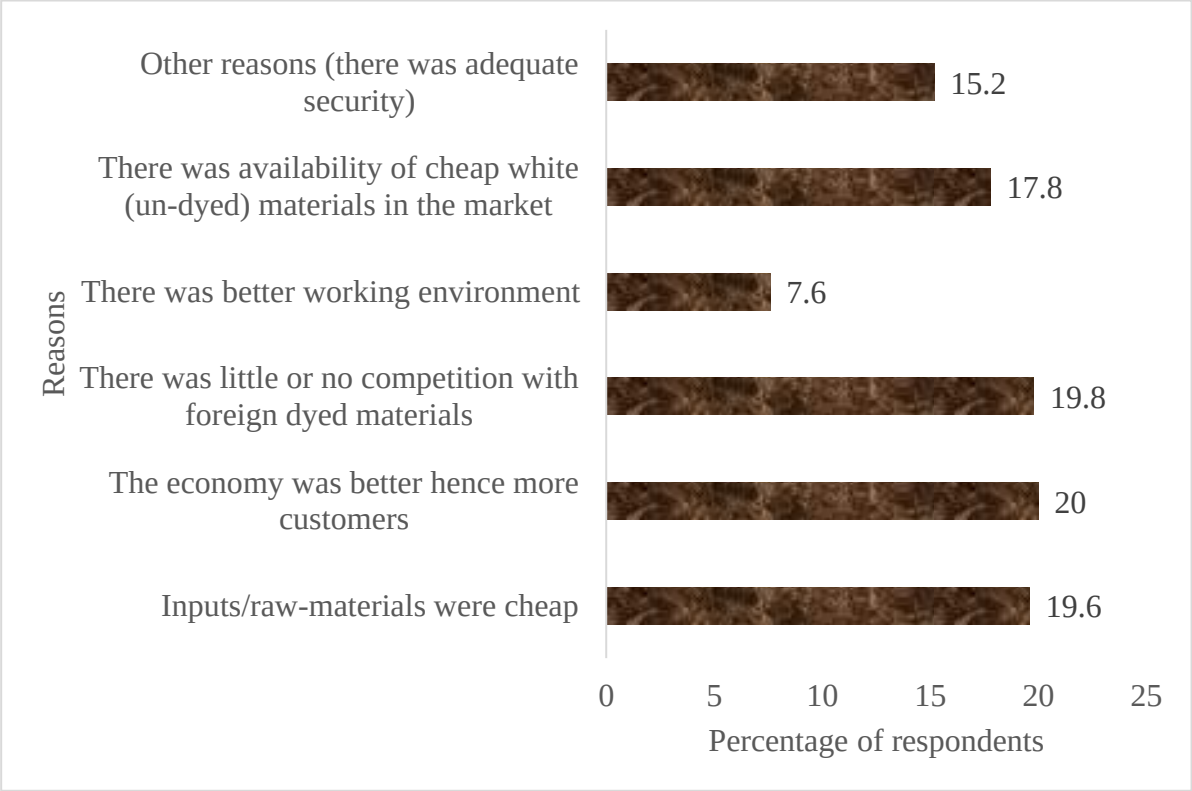


Figure 4.19: Reasons why the dyeing occupation blossom within the last five years

Occupational vat dyeing as at 2018*:* Vast majority of the dyers are of the opinion that the dyeing occupation is no longer thriving. Figure 4.20 shows that 70.2 % of the dyers can dye not more than 400 yards (not >365.76 m) of material. This indicated that the business has declined significantly over a period of 5 to 6 years. This corroborates well with the fact that most SMEs in Nigeria die within the first 5 years of existence and only about 5-10 % survive, thrive and grow (Agwu and Emeti, 2014; Aremu and Adeyemi, 2011). Among the reasons given for the decline in the business, the dyers consider poor economy as the most vital as shown in Figure 4.21. Nigerian economy has continued to decline with the location of the study area having the highest poverty level.

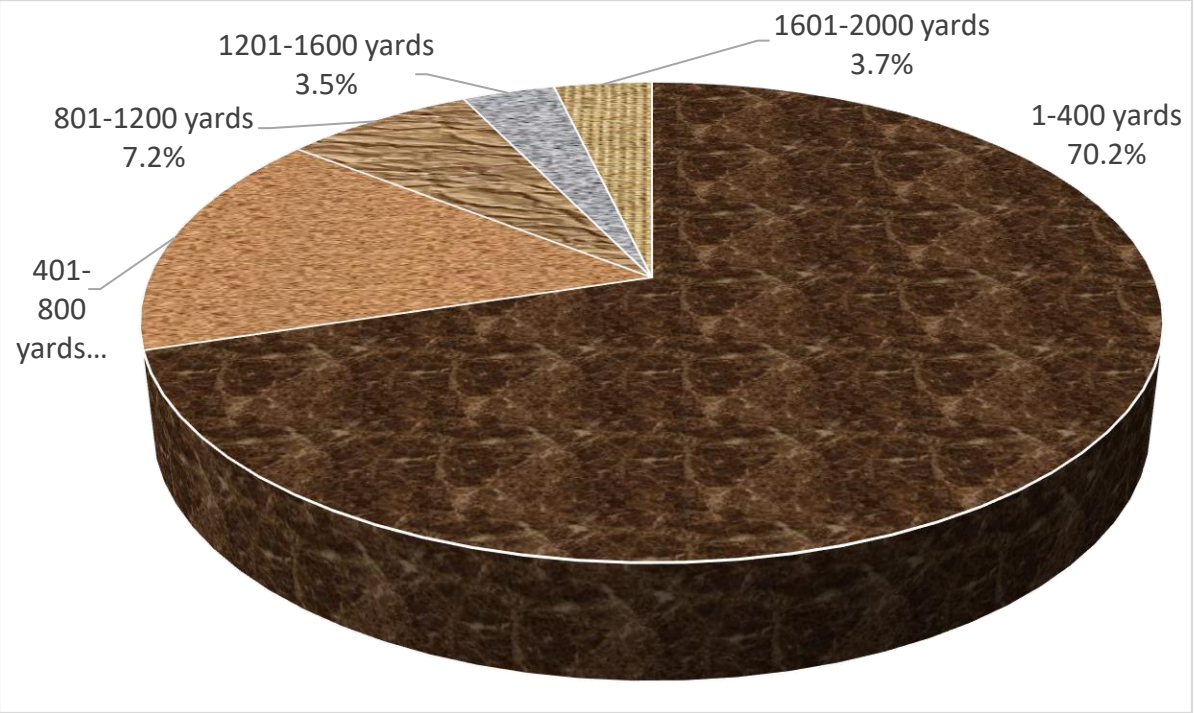


Figure 4.20: Weekly dyeing rate as at 2018

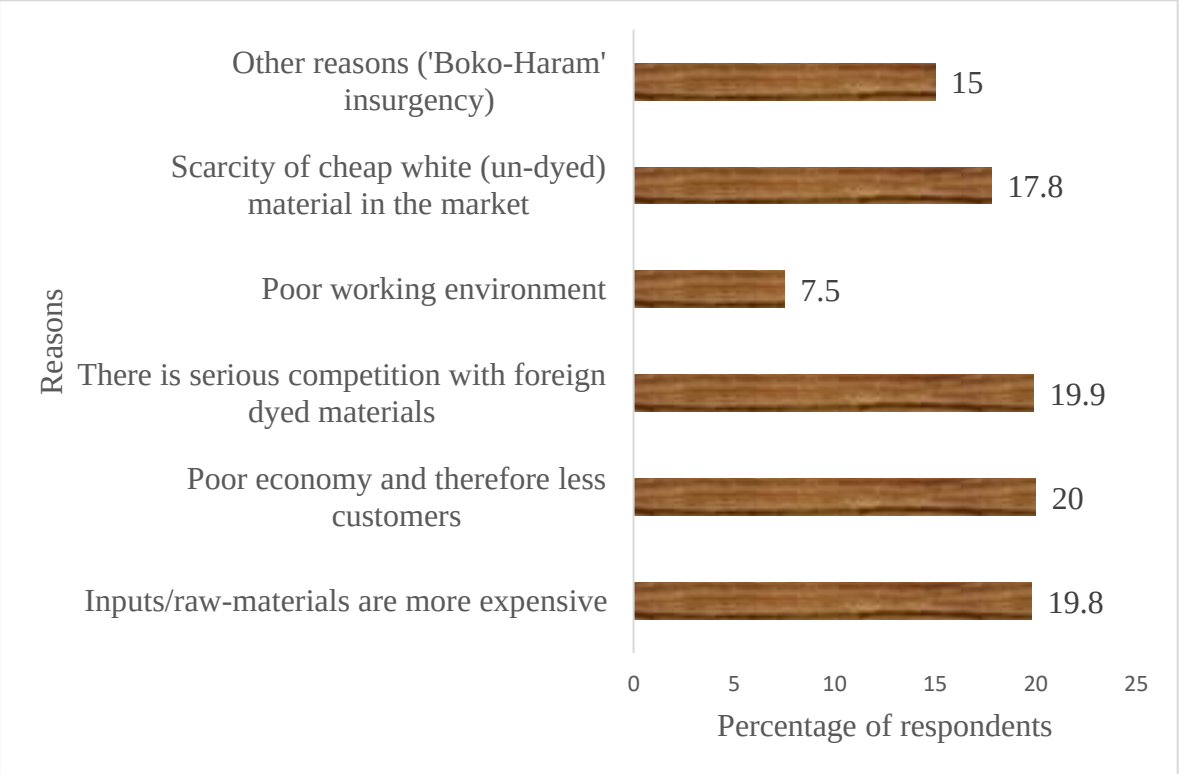


Figure 4.21: Reasons why the dyeing occupation declined

The role of Government*:* A larger proportion of the dyers believed that government can help revive the dyeing occupation. The major support required by the dyers are for the Government to improve the economy and stop importation of coloured textiles as shown in Figure 4.22. The dyers constantly look for competitive advantage in order to sustain the venture. One such move is the modification of their dyeing methods e.g., "shadow effect" which is quite appealing thus attracting customers.

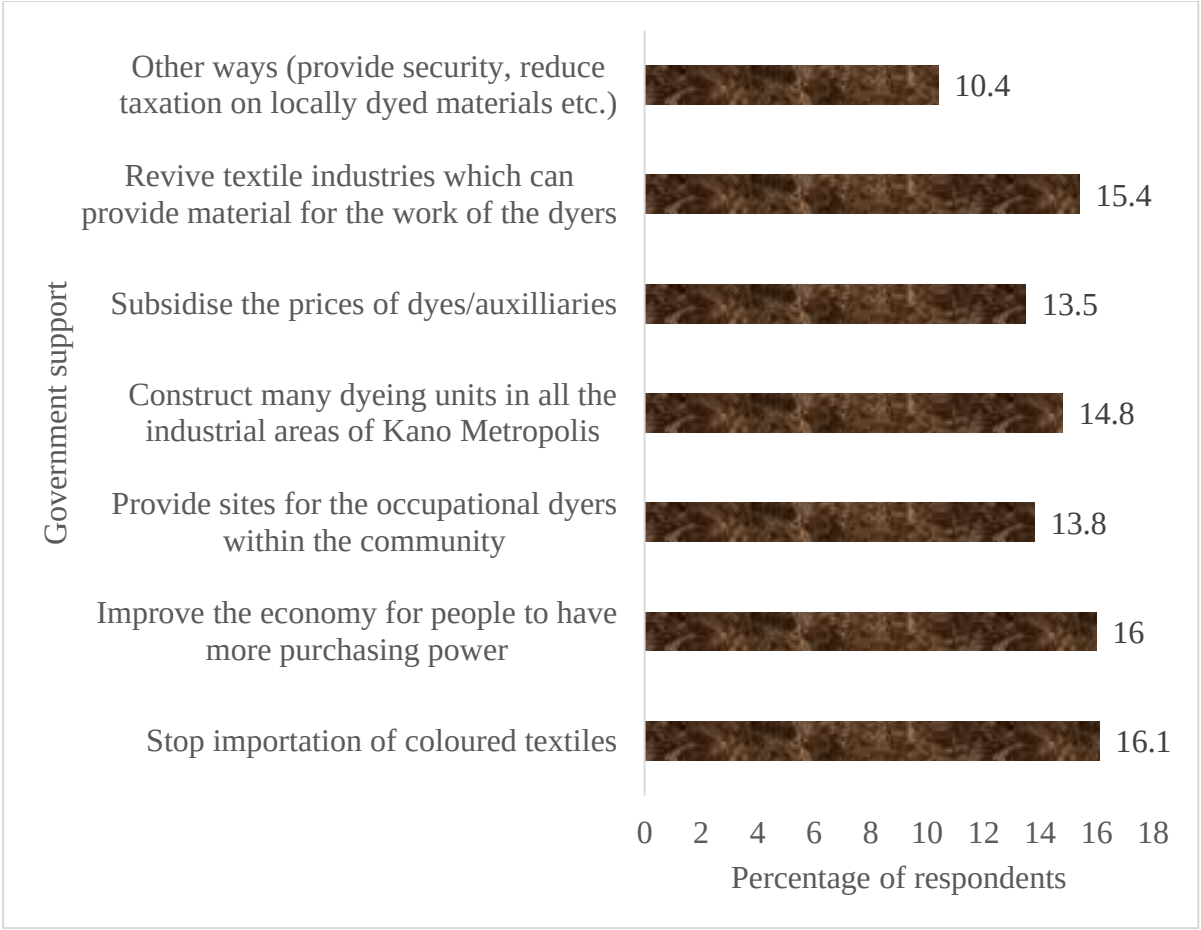


Figure 4.22: Support needed from government to revive the dyeing occupation

Occupational vat dyeing in years to come*:* To speculate the future prospect of the dyeing occupation, there is need to know the reasons for the decline of traditional indigo dyeing. Vuorema (2008) has attributed the disruption of traditional indigo dyeing globally to the

production of synthetic indigo and development of hydros as reducing agent enabling the dyeing process to be relatively short unlike the traditional processes. Additionally, indigo dyeing in West Africa was affected by economic penetration of local market by China (Ringuede, 2016). In the case of Nigeria, insecurity is also a very important factor that affected traditional indigo dyeing. Based on the challenges identified in this study, the modern vat dyers may have the same fate as the traditional indigo dyers especially the decline in local fabric production, importation of coloured textiles, insecurity, and economic realities. When the venture declines, thousands of youths will be out business resulting in high incidence of drug abuse. Dyed materials may not be easily affordable due to high cost as they may likely be only imported in the future (Figure 4.23).

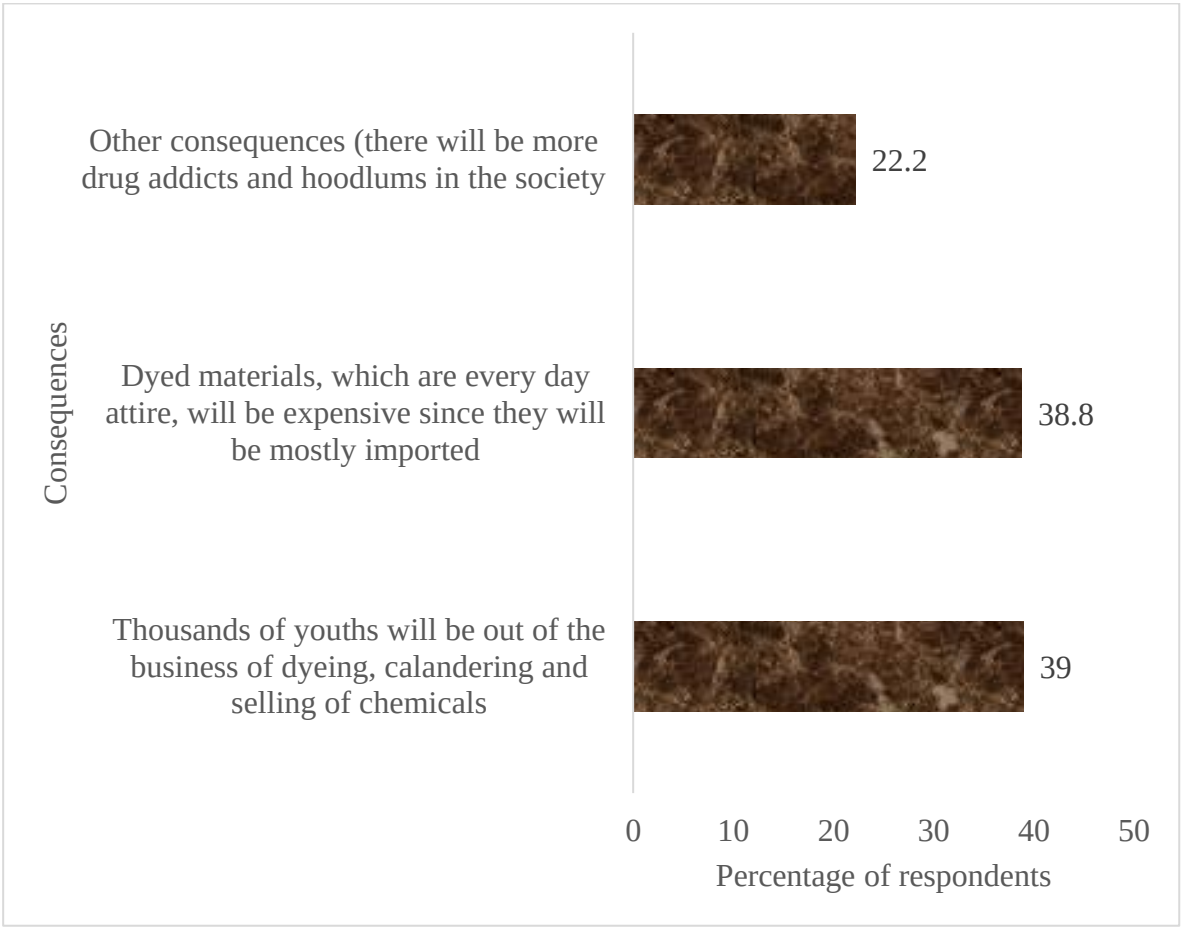


Figure 4.23: Consequences due to decline of the dyeing occupation

4.1.6 Waste management and potential environmental impacts

4.1.6.1 Waste management

As shown in Figure 4.24, most of the dyers work in a dyehouse where the liquid waste (dye effluent/mercerizing wastewater) is discharged into open drain. Effluent from tannery and dyeing industries in Kano Metropolis are similarly discharged into open drains affecting the natural waters in the vicinity (Nabegu, 2016). It has been observed that the open drains (gutters) are shallow (Plate XIX) and stagnate wastewater (Plate XX). The stagnation of wastewater could be due to the fact that littering of refuse in drainages is common along the streets of Kano Metropolis (Balogun *et al.*, 2021).

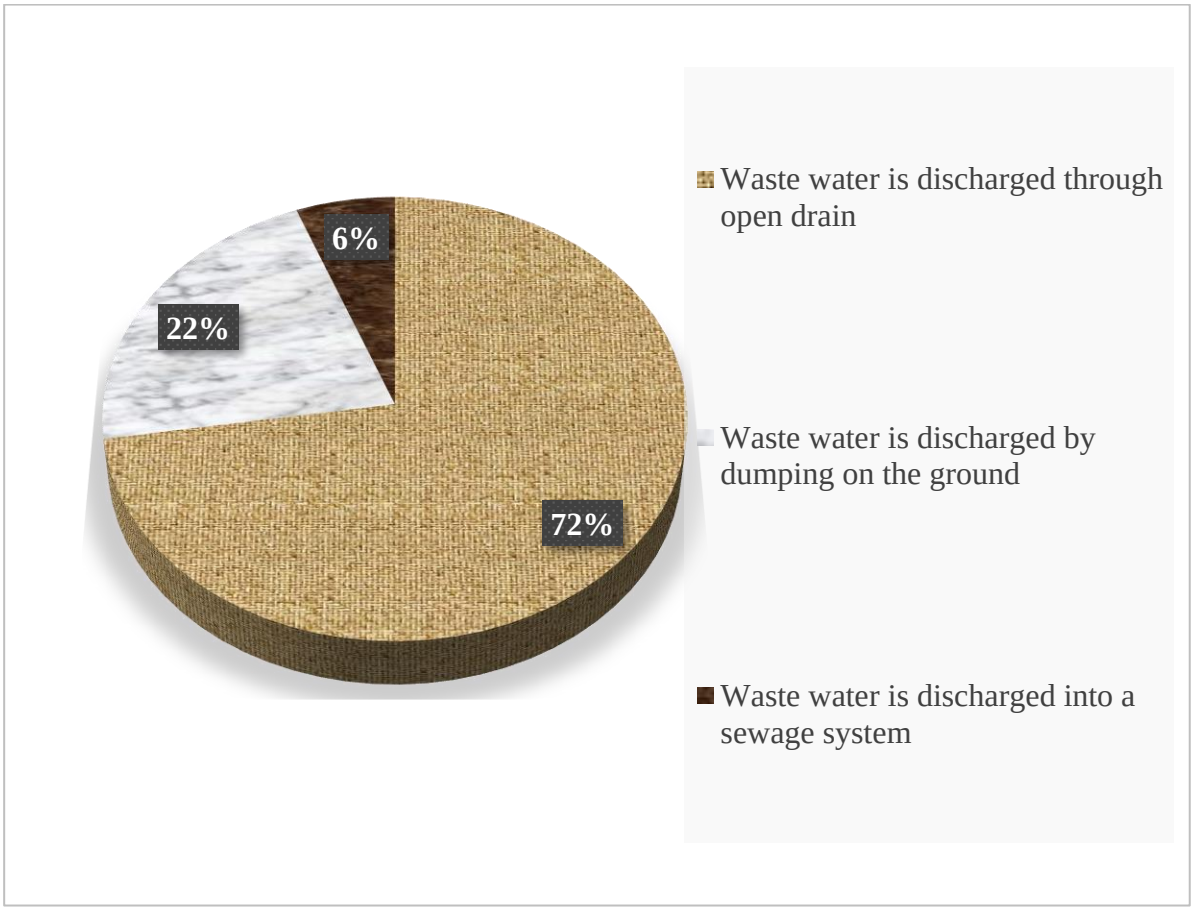


Figure 4.24: Ways of discharging dye/mercerization wastewaters



Plate XIX: Shallow drainage (Field work, 2018)



Plate XX: Stagnant effluent in a drainage (Field work, 2018)

Some of the dyehouses work far away from drainage system which was why certain proportions of the dyers either dump the effluent on the ground or into a sewage system. Recently, residents of Kano Metropolis lamented the lack of drainage on the streets of the city (Murtala, 2018). Discharge of dye wastewater into poor drainage system by small scale dyeing

industries has been reported previously (Selase *et al.,* 2021; Makinde *et al.,* 2010; Upadhyay and Panday, 2015; Howard *et al.,* 2019). Local batik/tie-dye workers in Ghana dispose of their wastewater into sewage system, onto the ground, into septic tank which is emptied from time to time, and by recycling (Selase *et al.* 2021).

The effluent discharged by the occupational dyers is not recycled or treated to remove toxic substances. Similarly, companies producing readymade clothing in Bangladesh (Islam and Islam, 2021) and small-scale batik industries in Indonesia (Sulthonuddin and Herdiansyah, 2021) do not have wastewater treatment plants. Even in textile industries, it is difficult to properly dispose of wastewater which is one of the major challenges that affects the global world (Al-Tohamy, 2022) where this problem is more serious in developing countries (Rosa *et al.,* 2017) like Nigeria.

Generally, poor working conditions and low economic status associated with small scale industries do not allow an efficient wastewater treatment before disposal (Bazin *et al.,* 2012) and as such local dyeing industries in Nigeria do not operate any treatment process for their wastewater (Okareh *et al.,*2017; Adedeji and Ako, 2009). Adopting conventional treatment methods to treat huge volumes of wastewater being generated would be expensive in terms of initial installation cost and subsequent operational and maintenance costs (Manu, 2007).

The recent treatment approaches for dye wastewater include membrane separation, adsorption, advanced oxidation processes, bio-electrochemical treatment, photocatalytic degradation etc. (Shindhal *et al.,* 2020) where adsorption was found to be more suitable due to its ease of use, cost effectiveness, and high efficiency (Rapo and Tonk, 2021). Vat dye effluent has been

treated using bioremediation (Gurav *et al.,* 2011; Olaganathan and Patterson, 2009; Sirianuntapiboon *et al.,* 2006), adsorption (Golob and Ojstrsek, 2005), coagulation/flocculation (Manu, 2007), ultrafiltration (Golob and Ojstrsek, 2005), and electrochemical methods (Kariyajjanavar *et al.,* 2013).

Membrane filtration preceded by physico-chemical treatment was proposed for the reclamation of dye wastewater from a denim manufacturing textile mill in Turkey (Yukseler *et al.,* 2017). Mercerization wastewater can be reused as high amount of caustic soda may be recovered and reused (Yukseler *et al.,* 2017). Merkel *et al.* (2017) has recovered significant amount of caustic soda using electrodialysis. Dyers in Kano Metropolis mostly mercerize the fabric before dyeing which constitutes a lot of liquid waste where caustic soda can be reclaimed with appropriate technology.

Discussion with the dyers revealed that some of them have tried the use of septic tanks for wastewater disposal but that did not work because the tank could not be emptied after accumulation. According to them, there was little or no disposal problem when they were using natural indigo dye. Some of the dyers suggested that provision of adequate and appropriate drainage will solve the effluent problem while others opined that wastewater treatment plant will suffice. It was observed that the best option is to relocate the dyehouses to any of the four industrial estates in the Metropolitan Area.

Tie-dye workers in Ghana suggested the use of incinerator, sewer system, and wastewater treatment plant as waste management strategies (Selase *et al.,* 2021). Sulthonuddin and

Herdiansyah (2021) have suggested preventive measures for small scale batik industry in Indonesia which include educating communities on industrial waste management, provision of waste management facilities, monitoring activities for environmental quality, and educating the dyers on eco-friendly processes such as use of natural dyes.

It has been observed that the solid waste generated range from polyethene bags used as packages for caustic soda, hydros, and dyes, candle wax used for batik work, and polyester yarn used for creating patters during tie-dye, as well as sludge accumulated where liquid waste is continuously dumped on the ground. The dyers usually burn solid waste or allow it to litter in the environment. Similarly, a large proportion of tie-dye workers in Ghana dispose of their solid waste by burning (Selase *et al.,* 2021).

Conventionally, landfill and incineration are the two main strategies that are used for solid waste management where the former produces leachate which may result in soil and groundwater contamination while the latter produces hazardous gases such as dioxin and nitrogen oxides which are discharged into the atmosphere (Islam and Islam, 2021). Industries within residential areas in Kano Metropolis generate only 2.9 % of municipal solid waste (MSW) but those wastes are left on the street and clogs drainages (Nabegu, 2016) where it is very common to find the drainage lines being filled up with refuse after rainfall (Butu and Mshelia, 2014).

As shown in Table 4.6, some of the dyers have been visited/monitored by an environmental officer either to enlighten the dyers on waste management or educate them on the environmental impacts of dye effluent. The dyers revealed that some of them have been

penalized previously due to improper discharge of effluent. The dyers also disclosed that representatives of Kano State Ministry of Environment (KSMEN) occasionally pay them a visit to inspect their activities particularly the manner in which wastewater is discharged. The areas not visited by those officials are mostly in Gwale and Fagge Local Government Areas where the dyehouses are difficult to locate with most of them working in the house of owner.

Table 4.6: Visit by an environmental officer

Reasons for visit	Yes N=226 (%)	No N=226 (%)	Missing N=226 (%)	Total N=226 (%)
Ensure dye effluent is properly discharged	119 (52.7)	1 (0.4)	106 (46.9)	226 (100)
Advice on how to keep the environment clean	120 (53.1)	0 (0)	106 (46.9)	226 (100)

Many guidelines, recommendations, and propositions have been developed to ensure the protection of water which may soon become a scarce commodity. Countries such as the United States, Canada, Australia, France etc. have national environmental legislation which establishes dyehouse effluent limit values to comply while in some countries the emission limits are mainly recommended but not mandatory (Hessel *et al.*, 2007). In Nigeria, the Federal Ministry of Environment through the National Environmental Standards and Regulations Enforcement Agency (NESREA), KSMEN as well as local governments in the affected areas are responsible for ensuring the safe use and disposal of toxic chemicals (Nabegu, 2016).

Regulations and guidelines are set by NESREA even though the legislation of the agency is limited due to proof of causation which is often difficult to establish especially with regards

to water pollution originating from industrial operations (Adedeji and Ako, 2009). Recently, the agency warned manufacturers in Kano to desist from degrading the environment and also urged them to treat effluent at least to primary levels before discharge into the public drain (Essen, 2017). The dyehouses investigated are not registered nor recognised by the government hence may be difficult to regulate.

4.1.6.2 Potential environmental impacts

The World's annual waste generation amounts to 7-10 billion tonnes out of which approximately 2 billion tonnes is MSW (Yalcin-Enis *et al.*, 2019). In developing countries such as Nigeria, the sitting of industries is determined by various criteria some of which are environmentally unacceptable like the establishment of industrial estates in most state capitals and large urban centres in the country (UNEP/WSSCC/WHO, 1997). Toxicity of chemicals used by industries in Kano Metropolis are not generally tested where most of those chemicals can be harmful to the environment. Tannery and dye effluent from factories (Nabegu, 2016) as well as high rate of MSW in Kano (Butu and Mshelia, 2014) largely contribute to environmental pollution. Wastewaters from the dyehouses visited may have serious effect on groundwater sources since 65 % of them are not more than 91 m away from residential buildings as shown in Figure 4.25.

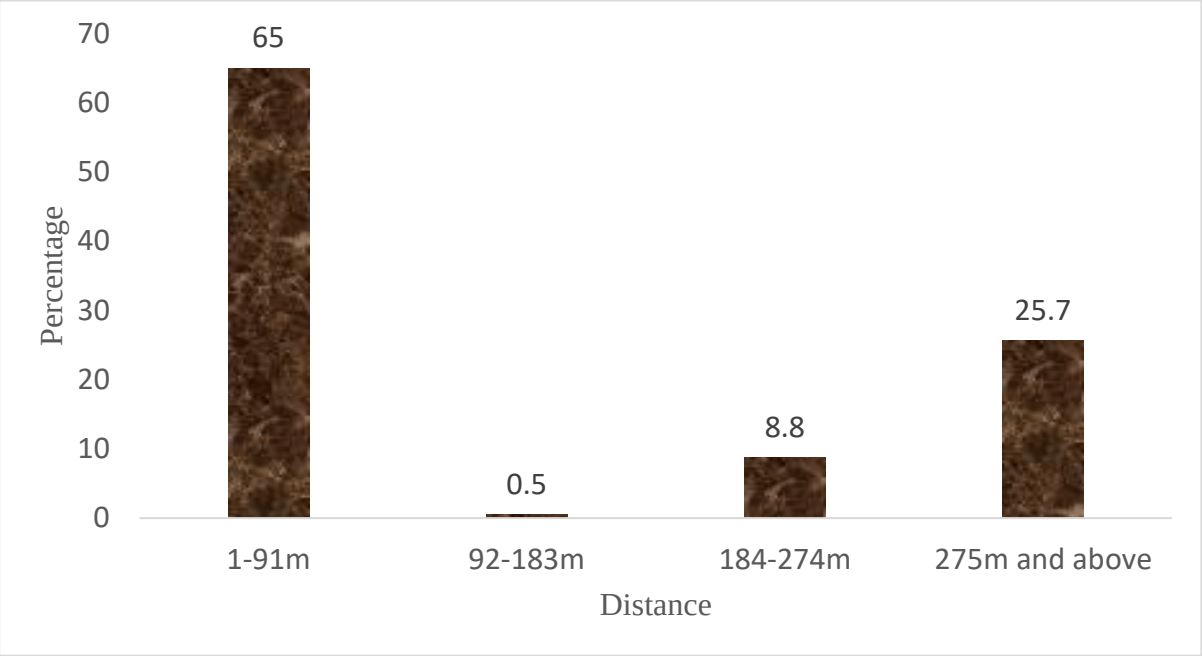


Figure 4.25: Distance from dyehouses to residential buildings

During the dyeing process, 100-200 l of water/kg of fabric is used and 85-95 % of that water is discharged as waste (Olaganathan and Patterson, 2009). Additionally, in batch dyeing, as carried out by the dyers investigated, the fabric remains in a single piece of equipment which is filled with water and then drained after both the actual dyeing and rinsing. Each time the fabric is exposed to a separate bath, it uses water about 5-10 times its weight (Chequer *et al.*, 2013). Dumping of such huge wastewater into the poor drainages or on the ground means that, ultimately, the effluent will penetrate the surrounding soil and seep into the ground.

Similarly, Oloyede *et al.* (2014) suggested that dye effluent from "Adire" dye workers in Abeokuta seep into the wells of residents in the production area. Wastewaters that flow in drainages corrodes the sewage pipes, affects drinking water quality and can be a breeding ground for bacteria and viruses. When effluent is allowed to flow in the fields it clogs the

pores of the soil resulting in loss of soil productivity, hardening of soil texture, and impedes penetration of roots (Kant, 2012).

Table 4.7 shows the perception of the dyers on the environmental impacts of dyeing/mercerizing wastewater. Most of them (68.2 %) strongly agreed with the perception that the wastewater seep into the ground. More than one half disagreed with the possibility of the wastewater going to treatment plant. A little above one half (53.3 %) are in agreement that the wastewater is highly coloured. Almost one half (49.6 %) strongly agreed that the wastewater can kill plants and aquatic organisms. About two third of the dyers are strongly in disagreement with the assertion that the wastewater does not smell.

Table 4.7: Perception of dyers on wastewater discharge

Perception	Strongly disagree N=226 (%)	Disagree N=226 (%)	Agree N=226 (%)	Strongly agree N=226 (%)	Total N=226 (%)
Wastewater discharged seep into the ground	1 (0.4)	1 (0.4)	70 (31)	154 (68.2)	226 (100)
Wastewater discharged goes straight to a treatment plant	69 (30.5)	137 (60.6)	13 (5.8)	7 (3.1)	226 (100)
Wastewater disposal unit is highly coloured	2 (0.9)	0 (0)	125 (55.3)	99 (43.8)	226 (100)
Vat dye effluent can kill plants and aquatic animals	4 (1.8)	1 (0.4)	109 (48.2)	112 (49.6)	226 (100)
Waste water discharged does not smell	144 (63.7)	73 (32.3)	3 (1.3)	6 (2.7)	226 (100)

Discussion revealed that most of the dyers are aware that wastewaters should not be disposed of directly onto soil surfaces or into water bodies. Similarly, dye workers in Bangladesh (48.3 %) agreed with the perception that fish culture and cattle rearing is hampered due to pollution caused by loom-dye effluent, agreed (48.33 %) that loom-dye effluent should not be disposed directly in cropland, and also agreed (66.67 %) that the loom—dye effluent should not be disposed directly in water bodies (Rahman *et al.,* 2020).

Typically, released vat dyebath contains spent caustic soda, reducing agent, dispersing agents, auxiliaries such as levelling and sequestering agents (Bechtold and Turcanu, 2009), and heavy metal impurities due to their production processes (Baptista, 2009; Rapo and Tonk, 2021). Vat dyes are highly eliminable due to their high degree of fixation and for the fact that they are water insoluble. They are not bioavailable due to their insolubility and the amount of unfixed dye is small because of their high exhaustion levels (Lacasse and Baumann, 2004). As most vat dyes are exhausted up to 95 %, a little of the dye is left in the bath and consequently the effluent load resulting from this unused dye is minimal (Chakraborty, 1992). Vat dye effluent is considered as a highly polluting wastewater (Bozic and Kokol, 2008; Rapo and Tonk, 2021).

The amounts of auxiliaries consumed in wet dyeing processes is much higher than dyes and those chemicals are generally non-reactive and are not absorbed by the substrate being dyed ending up in wastewater which may cause problems in the aquatic environment (Wang *et al.,* 2002). Dyers in Kano Metropolis use large amounts of caustic soda and hydros for dyeing and huge quantity of caustic soda for mercerization. It has been reported that stream containing 25 mg/l caustic soda caused the death of fish and highly concentrated solution kills crops and destroys vegetation (Bhupinder Kaur and Chanchal, 2016).

Caustic soda spills on soil causes groundwater pollution if precipitation occurs before clean-up and the greatest negative impact from the release of caustic soda solution into the environment is the resulting pH change (Gad, 2014). Presence of excess concentration of soluble salts such as caustic soda, sodium sulphate, sodium chloride etc. even in small quantities are found to be toxic to aquatic life (Ghaly *et al.,* 2014) and in arid and semi-arid regions increase in salinity of water increases the osmotic pressure of mammalian and aquatic species (Hessel *et al.,* 2007).

Salts of sulphur in the form of sulphates and sulphites contaminate sewage, lower its pH and show corrosive action where sewage comes in contact with concrete works, iron structures etc. (Kulandainathan *et al.,* 2007). They also affect the environment detrimentally by noxious odours, toxicity, and high COD of the wastewater (Bozic and Kokol, 2008). When hydros is exposed to water, its solid form liberates sulphur dioxide gas which is corrosive to equipment and buildings (Bajpai, 2018).

Dispersing agents in vat dye formulations (mostly formaldehyde condensation products) are water insoluble and poorly degradable and therefore remain in the wastewater (Lacasse and Baumann, 2004). Heavy metal and dyes remain in water and soil for long periods reducing soil fertility as well as the photosynthetic activity of aquatic plants resulting in the development of anoxic conditions for aquatic fauna and flora (Al-Tohamy, 2022). Fossil fuel used by the dyers as a source of power can pollute the environment as its use causes climate change (Yalsin-Enis *et al.,* 2019).

4.2 Geographical Locations of the Dyehouses

The coordinates of the dyehouses obtained by GIS (see Appendix C) were imported into goggle earth to obtain the location of the dyehouses on a map as shown in Figure 4.26. The dominance of dyehouses in Gwale corroborates well with the high percentage of dyers found in the area from questionnaire survey. The reason for this was discussed under demographic/socioeconomic characteristics of the dyers (Section 4.1.1).

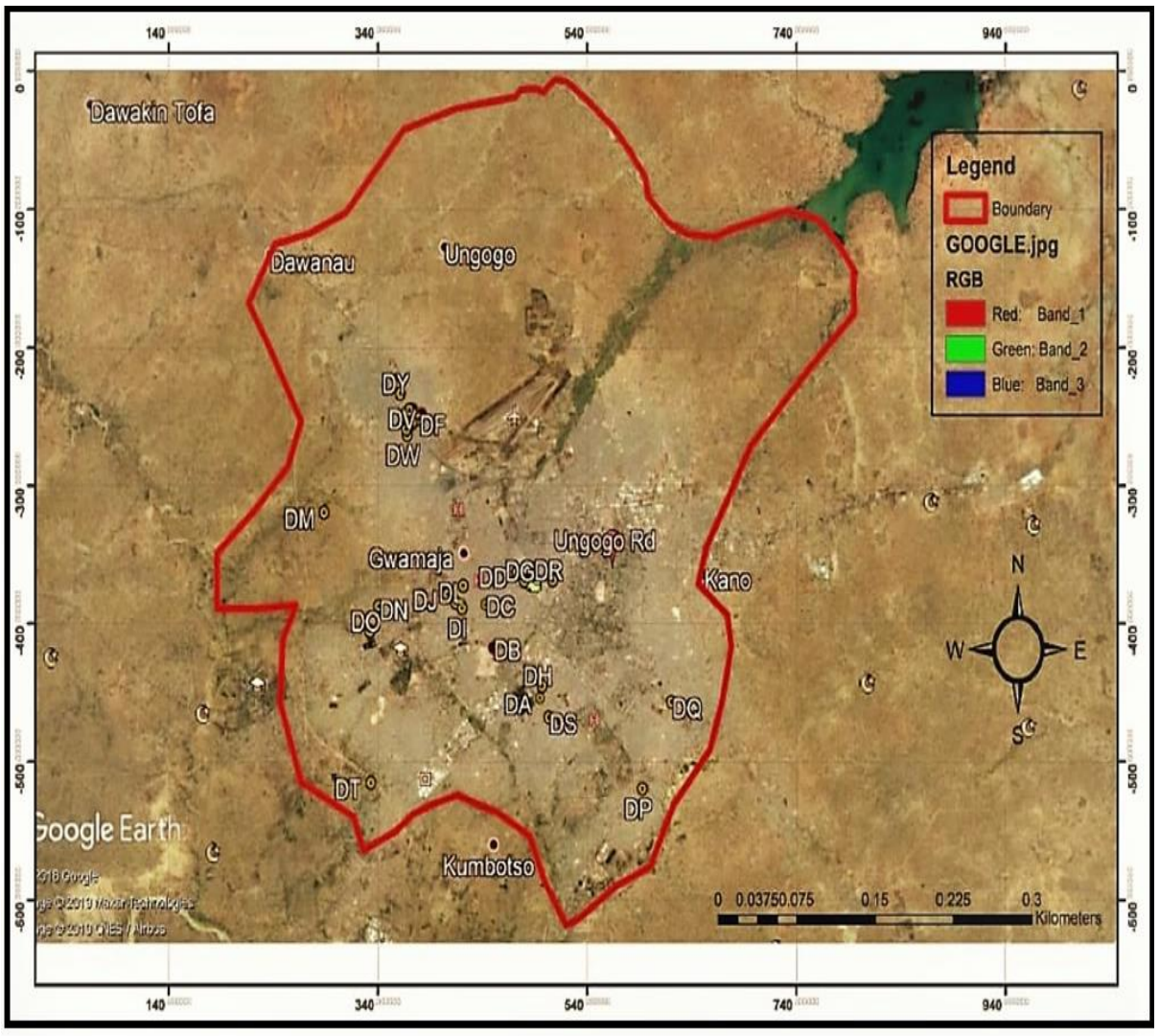


Figure 4.26: GeograpHical locations of the dyehouses visited (GIS laboratory, Ahmadu Bello University, Zaria)

4.3 Heavy Metal Content in Caustic Soda, Hydros, and Dye Powders

4.3.1 Heavy metal content in caustic soda and hydros

Calibration curves generated by MP-AES software for the determination of sodium (Na), cadmium (Cd), chromium (Cr), iron (Fe), lead (Pb), manganese (Mn), zinc (Zn), copper (Cu), and nickel (Ni) in caustic soda and hydros are shown in Figures D1 to D9, respectively (see Appendix D). Figure 4.27 shows that there is high conc. of Na in caustic soda. This may be due to the presence of impurities namely sodium chloride and sodium carbonate (Zahid *et al.*, 2017) which are Na sources. Hydros, however, is commonly used as Na source (Reza *et al.*, 2014) which may be a good reason for the higher conc. of Na in hydros than in caustic soda. No Pb is found in both samples and the conc. of Cr, Cu, and Mn are the same in caustic soda and hydros samples (Figure 4.28). The conc. of Fe and Ni are higher in hydros while conc. of Cd and Zn are higher in caustic soda.

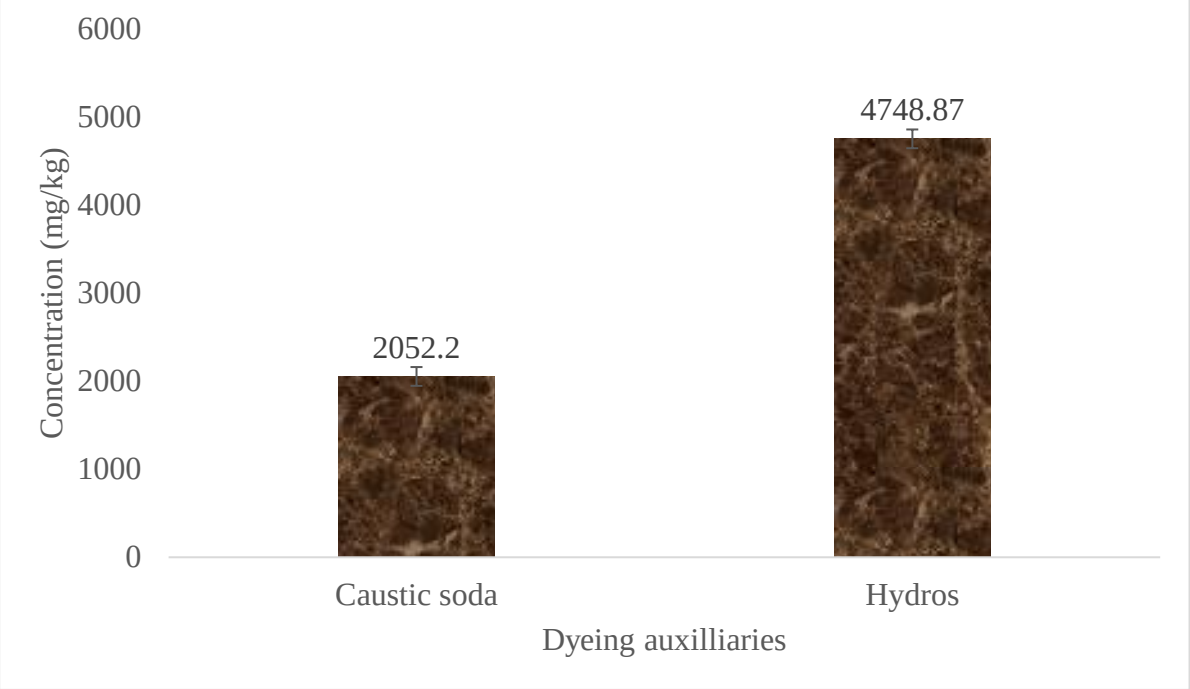
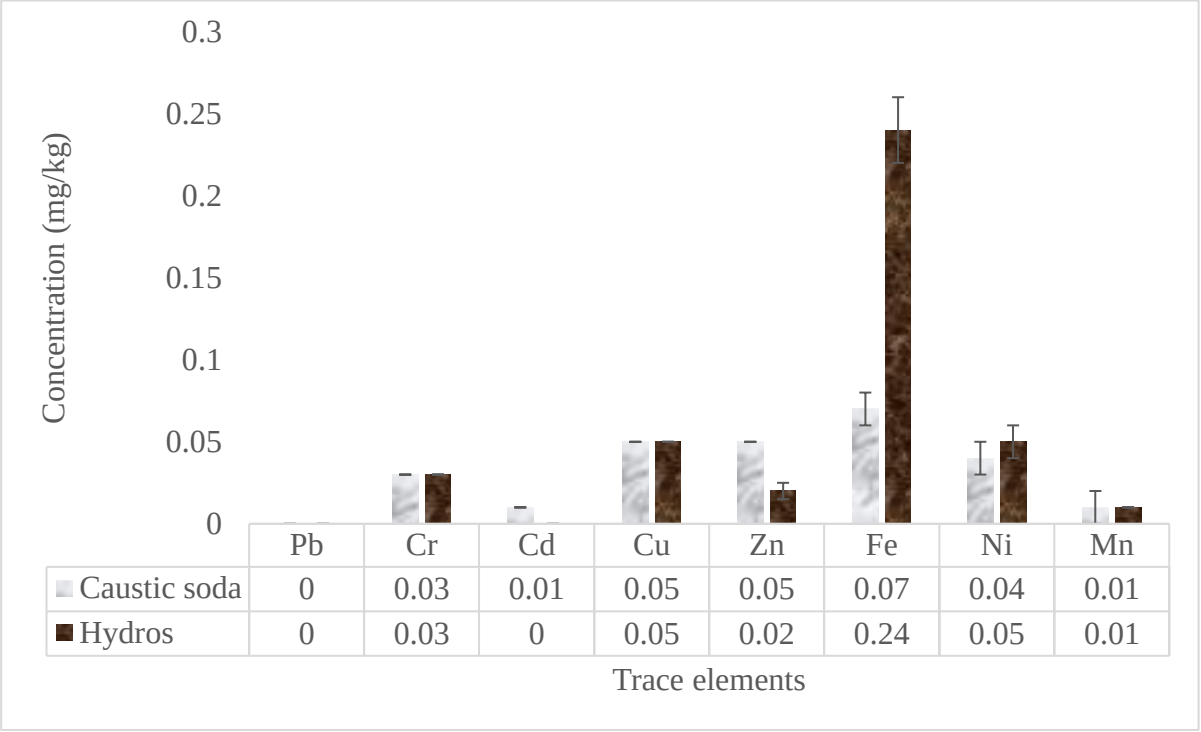


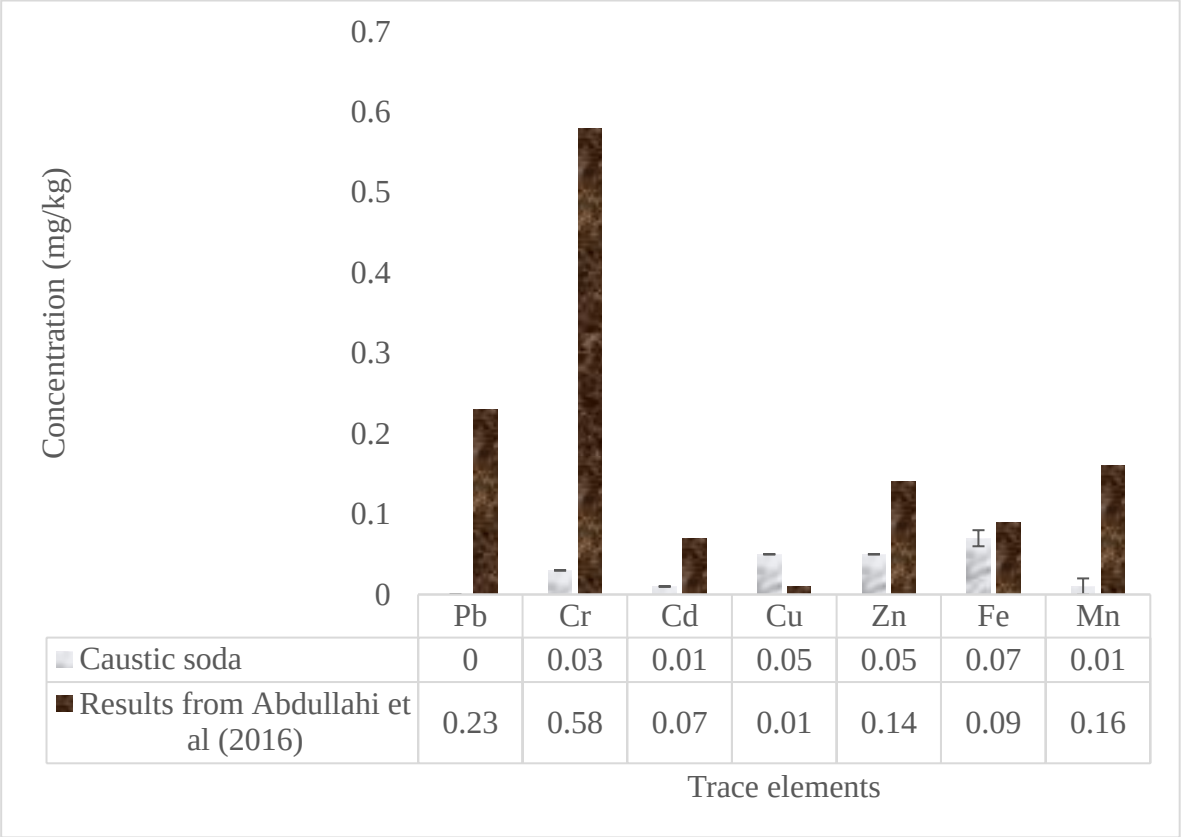
Figure 4.27: Sodium in main dyeing auxiliaries



	Pb	Cr	Cd	Cu	Zn	Fe	Ni	Mn
Caustic soda	0	0.03	0.01	0.05	0.05	0.07	0.04	0.01
Hydros	0	0.03	0	0.05	0.02	0.24	0.05	0.01

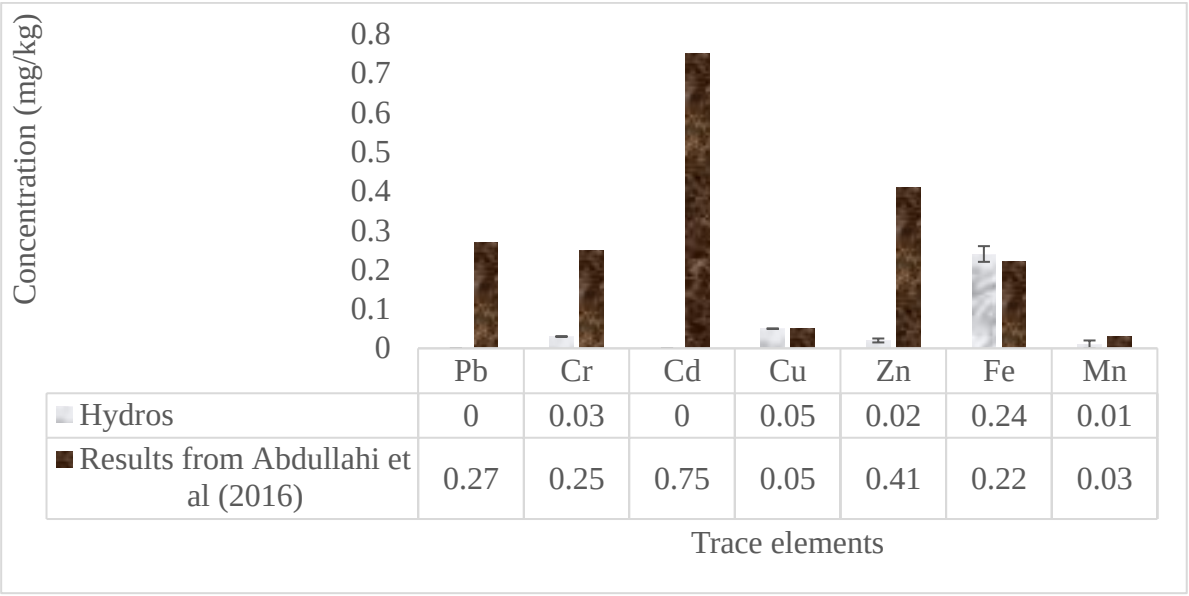
Figure 4.28: Contents of some heavy metals in main dyeing auxiliaries

Figure 4.29 shows that except for Cu, all the heavy metals investigated in caustic soda are lower than that found by Abdullahi *et al.* (2016) who used AAS for the determinations using similar samples purchased from local markets in Kano Metropolis. The conc. of Mn, Zn, and Cr in caustic soda reported by the authors are about 16, 3, and 19 times higher than that obtained in this study, respectively. As shown in Figure 4.30, the conc. of Cu, Mn, and Fe in hydros reported by Abdullahi *et al.* (2016) are close to the values obtained in this study while the conc. of Zn and Cr were about 21 and 8 times higher, respectively. These differences can be attributable to the difference in the precision of analytical method used and also differences in the production processes by different companies and also different batches of samples from the same manufacturer. The amalgam process, for example, produces hydros which is free from heavy metals (Bajpai, 2018).



	Pb	Cr	Cd	Cu	Zn	Fe	Mn
Caustic soda	0	0.03	0.01	0.05	0.05	0.07	0.01
Results from Abdullahi et al (2016)	0.23	0.58	0.07	0.01	0.14	0.09	0.16

Figure 4.29: Mean heavy metals concentrations in caustic soda compared to values obtained in a previous study



	Pb	Cr	Cd	Cu	Zn	Fe	Mn
Hydros	0	0.03	0	0.05	0.02	0.24	0.01
Results from Abdullahi et al (2016)	0.27	0.25	0.75	0.05	0.41	0.22	0.03

Figure 4.30: Mean heavy metals concentrations in hydros compared to previous study

4.3.2 Heavy metal content in dye powders

Calibration curves generated by MP-AES software for the determination of Na, Cd, Cr, Fe, Pb, Mn, Zn, Cu, and Ni in dye powders are shown in Figures D10 to D18 respectively (see Appendix D). Elemental analysis of textile dyes may provide valuable information with regards to conc. of elements which could help monitor the safety of handling and use of these dyes (Abel-Ghany, 2013). Figure 4.31 shows Na content in RSN, VR1, and VRR samples and the respective mean conc. are 92.9, 105.98, and 113.75 mg/kg. As shown in Figure 4.32, the mean Fe levels found in RSN, VR1, and VRR are 1.85, 1.99, and 6.26 respectively. Figure 4.33 shows that except for Pb, the highest mean heavy metal contents were found in VRR. The conc. of Pb is similar in the three dyes investigated. Cr and Cu are equally abundant in RSN and VR1. Mean conc. of Na, Fe, Cd, Ni, and Mn in samples analyzed are in the order VRR>RSN>VR1.

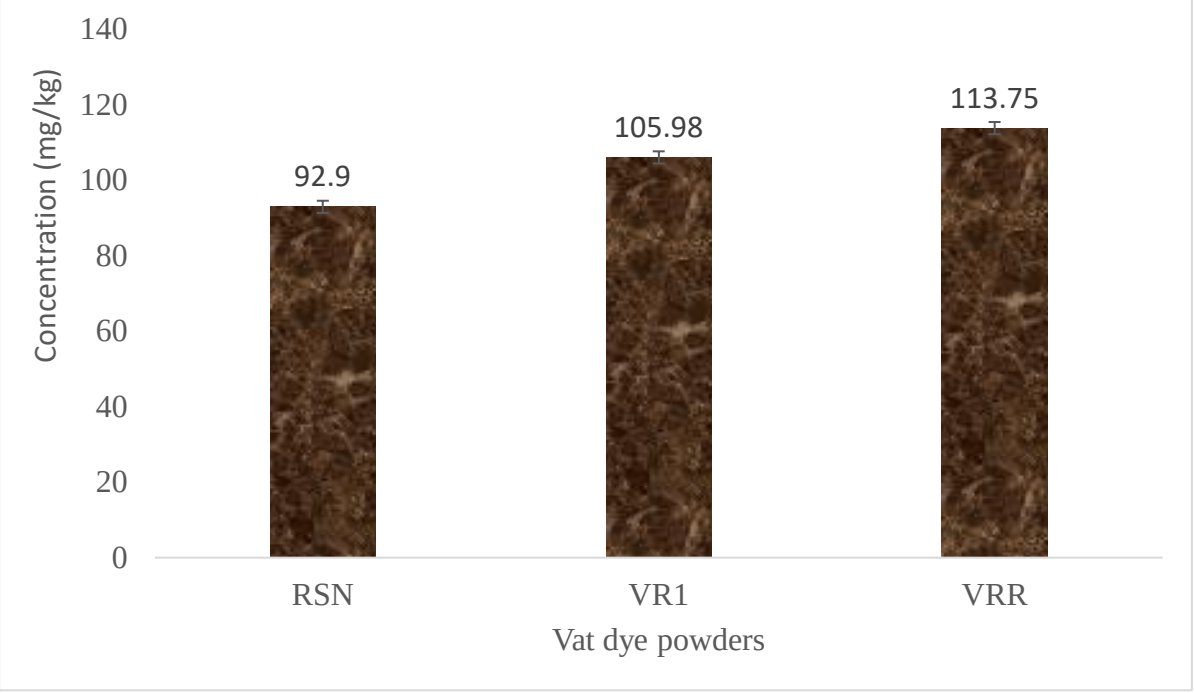


Table 4.31: Sodium in dye powders

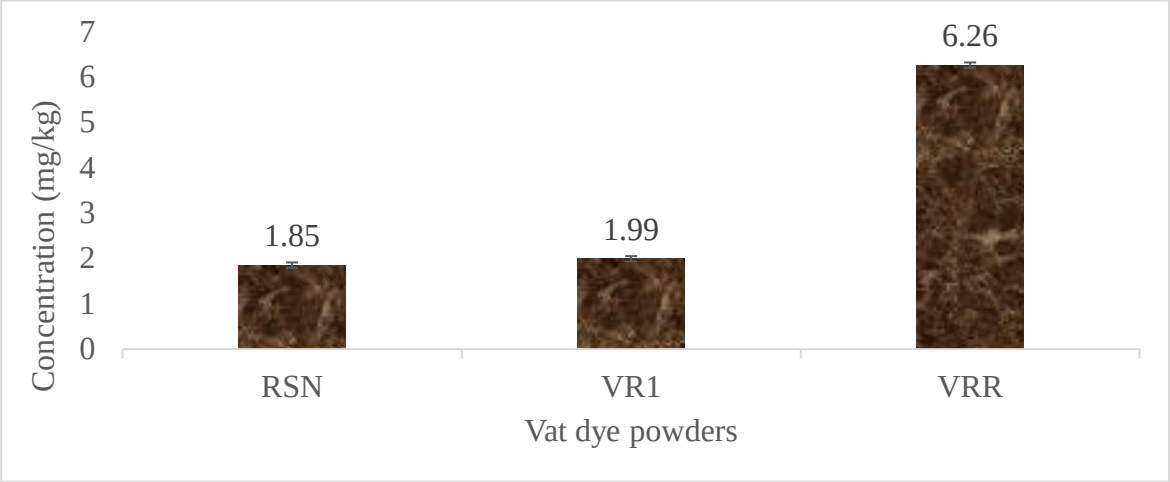
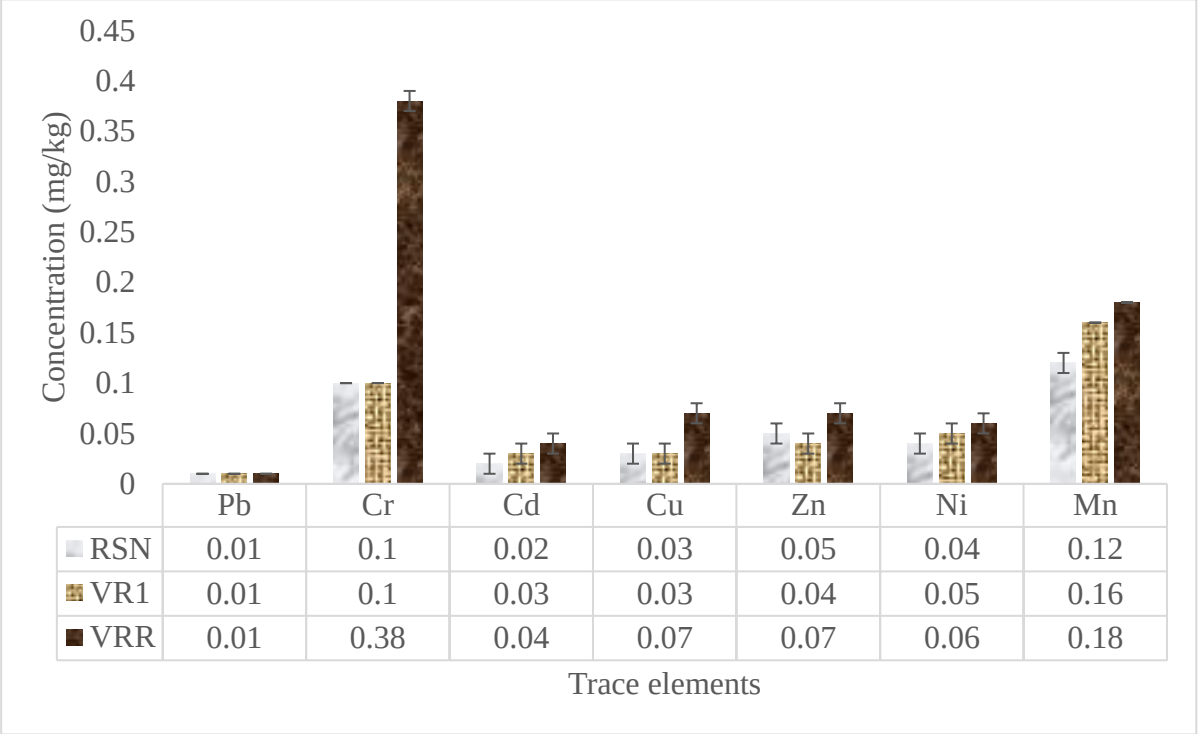


Figure 4.32: Iron in dye powders



	Pb	Cr	Cd	Cu	Zn	Ni	Mn
RSN	0.01	0.1	0.02	0.03	0.05	0.04	0.12
VR1	0.01	0.1	0.03	0.03	0.04	0.05	0.16
VRR	0.01	0.38	0.04	0.07	0.07	0.06	0.18

Figure 4.33: Selected heavy metals in dye powders

The conc. of Na ranged from 91.17 to 114.79 mg/kg. The lowest value was found in RSN whereas the highest value was in VRR. Fe conc. ranged from 1.84 to 6.33 mg/kg. The highest level was detected in VRR while the lowest level was found in RSN. Cr conc. ranged from

0.01 to 0.39 mg/kg and the lowest was detected in RSN and VR1. Conc. of Cd ranged from 0.02 to 0.04 mg/kg where lowest level was found in RSN. The conc. of Cu ranged from 0.03 to 0.07 mg/kg and the lowest was found in VR1 and RSN. Zn conc. ranged from 0.04 to 0.07 mg/kg where the lowest level was measured in VR1. The conc. of Ni ranged from 0.03 to 0.07 mg/kg with the lowest found in VR1. Conc. of Mn ranged from 0.12 to 0.18 mg/kg with the lowest value found in RSN. In all the metals investigated, the highest levels were found in sample VRR.

As shown in Table 4.8, among the metals investigated, Na is the most abundant. The mean heavy metal content (mg/kg) in the three samples investigated is in the following order: **Na** (104.21±10.5)>**Fe** (3.37±2.51)>**Cr** (0.19±0.16)>**Mn** (0.15±0.03)>**Ni** (0.05±0.01)>**Zn** (0.05±0.02)>**Cu** (0.04±0.02)>**Cd** (0.03±0.01)>**Pb** ($0.01\pm1.7\times10^{-2}$). The results obtained in this study may be related to the fact that the synthetic steps in the production of vat dyes requires the use of catalysts e.g., mercury (Hg), arsenic (As), Cr, Fe, etc., oxidizing agents e.g., manganese dioxide, and alkaline fusion using caustic soda (Baptista, 2009). Cobalt (Co), Cr, Cu, Ni, etc. form part of the most commonly used dyes especially dyes for leather materials, nylon, and wool (Zeiner *et al.*, 2007). Dyestuffs with metal free chromophores also contain metallic impurities originating from the rawmaterials used in their manufacture (Sungur and Gülmez, 2015). Heavy metals such as Hg, Cr, Cd, Pb, As, etc. are normally used in the production of textile dyes and pigments (Al-Tohamy, 2022).

Table 4.8: Mean heavy metals concentrations in dyes from current study compared to values obtained in previous studies and international standard

Metals (mg/kg)	Concentration in RSN (mg/kg)	Concentration in VR1 (mg/kg)	Concentration in VRR (mg/kg)	Mean± SD	Abdullahi *et al* (2016)	Abel-Ghany (2013)	Anliker (1979)
Na	92.9±1.62	105.98±0.33	113.75±1.52	104.21±10.5	-	-	-
Pb	0.01±1.7E-17	0.01±1.7E-17	0.01±1.7E-17	0.01±1.7E-2	0.55	14.86	100
Cr	0.1±1.7E-17	0.1±1.7E-17	0.38±0.01	0.19±0.16	0.36	21.28	100
Cd	0.02±0.00	0.03±0.00	0.04±0.01	0.03±0.01	0.14	1.01	20
Cu	0.03±0.00	0.03±0.00	0.07±0.00	0.04±0.02	0.14	4.958	250
Zn	0.05±0.01	0.04±0.01	0.07±0.01	0.05±0.02	0.64	21.35	1500
Fe	1.85±0.01	1.99±0.01	6.26±0.06	3.37±2.51	0.25	-	2500
Ni	0.04±0.01	0.05±0.01	0.06±0.01	0.05±0.01	-	-	200
Mn	0.12±0.01	0.16±2.3E-17	0.18±3.4E-17	0.15±0.03	0.23	5.07	1000

Mass fractions of heavy metals in dyes (in mg/kg) are 1 to 1.4 (As), up to 1.0 (Cd), 3 to 8.3 (Cr), 1 to 3.2 (Co), 33 to 110 (Cu), 6 to 52 (Pb), 0.5 to 1.0 (Hg), and (Zn) 3 to 32 with vat dyes having the highest chromium, cupper, and mercury levels (Barclay and Buckley, 2000). Abdullahi *et al.* (2016) used AAS to determine heavy metal content in red, blue and green vat dyes purchased from local market in Kano Metropolis (similar dyes used in this study). The authors reported higher metal content, except for iron, where they detected mean metal levels in lead, chromium, cadmium, copper, zinc, and manganese that are about 55, 2, 5, 4, 13, and 2 times higher than values obtained in this study respectively (Table 4.8).

Abel-Ghany (2013) assessed metal levels in 9 dyes purchased from local market in Cairo using ICP-AES and reported higher levels of heavy metal concentrations compared to values obtained in this study. Anliker (1979) reported heavy metal levels recommended by the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) which was introduced in 1978 and still valid. This large variation in metal content among the current results and those reported previously may be because different dye classes will have different levels of metals due to differences in synthetic methods. All the metal content measured in this study are within ETAD limits (Table 4.8).

4.4 Physico-chemical Parameters and Some Heavy Metals in Vat Dye Effluent and Groundwater Samples

4.4.1 Physico-chemical parameters in vat dye effluent and groundwater samples

Table 4.9 shows mean effluent pollutants conc. from current study compared to values reported previously and national standard. Tables E1 to E3 (see Appendix E) show physico-

chemical parameters and heavy metals in effluent from VR1, RSN, and VRR, respectively. Table 4.10 shows mean water pollutants compared to values obtained in previous studies, national and international standards. Appendix F shows individual physico-chemical parameters and heavy metal content in the twelve water samples investigated. The physico-chemical parameters assessed in dye effluent and groundwater samples include pH, DO, BOD, conductivity (Cd), TDS, and sulphate. Additionally, colour and COD are also determined in effluent samples while temp. was assessed in groundwater samples.

Table 4.9: Mean effluent pollutants conc.

Parameters	Mean± SD (DA-DR)	Mounteer *et al.* (2018)	Santhi and Moses (2008)	Abebe and Galebo (2019)	Yusuff and Sonibare (2004)	FEPA standard
pH	11.50±0.15	11	11.87	11.89	10.11.5	6-9
Colour	616.71±131.58	1230	-	-	612-4637	5
DO	1.49±0.10	-	-	-	1.2-7.0	NS
BOD	405.81±59.33	-	462	480	163-645	50
COD	1550.32±344.72	2412	1560	1590	-	80
Conductivity	2147.76±159.30	1656	-	-	-	NS
TDS	4401.04±591.93	-	6811	7895	250-2200	2000
Sulphate	53.21±8.60	24.1	159	-	-	50
Sodium	856.72±562.18	-	3125	-	-	-
Iron	0.85±0.33	-	-	-	0.45-2.14	20
Nickel	0.13±0.03	-	-	-	-	<1
Chromium	0.14±0.21	-	-	-	0.5	<1
Lead	2.45±1.23	-	-	-	-	<1

pH: no units, Colour: pt-co, Conductivity: µs/cm, All other parameters: mg/l, FEPA: Federal Environmental Protection Agency

Table 4.10: Mean water pollutants conc.

Parameters	Mean± Standard deviation (WA-WL)	Yahaya *et al.* (2017)	Tahir *et al.* (2015)	Dabo and Saleh (2017)	SON standard	WHO standard
pH	6.45±0.45	7.7	6.32	7.3	6.5-8.7	6.5-8.5
Temperature	30.94±0.90	27.85	33.6	27	-	27-28
DO	4.05±0.80	4.67	-	2.64	-	7.5
BOD	1.49±0.55	1.25	-	0.93	-	-
Conductivity	1112.26±162.28	590.9	558	504	1000	1000
TDS	786.22±481.70	119.13	312	1056	500	500
Sulphate	20.78±2.85	-	22.2	-	100	-
Sodium	808.75±312.40	-	35	-	200	-
Iron	1.23±0.91	0.6	0.3	0.25	0.3	0.3
Nickel	0.10±0.01	-	0.018	-	0.02	0.07
Chromium	0.08±0.04	0.57	0.04	0.56	0.05	0.05
Lead	2.27±0.06	0.11	0.11	0.25	0.01	0.01

pH: no units, Temperature: ^{o}C, Conductivity: µs/cm, All other parameters: mg/l, SON: Standard organization of Nigeria, WHO: World Health Organization

4.4.1.1 pH

The pH determined in effluent ranged from 11.11 to 11.8 with mean value of 11.50±0.15 (Table 4.9). The lowest level was found in sample DP whereas the highest was detected in DI. Mean pH value determined in this study is out of range of Federal environmental protection agency (FEPA) recommended limits. Vat dye wastewaters investigated

previously by Mounteer *et al.* (2018), Santhi and Moses (2008), and Abebe and Galebo (2019) have mean pH values similar to this study may be due to the fact that leuco vat dyeing is usually carried out at that alkaline pH region (Chakraborty, 2010).

pH in groundwater ranged from 5.54 to 7.20 with an average of 6.45±0.45 (Table 4.10). The lowest level was detected in sample WA and the highest value found in WC. The mean pH value found in this study is out of range of permissible limits set by standards organization of Nigeria (SON) and World health organization (WHO). Previous studies reported slightly alkaline pH of groundwaters in the same study area (Yahaya *et al.,* 2017; Dabo and Saleh, 2017). Tahir *et al.* (2015) reported a more acidic pH than the value measured in this study.

pH determines the presence or absence of ionic species of water/effluent. Strength of pH alters the rate of biological reaction for the survival of microorganisms and also affects the soil permeability which results in contaminating groundwater sources (Elango *et al.,* 2017). Although pH usually has no direct impact on consumers, it is one of the most important operational water quality parameters as toxicity of metals increases with the basic pH (Mandour, 2012). It is suggested that water undergoes anaerobic fermentation processes as a result of formation of ammonia and organic acids where hydrolysis of those acidic materials decreases the pH value and make water more acidic (Elango *et al.,* 2017). Acidic waters can cause corrosion of pipes and may pose negative effects on gastrointestinal tracts when consumed thereby resulting in diarrhea (Zacchaeus *et al.,* 2020).

4.4.1.2 DO

The conc. of DO in effluent samples ranged from 1.31 to 1.68 mg/l with a mean value of 1.49±0.1 mg/l. The lowest value was found in sample DH and the highest in DR. FEPA did not specify limits for DO of industrial effluent. Conc. of DO in groundwater ranges from 2.93 to 5.40 mg/l with an average of 4.05±0.8 mg/l. The lowest value was measured in sample WK whereas the highest value was detected in sample WG. The mean DO value is lower than the recommended limit set by WHO. SON did not recommend any limit for DO of drinking water. The mean DO conc. measured in this study is higher than that reported by Dabo and Saleh (2017) and lower than that detected by Yahaya *et al.* (2017).

Dissolved oxygen test measures the conc. of oxygen dissolved in water or wastewater and is significantly affected by temperature, salinity, and atmospheric pressure. Saturation conc. of oxygen in deionized water at 1 ^{o}C and standard air pressure is 14.2 mg/l and species that live in water are sensitive to relatively small changes in the already extremely low quantity of oxygen available. For example, Trout fish die when the DO conc. is less than 5 mg/l (Woodard, 2001). The presence of organic substances in water also affects the DO. The decrease in DO levels does not only affect the ecological balance but also poses environmental problems because it reduces the population of beneficial microorganisms that naturally degrade harmful organic substances (Ratna and Padhi, 2012).

4.4.1.3 BOD

BOD conc. in effluent ranges from 307.32 to 490.44 mg/l with an average value of 405.81±59.33 mg/l. The lowest value was obtained in sample DC while the highest value was measured in DD. The average value obtained in this study exceeds the FEPA limit of 50 mg/l.

Santhi and Moses (2008) and Abebe and Galebo (2019) have measured the BOD of effluent from vat dyebaths as 462 and 480 mg/l, respectively. A BOD of 3670 mg/l was found in effluent containing C. I. Vat Blue 4 from a dyeing unit in India (Olaganathan and Patterson, 2009). BOD conc. in groundwater ranges from 0.69 to 3.44 mg/l with a mean value of 1.49±0.55 mg/l. The highest value was measured in sample WA whereas the lowest value was in WE. No BOD limit is set by both SON and WHO. Previous studies reported mean BOD values of 1.25 mg/l (Yahaya *et al.,* 2017) and 0.93 mg/l (Dabo and Saleh, 2017).

The simplest way of estimating the biodegradability of a wastewater sample is to estimate the amount of oxygen required to stabilize the waste. The second oxygen demand is nitrification (oxidation of ammonia) where a significant amount of oxygen is consumed such that the total oxygen demand is comparable with carbonaceous demand. The process generates H^+ ions which increase the acidity of the wastewater as shown in Equation 4.1. Low or nil BOD shows good quality water while high BOD indicates that the water is highly contaminated and not suggested for drinking purposes. Increase in BOD also leads to microbial oxygen demand reducing DO which may induce hypoxia conditions with subsequent adverse effects on aquatic biota (Elango *et al.,* 2017).

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$$

Equation 4.1: Nitrification process (Scholz, 2016)

4.4.1.4 Cd and TDS

Cd in effluent ranged from 1958.22 to 2540.0 µs/cm with an average of 2147.76±159.3 µs/cm. The highest value was measured in sample DN while the lowest was detected in DI. No Cd limit is set by FEPA. Mounteer *et al.* (2018) reported conductivity of 1656 µs/cm from a raw textile mill effluent containing vat dye. Cd in groundwater ranges from 923.32 to 1358.49

µs/cm with a mean value of 1112.26±162.28 µs/cm. The mean value obtained in groundwater is almost twice the values reported previously (Yahaya *et al.,* 2017; Tahir *et al.,* 2015) and exceeds the limit of 1000 µs/cm set by SON and WHO.

Cd reflects the total amount of salt in water (Ca^{2+}, Mg^{2+}, Na^{+}, CO_3^{2-}, SO_4^{2-}) and is used to determine salinity of water (Hussain, 2013). High conductivity level recorded could be linked to sewage materials as well as leaching of inorganic contaminants. Large quantity of mercerization wastewater containing caustic soda could also be the reason for the high Cd. Electrical Cd is related to TDS as it measures the ionic content of water sample which determines its ability to conduct an electric current. As TDS conc. increases, the ionic strength also increases (Popoola *et al.*, 2019).

TDS in effluent ranged from 3168.4 to 5104.32 mg/l with a mean value of 4401.04±591.93 mg/l. The lowest value was detected in sample DI whereas the highest value was found in DQ. Mean TDS value in effluent was above FEPA recommended limit of 2000 mg/l. It is lower than mean values reported previously (Mounteer *et al.,* 2018; Santhi and Moses, 2008) but higher than that measured by Abebe and Galebo (2019). TDS in groundwater ranges from 18.78 to 1678 mg/l with an average of 786.22±481.70 mg/l which exceeds the maximum permissible limit of 500 mg/l set by SON and WHO. The mean TDS is higher than that reported by Yahaya *et al.* (2017) and Tahir *et al.* (2015) but lower than the value measured by Dabo and Saleh (2017). Textile industries show higher TDS values than other industries mainly due to the fixing, bleaching, and dyeing agents used for fabric processing at different stages. High TDS value of water is not recommended for drinking and irrigation purposes as it may cause salinity problem (Elango *et al.,* 2017).

4.4.1.5 Sulphate

Conc. of sulphate in effluent ranged from 32.18 to 64.3 mg/l with a mean value of 53.21±8.60 mg/l. The lowest value was measured in sample DR whereas the highest value was found in sample DH. The mean value in effluent exceeds the maximum of 50 mg/l set by FEPA. Santhi and Moses (2008) reported sulphate conc. of 159 mg/l from a Jade Green XBN vat dyebath. Sulphate conc. in groundwater ranges from 13.37 to 26.77 mg/l with an average of 20.78±2.85 mg/l. Mean sulphate conc. obtained in groundwater is within the maximum permissible limit of 100 mg/l set by SON. Tahir *et al.* (2015) reported a higher sulphate conc. in groundwater.

Sulphate is widely distributed in nature and may be present in natural waters in conc. ranging from a few to thousands mg/l. Bacteria and dissolved oxygen play leading roles in determining the fate of sulphur containing compounds in aquatic systems where sulphate reducing bacteria use sulphate ion as an oxygen source for the assimilation of organic matter in the same way DO is used by aerobic bacteria (Kularatne *et al.*, 2003). Sulphates are sulphuric acid products used in the production of fertilizers, chemicals, dyes, glass, paper, textiles etc. and are discharged into water from mines and smelters from kraft pulp, paper, textile mills and tanneries (WHO, 2004). Natural source of sulphate is linked with the dissolution of sulphate/evaporites minerals such as gypsum and anthropogenic sources could be from municipal and industrial effluents mainly due to sulphur-based waste products (Aladejana *et al.,* 2020). During vat dyeing process, hydros is converted into sulphite (toxic to fish and bacteria) and in some cases this is further oxidized into sulphate which may cause corrosion of concrete pipes (Chavan, 2011). Accumulation of sulphate in water may lead to increase in water pH causing acidosis (Popoola *et al.*, 2019).

4.4.1.6 Colour

Colour in effluent ranges from 405.3 to 920.12 pt-co with a mean value of 616.71±131.58 pt-co. The highest value was obtained in sample DB while the lowest value was found in DJ. The mean colour value is above FEPA limit and lower than the values reported by Mounteer *et al.* (2018) and Yusuf and Sonibare (2004). Colour is based on the use of the Adams-Nickerson chromatic value formula for calculating single number colour difference values i.e., uniform colour difference and this modification was developed by members of ADMI. Colour of effluent is one of the major problems in the textile industry and it is a widely accepted primary pollutant in wastewater. Colour diminishes the photosynthetic activity of aquatic life and it affects other parameters such as DO, BOD etc., Colour is difficult to remove by conventional treatment methods (Elango *et al.,* 2017) and high colour renders water unfit for use at the downstream of the disposal point and continuously threatens the biodiversity (Karim *et al.,* 2018).

4.4.1.7 COD

Concentration of COD in effluent ranges from 1203.84 to 2218.44 mg/l with an average value of 1550.32±344.72 mg/l. the lowest value was found in sample DJ whereas the highest value was measured in DB. The mean value far exceeds FEPA recommended limit of 80 mg/l and is in the same range as values reported previously (Mounteer *et al.,* 2018; Yusuf and Sonibare, 2004). COD test oxidizes materials that microorganisms cannot metabolize in 5 days or that are toxic (Scholz, 2016). COD is a measure of the amount of oxygen required to oxidize the organic matter and possibly some inorganic materials in a sample and also provides a direct measure of the potential impact of oxygen consumption on the oxygen content of water body (Walker *et al.,* 2019). Rise in COD value after dyeing with vat dyes may be due to the use of

hydros and in an open bath. Excess air oxidized a part of the total hydros to sulphate and the rest contributes to COD. The quantity of hydros converted to sulphate and the rest left in the bath are nearly 50:50 (Chakraborty, 1992).

If COD is much greater than the BOD in raw wastewater, then the waste is not readily biodegradable which may be toxic to microorganisms and if they are similar then the waste is readily biodegradable (Scholz, 2016). In the case of biodegradable organics, COD is 1.3 to 1.5 times the BOD and when the ratio is twice, there is good reason to suspect that a significant portion of the organic material in the samples is not biodegradable by ordinary microorganisms (Woodard, 2001). The COD measured in effluent samples is almost 4 times the BOD which indicates that the wastewater is not readily biodegradable.

4.4.1.8 Temperature

Temp. in groundwater ranged from 29 to 33 ^{o}C with an average value of 30.94±0.9 ^{o}C. The lowest value was measured in sample WF and the highest in WE. The mean temperature exceeds WHO recommended limit of 27-28 ^{o}C and is higher than the temperature measured by Yahaya *et al.* (2017) and Dabo and Saleh (2017) but lower than that obtained by Tahir *et al.* (2015). Temp. is one of the most essential parameters of water as it is significant for the growth and activity of ecological life as it affects the solubility of oxygen in water (Shawai *et al.*, 2018).

4.4.2 Heavy metals in effluent and groundwater samples

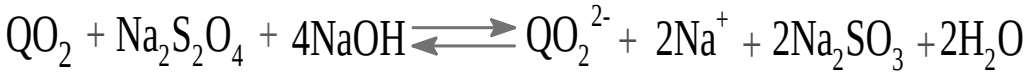
Figures D19 to D23 (see Appendix D) show calibration curves generated by MP-AES software for the determination of Ni, Pb, Cr, Fe, and Na, respectively, in effluent and groundwater

samples. In recent years, there has been an increasing ecological and global public health concerns associated with environmental contamination by heavy metals and although they are found naturally, most environmental contamination and human exposure result from anthropogenic activities such as industrial activities, domestic and agricultural use of metals etc. (Tchounwou *et al.*, 2012). The heavy metals investigated in dye effluent and groundwater samples include Na, Fe, Ni, Cr, and Pb as shown in Table 4.9 and Table 4.10 respectively.

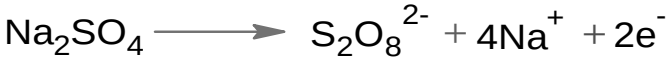
4.4.2.1 Sodium

High level of Na in a sample may cause interferences in atomic spectrometric methods because Na is one of the so-called easily ionized elements which is a well-known and common interferent (Baranyai *et al.,* 2020). According to the authors, Na conc. naturally present in human blood serum samples affected the intensity values of other measured elements.

The conc. of Na in effluent ranged from 0.00 to 1398.91 mg/l with an average value of 856.72±562.18 (Table 4.9). The highest conc. was found in sample DN. Na was not determined in samples DA, DE, DH, DI, and DJ. High Na content found in this study may be attributable to the fact that caustic soda and hydros were found to have high Na content which will invariably contribute to the overall Na conc. in the dyebath. Reduction of vat dye in an alkaline solution produces Na in the dyebath as shown in Equation 4.2. Oxidation of sulphate also give rise to Na as shown in Equation 4.3. Santhi and Moses (2008) found Na conc. of 3125 mg/l in Jade Green XBN dyebath effluent in which hydros was used as the reducing agent. The limit of Na in effluent samples has not been set by FEPA.



Equation 4.2: Reduction of quinone (QO_2) with hydros to give leuco dye (QO_2^{2-}) (Broadbent, 2001)



Equation 4.3: Oxidation of sulphate (Kariyajjanavar *et al.,* 2013)

Na found in groundwater samples ranged from 0.00 to 1187.36 mg/l with an average of 808±312.4 (Table 4.10). The highest value was obtained in sample WK and Na has not been determined in sample WG. The mean Na level obtained in this study is higher than that reported previously and exceeds the limit of 200 mg/l set for safe drinking water quality by SON. WHO, however, has not set limit for Na in drinking water. Tahir *et al.* (2015) reported 35 mg/l as the mean Na conc. in deep and shallow boreholes in Kano Metropolis. Sa'eed and Mahmoud (2014) detected mean Na conc. in Fagge Local Government Area as 3.7 mg/l while Suleiman *et al.* (2020) determined the conc. of about 23.3 mg/l in Gwale. However, a maximum level of Na up to 863 mg/l was measured in the shallow tube well of Barguna district of Bangladesh (Islam *et al.,* 2017).

Na occurs naturally in groundwater and is believed to have been released by weathering of plagioclase feldspars. The rock types in Kano Metropolis are characterized by enrichment in Na, calcium (Ca), and potassium (K) ions (Tahir *et al.,* 2015). Frequent discharge of the vat dye effluent with high Na content in to shallow and stagnant drainages which are in close proximity to groundwater source (not more than 91 m away) may be responsible for the high Na conc. Aghazadeh *et al.* (2017) also attributed the high conc. of Na to cation exchange among minerals, anthropogenic activities, and poor drainage conditions.

Na is one of the leading constituents of blood plasma of humans and because of that alteration of its normal conc. in the body may have direct and vital effects on the osmotic pressure of the plasma, on plasma volume, on acid-base balance, and on the maintenance of electric activity of body cells (Hasan *et al.,* 2020). Elevated Na intake has been associated with hypertension, cardiovascular disease and stroke. Sodium intake for adults equals to 2 g/day which is equivalent to 5 g salt/day (WHO, 2012).

4.4.2.2 Iron

Fe in effluent samples ranged from 0.1 to 1.30 mg/l with an average of 0.85±0.33 mg/l. The lowest conc. was found in sample DJ whereas the highest was found in DP. The mean Fe content detected in this study is within FEPA permissible limit of 20 mg/l. Yusuf and Sonibare (2004) reported 1.24 mg/l as mean Fe conc. in composite textile effluents from five different textile mills in Kaduna Metropolis.

Fe in groundwater samples ranged from 0.81 to 3.99 mg/l with an average of 1.23±0.91 mg/l. The lowest level was found in sample WL while the highest was found in WI. Mean Fe level is higher than that reported previously and is above permissible limit set by SON and WHO for drinking water quality. Yahaya *et al.* (2017) found 0.6 mg/l mean iron concentration in groundwater samples from wells located in industrial areas of Kano Metropolis. A mean Fe conc. of 0.3 mg/l was found around residential areas in Kano Metropolis (Tahir *et al.,* 2015). Mean Fe conc. in drinking water sources in Kano Metropolis (boreholes, wells, and tap water) was reported as 0.25 mg/l (Dabo and Saleh, 2017).

High Fe content is a characteristic of groundwater in significant proportions practically in all states of Nigeria (Ezeigbo, 1988). Fe levels found in some states ranged from 0.3-1.5 mg/l in coastal aquifer in Ogun State (Aladejana *et al.,* 2020) to 2.2-4.71 mg/l in industrial and residential areas of Lagos Metropolis (Popoola *et al.,* 2019).

Even though conc. of Fe in effluent is within FEPA permissible limit for effluent discharge, frequent dumping of the wastewaters on the ground or in to a shallow drain may accumulate and increase Fe content in the groundwater because of its proximity to the source of contamination. High level of Fe may also be attributable to the dissolution of iron bearing rocks and/or soils. It can also be due to leaching from rusting in the old galvanized metal pipe work in the distribution channel (Audu and Idowu, 2015) since Fe is used in coatings of many pipes and can deteriorate and find its way into the water supply (Mandour, 2012). Fe exists in its natural form as ores (magnetite taconite and hematite) in rocks, soil, and minerals making about 5 % of the earth's crust (Popoola *et al.,* 2019) and can be dissolved and transported out of the soil and carried into groundwater (Mandour, 2012). Fe is an essential element that is required by all forms of life. It is a natural constituent of all nutrients of plant and animal origin (Geiger and Cooper, 2010). In humans, it is an essential element for haemoglobin and myoglobin, and its deficiency leads to anaemia and loss of wellbeing. Overload of Fe causes severe health problems such as liver cancer, diabetes, cirrhosis of liver, heart disease, etc. (Zhang *et al.,* 2020).

4.4.2.3 Nickel

Ni conc. in effluent ranged from 0.08 to 0.19 mg/l with an average of 0.13±0.03 mg/l. The lowest level was detected in sample DL and the highest level measured in DH. The mean Ni

level is within FEPA permissible limit. The conc. of Ni in groundwater ranged from 0.09 to 0.14 mg/l with a mean value of 0.1±0.01 mg/l. The lowest level was determined in sample DC and the highest concentration in DL. The average Ni conc. detected in this study is above the SON and WHO limits which may be deleterious to consumers of the water samples tested. Mean Ni level of 0.018 mg/l was reported to be present in groundwater samples around Kano Metropolis (Tahir *et al.,* 2015). Ni is a naturally occurring metal existing in various mineral forms and it is present in all compartments of the environment and ubiquitous in the biosphere (EPSA, 2015). The primary source of Ni in drinking water is leaching from metals in contact with the water such as pipes and fittings and it may also be present in some groundwater as a consequence of dissolution from Ni ore bearing rocks (Tiwari *et al.,* 2013). The source of Ni measured in this study may be attributable to municipal waste scattered virtually all around the study area. Ni present in dye/auxiliaries and consequently in dye effluent may also contribute to its concentration in groundwater.

Ni is used as alloy in nickel-plating and in the manufacture of batteries. Its toxicity is usually enhanced by the presence of other metals such as Co, Cu, Fe, and Zn in drinking water (Mandour, 2012). Ni is present in a number of enzymes in plants and microorganisms. In humans, it influences ion adsorption, metabolism, and may be an essential component of the haemopoietic process (Tiwari *et al.*, 2013). Short-term inhalation exposure causes damage to the lungs and kidneys. Effects of ingestion through drinking water include gastrointestinal diseases e.g., nausea, vomiting, diarrhea, and neurological effects. Long-term exposure via skin contact can result in nickel dermatitis consisting of itching of the fingers, hands, and forearms (Geiger and Cooper, 2010).

4.4.2.4 Chromium

Cr conc. in effluent samples ranged from 0.02 to 1.24 mg/l with a mean value of 0.14±0.21 mg/l. The highest value was detected in sample DD whereas the lowest was found in DO. Mean Cr conc. found in the effluent studied is within FEPA limit. Yusuf and Sonibare (2004) have detected 0.5 mg/l in effluent from textile industries in Kaduna. Conc. of Cr in groundwater ranged from 0.04 to 0.18 mg/l with an average value of 0.08±0.04 mg/l. The lowest value was found in sample WC and WG while the highest value was obtained in sample WI. The mean Cr value obtained in this study is lower than that previously measured in groundwaters around Kano Metropolis (Yahaya *et al.,* 2017; Dabo and Saleh, 2017) except for values reported by Tahir *et al.* (2015). The mean Cr content in groundwater samples is above the limits set by SON (0.02 mg/l) and WHO (0.05 mg/l).

Cr exists naturally as element in rocks, soils, volcanic emissions, plants, and animals. Natural deposits erosion and coating removal from water pipes may contribute to chromium present in groundwater samples (Popoola *et al.,* 2019). Cr has several oxidation states, the common ones being divalent (Cr^{+2}), trivalent (Cr^{+3}), and hexavalent (Cr^{+6}) where Cr^{+3} is an essential nutrient while Cr^{+6} is listed as a known human carcinogen (Walker *et al.,* 2019). Hexavalent Cr is widely used in numerous industrial processes including chrome pigment production, chrome plating, stainless steel manufacturing, leather tanning, etc. (Sun *et al.,* 2015). Trivalent Cr is required by human body for insulin secretion that helps to maintain normal glucose metabolism in the body (Vetrimurugan *et al.,* 2017). The short-term effects of hexavalent Cr include shortness of breath, coughing, wheezing, and other effects on the respiratory tract. Inhalation and ingestion may also cause gastrointestinal effects including abdominal pain, vomiting, and hemorrhage (Geiger and Cooper, 2010). The long-term exposure to Cr could

cause kidney damage, lung cancer, high blood pressure, and bone defects (Popoola *et al.,* 2019). Cr contaminated water in Greece indicated increased incidence in liver cancer, mortality, lung cancer, cancer of the kidney, and other genitourinary organs among women (Linos *et al.,* 2011).

4.4.2.5 Lead

Conc. of Pb in effluent ranged from 0.05 to 4.09 mg/l with an average of 2.45±1.23 mg/l. The lowest value was found in sample DC while the highest level was detected in DR. mean Pb conc. in this study far exceeded the FEPA permissible limit. Pb conc. in groundwater ranged from 2.16 to 2.38 mg/l with an average value of 2.27±0.06 mg/l. The mean Pb content detected in this study far exceeds SON and WHO permissible limits of 0.01 mg/l and is also higher than the results obtained in previous studies. Previous mean conc. of Pb found in groundwater samples in Kano Metropolis include 0.11 mg/l (Yahaya *et al.,* 2017; Tahir *et al.,* 2015) and 0.25 mg/l (Dabo and Saleh, 2017). The groundwater samples investigated are not fit for drinking due to excess Pb levels.

Pb is used in the production of lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors etc. Uncontrolled disposal of lead acid batteries can cause relative high levels of lead in groundwater (Oyeku and Eludoyin, 2010). High Pb conc. may originate from corrosion of brass fitting of certain types of submersible pumps used in groundwater wells (Sa'eed and Mahmoud, 2014). High conc. of Pb could also be as a result of composed manure deposited on farms, littered petrol in cars, generators, and water pumps (Yusuf *et al.,* 2018). High Pb level can also be attributed to leaching of natural deposits of Pb ores in the soil into the groundwater (Popoola *et al.,* 2019). Presence of Pb in water beyond permissible level could

result in hypertension, interference of vitamin D and calcium metabolism, and damage to tissues and organs (Popoola *et al.*, 2019). Exposure to Pb results in significant behavioural and cognitive deficits such as impairment of activity, attention, adaptability, learning ability and memory, as well as increased distractibility. Acute intoxication with Pb results in headaches, muscle tremor, abdominal cramps, kidney damage, etc. while chronic lead intoxication causes tiredness, irritability, joint pain, and gastrointestinal symptoms (WHO, 2011b).

4.5 Occupational Vat Dyeing Parameters

The rate of reduction of vat dyes depends on particle size of the dye, temperature, time, pH, and access of the reducing agent. The factors influencing the rate of dyeing, however, include type of substrate, temp., LR, and conc. of dye and auxiliaries (Shamey and Hussein, 2005). Survey results have shown that most of the dyers carryout vatting for not more than 2 min. and accomplish dyeing in less than 10 min. (section 4.1.4.3). As discussed under section 4.1.4.4, the average LR has been estimated to be 40:1. In order to determine dyeing temp. and quantity of caustic soda and hydros used in the dyeing of 10 % shade of RSN, vatting and dyeing time as well as LR were kept at constant levels of 2 min., 10 min., and 100:1, respectively. The results obtained from a dyebath each in 18 dyehouses investigated are shown in Table 4.11.

Table 4.11: Dyeing conditions used by the occupational dyers

	Parameter± SD		
Dyehouses	Temp. (^{o}C)	NaOH conc. (g/l)	Hydros conc. (g/l)
DA	80±1.00	15.47±0.37	16.58±0.34
DB	76±1.53	21.58±0.32	21.40±1.11
DC	77±1.53	21.53±0.37	19.52±1.51

DD	74±1.00	21.59±0.41	20.74±0.47
DE	69±1.00	22.45±0.32	20.64±1.06
DF	73±1.53	22.67±0.38	21.67±0.26
DG	75±0.58	21.42±1.13	19.61±1.25
DH	77±0.58	21.65±0.38	19.15±0.55
DI	73±1.00	21.76±0.77	19.55±0.80
DJ	78±2.08	21.33±0.23	19.58±0.32
DK	70±2.08	20.90±0.38	20.53±0.48
DL	76±2.08	21.59±0.35	21.57±0.40
DM	80±3.00	21.28±0.50	17.20±1.21
DN	78±2.65	18.19±0.51	16.56±0.44
DO	78±0.58	33.39±6.80	19.48±3.83
DP	81±2.65	20.05±0.50	15.33±1.54
DQ	84±2.08	20.38±1.28	16.65±2.15
DR	78±2.65	18.57±1.40	16.11±1.59
Mean± SD	76±4	21.43±3.46	18.99±2.05

4.5.1 Temperature

The temp. of the dyebath just before dyeing ranged from 68 to 83 ^{o}C with a mean value of 76±4 ^{o}C. The lowest temp. was found in dyehouse K (DK) while the highest was found in DP and DQ. The equipment type and fuel used by the dyers (discussed in sections 4.1.3.2 and 4.1.3.3 respectively) could not provide a precise temp. control. This is in line with a report by Jena *et al.* (2015) that traditional hand dyers use fossil fuel which bring about difficulties in precise temperature control. According to Patra *et al.* (2018), improper temperature control, applicable to non-industrial dyers, results in increased dyeing cost for un-utilized and expensive vat dyes. Precise temperature control is necessary for some vat dyes to get better colour absorption (Chakraborty and Chavan, 2004).

According to Wardman (2018), it is a requirement to maintain uniform temp. in a dyeing machine. In practical vat dyeing, the temp. at the start of dyeing is determined by the classification of the dye used either IK, IW, or IN (Aspland, 1997). It has been reported that temperature can be gradually raised to about 80 ^{o}C and lowered to 40-50 ^{o}C towards the end of vat dyeing cycle (Aspland, 1992) which is slightly different from the practice of the occupational dyers. Since the heating source is not continuous, the temp. of the dyebath drops over period of dyeing which is usually a few min.

4.5.2 Caustic soda and hydros conc.

Caustic soda conc. ranged from 15.07 to 40.86 g/l with a mean value of 21.43±3.46 g/l. The lowest value was found in dyehouse A (DA) while the highest value was found in DF. According to Lacasse and Baumann (2004), to dye deep colour of Indanthrene vat dye on 100 kg of cotton (LR=10:1), 24 ml/l of caustic soda is required. Khatri *et al.* (2017) used 20 g/l caustic soda in the reduction of RSN for the dyeing of regenerated cellulose nanofibers at 60 ^{o}C for 50 min. Aspland (1992b) and Chakraborty (2010) recommended 4.8 g/l (for a 2 % shade) and 10 g/l, respectively, where the quantity increases with increase in dye conc. and LR.

Vat dye is reduced chemically by hydros in highly alkaline medium provided by caustic soda (Bozic *et al.,* 2009). Caustic soda serves as a pH regulator in vat dyeing as leuco compound can exist either as monosodium or disodium salt as well as in the form of free leuco acid. Affinity, substantivity, and fastness properties are highly influenced by a noticeable change in pH (Chakraborty, 1992). Caustic soda is found in household products including drain cleaners,

paint removers, detergent, alkali batteries, and is used in the manufacture of soap, paper and rayon among others (Gad, 2014).

Conc. of hydros ranged from 14.13 to 21.93 g/l with an average value of 18.99±2.05 g/l. the lowest value was found in dyehouse P (DP) and the highest value in DF. 20 g/l of hydros has been used in the dyeing of cellulose nanofibers to obtain maximum colour yield with RSN (Khatri *et al.* 2017). Nwadiakwu (2016) suggested 8 g/l of hydros to be used by the occupational dyers in Lagos, Nigeria. Aspland (1997) and Chakraborty (2010) recommended the use of 4 g/l and 10 g/l, respectively, where according to them the conc. increases with percentage shade and LR. The quantity of hydros to be used depends on how many keto groups in the dye molecules are to be reduced where 1 mole of hydros is required to reduce 2 keto groups to the enol form (Shim *et al.,* 2006).

Dyeing time, LR, percentage shade, dyeing temp., and nature of the dyebath (open or closed) influence the quantity of hydros to be used in vat dyeing. Addition of too little hydros results in oxidation which removes the dye from solution, incorrect heavy colour selvedge and poor fastness to washing while too much hydros can lead to the destruction of the dye chromophore which leads to loss of colour yield (Teli *et al.,* 2001). Too excess hydros retards rate of dyeing and large excess results in over-reduction as well as wastage of dye. Manufacturers recommendation is to be consulted to know the right quantity required. In practice, one half of caustic soda is used for reduction, one quarter is added at the start of dyeing, and the remaining to be added at different times during the dyeing process (Chakraborty, 2010).

Hydros is the most common reducing agent used industrially because of its effective reducing power and its availability in an easy-to-handle solid form (Saikhao *et al.,* 2018). It is used in reductive bleaching effective for colour stripping which can remove many types of dyes. Most acid and direct dyes are permanently decolourized by hydros because it breaks the azo group (Bajpai, 2018). Hydros can be used for water treatment, gas purification, cleaning as well as an oxygen scavenger. It has also been used in food preparations especially in molasses to brighten the colour (Reza *et al.*, 2014).

4.6 Results from Mercerization Experiments

Significant input variables are well known for mercerization process of cotton which include but not limited to caustic soda conc., temp., and treatment time (Khajavi *et al.*, 2015; Gemci, 2010). CCD (containing 5 levels of each factor viz. low and high factorial, low and high axial, and centre) was used to fit a model, develop regression equations, and then optimize key factors influencing shrinkage and elongation of CF and BF. In the regression equations, the parameter with the highest absolute value of the coefficient has the greatest effect on the response. Normal mercerization requires the use of a conc. solution of caustic soda at uniform temp. not exceeding 18 ^{o}C. Caustic soda solution of mercerizing strength and at low temp. is highly viscous and of low surface activity (Duckworth and Wrennall, 1977) and therefore affects the degree of uniformity of penetration into the textile structure. This is why the temp. was varied from room temp. to 100 ^{o}C. Temp. above room temp. were controlled by appropriate hot plate heating rates.

The process of surface modification of polyester fibres by alkaline solution also known as weight reduction is well known (Tavanai, 2009). Hot caustic treatment of cotton/polyester

fabric (240 g/l caustic conc., 60-90 ^{o}C, and 2-20 min. treatment time) has been reported by Montazer and Sadighi (2006). Haji *et al.* (2011) treated cotton/polyester fabric with 40 g/l caustic soda at elevated temp. to impart silky surface to the polyester fibres and improve water and dye absorption on both fibres in the fabric. As shown in Table 3.2 (section 3.1.1), BF used in this study consists of polyester warp (BFPWA) and cotton weft (BFCWE) while the CF consists of cotton warp (CFWA) and cotton weft (CFWE) yarns.

4.6.1 Shrinkage

As shown in Table 4.12, the average shrinkage values of CF are higher than those of BF under the same conditions of treatment. BFPWA shrinkage is minimal because polyester fibres shrink very little. The mean shrinkage values of BF and CF are respectively 8.82±0.11 % and 11.97±0.28 %. Haghighatkish and Yousefi (1992) reported that polyester yarns do not shrink measurably at 30 ^{o}C in aqueous caustic soda solution. CFWA shrink as high as 21 % in 349 g/l caustic soda at 85 ^{o}C for 8 min. which is the highest shrinkage measured. The maximum shrinkage of cotton fibres during slack mercerization varies from 15-19 % depending on the type of cotton which is why the amounts of shrinkage reported in the literature differ considerably (Sloan *et al.,* 1963). For example, Egyptian cotton was found to shrink more than American cotton under the same treatment condition (Goldthwait, 1965).

Table 4.12: Shrinkage values obtained from mercerized and unmercerized samples

Run No.	NaOH Conc. (g/l)	Temp. (^{o}C)	Time (min.)	Fabric (type)	Warp shrinkage (%)	Weft shrinkage (%)	Average Shrinkage (%)
1	201	45	8	BF	1.3	17	9.2
2	201	45	3	CF	12.7	8	10.3
3	275	65	6	CF	18.3	8.7	13.5
4	349	85	8	BF	0.7	15.7	8.2
5	201	85	8	CF	17.3	8	12.8
6	275	65	6	BF	0.3	15	**7.7**

7	349	45	8	CF	20.3	10.3	15.3
8	275	65	6	CF	20	5.7	12.8
9	275	65	6	BF	4.7	16.7	10.7
10	201	85	8	BF	0.0	11.7	5.8
11	275	65	6	CF	20.3	5.3	12.8
12	275	65	6	CF	20	3.3	11.7
13	349	85	3	CF	17.3	13.3	15.3
14	201	45	3	BF	2.0	15.7	8.8
15	349	45	3	CF	20.7	10.7	15.7
16	349	85	8	CF	21	10.7	15.8
17	349	45	3	BF	1.7	19.0	10.3
18	275	65	6	BF	0.3	14.0	7.2
19	275	65	6	BF	3.7	15.3	9.5
20	349	85	3	BF	4.7	18.0	11.3
21	201	45	8	CF	16	7.3	11.7
22	201	85	3	BF	0.3	15.0	7.7
23	201	85	3	CF	13.3	8.3	10.8
24	349	45	8	BF	6.7	20.0	13.3
25	275	65	10	CF	17.7	0.7	9.2
26	275	65	1	CF	16.7	5.3	11.0
27	400	65	6	CF	18.7	5.3	12.0
28	275	65	6	CF	13.7	3.3	8.5
29	275	32	6	BF	1.3	16.7	9.0
30	275	65	6	BF	2.7	17.0	9.8
31	400	65	6	BF	2.3	16.7	9.5
32	275	32	6	CF	14.7	5.3	10.0
33	275	65	6	CF	19.7	7.7	13.7
34	275	99	6	CF	16.7	7.7	12.2
35	275	65	10	BF	4.3	15.7	10.0
36	150	65	6	CF	11.7	4.0	4.3
37	275	65	6	BF	0.7	16.0	9.3
38	275	65	1	BF	2.0	15.7	8.8
39	150	65	6	BF	0.3	4.7	2.5
40	275	99	6	BF	1.7	13.7	7.7
41	0	65	6	UMCF	2.0	0.0	1.0
42	0	65	6	UMBF	0.0	0.0	0.0

BF: blend fabric, CF: cotton fabric, UMCF: unmercerized cotton fabric, UMBF: unmercerized blend fabric

BFCWE shrinks more than CFWE may be because the former has higher number of picks and lower yarn count than the latter implying that the structure is more open to swell and shrink. Sameii *et al.* (2008) attributed higher shrinkage to higher weave density. CFWA shrinks more than the CFWE which may also be attributable to openness of structure with lower yarn count

of the former. The amount of shrinkage of fibres in cotton textile structures especially yarns and fabrics during mercerization depends on restrictions imposed by twist and weave as well as whether tension is applied or not (Goldthwait, 1965). Caustic alkali causes cotton fibres to swell greatly if unrestricted and to shrink. It is the swelling of the fibres that causes the fabric to shrink. When fibres in cotton cloth swell during mercerization without tension, they do so outwardly in every other direction and because fibres are spiral structures they tend to shorten as they increase in diameter. When the yarns in a piece of cloth increase in diameter and shrink, the whole piece shrinks (Goldthwait and Murphy, 1955). Shrinkage of PET fabrics may be due to the fact that caustic soda swells PET chains by diffusion and the mobility of the swelled PET chains increase with hydroxyl group activity. The swelled amorphous region changes to crystal structure by recrystallization hence shrinkage increases because of the structural relaxation of the amorphous region (Kim *et al.,* 2009).

4.6.1.1 Model fitting and analysis of variance (ANOVA) for shrinkage

The choice of model based on sum of squares; lack of fit tests; and model summary statistics; as well as analysis of variance (ANOVA) for the response "shrinkage" was generated by DX7. Lack of fit shown in Table 4.13 compares residual error to the "pure error" from replicated design points. The selected model should have insignificant lack of fit. Lack of fit in this case is not significant and therefore the model can be used as a response predictor. The linear model selected exhibits low standard deviation, high coefficient of determination (67.56 %) and low PRESS. As shown in Table 4.14, the model F-value of 17.70 implies the model is significant and there is only 0.01 % chance that a "model F-value" this large could occur due to noise. Values of "Prob>F" less than 0.05 will indicate that the model terms are significant. Only caustic soda conc. (factor A) and fabric type (factor D) are significant model terms while temp.

(factor B) and time (factor C) do not show significant effect on shrinkage within the selected range of the factors.

The "lack of fit F-value "of 0.5508 implies the lack of fit is not significant relative to pure error. There is 55.08 % chance that a "lack of fit F-value "this large could occur due to noise. Non-significant lack of fit is good for the model to fit. The predicted determination coefficient (Pred R^2=0.5479) is in reasonable agreement with the adjusted determination coefficient (Adj R^2=0.6375) which is also satisfactory to confirm the fitness of the model. "Adeq Precision" measures the signal-to-noise ratio where a ratio greater than 4 is desirable. The ratio of 16.063 indicates an adequate signal which implies that this model could be used to navigate the design space (Nasirizadeh *et al.*, 2012). The negative sign in front of the terms in the first order regression model shown in Equation 4.4 and Equations 4.5a and 4.5b indicates antagonistic effect whereas the positive sign shows synergistic effect.

Table 4.13: Model fitting for shrinkage

Sequential model sum of squares [Type I]						
Source	Sum of Squares	df	Mean Square	F-Value	P-Value>F	
Mean vs Total	4320.16	1	4320.16			
Block vs Mean	36.74	1	36.74			
Linear vs Block	**202.79**	**4**	**50.70**	**17.7**	**<0.0001**	**Suggested**
2FI vs Linear	14.22	6	2.37	0.8	0.5794	
Quadratic vs 2FI	18.96	3	6.32	2.46	0.0860	
Cubic vs Quadratic	14.38	10	1.44	0.43	0.9076	Aliased
Residual	49.80	15	3.32			
Total	4657.05	40	116.43			
Lack of fit tests						
Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Linear	74.19	26	2.85	0.99	0.5508	Suggested
2FI	59.97	20	3	1.04	0.5113	
Quadratic	41.01	17	2.41	0.83	0.6451	
Cubic	26.63	7	3.8	1.31	0.3530	Aliased
Pure Error	23.17	8	2.9			
Model summary statistics						
Source	Standard Deviation	R squared	Adjusted R squared	Predicted R squared	PRESS	

Linear	1.69	0.6756	0.6375	0.5479	135.68	Suggested
2FI	1.72	0.7230	0.6241	0.4423	167.40	
Quadratic	1.6	0.7862	0.6750	0.4699	159.11	
Cubic	1.82	0.8341	0.5797	-0.6885	506.80	Aliased

Table 4.14: Analysis of variance (ANOVA) test for significance (shrinkage)

Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Block	36.74	1	36.74			
Model	**202.79**	**4**	**50.70**	**17.7**	**<0.0001**	**Significant**
A-NaOH conc.	102.15	1	102.15	35.67	<0.0001	
B-Temp.	1.06	1	1.06	0.37	0.5465	
C-Time	0.029	1	0.029	0.01	0.9204	
D-Fabric	99.54	1	99.54	34.76	<0.0001	
Residual	97.36	34	2.86			
Lack of Fit	**74.19**	**26**	**2.85**	**0.5508**	**0.5508**	**Not Significant**
Pure Error	23.17	8	2.90			
Cor Total	336.89	39				

Std. Dev.	1.69	R-squared	0.6756
Mean	10.39	Adj R-squared	0.6375
C. V. %	16.28	Pred R-squared	0.5479
PRESS	135.68	Adeq Precisior	16.063

Factor	Coefficient Estimate	df	Standard Error	95 % Confidence interval		VIF
				Low	High	
Intercept	10.20	1	0.27	9.64	10.75	
BLOCK 1	0.98	1				
BLOCK 2	-0.98					
A-NaOH conc.	1.93	1	0.32	1.28	2.59	1.00
B-Temp.	-0.20	1	0.32	-0.86	0.46	1.00
C-Time	0.033	1	0.32	-0.63	0.69	1.00
D-Fabric	-1.58	1	0.27	-2.12	-1.03	1.00

Shrinkage =+10.20+1.93* A-0.20* B+0.033* C-1.58* D …..4.4

Shrinkage (CF) =+5.19571+0.026020* NaOH conc.-9.89359E-003*Temperature+0.012190* Time ……4.5a

Shrinkage (BF)=+2.04071+0.026020* NaOH conc.-9.89359E-003* Temperature +0.012190* Time ……4.5b

4.6.1.2 Diagnostics for shrinkage

The consistency of the data for response “shrinkage” was confirmed from normal probability plot of residuals plotted by DX7 as shown in Figure 4.34. The points are fairly close to a

straight line indicating the validity of the experimental data since the residuals are normally distributed (Wagaw and Chavan, 2012: Myers *et al.*, 2009). The size of the studentized residual should be independent of its predicted value meaning that the spread of the residuals should be approximately the same across all levels of the predicted values. In this case, the plot obtained is okay as shown in Figure 4.35.

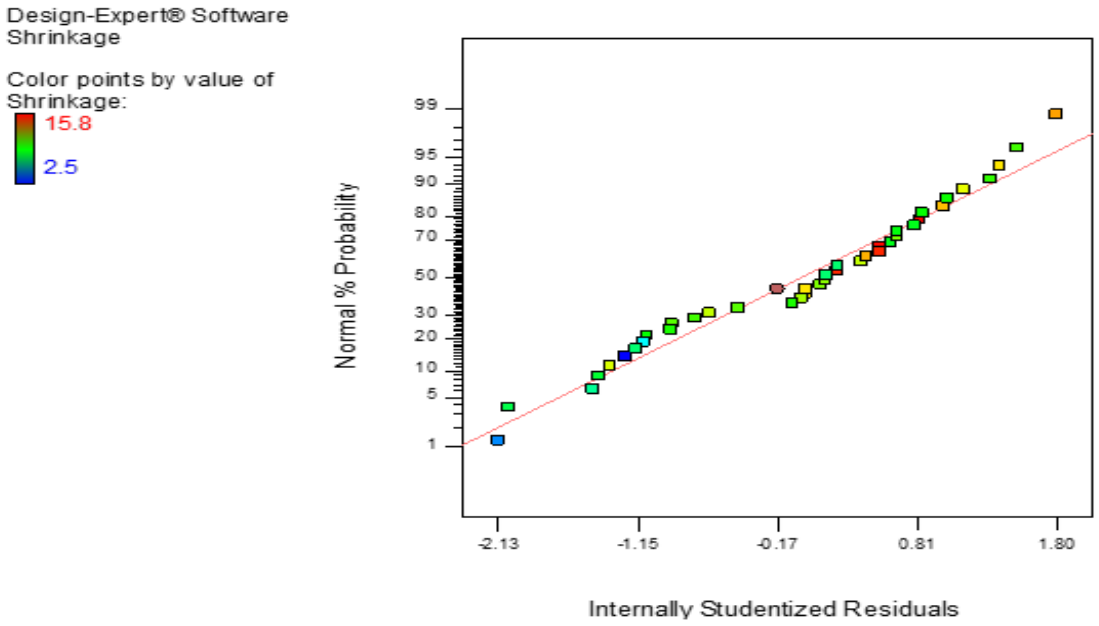


Figure 4.34: Normal Probability plot of residuals

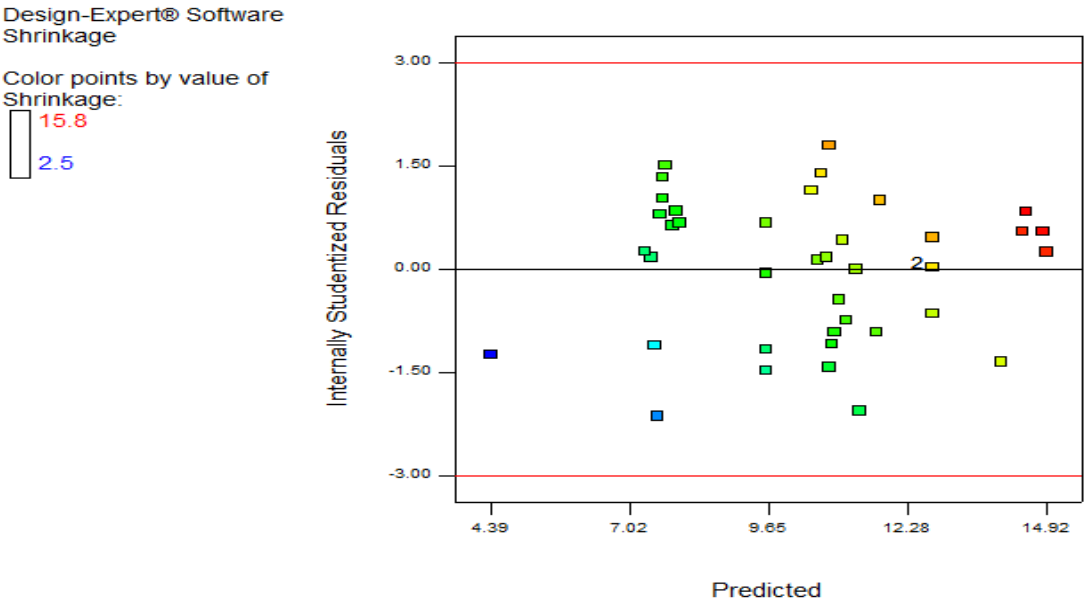


Figure 4.35: Studentized residuals versus predicted

The plot of externally studentized residuals identifies if there are outliers. The plot shown in Figure 4.36 is okay as all the points fall well within the red lines set at plus or minus 3.53. Box-Cox plot was developed to analytically calculate the best power low transformation. Figure 4.37 shows that the current transformation points to a value of 1 for "Lambda" which indicates the power applied to the response values. A lambda of 1 indicates no transformation. If 95 % confidence interval includes 1, then no transformation is recommended as in this case. As shown in Table 4.15, the value of residuals (difference between experimental data and the predicted value) is low showing the precision of the experiments.

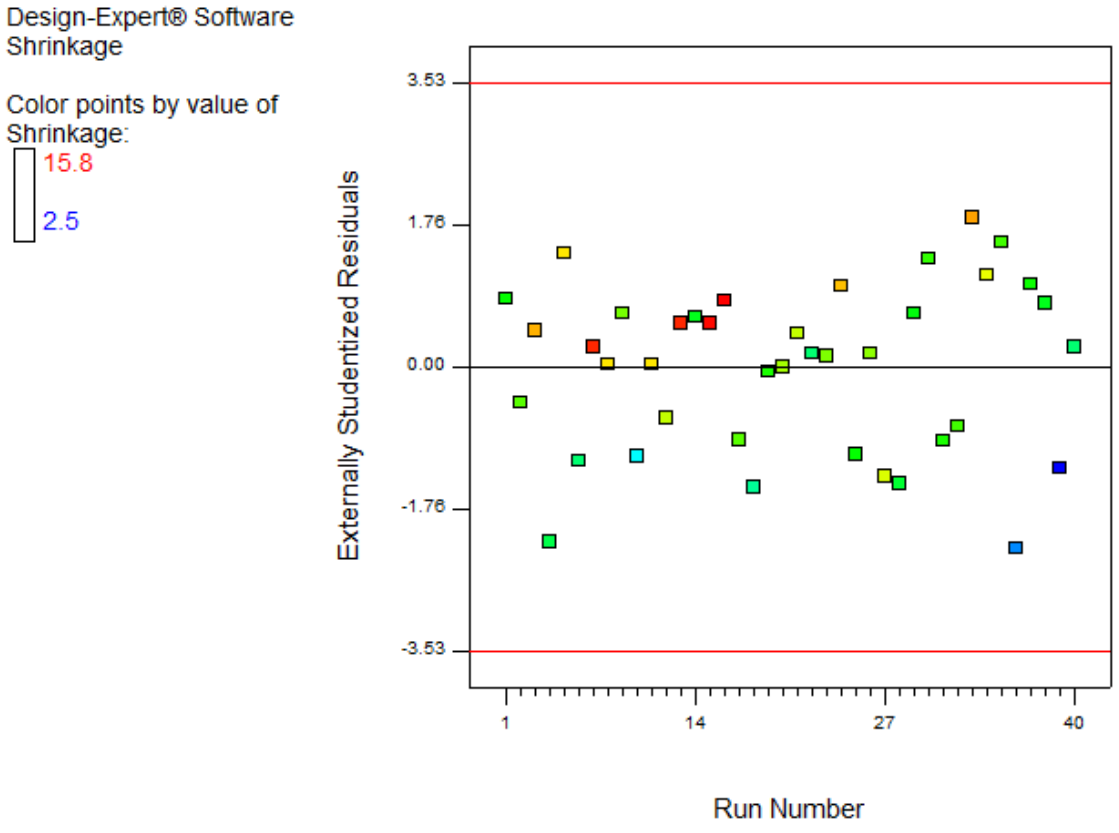


Figure 4.36: Externally studentized residuals

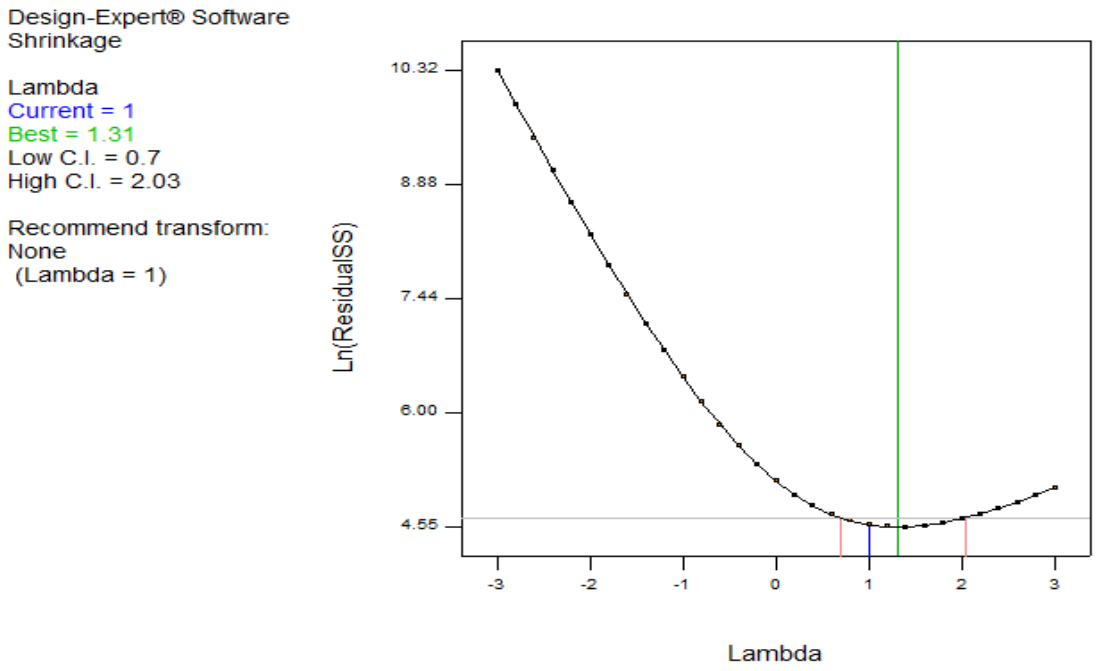


Figure 4.37: Box-Cox plot

Table 4.15: Diagnostics case statistics (shrinkage)

SO	AV	PV	Res.	Lev.	ISR	ESR	IFVD	CD	RO
1	10.30	10.98	-0.68	0.177	-0.445	-0.440	-0.204	0.007	2
2	15.70	14.85	0.85	0.177	0.553	0.547	0.253	0.011	15
3	10.80	10.59	0.21	0.177	0.138	0.136	0.063	0.001	23
4	15.30	14.46	0.84	0.177	0.549	0.544	0.252	0.011	13
5	11.70	11.05	0.65	0.177	0.424	0.419	0.194	0.006	21
6	15.30	14.92	0.38	0.177	0.250	0.246	0.114	0.002	7
7	12.80	10.65	2.15	0.177	1.397	1.418	0.657	0.070	5
8	15.80	14.52	1.28	0.177	0.832	0.828	0.384	0.025	16
9	12.80	12.75	0.048	0.067	0.029	0.029	0.008	0.000	11
10	13.50	12.75	0.75	0.067	0.457	0.452	0.121	0.002	3
11	12.80	12.75	0.048	0.067	0.029	0.029	0.008	0.000	8
12	11.70	12.75	-1.05	0.067	-0.644	-0.638	-0.171	0.005	12
13	4.30	7.54	-3.24	0.191	-2.131	-2.256	-1.096	0.179	36
14	12.00	14.05	-2.05	0.191	-1.346	-1.363	-0.662	0.071	27
15	10.00	11.13	-1.13	0.191	-0.741	-0.736	-0.358	0.022	32
16	12.20	10.46	1.74	0.191	1.140	1.145	0.557	0.051	34
17	11.00	10.74	0.26	0.191	0.170	0.167	0.081	0.001	26
18	9.20	10.85	-1.65	0.191	-1.085	-1.088	-0.529	0.046	25
19	13.7	10.80	2.90	0.088	1.796	1.860	0.576	0.052	33
20	8.50	10.80	-2.30	0.088	-1.421	-1.443	-0.447	0.032	28
21	8.80	7.83	0.97	0.177	0.633	0.627	0.290	0.014	14
22	10.30	11.70	-1.40	0.177	-0.909	-0.907	-0.420	0.030	17

23	7.70	7.43	0.27	0.177	0.173	0.171	0.079	0.001	22
24	11.30	11.30	-2E3	0.177	-0.001	-0.001	-0.000	0.000	20
25	9.20	7.89	1.31	0.177	0.851	0.847	0.392	0.026	1
26	13.30	11.76	1.54	0.177	1.002	1.002	0.464	0.036	24
27	5.80	7.50	-1.70	0.177	-1.106	-1.110	-0.514	0.044	10
28	8.20	11.37	-3.17	0.177	-2.062	-2.172	-1.006	0.152	4
29	7.70	9.60	-1.90	0.067	-1.161	-1.167	-0.312	0.016	6
30	10.70	9.60	1.10	0.067	0.674	0.669	0.179	0.005	9
31	7.20	9.60	-2.40	0.067	-1.466	-1.493	-0.399	0.026	18
32	9.50	9.60	-0.10	0.067	-0.060	-0.059	-0.016	0.000	19
33	2.50	4.39	-1.89	0.191	-1.241	-1.251	-0.608	0.061	39
34	9.50	10.89	-1.39	0.191	-0.916	-0.913	-0.444	0.033	31
35	9.00	7.97	1.03	0.191	0.675	0.669	0.325	0.018	29
36	7.70	7.31	0.39	0.191	0.257	0.253	0.123	0.003	40
37	8.80	7.59	1.21	0.191	0.797	0.793	0.385	0.025	38
38	10.00	7.70	2.30	0.191	1.514	1.544	0.750	0.090	35
39	9.80	7.64	2.16	0.088	1.335	1.352	0.419	0.029	30
40	9.30	7.64	1.66	0.088	1.026	1.027	0.318	0.017	37

SO: Standard order, AV: Actual value, PV: Predicted value, Res.: Residual, Lev.: Leverage, ISR: Internally studentized residuals, ESR: Externally studentized residuals, IFVD: Influence on fitted values drifts, CD: Cooks distance, RO: Run order

4.6.1.3 Main effects

The individual effects of caustic soda conc., temp., and treatment time on shrinkage of BF and CF are respectively shown in Figures 4.38 to 4.43. Figure 4.44 shows shrinkage behaviour by fabric type. ANOVA shown in Table 4.14 indicated that there is no interaction among factors and therefore only main effects are at play.

Caustic soda concentration: The individual (main) effect of caustic soda conc. (Figures 4.38 and 4.39 for BF and CF respectively) on shrinkage was determined at constant temp. (65 ^{o}C) and time (6 min.). As caustic soda conc. increases from 201 to 349 g/l, the percentage shrinkage increases for both BF and CF. Moghassem and Valipour (2013) reported increase in dimensional stability with increase in caustic soda conc. from 200 to 250 g/l.

The degree of swelling during mercerization depends on the conc. of caustic soda. At low conc., caustic soda molecules are hydrated by large number of water molecules and the diameter of the hydrated ions is too large to penetrate into the macromolecular structure of cotton. As conc. of caustic soda increases, the number of water molecules available for the formation of hydrates decreases and thus hydrated ion pairs are formed which are capable of penetrating into the fibre structure by breaking hydrogen bonds and van der Waals forces between cellulose chains resulting in fibre swelling and the corresponding increase in shrinkage (Brahma *et al.*, 2018; Khajavi *et al.*, 2015; Wagaw and Chavan, 2012).

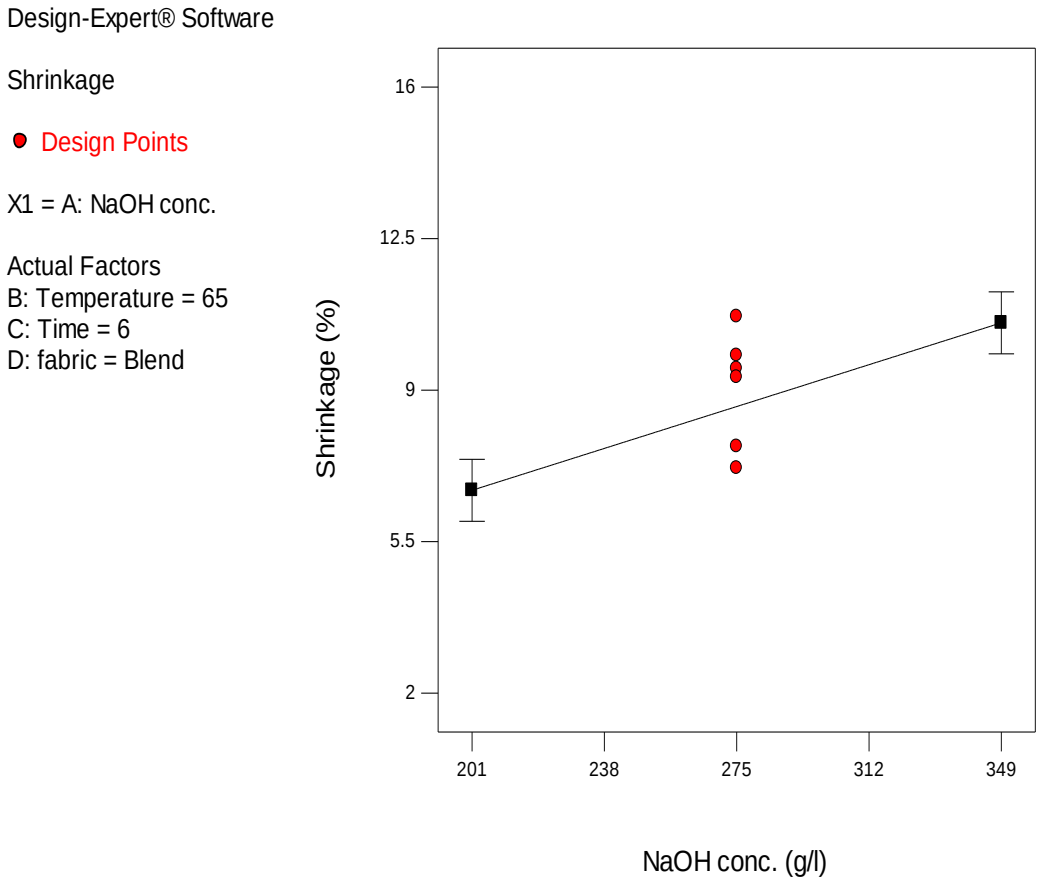


Figure 4.38: Effect of caustic soda conc. on the shrinkage of BF

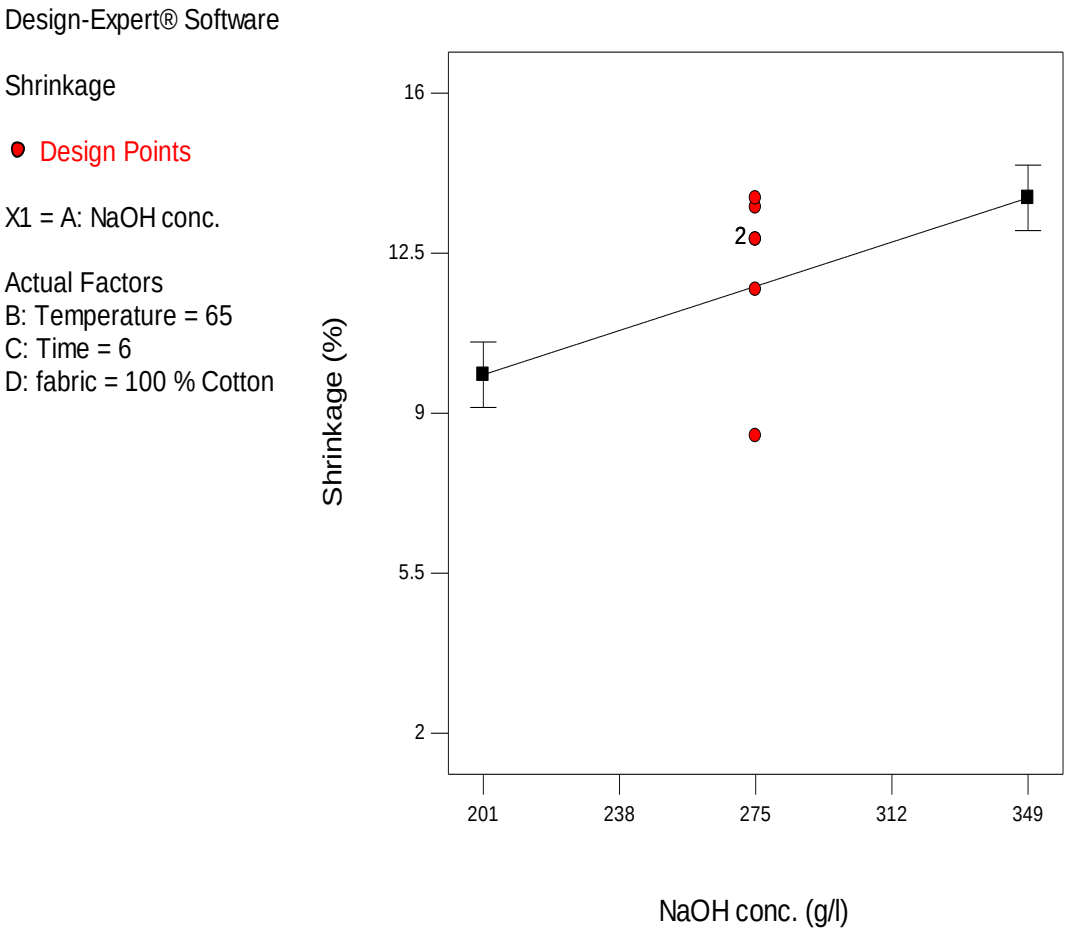


Figure 4.39: Effect of caustic soda conc. on the shrinkage of CF

Temperature: The effect of temperature (Figures 4.40 and 4.41 respectively for BF and CF) on shrinkage was determined at constant caustic soda conc. (275 g/l) and time (6 min.). As temp. increases from 45 to 85 ^{o}C, shrinkage slightly decreases for both BF and CF. This is collaborated with the small antagonistic effect of temperature (coefficient of B) shown in Equation 4.1. Shrinkage of fabric during hot mercerization is much less than that occurring during normal mercerizing (Duckworth and Wrennall, 1977). Kokot and Stewart (1995) reported decrease in longitudinal shrinkage of cotton with increase in mercerization temp.

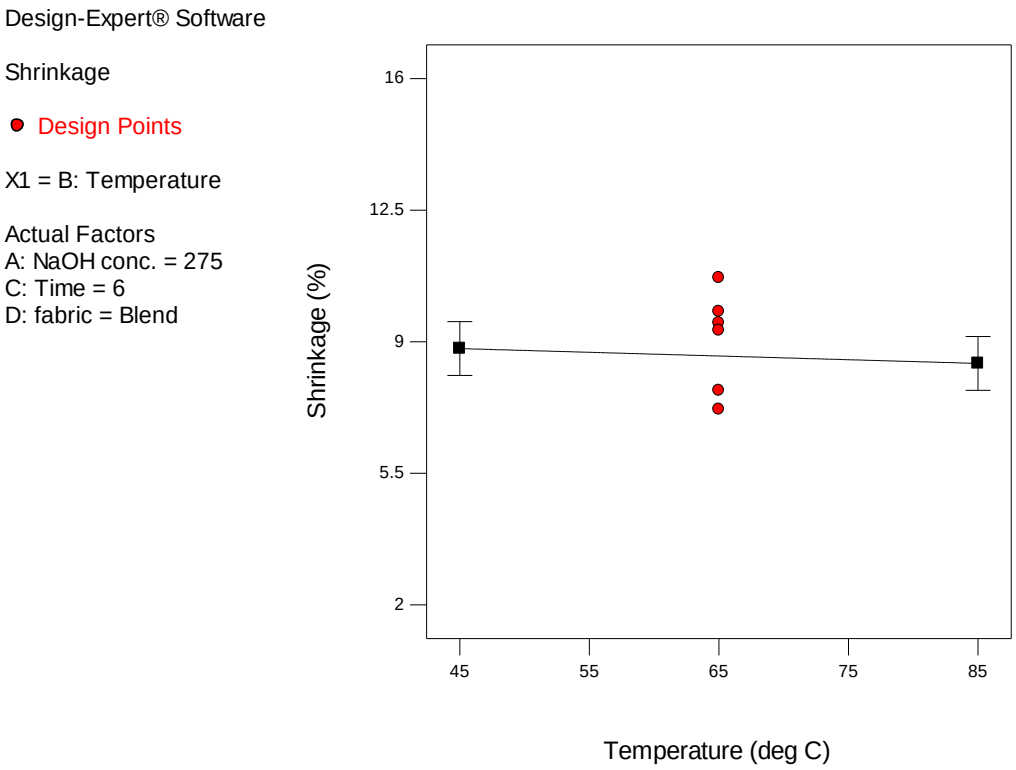


Figure 4.40: Effect of temp. on the shrinkage of BF

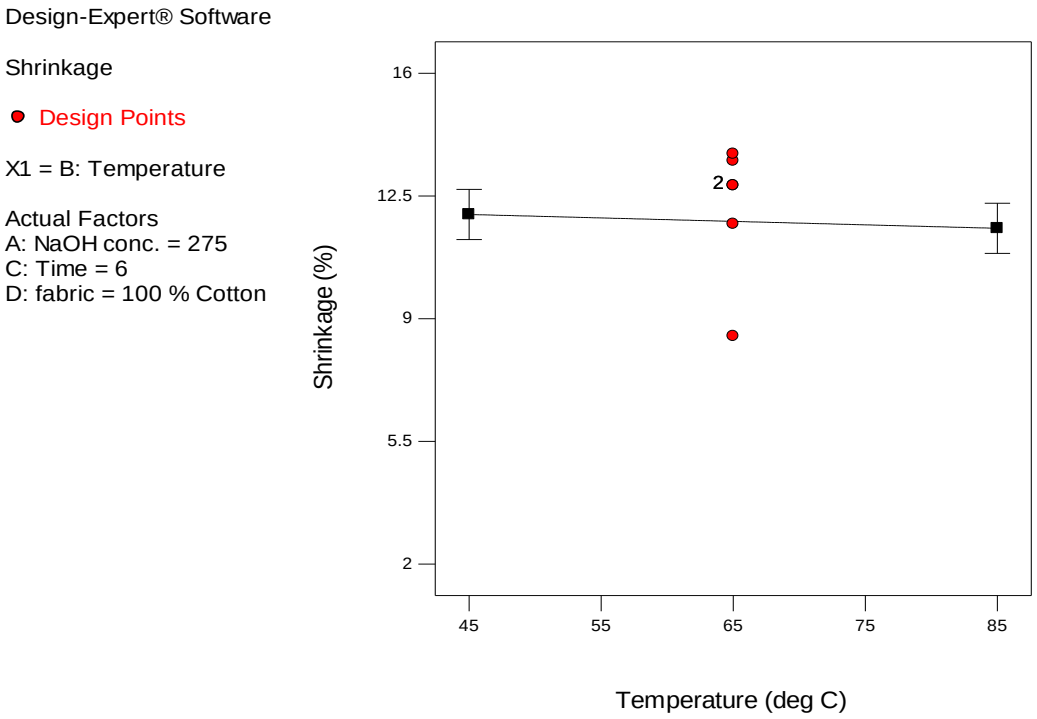


Figure 4.41: Effect of temp. on the shrinkage of CF

Time: The effect of time (Figures 4.42 and 4.43, respectively, for BF and CF) on shrinkage was determined at constant caustic soda conc. (275 g/l) and temp. (65 ^{o}C). As mercerization time increases from 3 to 8 min., shrinkage slightly increases for both BF and CF. This is also corroborated with the little synergistic effect of time (coefficient of C) shown in Equation 4.1. Previous studies similarly reported increase in shrinkage of cotton with increase in treatment time (Gemci, 2010; Moghassem and Valipour, 2013).

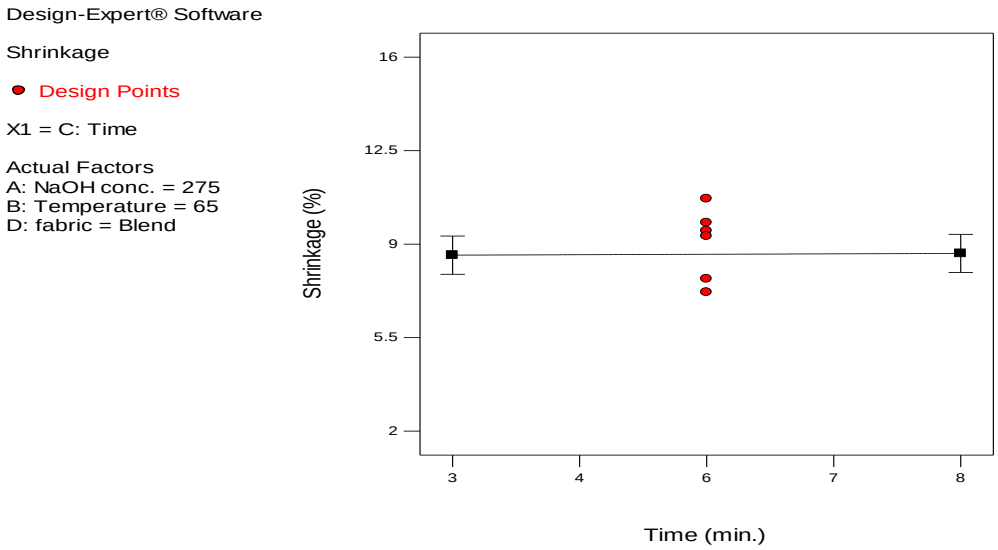


Figure 4.42: Effect of time on the shrinkage of BF

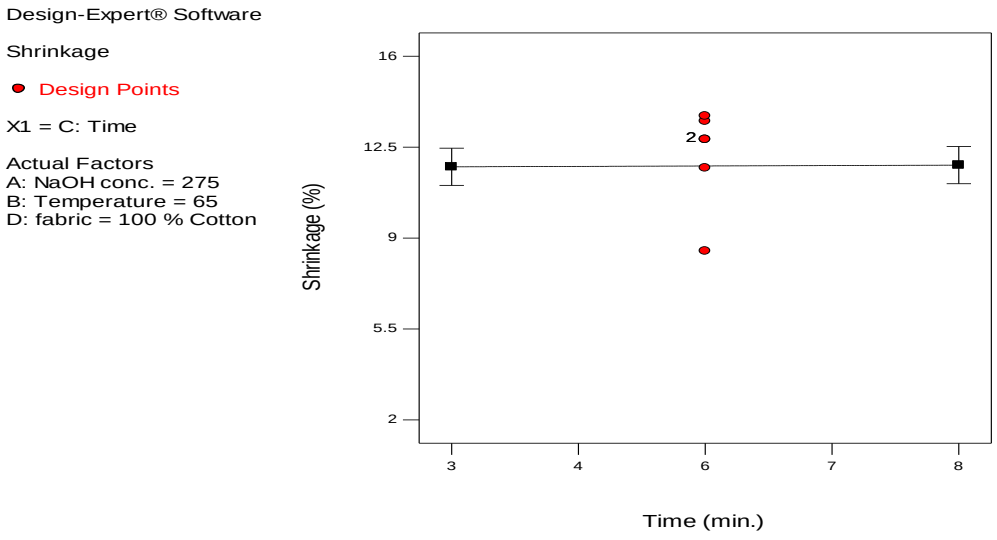


Figure 4.43: Effect of time on the shrinkage of CF

Fabric type: The effect of fabric type (Figure 4.44) on shrinkage was determined at constant caustic soda conc. (275 g/l), temp. (65 ^{o}C), and treatment time (6 min.). CF shrink much more than BF which is attributable to the presence of polyester yarns in the latter fabric. It is well known that synthetic fibres do not swell as much as cotton fibres and this affected the average shrinkage value of the BF.

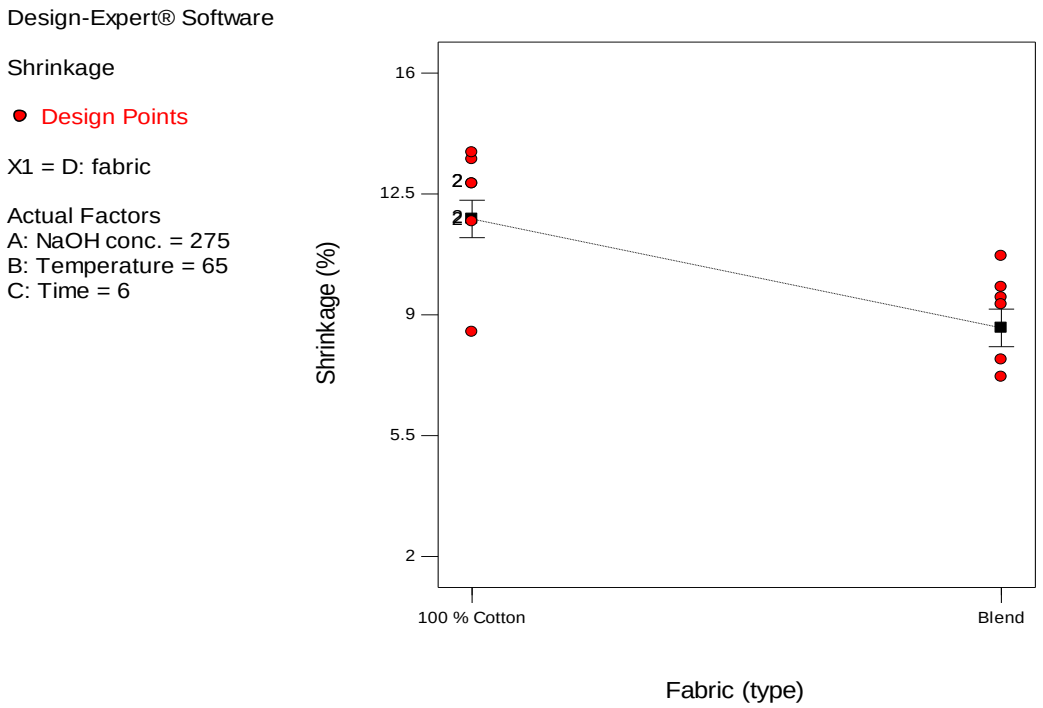


Figure 4.44: Shrinkage behaviour by fabric type

4.6.1.4 Contour and 3D plots

For response surface designs, perturbation plot shows how the response changes as each factor moves from a chosen reference point with all other factors held constant at the reference value. Figures 4.45 and 4.46 (for BF and CF, respectively) show that factor C (time) produces a relatively small effect as it changes from the reference point. Caustic soda conc. (factor A) and temp. (factor B) are further away from the reference point and are therefore chosen to generate contour and 3D plots since those plots show only two factors at a time.

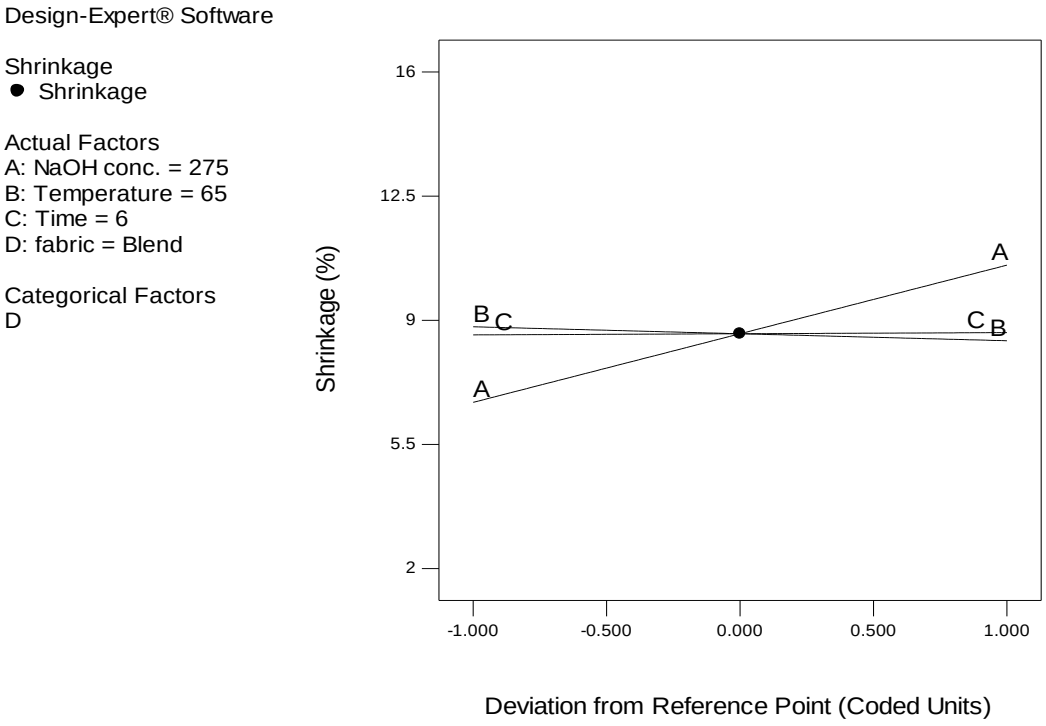


Figure 4.45: Perturbation plot for shrinkage of BF

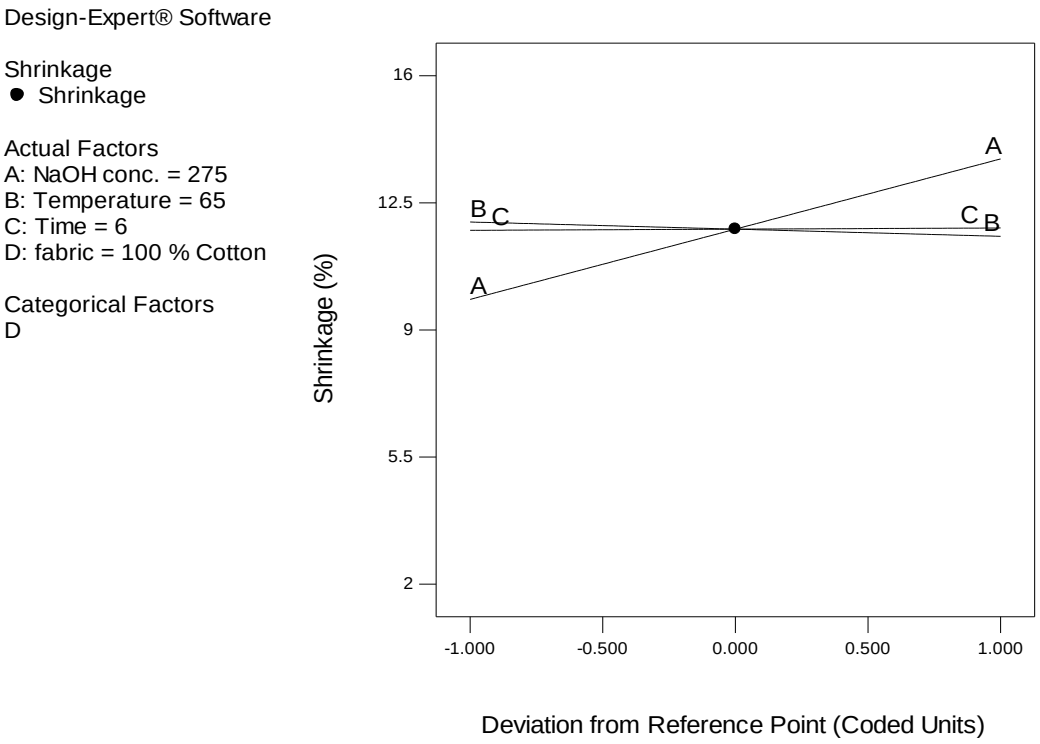


Figure 4.46: Perturbation plot for shrinkage of CF

The contour plots are shown in Figures 4.47 and 4.48 (respectively for BF and CF) while 3D plots are shown in Figures 4.49 and 4.50 (respectively for BF and CF). Contour and 3D plots are maps much like those used by a geologist for topography but instead of displaying elevation they show response (Anderson and Whitcomb, 2017) which in this case is the shrinkage. Each contour represents a combination of input factors (caustic soda conc. and temp.) to produce a constant response (shrinkage) with respective labels. The actual runs are shown as dots and the dots at the centre point (at 275 g/l caustic soda conc.) indicates the number of replicates at this set of conditions. The shape of the contours and 3D plots are "plain" because the model selected is linear.

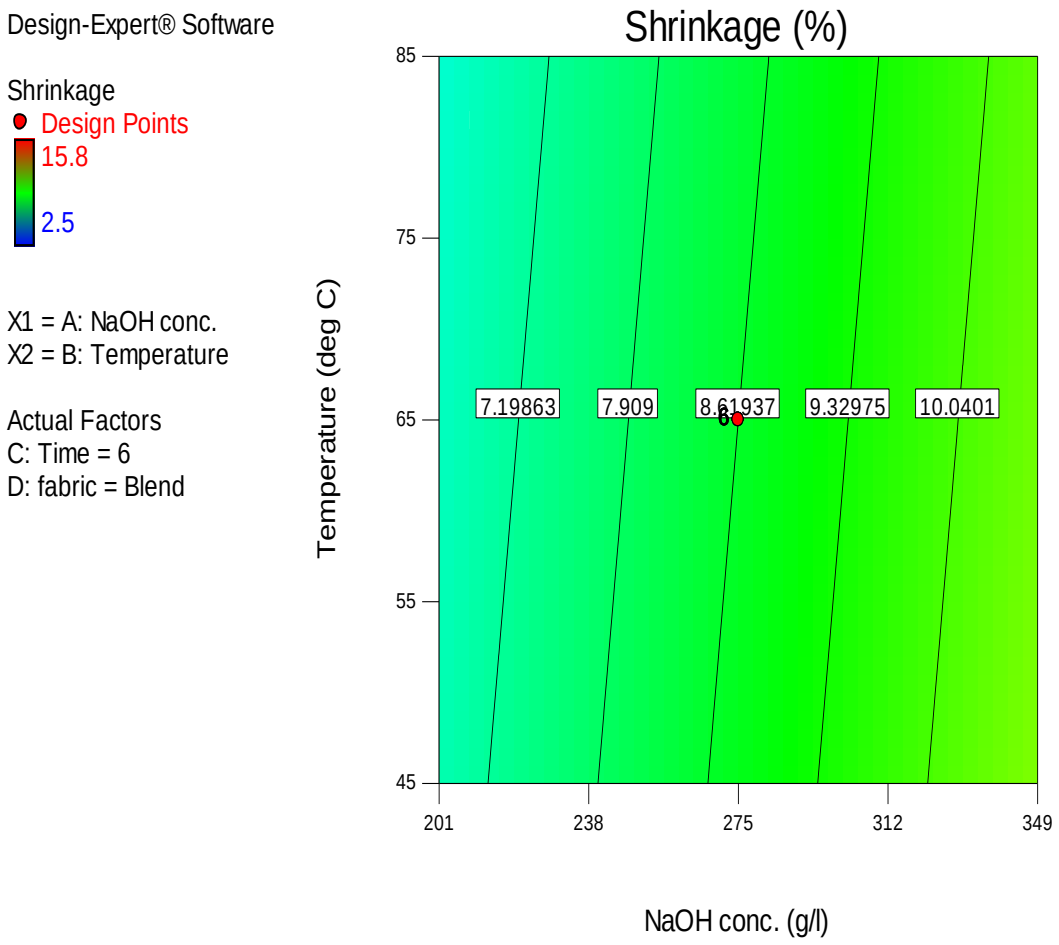


Figure 4.47: Contour plot for shrinkage of BF

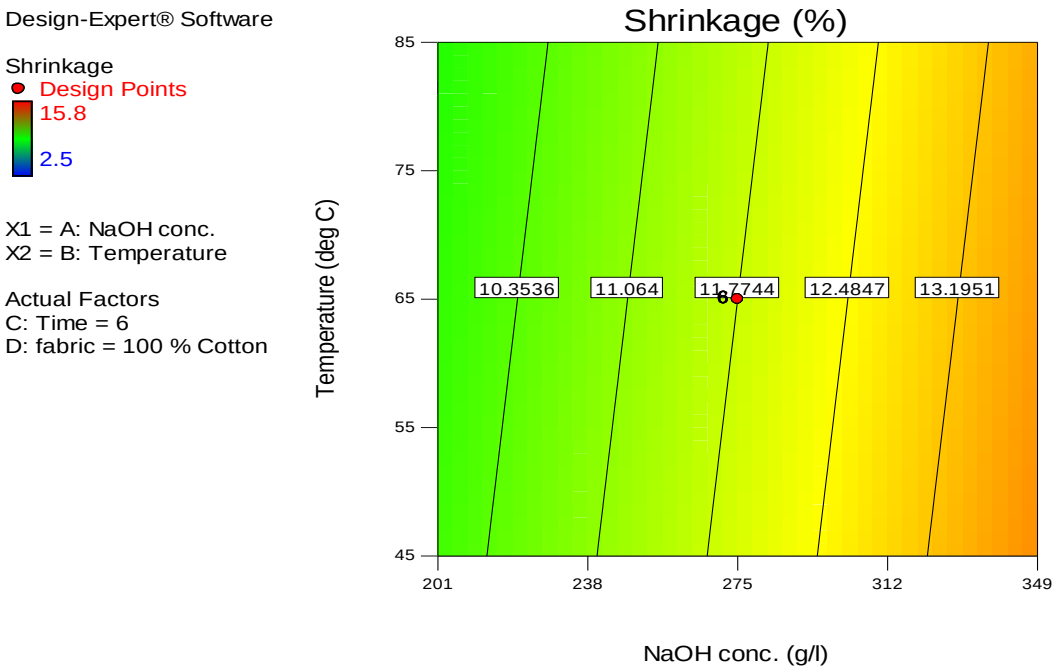


Figure 4.48: Contour plot for shrinkage of CF

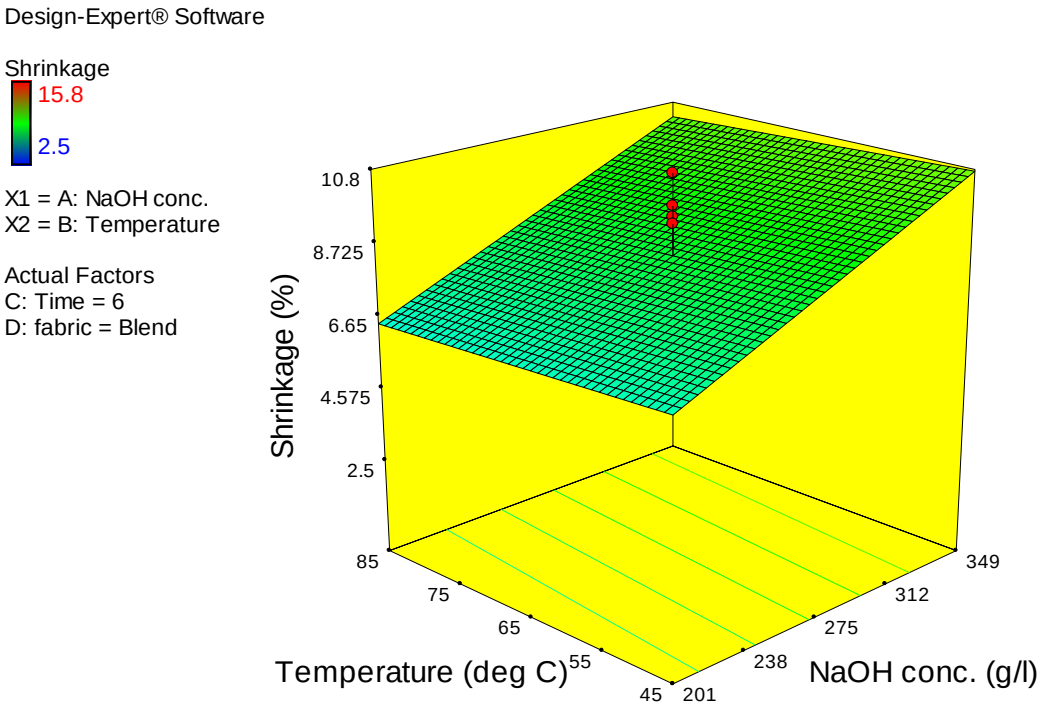


Figure 4.49: 3D plot for shrinkage of BF

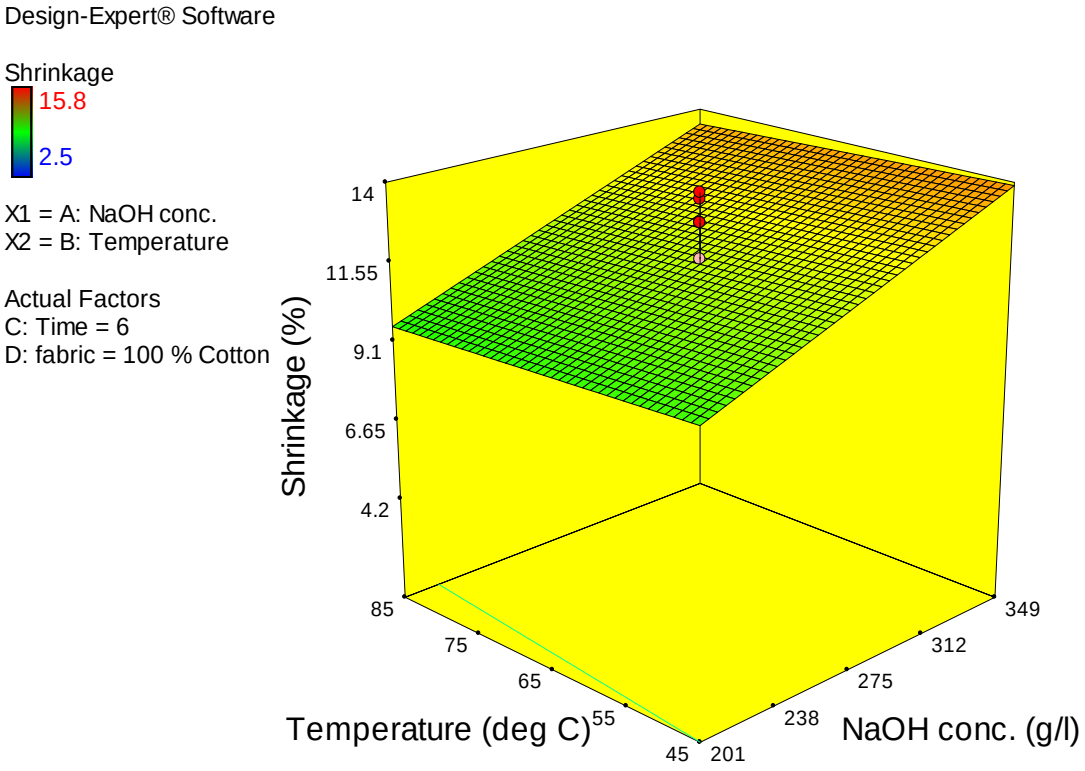


Figure 4.50: 3D plot for shrinkage of CF

4.6.2 Tensile strength

Figures G1 and G2 show load elongation curves for BFPWA and CFWA, respectively while Figures G3 to G82 show load elongation curves for warp and weft in that order for samples 1 to 40 (see Appendix G). Warp and weft way as well as the average tensile strength values obtained from mercerization of BF and CF are shown in Table 4.16. The strength values of the untreated samples are also presented. BFPWA have higher strength values than BFCWE, CFWA, and CFWE under the same treatment conditions which is mainly because it is a synthetic yarn which is usually higher in strength than natural fibres.

Table 4.16: Tensile strength values obtained from mercerized and unmercerized fabrics

Run No.	NaOH Conc. (g/l)	Temp. (^oC)	Time (min.)	Fabric (type)	Tensile Strength± SD (N)		Average Tensile strength (N)
					Warp	Weft	
1	201	45	8	BF	411.32±16.8	119.87±14.6	265.6
2	201	45	3	CF	187.42±46.2	51.69±14.0	119.56
3	275	65	6	CF	181.89±30.3	93.55±15.7	137.72
4	349	85	8	BF	167.64±8.8	103.08±17.8	135.36
5	201	85	8	CF	180.33±40.4	94.97±10.6	137.65
6	275	65	6	BF	399.6±12.5	122.51±10.5	261.06
7	349	45	8	CF	182.7±42.3	92.33±20.9	137.52
8	275	65	6	CF	191.29±27.5	90.14±21.2	140.72
9	275	65	6	BF	389.62±32.2	115.64±24.8	252.63
10	201	85	8	BF	348.64±54.6	114.47±20.3	231.56
11	275	65	6	CF	160.06±30.6	66.35±13.1	113.21
12	275	65	6	CF	152.39±60.8	69.41±17.7	110.90
13	349	85	3	CF	161.46±29.7	62±12.2	111.73
14	201	45	3	BF	414.34±20.7	103.59±22.1	258.97
15	349	45	3	CF	167.91±13.7	72.43±26.6	120.17
16	349	85	8	CF	204.48±26.6	87.03±11.7	154.76
17	349	45	3	BF	417.93±20.6	127.79±8.8	272.86
18	275	65	6	BF	393.73±12.8	113.54±21.8	253.64
19	275	65	6	BF	373.58±14.9	111.81±15.7	242.7
20	349	85	3	BF	343.99±20.3	108.49±23.1	226.23
21	201	45	8	CF	196.85±11.5	85.92±19.0	141.39
22	201	85	3	BF	404.81±9.4	122.67±5.0	263.74
23	201	85	3	CF	183.26±18.9	92.6±8.2	137.93
24	349	45	8	BF	171.14±43.3	71.8±11.9	121.47
25	275	65	10	CF	423.61±25.4	133.44±11.5	278.54
26	275	65	1	CF	204.86±7.1	84.48±17.7	144.67
27	400	65	6	CF	183.35±31.3	68.7±29.5	126.03
28	275	65	6	CF	183.65±26.0	71.12±14.7	127.39
29	275	32	6	BF	426.07±68.3	116.1±10.4	271.09
30	275	65	6	BF	395.47±15.2	136±6.9	265.74
31	400	65	6	BF	295.72±24.7	125.96±10.2	210.84
32	275	32	6	CF	168.41±14.8	68.05±15.9	118.23
33	275	65	6	CF	156.9±25.0	69.16±24.0	113.03
34	275	99	6	CF	189.36±25.3	94.84±11.8	142.1
35	275	65	10	BF	359.09±18.1	126.63±7.7	242.86
36	150	65	6	CF	174.78±25.2	77.82±6.1	126.3
37	275	65	6	BF	383.22±32.2	124.47±14.1	253.85
38	275	65	1	BF	385.65±21.4	123.75±6.3	254.7
39	150	65	6	BF	364.44±15.6	109.3±8.3	236.87
40	275	99	6	BF	155.50±19.1	102.69±22.0	129.10
41	0	-	-	UMCF	147.15±41.7	59.39±19.6	103.27

42	0	-	-	UMBF	358.33±6.2	107.28±7.5	232.81

BF: blend fabric, CF: cotton fabric, UMCF: Unmercerized cotton fabric, UMBF: Unmercerized blend fabric

All mercerized CFWA and CFWE have higher strength values than that of the original untreated sample (UMCF). The major reason for increase in tensile strength may be an alleviation of internal stress and removal of false twists of the fibres in the fabric during swelling process as presence of many convolutions and false twists in the fibres causes weak spots (Lin *et al.,* 2022). Mercerized samples have enhanced longitudinal shrinkage and lateral swelling of fibres which make the fibres appear closer to each other with increased thickness which results in higher tensile strength (Patil *et al*., 2019).

Increase in tensile strength with slack mercerization can also be attributable to the reduction of the crystallinity of the fibres, decrease in the length of their crystallites, and increase in the orientation of the crystallites with respect to fibre axis. From Table of strength and extensibility data, there is considerable variation from the results of different workers because tensile properties can be affected by the condition of processing and testing and also by the species and varieties of cotton (Zeronian *et al.,* 1990).

CFWA are generally stronger than CFWE may be due to the fact that warp yarns are usually sized in preparation for weaving and are normally more twisted to withstand weaving tension (twist improves the strength of yarn). Hari *et al.* (1985) has attributed increase in tensile strength to improve in packing of fibres due to swelling and shrinkage within the yarn which leads to higher interface friction and consequent increase in tensile strength. Except for samples from run number 4, 10, 20, 24, 31, and 40, mercerized BFPWA is stronger than the

original UMBF warp. All the 6 samples with inferior strength values were mercerized either in very high caustic soda conc. (samples 4, 20, 24, 31) high temp. (samples 4, 10, 20, 40) or both which may cause polyester hydrolysis as described by Nateri and Goodarz (2013). For CF, increase in caustic soda conc. (Younesi *et al.,* 2019) and temp. (Khajavi *et al.,* 2015) caused increase in tensile strength.

For the BFPWA, some researchers have noticed a loss of fibre/yarn tenacity as a result weight reduction (Tavanai *et al.,* 2009). The author treated polyester with 350 g/l caustic soda at 55-60 ^{o}C for 15-60 min. and reported reduction in tenacity and extensibility of the yarns in a woven fabric due to weight reduction (hydrolysis). BFWE have higher strength values than CFWE under the same treatment conditions which may be attributable to higher yarn density in the former than in the latter. The mean strength values for BF and CF are respectively 236.95±18.13 N and 136.98±13.7 N.

4.6.2.1 Model fitting and analysis of variance (ANOVA) for tensile strength

As shown in Table 4.17, the selected model was quadratic which was found to have significant lack of fit in ANOVA (Table 4.18). The selected model should have insignificant lack of fit. Lack of fit in this case is significant (because the probability value of 0.0007 is far lower than the threshold value of 0.05) and therefore the model can not be used as a response predictor. The predicted determination coefficient (Pred R^2=0.3976) is not as close to the adjusted determination coefficient (Adj R^2=0.7254) which indicate a large block effect or a possible problem with the model and/or data. Model reduction to “linear” still has significant lack of fit. Similarly, Khajavi *et al.* (2015) could not fit a model for the tenacity of conventionally mercerized samples within the selected range of tenacity values.

Table 4.17: Model fitting for tensile strength

Source	Sum of Squares	df	Mean Square	F-Value	P-Value>F	
Sequential model sum of squares [Type I]						
Mean vs Total	1.4E+006	1	1.4E+006			
Block vs Mean	259.42	1	259.42			
Linear vs Block	1.03E+005	4	25790.62	16.31	< 0.0001	
2FI vs Linear	15451.49	6	2575.25	1.88	0.1194	
Quadratic vs 2FI	**9972.17**	**3**	**3324.06**	**2.93**	**0.0531**	**Suggested**
Cubic vs Quadratic	19258.47	10	1925.85	3.18	0.0215	Aliased
Residual	9095.95	15	606.40			
Total	1.56E+006	40	38885.82			
Lack of fit tests						
Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Linear	52688.56	26	2026.48	14.88	0.0003	
2FI	37237.07	20	1861.85	13.67	0.0004	
Quadratic	**27264.90**	**17**	**1603.82**	**11.78**	**0.0007**	**Suggested**
Cubic	8006.43	7	1143.78	8.40	0.0038	Aliased
Pure Error	1089.53	8	136.19			
Model summary statistics						
Source	Standard Deviation	R squared	Adjusted R squared	Predicted R squared	PRESS	
Linear	39.77	0.6573	0.6170	0.4923	79677.79	
2FI	37.00	0.7558	0.6686	0.4037	93579.17	
Quadratic	**33.68**	**0.8193**	**0.7254**	**0.3976**	**94541.93**	**Suggested**
Cubic	24.63	0.9420	0.8532	-0.4222	2.2E+005	Aliased

Table 4.18: Analysis of variance (ANOVA) test for significance (tensile strength)

Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Block	259.42	1	259.42			
Model	**1.3E+005**	**13**	**9891.24**	**8.72**	**<0.0001**	**significant**
A-NaOH conc.	1976.73	1	1976.73	1.74	0.1987	
B-Temp.	813.51	1	813.51	0.72	0.4051	
C-Time	423.24	1	423.24	0.37	0.5468	
D-Fabric	99949.01	1	99949.01	88.12	<0.0001	
AB	388.78	1	388.78	0.34	0.5635	
AC	502.99	1	502.99	0.44	0.5115	
AD	1565.03	1	1565.03	1.38	0.2512	
BC	804.43	1	804.43	0.71	0.4077	
BD	2793.22	1	2793.22	2.46	0.1291	
CD	9397.04	1	9397.04	8.29	0.0081	

A^2	1301.29	1	1301.29	1.15	0.2943	
B^2	3005.16	1	3005.16	2.65	0.1161	
C^2	4709.81	1	4709.81	4.15	0.0523	
Residual	28354.43	25	1134.18			
Lack of Fit	**27264.90**	**17**	**1603.82**	**11.78**	**0.0007**	**Significant**
Pure Error	1089.53	8	136.19			
Cor Total	1.6E+005	39				

Std. Dev.	33.68	R-squared	0.8193
Mean	186.96	Adj R-squared	0.7254
C. V. %	18.01	Pred R-squared	0.3976
PRESS	94541.93	Adeq Precisior	9.926

Factor	Coefficient Estimate	df	Standard Error	95 % Confidence interval		VIF
				Low	High	
Intercept	190.33	1	9.82	170.11	210.56	
BLOCK 1	-2.68	1				
BLOCK 2	2.68					
A-NaOH conc.	-8.51	1	6.44	-21.78	4.76	1.00
B-Temp.	-5.46	1	6.44	-18.73	7.81	1.00
C-Time	3.94	1	6.44	-9.34	17.21	1.00
D-Fabric	49.99	1	5.32	39.02	60.95	1.00
AB	4.93	1	8.42	-12.41	22.27	1.00
AC	-5.61	1	8.42	-22.95	11.73	1.00
AD	-7.57	1	6.44	-20.84	5.70	1.00
BC	7.09	1	8.42	-10.25	24.43	1.00
BD	-10.11	1	6.44	-23.38	3.16	1.00
CD	-18.55	1	6.44	-31.82	-5.28	1.00
A^2	-6.72	1	6.28	-19.65	6.20	1.00
B^2	-10.21	1	6.28	-23.14	2.71	1.00
C^2	12.79	1	6.28	-0.14	25.71	1.00

4.6.2.2 Diagnostics (tensile strength)

Diagnosis of residuals showed abnormality hence the selected model is not statistically solid. Figure 4.51 shows that many residuals are not really close to a straight line indicating that they are not normally distributed. As shown in Figure 4.52, the sizes of the studentized residuals are not approximately the same across all levels of the predicted values. Figure 4.53 shows that there is a point outside the residuals demarcated by a red line indicating that there is an outlier. As shown in Figure 4.54**,** A lambda of 1 indicates no transformation. If 95 % confidence interval includes 1, then no transformation is recommended. Table 4.19 shows that

the difference between the predicted values and the experimental results are really high coupled with the warnings shown in run order 24, 25, 38, and 40 with regards to either ESR, IFVD, and CD.

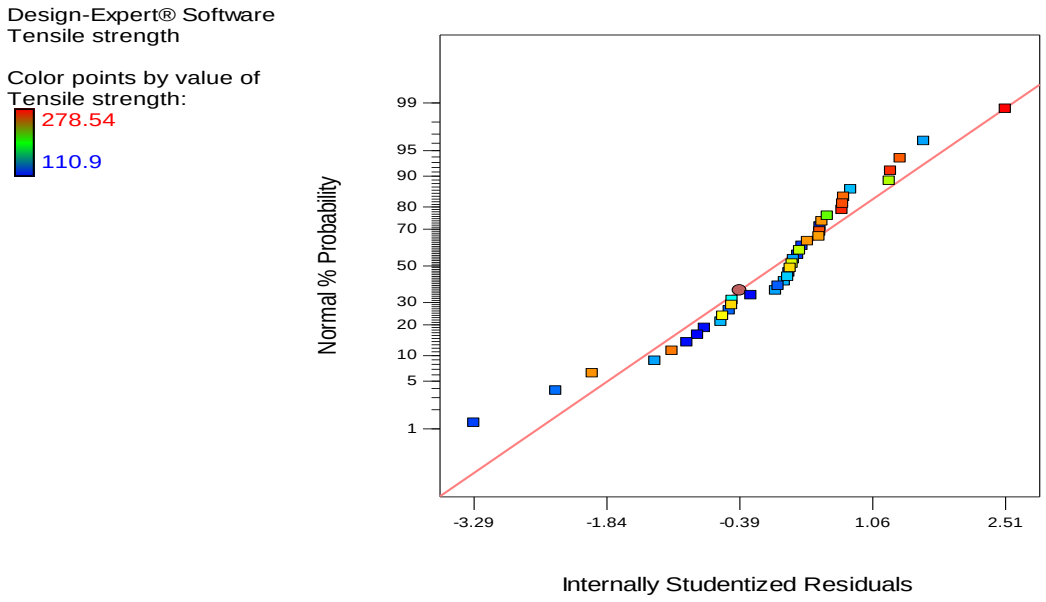


Figure 4.51: Normal probability plot of residuals

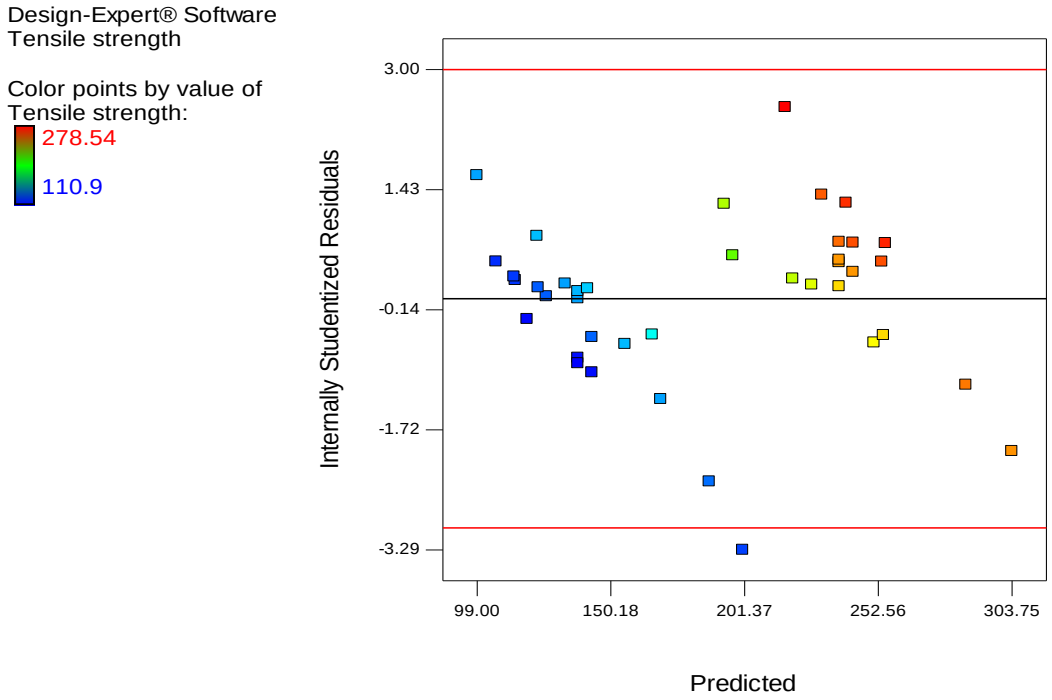


Figure 4.52: Studentized residuals versus predicted

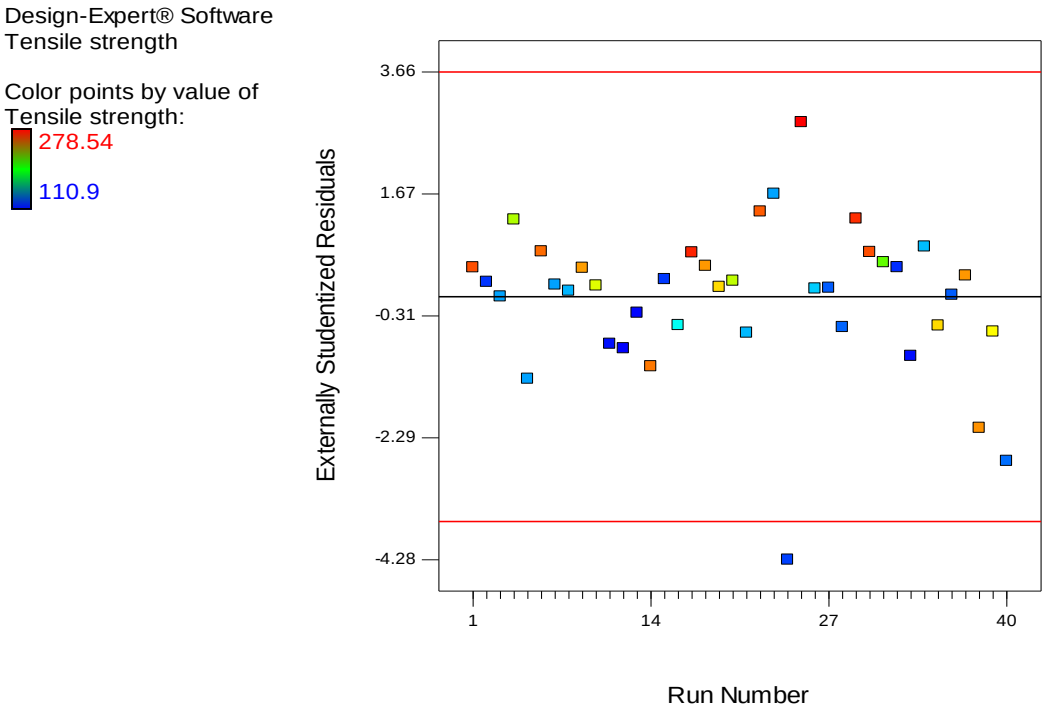


Figure 4.53: Externally studentized residuals

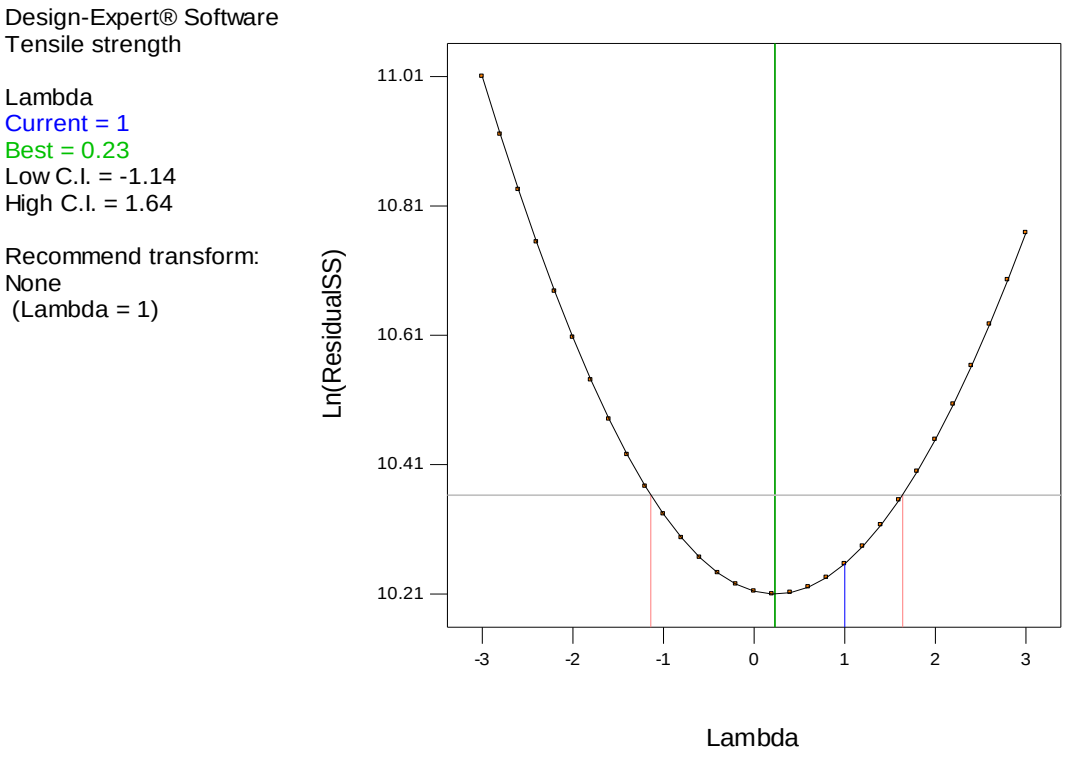


Figure 4.54: Box-Cox plot

Table 4.19: Diagnostics case statistics (tensile strength)

SO	AV	PV	Res.	Lev.	ISR	ESR	IFVD	CD	RO
1	119.56	113.73	5.83	0.488	0.242	0.237	0.232	0.004	2
2	120.17	113.21	6.96	0.488	0.289	0.284	0.277	0.005	15
3	137.93	99.00	38.93	0.488	1.615	1.672	1.632	0.166	23
4	111.73	118.19	-6.46	0.488	-0.268	-0.263	-0.257	0.005	13
5	141.39	155.73	-14.34	0.488	-0.595	-0.587	-0.573	0.022	21
6	137.52	132.78	4.74	0.488	0.197	0.193	0.188	0.002	7
7	137.65	169.36	-31.71	0.488	-1.316	-1.336	-1.304	0.110	5
8	154.76	166.13	-11.37	0.488	-0.472	-0.464	-0.453	0.014	16
9	113.21	137.66	-24.45	0.122	-0.775	-0.769	-0.287	0.006	11
10	137.72	137.66	0.056	0.122	0.002	0.002	0.001	0.000	3
11	140.72	137.66	3.06	0.122	0.097	0.095	0.035	0.000	8
12	110.90	137.66	-26.76	0.122	-0.848	-0.843	-0.315	0.007	12
13	126.30	125.59	0.71	0.468	0.029	0.028	0.026	0.000	36
14	126.03	122.44	3.59	0.468	0.146	0.143	0.134	0.001	27
15	118.23	106.31	11.92	0.468	0.485	0.478	0.448	0.014	32
16	142.10	121.97	20.13	0.468	0.820	0.814	0.764	0.039	34
17	144.67	141.39	3.28	0.468	0.134	0.131	0.123	0.001	26
18	278.54	217.02	61.52	0.468	2.505	2.836	*** 2.66**	0.368	25
19	113.03	143.03	-30.00	0.150	-0.966	-0.965	-0.405	0.011	33
20	127.39	143.03	-15.64	0.150	-0.504	-0.496	-0.208	0.003	28
21	258.97	286.16	-27.19	0.488	-1.128	-1.135	-1.107	0.081	14
22	272.86	255.36	17.50	0.488	0.726	0.719	0.701	0.033	17
23	263.74	230.98	32.76	0.488	1.359	1.384	1.350	0.117	22
24	226.23	219.90	6.33	0.488	0.263	0.258	0.251	0.004	20
25	265.60	253.97	11.63	0.488	0.482	0.475	0.463	0.015	1
26	121.47	200.74	-79.27	0.488	*** -3.28**	**** -4.28**	*** -4.17**	0.687	24
27	231.56	227.15	4.41	0.488	0.183	0.179	0.175	0.002	10
28	223.53	193.64	29.89	0.488	1.240	1.254	1.224	0.098	4
29	261.06	237.64	23.42	0.122	0.742	0.735	0.274	0.005	6
30	252.63	237.64	14.99	0.122	0.475	0.468	0.175	0.002	9
31	253.64	237.64	16.00	0.122	0.507	0.499	0.186	0.002	18
32	242.70	237.64	5.06	0.122	0.160	0.157	0.059	0.000	19
33	236.87	251.03	-14.16	0.468	-0.577	-0.569	-0.534	0.020	39
34	210.84	196.95	13.89	0.468	0.565	0.558	0.523	0.019	31
35	271.09	240.30	30.79	0.468	1.254	1.269	1.191	0.092	29
36	129.10	187.93	-58.83	0.468	-2.395	-2.674	*** -2.51**	0.337	40
37	254.70	303.75	-49.05	0.468	-1.997	-2.135	*** -2.00**	0.234	38
38	242.86	254.60	-11.74	0.468	-0.478	-0.471	-0.442	0.013	35
39	265.74	243.00	22.74	0.150	0.732	0.725	0.305	0.006	30
40	253.85	243.00	10.85	0.150	0.349	0.343	0.144	0.001	37

SO: Standard order, AV: Actual value, PV: Predicted value, Res: Residual, Lev: Leverage, ISR: Internally studentized residuals, ESR: Externally studentized residuals, IFVD: Influence on fitted values drifts, CD: Cooks distance, RO: Run order

4.6.2.3 Main and interaction effects

Since the model for tensile strength did not fit and diagnosis show anomaly, there is no need to generate regression equations or factor effects as the model may not be a good response predictor.

4.6.3 Elongation

Warp and weft way as well as average elongation values obtained from mercerization of BF and CF are presented in Table 4.20. Elongation values for the 2 unmercerized samples are also presented. The elongation of original untreated UMBF warp was about three times higher than that of the original unmercerized CFWA indicating that the former is more elastic than the latter before treatment. Caustic treatment of BFPWA has imparted little increase in elongation compared with that of the original untreated sample (with elongation of 25.03 mm). There is much higher increase in elongation of CFWA than that of CFWE. BFCWE have higher elongation than CFWE which may be due to the fact that the former has higher thread density and lower count than that of the latter. The mean average elongation values for BF and CF are, respectively, 24.96±1.4 mm and 21.28±2.6 mm.

Table 4.20: Elongation values obtained from mercerized and unmercerized samples

Run No.	NaOH Conc. (g/l)	Temp. (°C)	Time (min.)	Fabric (type)	Elongation± SD (mm)		Average Elongation (mm)
					Warp	Weft	
1	201	45	8	BF	27.63±0.9	28.81±1.7	26.22
2	201	45	3	CF	18.95±0.9	16.7±2.2	17.83
3	275	65	6	CF	21.05±1.3	19.21±2.0	20.13
4	349	85	8	BF	27.43±0.5	23.67±1.7	25.55
5	201	85	8	CF	21.97±1.5	19.2±1.3	20.59
6	275	65	6	BF	27.4±0.8	26.37±2.9	26.89
7	349	45	8	CF	27.95±2.0	20.21±1.9	24.08
8	275	65	6	CF	25.66±1.7	20.4±2.1	23.03

9	275	65	6	BF	26.05±1.3	22.92±2.1	24.49
10	201	85	8	BF	26.08±2.0	20.65±2.2	23.37
11	275	65	6	CF	21.52±3.0	17.18±1.6	19.35
12	275	65	6	CF	23.18±4.5	18.48±1.7	20.83
13	349	85	3	CF	25.45±2.0	18.6±1.1	22.03
14	201	45	3	BF	26.15±1.5	20.13±2.3	23.14
15	349	45	3	CF	22.81±1.9	17.83±2.8	20.32
16	349	85	8	CF	27.99±1.2	22.09±1.5	25.04
17	349	45	3	BF	29.4±0.6	15.92±1.3	22.66
18	275	65	6	BF	27.64±0.5	23.32±3.5	25.48
19	275	65	6	BF	26.93±0.6	24.38±1.8	25.66
20	349	85	3	BF	26.09±1.2	24.06±1.7	25.08
21	201	45	8	CF	21.68±1.4	17.7±1.1	19.69
22	201	85	3	BF	26.75±0.7	22.95±1.2	24.85
23	201	85	3	CF	22.5±1.9	19.38±1.5	20.94
24	349	45	8	BF	32.9±1.9	17.84±1.4	25.37
25	275	65	10	CF	28.39±1.7	21.87±2.5	25.13
26	275	65	1	CF	25.35±0.9	19.35±1.2	22.35
27	400	65	6	CF	24.39±1.8	18.58±2.7	21.49
28	275	65	6	CF	23.58±1.9	17.71±0.9	20.65
29	275	32	6	BF	27.29±2.1	24.97±1.6	26.13
30	275	65	6	BF	27.18±0.7	22.75±0.8	24.97
31	400	65	6	BF	22.84±0.9	21.88±2.4	22.36
32	275	32	6	CF	24.4±2.1	18.73±1.2	21.57
33	275	65	6	CF	25.2±2.4	16.37±2.2	20.79
34	275	99	6	CF	25.71±1.0	20.53±1.0	23.12
35	275	65	10	BF	26.06±1.1	26.49±1.2	26.28
36	150	65	6	CF	16.57±0.8	16.53±2.7	16.55
37	275	65	6	BF	27.78±0.9	26.29±1.4	27.04
38	275	65	1	BF	28.2±1.1	24.65±1.6	26.42
39	150	65	6	BF	26.78±0.8	14.85±0.9	20.82
40	275	99	6	BF	30.11±1.0	22.89±3.0	26.51
41	-	-	-	UMCF	8.42±3.6	12.87±1.4	10.65
42	-	-	-	UMBF	25.03±2.2	10.85±2.7	17.94

BF: blend fabric, CF: cotton fabric, UMCF: Unmercerized cotton fabric, UMBF: Unmercerized blend fabric

Slacked mercerized fabric usually gains elastic properties (Shamey and Hussein, 2005; Goldthwait and Murphy, 1955). Swelling cause cotton materials whether fibre, yarn, or fabric to tend to shrink in concentrated alkali solution thereby improving elasticity. Zeronian *et al.* (1990) attributed the increase in elasticity of mercerized samples to increase in the mobility of

crystallites in cotton as they are shortened with the corresponding increase in the number of less ordered (amorphous) regions.

It is reasonable to suggest that fabric extensibility generally increases with increase in areal density. Slacked mercerized fabrics are heavy with high density due to shrinkage thus have high extensibility at low stress deformation (Patil *et al.,* 2019). Increase in elongation due to caustic soda treatment may also be attributable to the fact that the crystalline structure of cellulose is translated from cellulose I to cellulose II which consist of anti-parallel arrangements of cellulose molecular chains (Tatsumi *et al.,* 2022) and this arrangement renders increased free volume between chains causing molecules to slide over each other more easily (Younesi *et al.,* 2019).

4.6.3.1 Model fitting and analysis of variance (ANOVA) for elongation

As shown in Table 4.21, the suggested model is quadratic with insignificant lack of fit because the probability value of 0.8466 exceeds the threshold value of 0.05 (Table 4.22). The quadratic model selected exhibits low standard deviation, high coefficient of determination and low PRESS. Values of "Prob>F" less than 0.05 will indicate that the model terms are significant. Caustic soda conc. (factor A), temp. (factor B), time (factor C), fabric type (factor D), AD, BC, A^2, and C^2 are significant model terms.

The predicted determination coefficient (Pred R^2=0.7825) is in reasonable agreement with the adjusted determination coefficient (Adj R^2=0.8490) which is also satisfactory to confirm the fitness of the model. "Adeq Precision" ratio of 17.908 indicates an adequate signal which implies that this model could be used to navigate the design space. The negative sign in front

of the terms in the second order polynomial model shown in Equation 4.6 and Equations 4.7a and 4.7b indicates antagonistic effect whereas the positive sign shows synergistic effect.

Table 4.21: Model fitting (elongation)

Sequential model sum of squares [Type I]						
Source	Sum of Squares	df	Mean Square	F-Value	P-Value>F	
Mean vs Total	21381.38	1	21381.38			
Block vs Mean	0.53	1	0.53			
Linear vs Block	173.84	4	43.46	14.09	<0.0001	
2FI vs Linear	24.37	6	4.06	1.41	0.2445	
Quadratic vs 2FI	**52.76**	**3**	**17.59**	**15.88**	**<0.0001**	**Suggested**
Cubic vs Quadratic	13.99	10	1.40	1.53	0.2205	Aliased
Residual	13.70	15	0.91			
Total	21660.59	40	541.51			
Lack of fit tests						
Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Linear	92.26	26	3.55	2.26	0.1163	
2FI	67.89	20	3.39	2.16	0.1327	
Quadratic	**15.11**	**17**	**0.89**	**0.56**	**0.8466**	**Suggested**
Cubic	1.12	7	0.16	0.10	0.9966	Aliased
Pure Error	12.58	8	1.57			
Model summary statistics						
Source	Standard Deviation	R squared	Adjusted R squared	Predicted R squared	PRESS	
Linear	1.76	0.6238	0.5795	0.4537	152.25	
2FI	1.70	0.7113	0.6081	0.4377	156.69	
Quadratic	**1.05**	**0.9006**	**0.8490**	**0.7825**	**60.60**	**Suggested**
Cubic	0.96	0.9508	0.8755	0.8400	44.59	Aliased

Table 4.22: Analysis of variance (ANOVA) test for significance (elongation)

Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Block	0.53	1	0.53			
Model	**250.99**	**13**	**19.31**	**17.43**	**<0.0001**	**Significant**
A-NaOH conc.	21.79	1	21.79	19.68	0.0002	
B-Temp.	4.75	1	4.75	4.29	0.0489	
C-Time	11.21	1	11.21	10.12	0.0039	
D-Fabric	136.09	1	136.09	122.87	<0.0001	
AB	0.36	1	0.36	0.33	0.5737	
AC	2.92	1	2.92	2.64	0.1167	
AD	10.65	1	10.65	9.62	0.0047	
BC	5.95	1	5.95	5.38	0.0289	
BD	1.89	1	1.89	1.71	0.2032	

CD	2.59	1	2.59	2.34	0.1388	
A^2	36.00	1	36.00	32.5	<0.0001	
B^2	2.69	1	2.69	2.43	0.1314	
C^2	8.96	1	8.96	8.09	0.0087	
Residual	27.69	34	2.86			
Lack of Fit	**15.11**	**26**	**2.85**	**0.56**	**0.8466**	**Not Significant**
Pure Error	12.58	8	2.90			
Cor Total	279.21	39				

Std. Dev.	1.05	R-squared	0.9006
Mean	23.12	Adj R-squared	0.8490
C. V. %	4.55	Pred R-squared	0.7825
PRESS	60.60	Adeq Precisior	17.908

Factor	Coefficient Estimate	df	Standard Error	95 % Confidence interval		VIF
				Low	High	
Intercept	23.32	1	0.31	22.69	23.95	
BLOCK 1	-0.12	1				
BLOCK 2	0.12					
A-NaOH conc.	0.89	1	0.20	0.48	1.31	1.00
B-Temp.	0.42	1	0.20	2.123E-003	0.83	1.00
C-Time	0.64	1	0.20	0.23	1.06	1.00
D-Fabric	1.84	1	0.17	1.50	2.19	1.00
AB	0.15	1	0.26	-0.39	0.69	1.00
AC	0.43	1	0.26	-0.11	0.97	1.00
AD	-0.62	1	0.20	-1.04	-0.21	1.00
BC	-0.61	1	0.26	-1.15	-0.068	1.00
BD	-0.26	1	0.20	-0.68	0.15	1.00
CD	-0.31	1	0.20	-0.72	0.11	1.00
A^2	-1.12	1	0.20	-1.52	-0.71	1.02
B^2	0.31	1	0.20	-0.098	0.71	1.02
C^2	0.56	1	0.20	0.15	0.96	1.02

Elongation =+23.32+0.89* A+0.42* B+0.64* C+1.84* D+0.15* A * B+0.43* A * C-0.62* A * D-0.61* B * C-0.26* B * D-0.31* C * D-1.12* A^2+0.31* B^2+0.56* C^2 …4.6

Elongation (CF)=+2.96868+0.11332* NaOH conc.-0.031010*Temperature-0.34940* Time+1.01249E-004* NaOH conc. * Temperature+2.14960E-003* NaOH conc. * Time-0.011437* Temperature * Time-2.02390E-004* NaOH conc.^{2}+7.69879E-004*Temperature^2+0.077909* Time^2 ….4.7a

Elongation (BF)=+14.26310+0.096519* NaOH conc.-0.057415* Temperature-0.57957*Time+1.01249E-004* NaOH conc. * Temperature+2.14960E-003* NaOH conc. * Time-0.011437* Temperature * Time-2.02390E-004* NaOH conc.^{2}+7.69879E-004*Temperature^2+0.077909* Time^2 …..4.7b

4.6.3.2 Diagnostics for elongation

Diagnosis shown in Figures 4.55 to 4.58 indicated that there is no anomaly and therefore the model is statistically solid. Table 4.23 shows that the experimental values are in reasonable agreement with predicted values with the highest residual observed in run order 37 (1.75 mm).

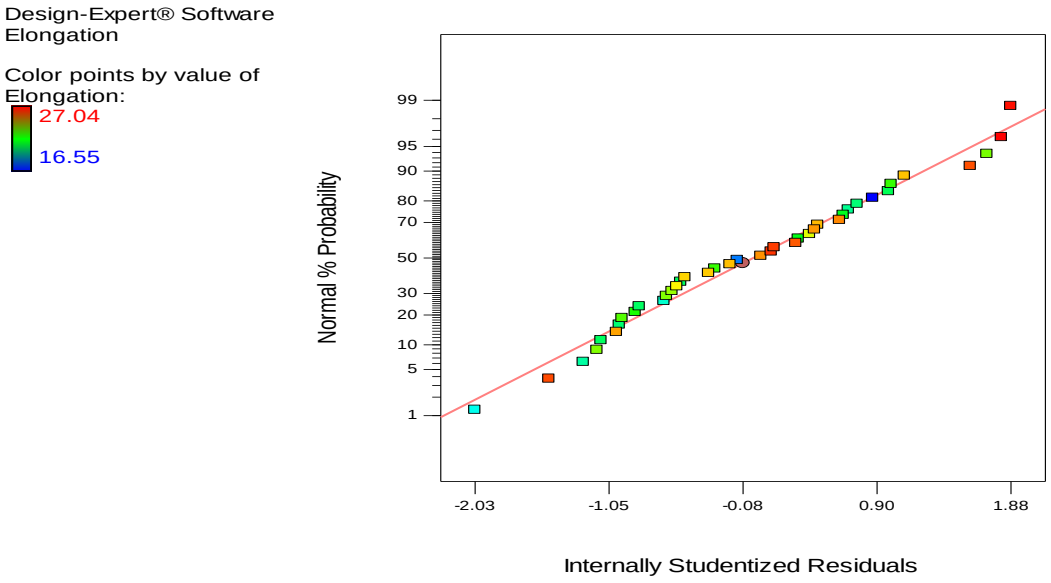


Figure 4.55: Normal probability plot of residuals

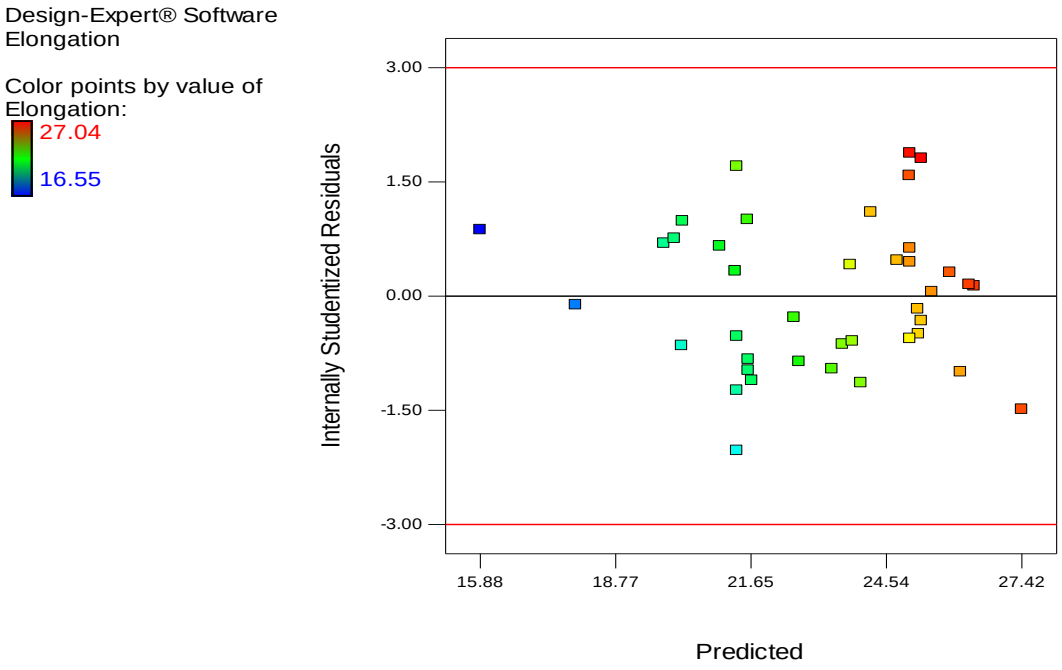


Figure 4.56: Studentized residuals versus predicted

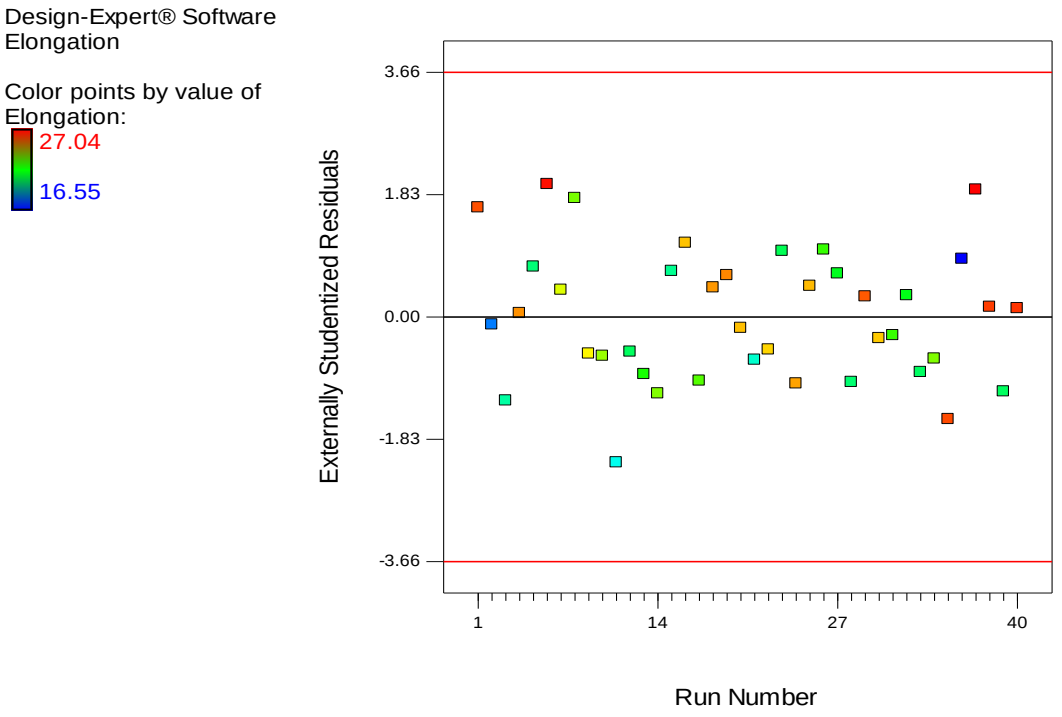


Figure 4.57: Externally studentized residuals

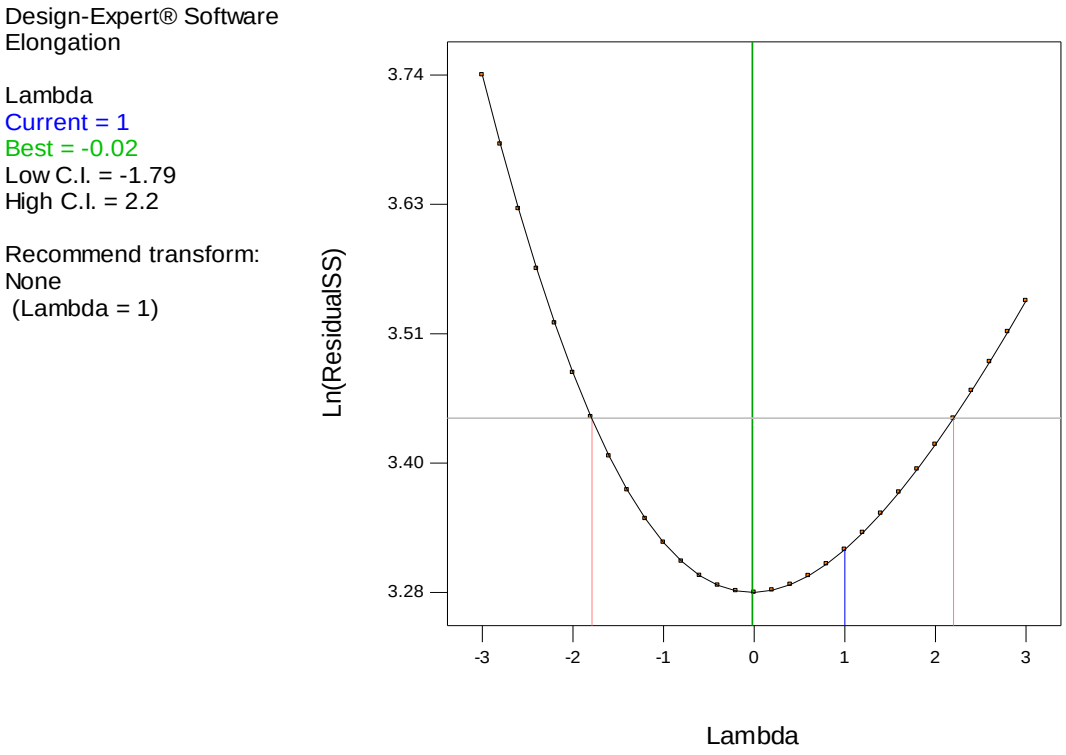


Figure 4.58: Box-Cox plot

Table 4.23: Diagnostics case statistics (elongation)

SO	AV	PV	Res.	Lev.	ISR	ESR	IFVD	CD	RO
1	17.83	17.92	-0.088	0.488	-0.116	-0.114	-0.111	0.001	2
2	20.32	19.80	0.52	0.488	0.693	0.685	0.689	0.030	15
3	20.94	20.20	0.74	0.488	0.986	0.985	0.961	0.062	23
4	22.03	22.68	-0.65	0.488	-0.861	-0.856	-0.835	0.047	13
5	19.69	20.18	-0.49	0.488	-0.650	-0.643	-0.627	0.027	21
6	24.08	23.77	0.31	0.488	0.411	0.404	0.394	0.011	7
7	20.59	20.02	0.57	0.488	0.757	0.750	0.732	0.036	5
8	25.04	24.21	0.83	0.488	1.101	1.106	1.079	0.077	16
9	19.35	21.35	-2.00	0.122	-2.029	-2.176	-0.812	0.038	11
10	20.13	21.35	-1.22	0.122	-1.238	-1.252	-0.467	0.014	3
11	23.03	21.35	1.68	0.122	1.703	1.775	0.662	0.027	8
12	20.83	21.35	-0.52	0.122	-0.528	-0.521	-0.194	0.003	12
13	16.55	15.88	0.67	0.488	0.871	0.866	0.813	0.045	36
14	21.49	20.99	0.50	0.488	0.656	0.648	0.608	0.025	27
15	21.57	21.32	0.25	0.488	0.328	0.322	0.302	0.006	32
16	23.12	23.61	-0.49	0.488	-0.633	-0.625	-0.586	0.023	34
17	22.35	21.58	0.77	0.488	1.005	1.005	0.943	0.059	26
18	25.13	24.77	0.36	0.488	0.469	0.462	0.434	0.013	25
19	20.79	21.60	-0.81	0.150	-0.831	-0.826	-0.347	0.008	33
20	20.65	21.60	-0.95	0.150	-0.976	-0.975	-0.409	0.011	28
21	23.14	24.00	-0.86	0.488	-1.139	-1.146	-1.118	0.082	14
22	22.66	23.38	-0.72	0.488	-0.956	-0.955	-0.931	0.058	17
23	24.85	25.23	-0.38	0.488	-0.498	-0.491	-0.479	0.016	22
24	25.08	25.21	-0.13	0.488	-0.170	-0.166	-0.162	0.002	20
25	26.22	26.22	1.19	0.488	1.582	1.634	1.594	0.159	1
26	25.37	25.37	-0.75	0.488	-0.997	-0.997	-0.972	0.063	24
27	23.37	23.37	-0.45	0.488	-0.592	-0.584	-0.570	0.022	10
28	25.55	25.55	0.042	0.488	0.055	0.054	0.053	0.000	4
29	26.89	26.89	1.85	0.122	1.876	1.983	0.740	0.033	6
30	24.49	24.49	-0.55	0.122	-0.558	-0.550	-0.205	0.033	9
31	25.48	25.48	0.44	0.122	0.446	0.439	0.164	0.002	18
32	25.66	25.66	0.62	0.122	0.629	0.621	0.232	0.004	19
33	20.82	20.82	-0.85	0.488	-1.109	-1.115	-1.046	0.072	39
34	22.36	22.36	-0.22	0.488	-0.280	-0.275	-0.258	0.005	31
35	26.13	26.13	0.24	0.488	0.310	0.304	0.285	0.006	29
36	26.51	26.51	-0.10	0.488	0.131	0.129	0.121	0.001	40
37	26.42	26.42	-0.12	0.488	0.152	0.149	0.139	0.001	38
38	26.28	26.28	-1.14	0.488	-1.489	-1.529	-1.434	0.130	35
39	24.97	24.97	-0.32	0.150	-0.325	-0.319	-0.134	0.001	30
40	27.04	27.04	1.75	0.150	1.808	1.900	0.798	0.038	37

SO: Standard order, AV: Actual value, PV: Predicted value, Res: Residual, Lev: Leverage, ISR: Internally studentized residuals, ESR: Externally studentized residuals, IFVD: Influence on fitted values drifts, CD: Cooks distance, RO: Run order

4.6.3.3 Main and interaction effects

Figures 4.59 to 4.65 shows individual (main) effects. The warning sign on the Figures mean that the factor is involved in an interaction and it may be misleading to interpret the main effect plots. It will be helpful to know how mercerization parameters affected elongation of cotton fibres in previous studies. Increase in mercerization temp. from 20 to 65 ^{o}C resulted in marked increase in elongation of cotton fabric which was attributed to total penetration of caustic soda solution into the fibre structure where a far greater proportion of cellulose is modified and the fabric becomes highly plastic capable of being readily stretched (Patil *et al.*, 2019). According to Sameii *et al.* (2009), increasing mercerization temp. can decrease the viscosity of caustic soda solution and also decrease the hydrophobic effect of oily impurities thereby improving the elongation. Khajavi *et al.* (2015) have shown that process duration brought about increase in elongation of cotton fibres but no significant difference in the values of elongation at different conc. of caustic soda.

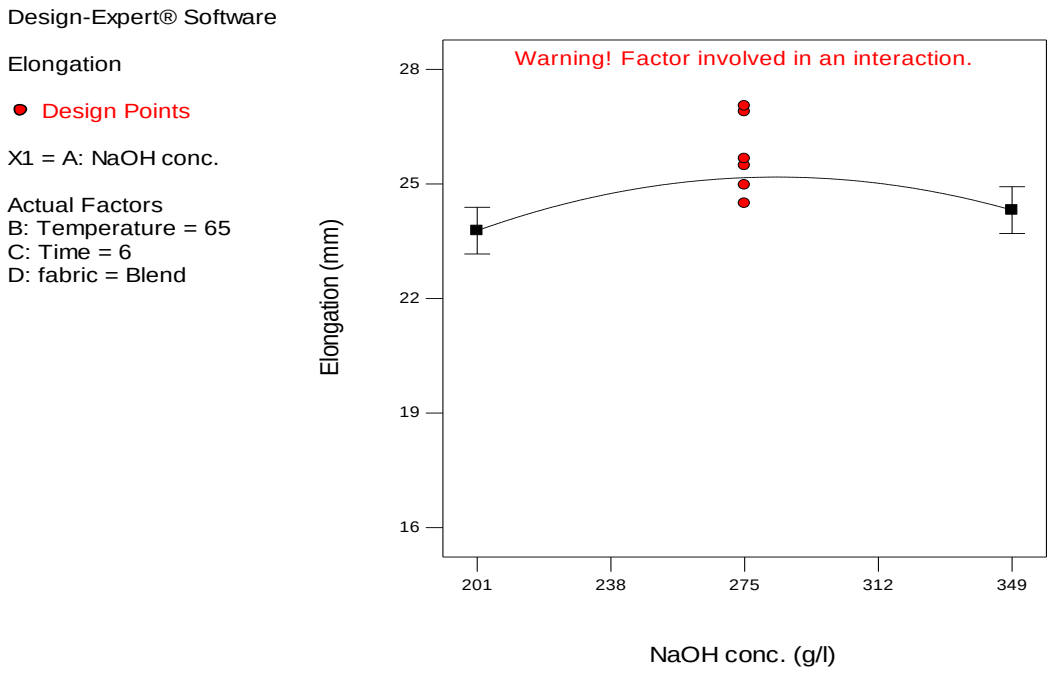


Figure 4.59: Effect of caustic soda conc. on elongation of BF

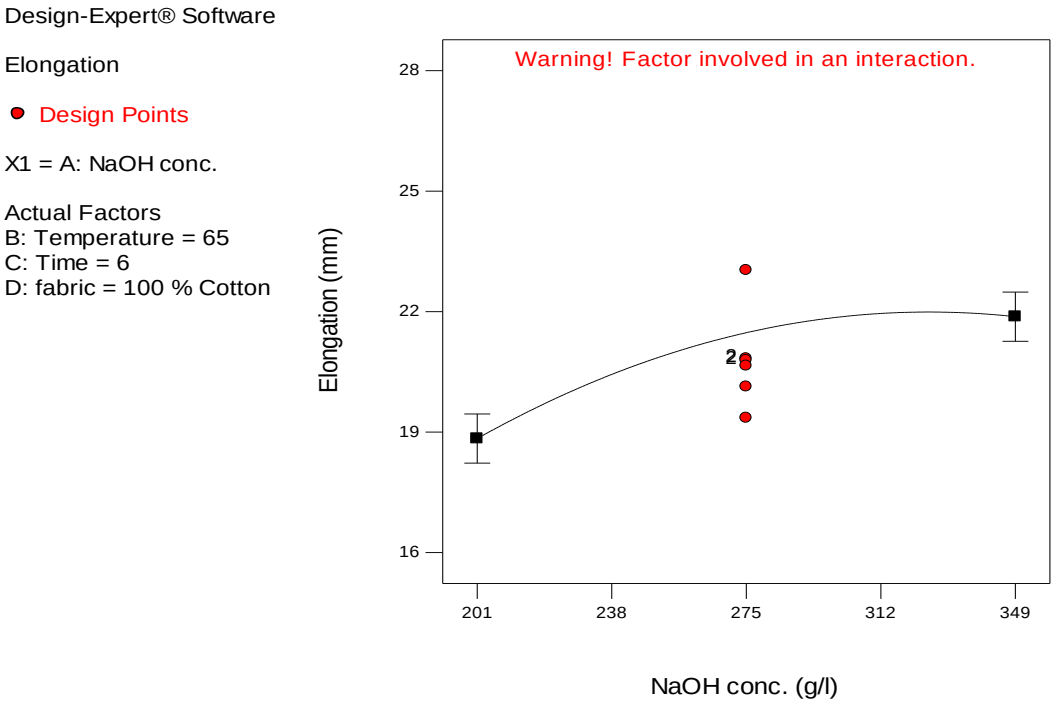


Figure 4.60: Effect of caustic soda conc. on elongation of CF

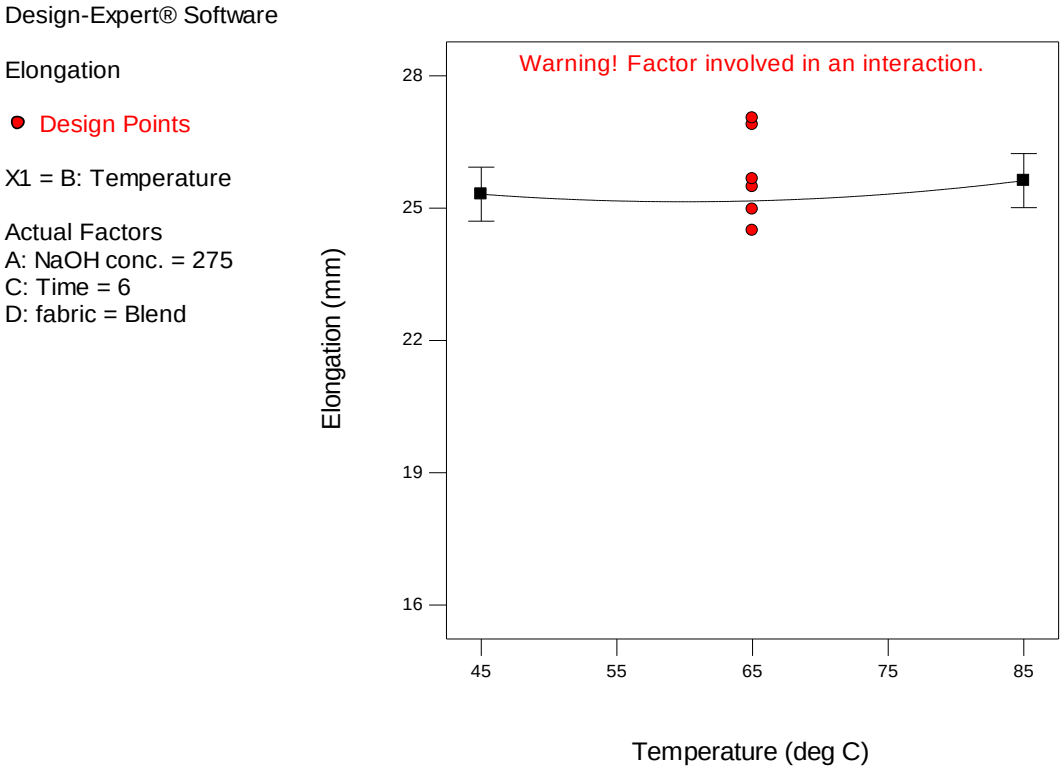


Figure 4.61: Effect of temp. on elongation of BF

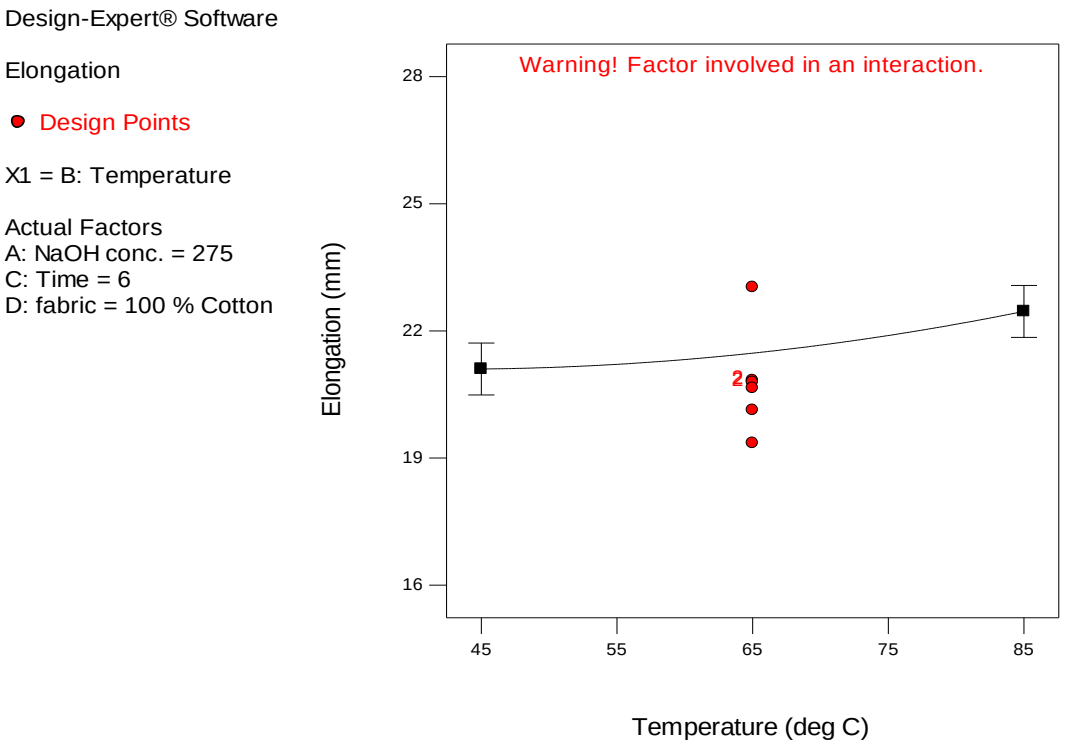


Figure 4.62: Effect of temp. on elongation of CF

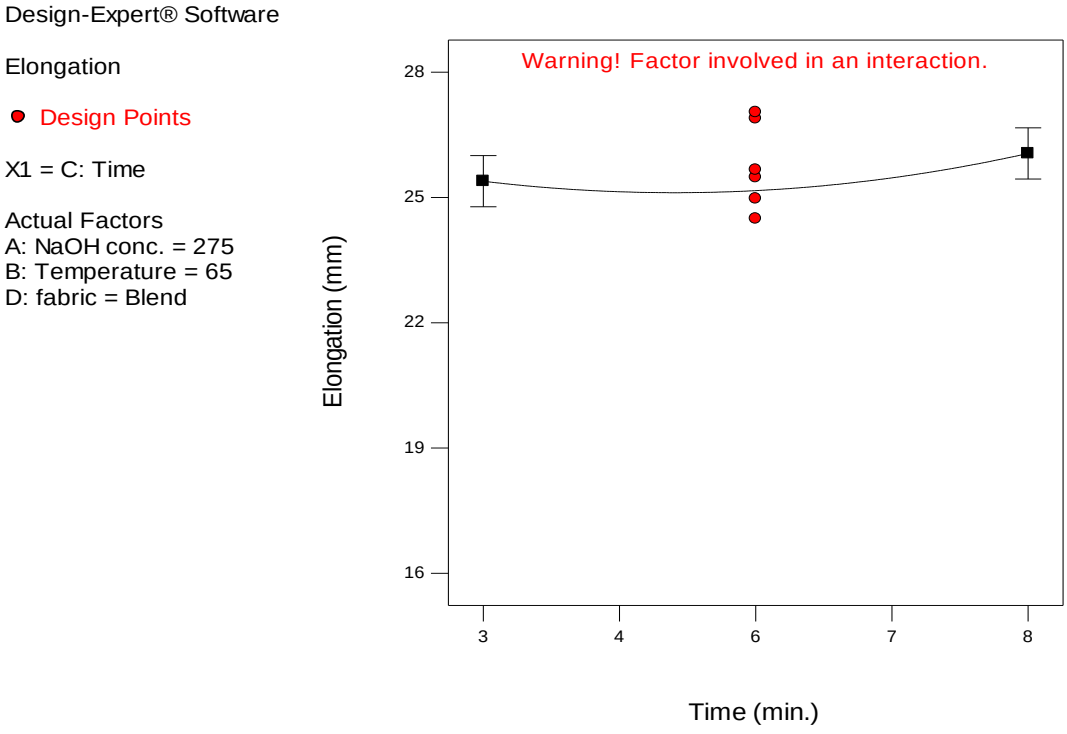


Figure 4.63: Effect of time on elongation of BF

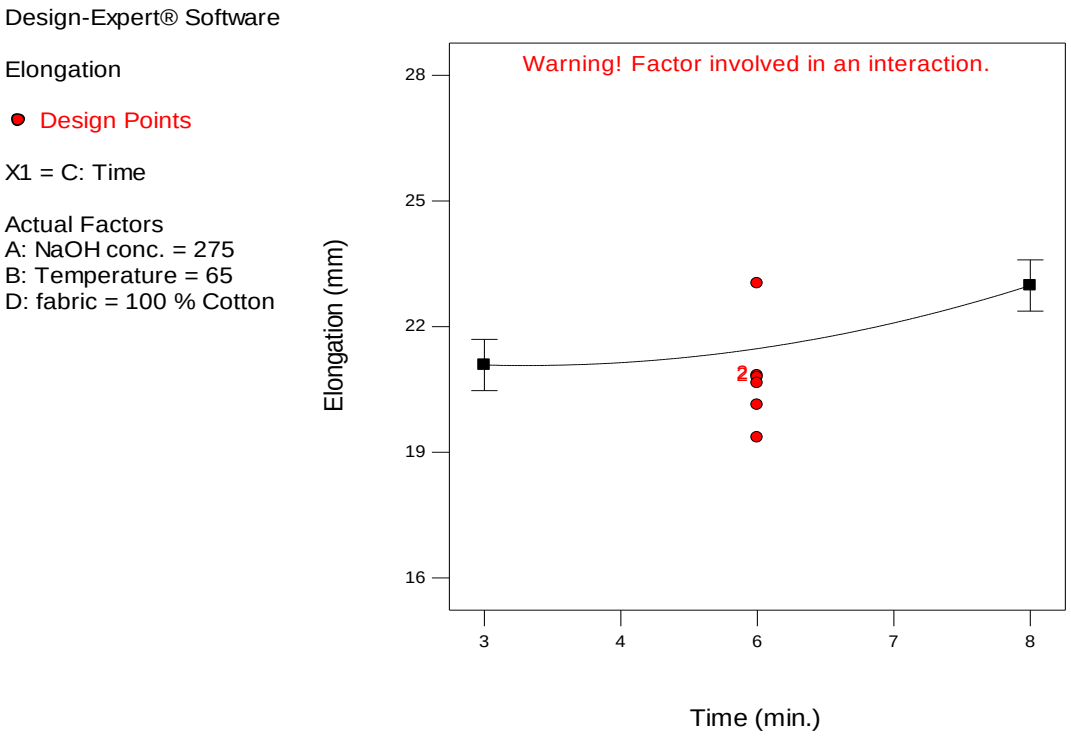


Figure 4.64: Effect of time on elongation of CF

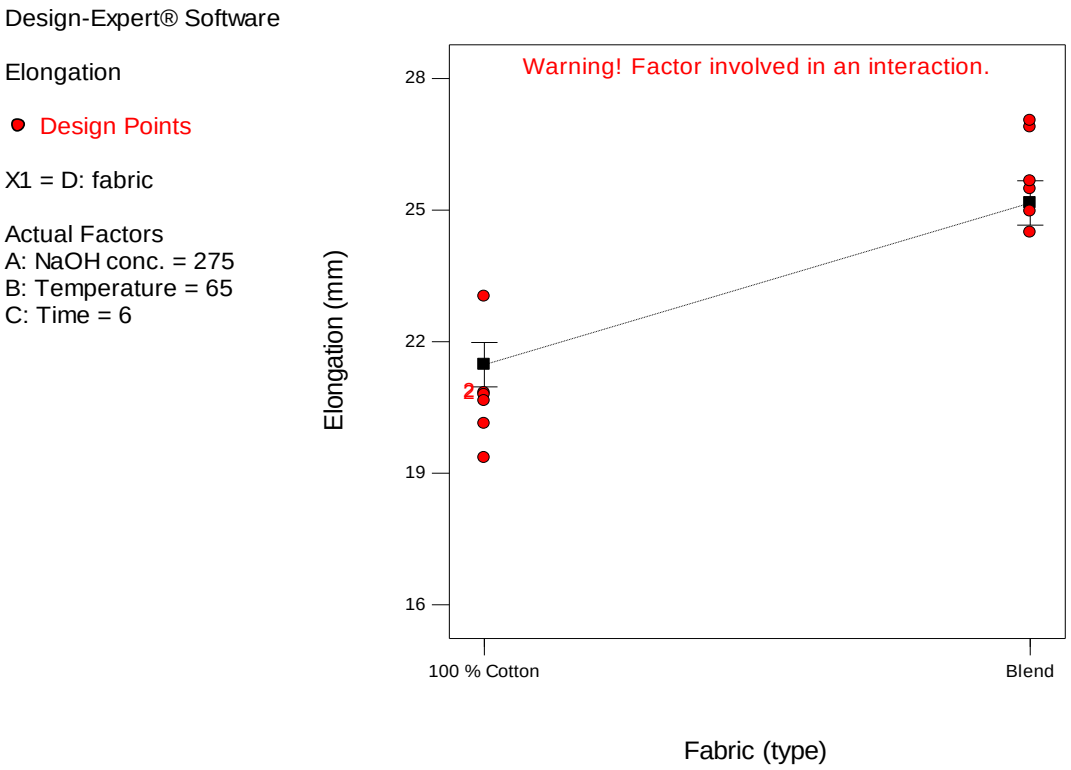


Figure 4.65: Fabric type and elongation

ANOVA shown in Table 4.22 indicated that there is an interaction among factors that affected elongation values which include caustic soda conc. and temp. (AB), caustic soda conc. and time (AC), caustic soda conc. and fabric type (AD), temp. and time (BC), temp. and fabric type (BD), time and fabric type (CD), A^2, B^2, and C^2. Interaction occurs when the effect of one factor on the response variable depends on the level of another factor (Anderson and Whitcomb, 2007). The "I-beam" shown in Figures 4.66 to 4.74 depict the 95 % least significant difference (LSD) interval for the plotted points. The points that have non overlapping intervals (non-parallel) are significantly different. In all the Figures, it is the side of the plot (left or right) in which the spread of the points is wider that is analyzed.

Caustic soda conc. and temp.: As shown in Figures 4.66 and 4.67, higher caustic soda conc. and high temp. results in higher elongation for BF and CF, respectively.

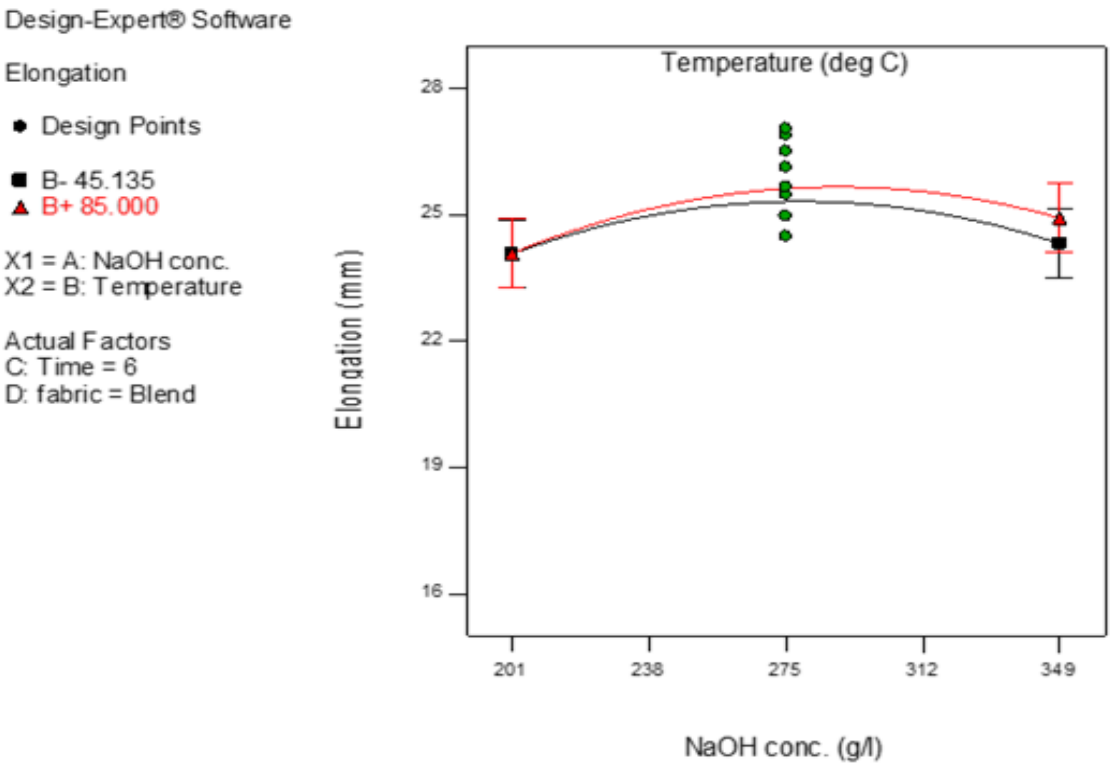


Figure 4.66: Interaction between caustic soda conc. and temp. to affect the elongation of BF

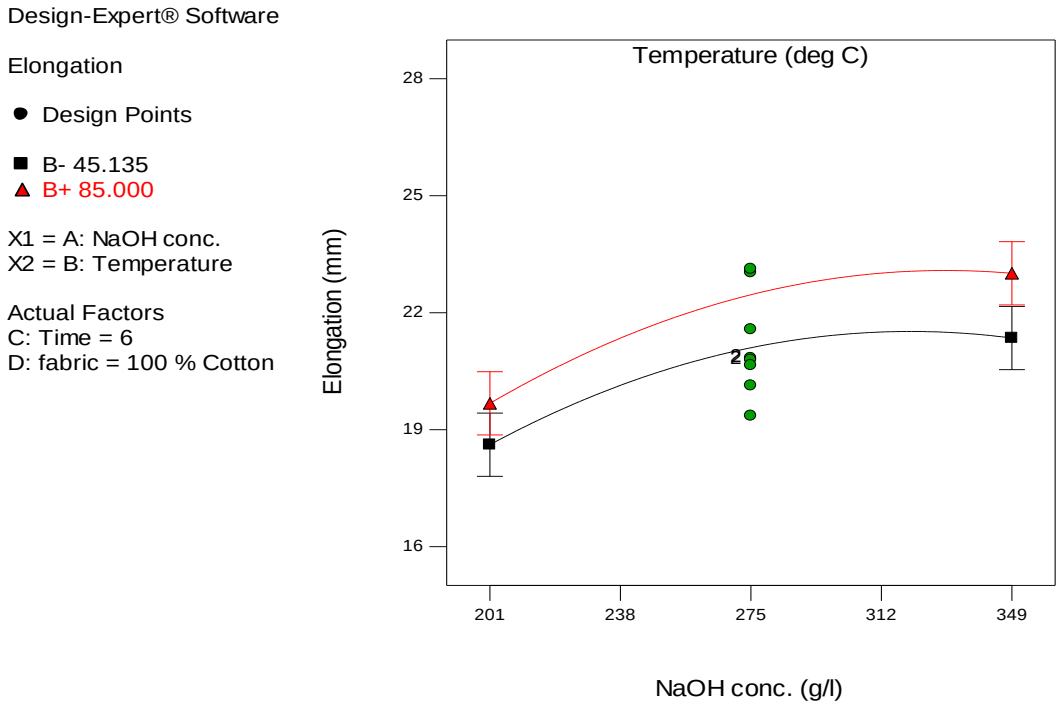


Figure 4.67: Interaction between caustic soda conc. and temp. to affect the elongation of CF

Caustic soda conc. and treatment time: Figures 4.68 and 4.69 show that high caustic soda conc. and long treatment time gives higher elongation of BF and CF, respectively.

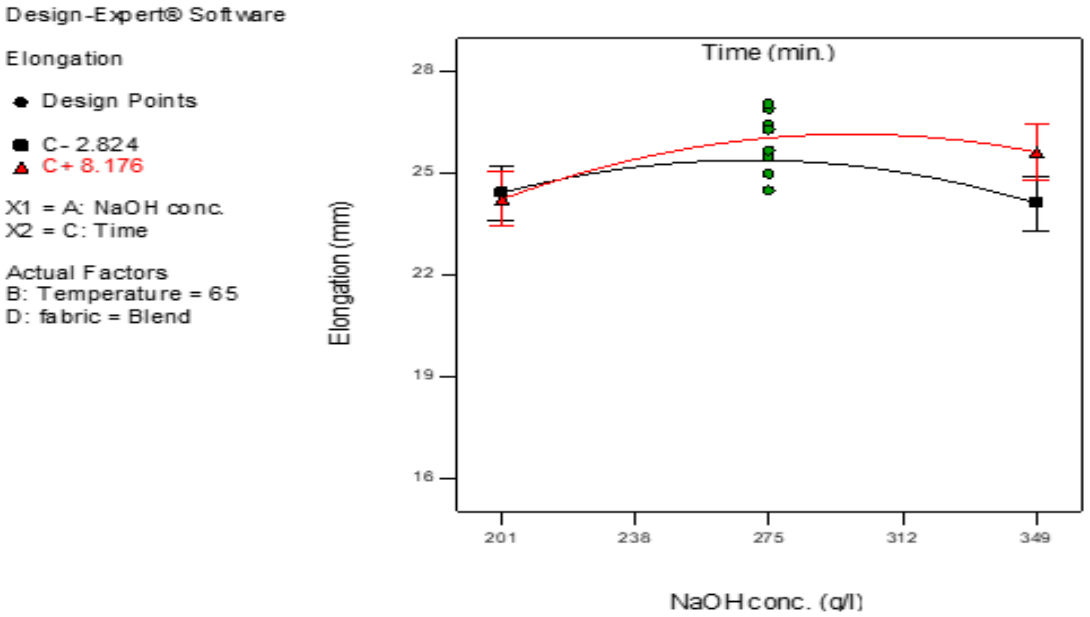


Figure 4.68: Interaction between caustic soda conc. and time to affect the elongation of BF

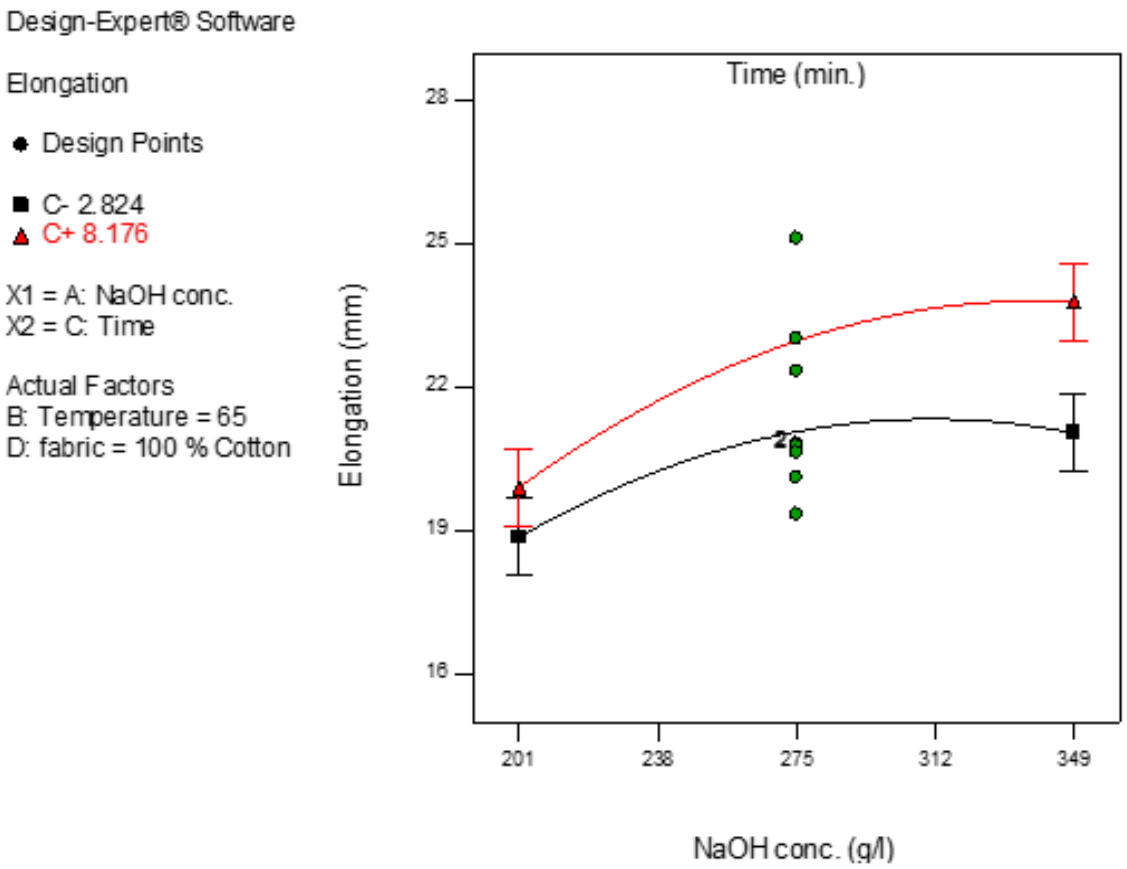


Figure 4.69: Interaction between caustic soda conc. and time to affect the elongation of CF

Temperature and treatment time: Figures 4.70 and 4.71 show that higher elongation value is obtained when the temperature is low with longer treatment time for BF and CF, respectively. Increase in time and temperature of alkali treatment leads to a decrease in the fabric elongation which could be due to polyester hydrolysis and cotton weakness as a result of production of oxycellulose and reduction of crystalline regions which also may be prolonged with the extension of treatment time and increase in temperature (Montazer and Sadighi, 2006).

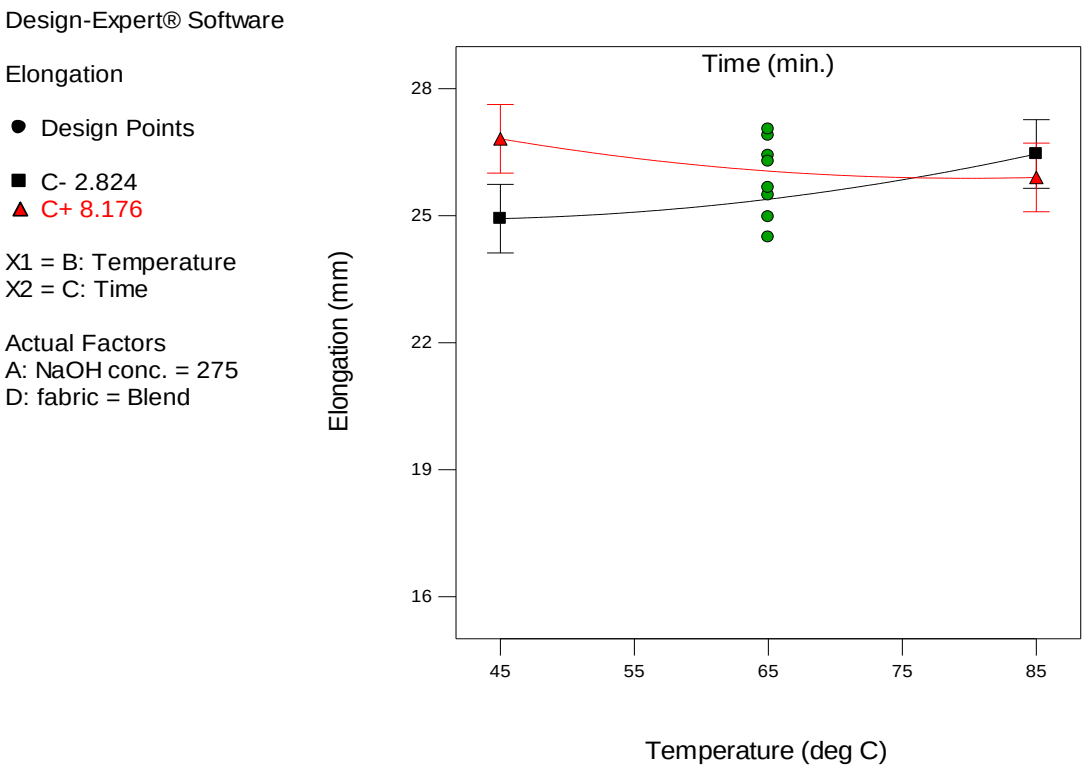


Figure 4.70: Interaction between temp. and time to affect the elongation of BF

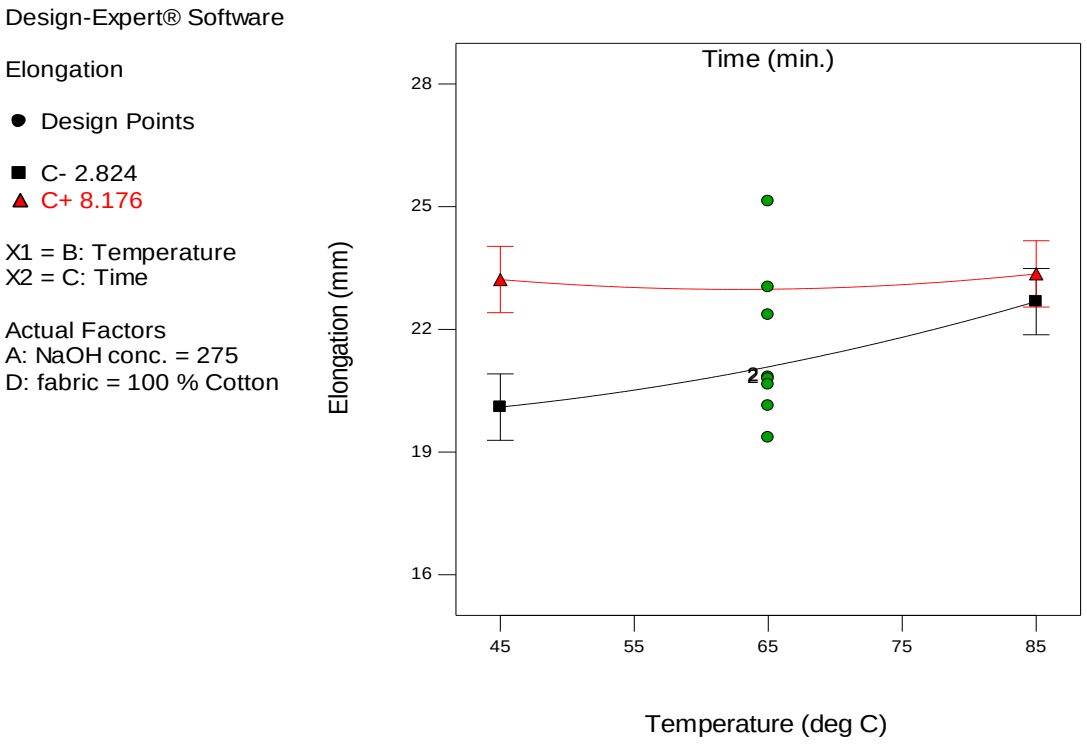


Figure 4.71: Interaction between temp. and time to affect the elongation of CF

Caustic soda conc. and fabric type: As shown in Figure 4.72, at all concentrations of caustic soda, the elongation of BF was higher than that of CF which is also higher with higher caustic soda conc.

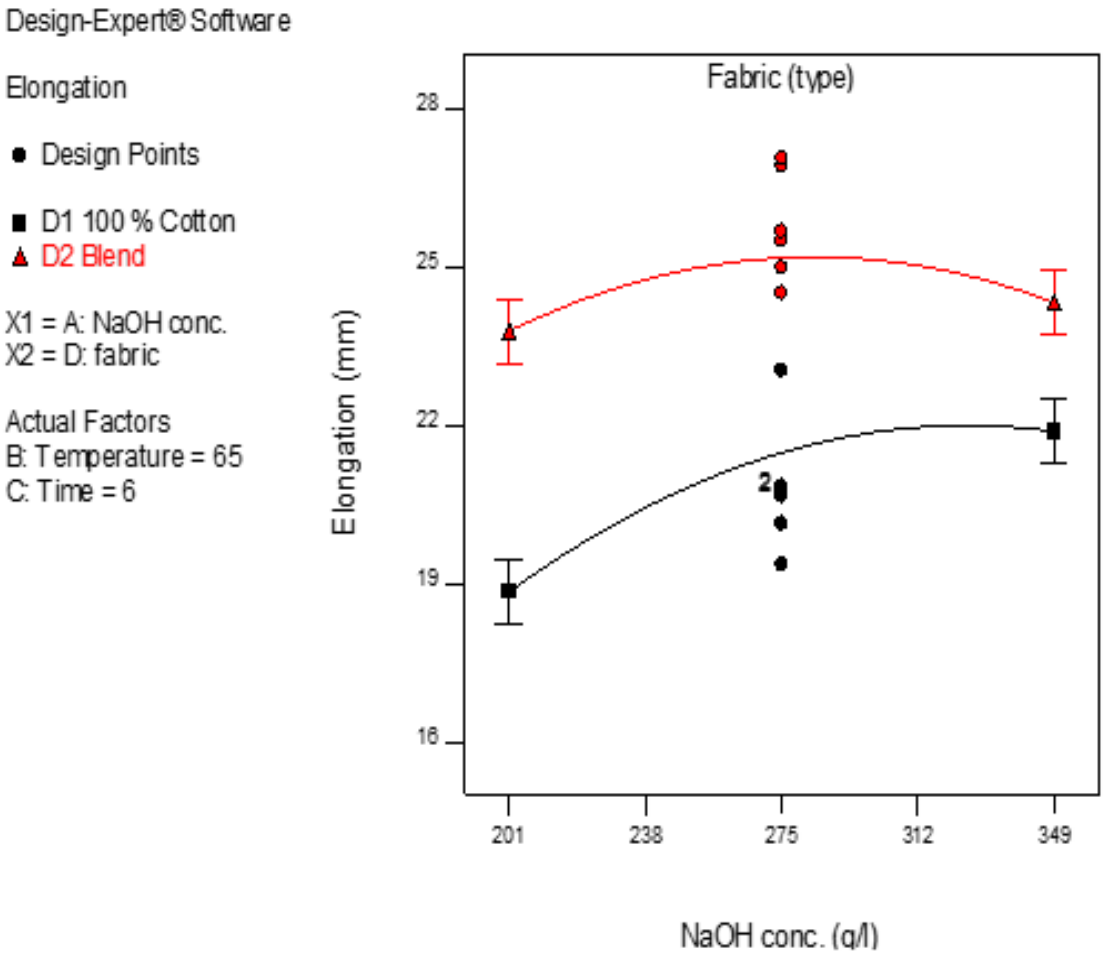


Figure 4.72: Interaction between caustic soda conc. and fabric type to affect the elongation

Temp. and fabric type: As shown in Figure 4.73, elongation of BF was higher than that of CF at all temp. Polyester fibres were reported to be more sensitive to temp. than cotton fibres during alkali treatment (Montazer and Sadighi, 2006).

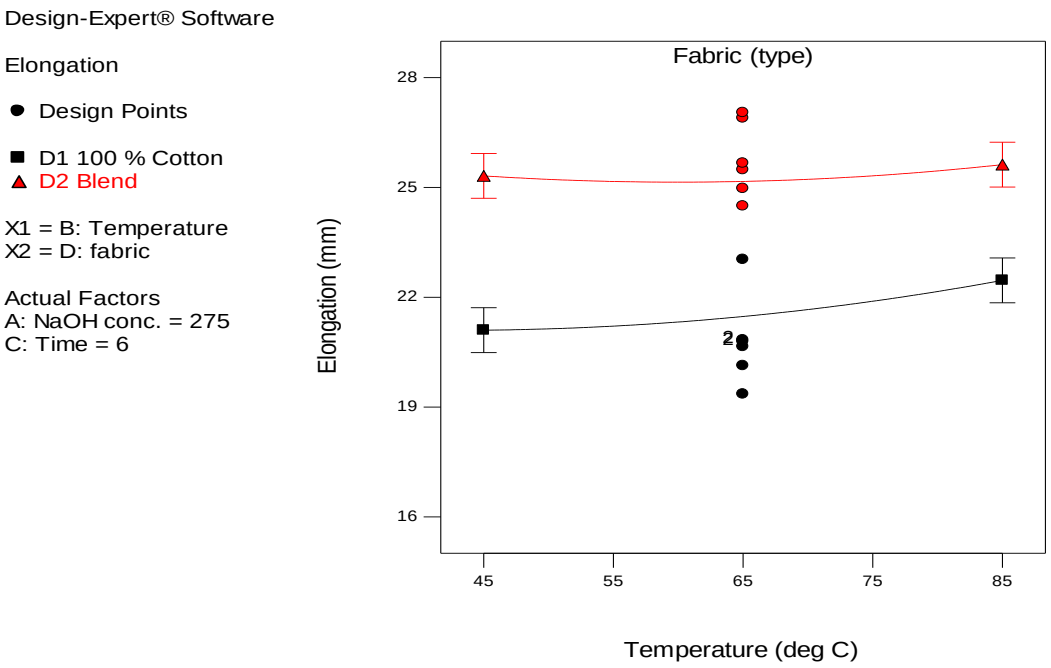


Figure 4.73: Interaction between temperature and fabric type to affect the elongation

Time and fabric type: Figure 4.74 show that at all treatment times, the elongation of BF was higher than that of CF.

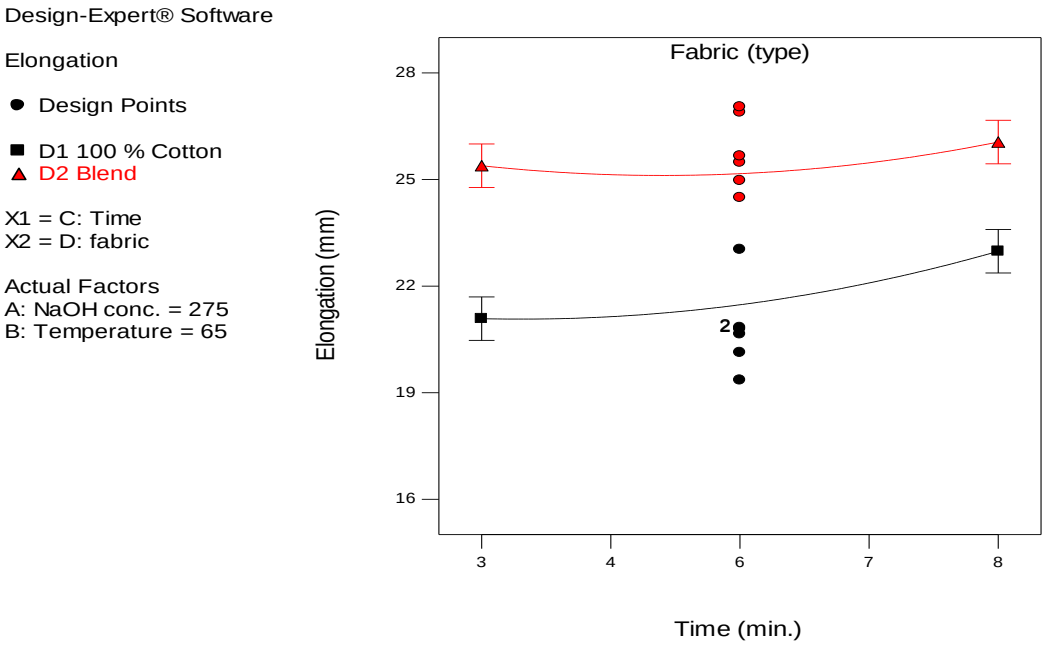


Figure 4.74: Interaction between time and fabric type to affect the elongation

4.6.4 Multi-response optimization of mercerization parameters using desirability function

The ramp of optimal conditions for BF and CF (Figures 4.75 and 4.76), histogram of desirabilities (Figures 4.77 and 4.78), as well as contour plots of elongation predictions (Figures 4.79 and 4.80) and shrinkage predictions (Figures 4.81 and 4.82) are shown.

The objective of this optimization is to simultaneously make elongation as high as possible and shrinkage to be as minimum as possible. In numerical optimization, desired goal is chosen for each factor and response. The possible goals in DX7 use five possibilities for a "goal" to construct desirability indices. The possibilities include: "maximize", "minimize", "target", "in range", and "none" (for responses only), and set to an exact value displayed as "equals to" (factors only). Fabric type, which is a categoric factor, has only 2 goals including "in range" and "equals to". Desirability ranges from zero to one for any given response. The program combines the individual desirabilities into a single number and then searches for the greatest overall desirability. A value of one represents the ideal case. A zero indicates that one or more responses fall outside desirable limits.

A multiple response method was applied for optimization of combinations of four factors (three numeric and one categoric) namely caustic soda conc., temp., time, and fabric type. The two responses optimized were average shrinkage and elongation. The criterion was set as follows: "in range" for temp. (45-85 ^{o}C) and time (3-8 min.), "equal to" 250 g/l for caustic soda conc., "in range" for fabric type (low level for CF and high level for BF), "maximize" average elongation, and "minimize" average shrinkage.

Desirability when coupled with optimization algorithms can provide best compromise when dealing with multiple demands. By seeking response changes from sixty starting points for two combinations of categoric factor levels (fabric type), one solution each for BF and CF were selected (from ten solutions) on the basis of the one that has relatively high elongation and minimum shrinkage with similar factor combinations because of the subsequent dyeing experiments to be carried out. The solutions were also chosen not by having high desirability only but from factor combinations that will make the process cheaper and faster while providing better responses (quality).

The dot on each ramp shown in Figures 4.75 and 4.76 (for BF and CF, respectively) reflects the factor setting or response prediction for that solution. The height of the dot shows how desirable it is. Figure 4.75 shows that mercerization of BF at 85 ^{o}C using 250g/l caustic soda conc. and 3 min. treatment time will result in 26.33 mm elongation and 7.7 % shrinkage with a desirability of 0.76. The ramp shown in Figure 4.76 indicated that the same mercerization conditions for CF is predicted to yield 22.14 mm elongation and 10.89 percentage shrinkage with a desirability of 0.443.

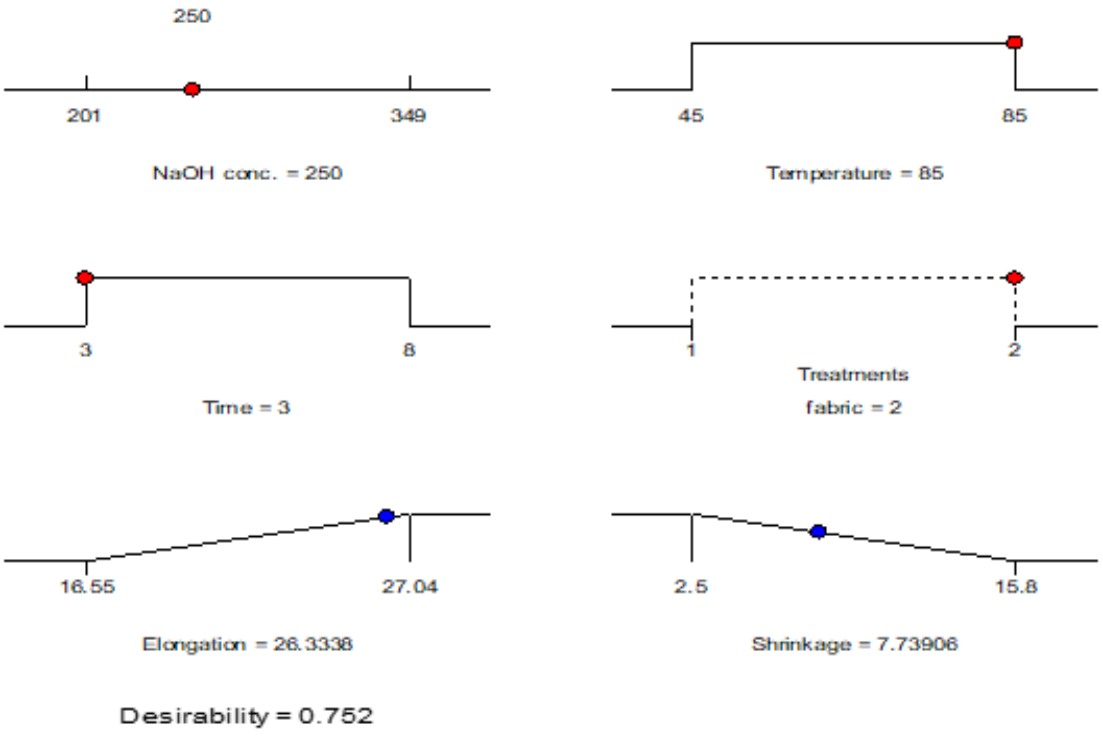


Figure 4.75: Ramp of optimal conditions for BF

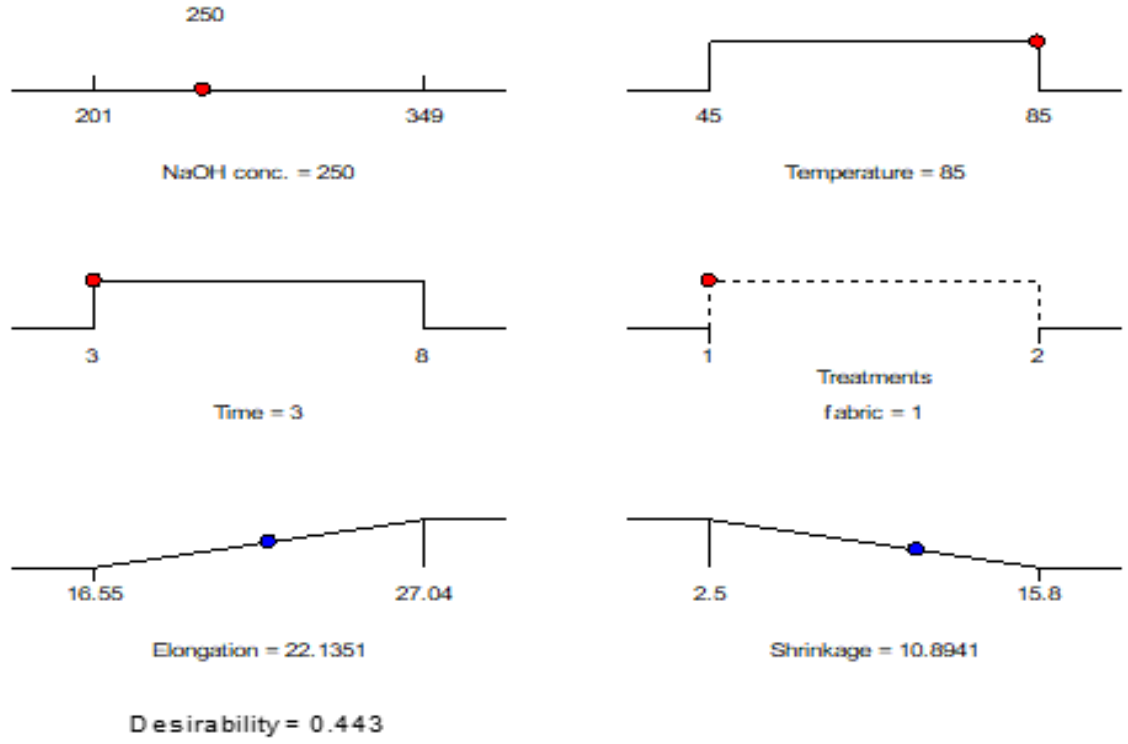


Figure 4.76: Ramp of optimal conditions for CF

Figures 4.77 and 4.78 show histograms depicting individual and combined desirabilities for BF and CF, respectively. Histogram shows how well each variable satisfied the criteria where values near one are good. Figures 4.79 and 4.80 (respectively for BF and CF) and Figures 4.81 and 4.82 (for BF and CF, respectively) show contour plots for elongation and percentage shrinkage prediction, respectively.

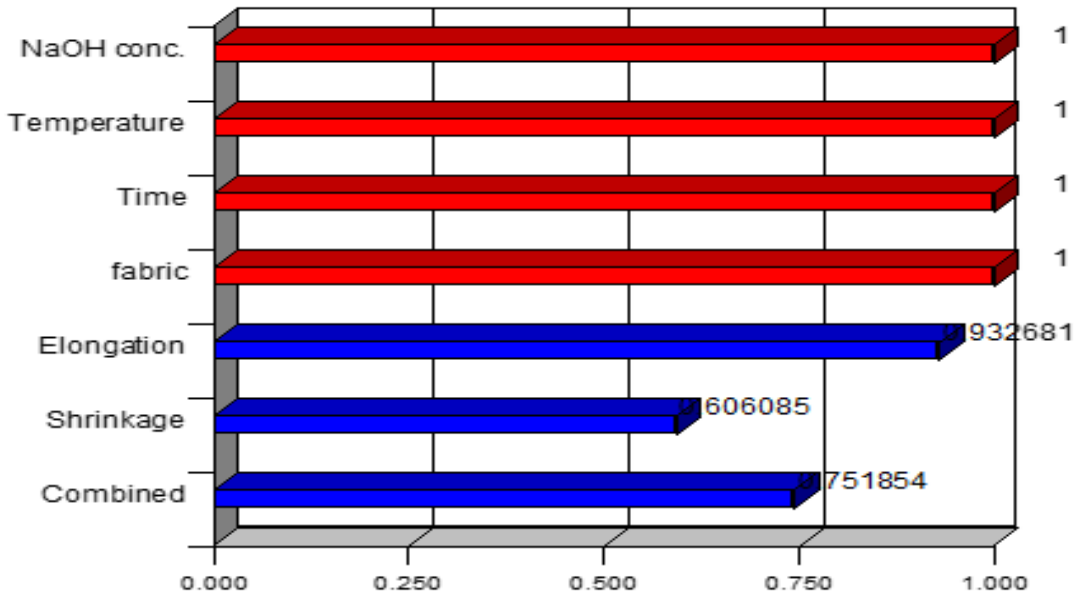


Figure 4.77: Histogram of individual and combined desirabilities for BF

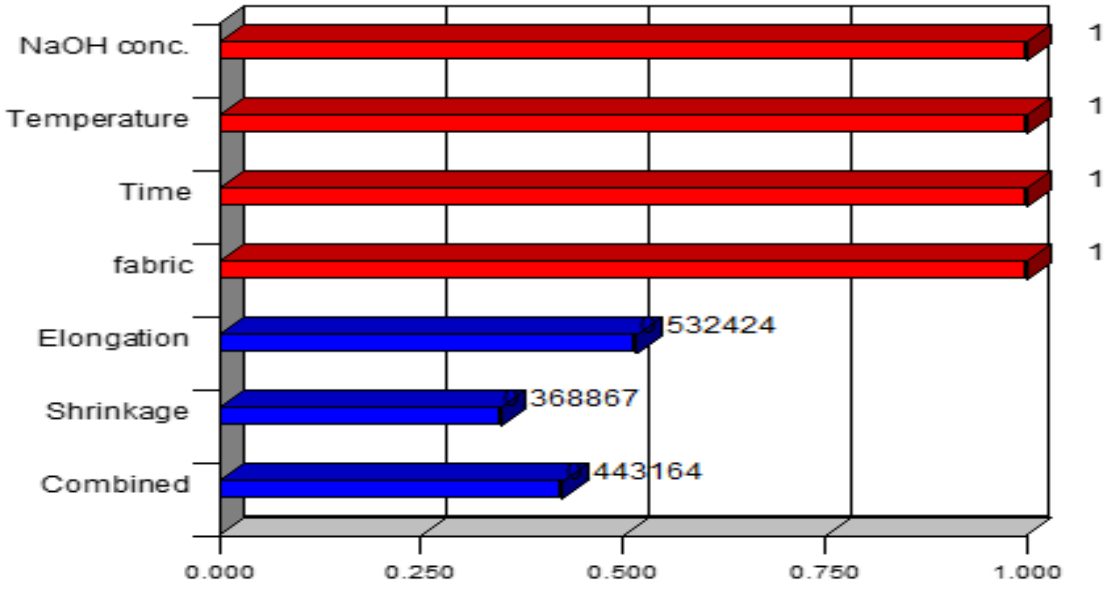


Figure 4.78: Histogram showing individual and combined desirabilities for CF

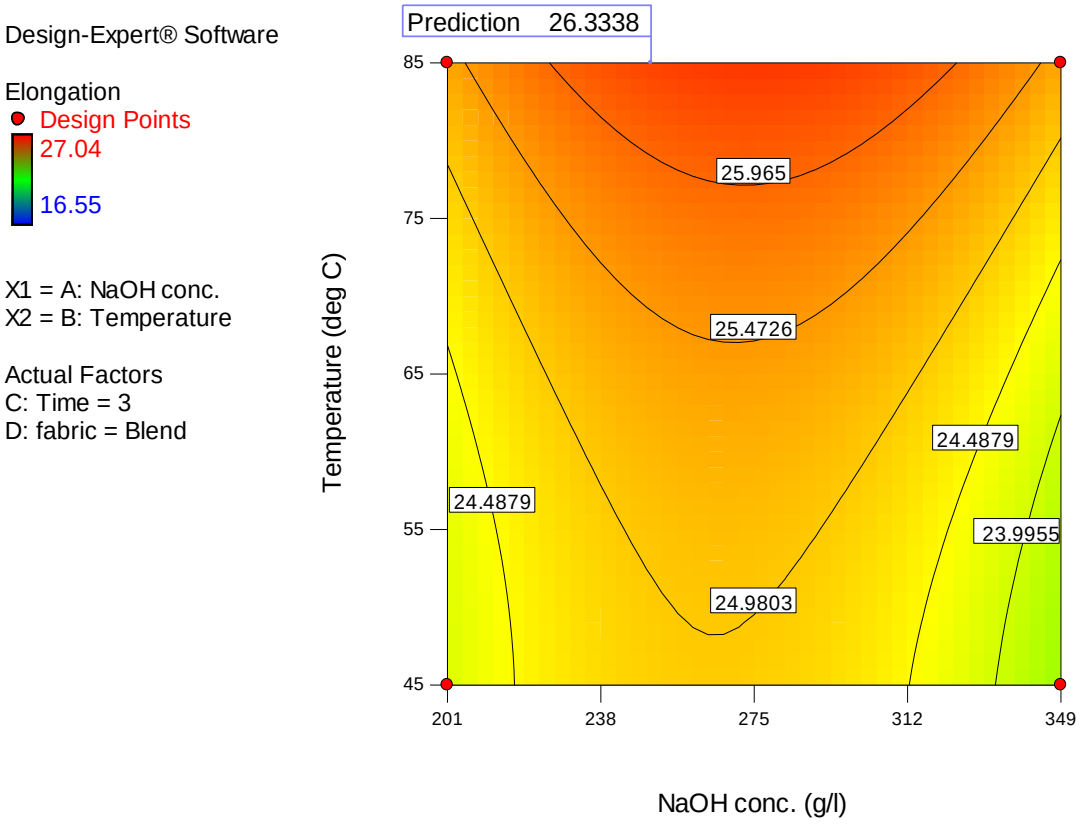


Figure 4.79: Contour plot of elongation prediction for BF

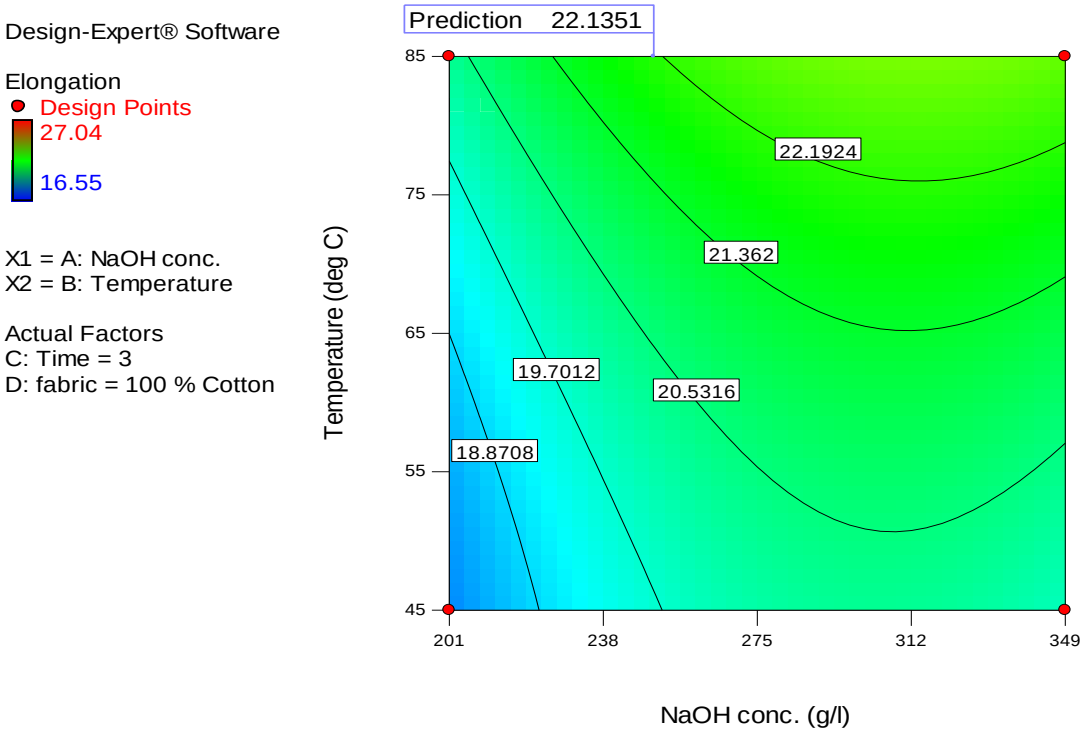


Figure 4.80: Contour plot of elongation prediction for CF

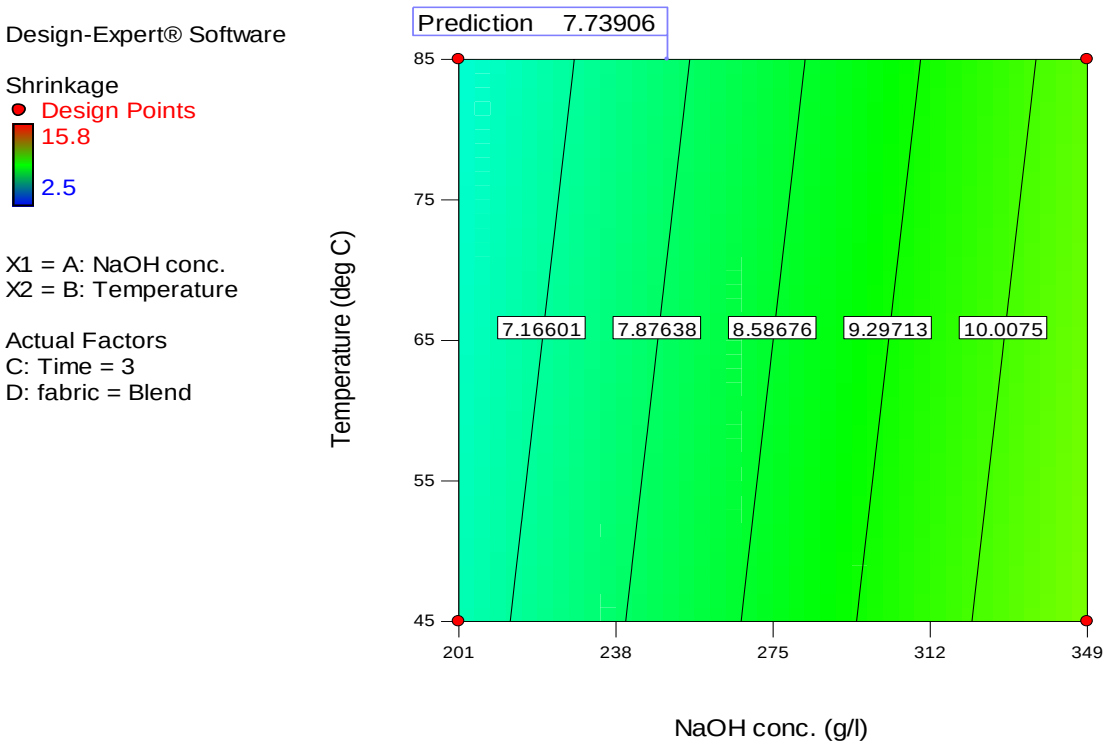


Figure 4.81: Contour plot of shrinkage prediction for BF

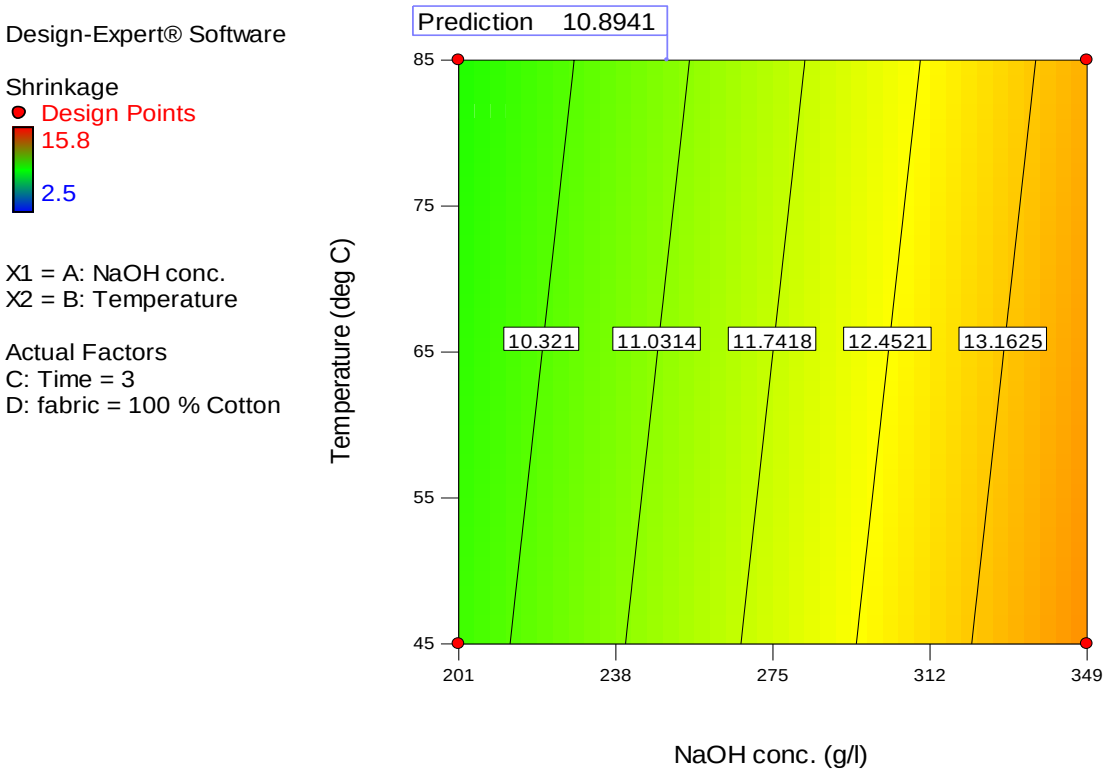


Figure 4.82: Contour plot of shrinkage prediction for CF

Caustic soda conc. of 250 g/l is economically and ecologically better as it will save mercerization cost and minimize wastewaters which may otherwise have negative environmental impacts. Mercerizing at 85 ^{o}C can easily be approximately controlled by the dyers as it is close to the boil and increase in cost of energy is almost negligible. Mercerizing in 3 min. will speed up the process as time is very important for the dyers (due to manual operation).

The optimum conditions predicted were checked experimentally. The experimental values obtained for average elongation (for five replicates) was 27.2±0.7 and 23.52±1.3 mm while the average shrinkage value was 7.1±0.4 and 9.9±3.6 %, respectively, for BF and CF were for 5 replications. Small errors between these values indicated that the experimental values obtained were in good agreement with the values predicted from the models. When compared to the original unmercerized sample, the elongation increased by about 51.62 % and 120.85 %, respectively, for BF and CF. Shrinkage is reduced by about 19.50 % for BF and 17.30 % for CF when compared to the mean average shrinkage of mercerized samples.

Khajavi *et al.* (2015) reported optimized conditions for conventional mercerization of plain-woven cotton fabric using 270 g/l NaOH, 6 min. treatment time., and temp. of 50 ^{o}C to obtain an elongation of 65 mm with a desirability of 0.762. Shrinkage value of 19.1 % was measured in a cotton fabric made up of open-end yarns mercerized at 85 ^{o}C using 300 g/l caustic soda and 5 min. treatment time (Sameii *et al.*, 2008). Moghassem and Valipour (2013) measured 16.8 % shrinkage of a cotton fabric mercerized at 80 ^{o}C using 250 g/l caustic soda and 4 min. treatment time. Kokot and Stewart (1995) measured 15 % shrinkage in a cotton fabric mercerized using 250 g/l caustic soda at 80 ^{o}C for 30 min.

4.7 Results from Dyeing Experiments

As shown in Table 4.24, 56 experiments were conducted with different factor combinations within two days (two blocks). All the fabrics were previously mercerized using 250 g/l caustic soda at 85 ^{o}C for 3 min. before the dyeing process. Table 3.7 (section 3.2.8.1) shows CCD of the dyeing experiment where the conc. of caustic soda and hydros as well as dyeing methods were varied. Two types of fabrics, CF and BF, were used as substrates and also varied in the experiments. The dye used in the experiment is RSN with C.I number 69800 according to colour index. The dye was selected because normally red or blue dyes are used to dye mercerized cotton as it is easier to observe differences in depth of those colours as well as assessment of lustre (Shamey and Hussein, 2005) and most likely the visual evaluation of levelness.

Table 4.24: Appearance rating of the dyed fabrics

Run No.	Run Type	NaOH conc. (g/l)	Hydros conc. (g/l)	Fabric (type)	Dyeing (method)	Appearance (%)
1	Centre	15	15	BF	WW	88
2	Centre	15	15	BF	Dry	87
3	Fact	20	20	BF	WW	94
4	Centre	15	15	BF	Dry	86
5	Fact	10	10	BF	WW	87
6	Fact	10	20	BF	WW	88
7	Fact	10	20	BF	Dry	97
8	Centre	15	15	BF	WW	98
9	Centre	15	15	CF	WW	50
10	Fact	10	10	CF	WW	41
11	Fact	10	10	CF	Dry	77
12	Centre	15	15	BF	WW	86
13	Fact	20	20	CF	WW	22
14	Fact	10	20	CF	Dry	91
15	Centre	15	15	CF	Dry	94
16	Centre	15	15	CF	Dry	88
17	Fact	20	10	BF	Dry	99
18	Fact	10	10	BF	Dry	83
19	Fact	20	10	CF	WW	42
20	Centre	15	15	CF	WW	46

21	Centre	15	15	CF	Dry	94
22	Centre	15	15	CF	WW	34
23	Fact	20	20	CF	Dry	81
24	Fact	20	10	CF	Dry	73
25	Centre	15	15	BF	Dry	85
26	Fact	20	20	BF	Dry	91
27	Fact	20	10	BF	WW	94
28	Fact	10	20	CF	WW	51
29	Axial	22	15	BF	WW	93
30	Axial	8	15	BF	Dry	82
31	Axial	22	15	CF	Dry	73
32	Axial	8	15	BF	WW	92
33	Axial	15	22	BF	WW	93
34	Axial	15	22	BF	Dry	92
35	Axial	22	15	BF	Dry	83
36	Centre	15	15	CF	WW	43
37	Axial	15	8	BF	Dry	80
38	Axial	8	15	CF	Dry	89
39	Axial	15	22	CF	Dry	85
40	Axial	15	8	BF	WW	92
41	Axial	22	15	CF	WW	14
42	Axial	15	8	CF	Dry	74
43	Centre	15	15	BF	WW	88
44	Centre	15	15	BF	Dry	94
45	Centre	15	15	CF	WW	29
46	Centre	15	15	CF	Dry	92
47	Centre	15	15	CF	WW	18
48	Centre	15	15	BF	WW	94
49	Axial	15	22	CF	WW	38
50	Axial	8	15	CF	WW	61
51	Centre	15	15	CF	Dry	97
52	Centre	15	15	BF	Dry	87
53	Axial	15	8	CF	WW	50
54	Centre	15	15	BF	Dry	92
55	Centre	15	15	BF	WW	89
56	Centre	15	15	CF	Dry	97
57	-	15	15	UMDCF	Dry	49

BF: blend fabric, CF: cotton fabric, UMD: unmercerized dyed cotton fabric WW: Wet-on-wet method, Dry: dry method

Of the many quality characteristics of dyed fabric, none is more important than the uniformity of the fabric appearance (Gunay, 2009). Levelness is related to uniformity of colouration as it determines the uniformity of dye distribution with respect to the depth of colour (Syed and

Wardman, 2011). Levelness is an essential quality of dyeing which is distinct and separate from shade and fastness and unlevelness is normally unacceptable in commercial dyeings except for stone-wash, acid-wash, or pigment-dyed textiles where an effect is sought to comply with fashion trend (Chang and Yeung, 1992).

Uniform distribution of shade within a dyed fabric is affected by several factors such as shade variation due to materials, equipment, controls, process, human factors, and logistics (Gunay, 2009). Traditionally, dye evenness was assessed visually and was therefore a subjective judgement (Syed and Wardman, 2011). Although levelness can be objectively determined (Chong and Yeung, 1992; Solymanian *et al.,* 2015), it is still measured subjectively (Solymanian *et al.,* 2015; Gunay, 2009). Visual assessment often does not quantify levelness and consequently the communication of levelness data between suppliers, laboratories, and manufacturers is difficult (Gunay, 2009).

As discussed under methods, dyeing was carried out at 60 ^{o}C for 10 min. Temperature region of 60 ^{o}C has been suggested for vat dyeing of cellulose without the addition of salt (Fox, 1948). The dyeing time was selected based on results obtained from survey (67 % of the dyers accomplish dyeing in less than 10 min.) and the fact that 80-90 % of vat dyes may be exhausted within 10 min. of dyeing (Broadbent, 2001). The low level of fabric type is CF and the high level is BF designated as “1” and “2”, respectively, in coded form. The low and high levels of dyeing methods are, respectively, “wet-on-wet” and “dry” (designated as “1” and “2” in coded form). The LR of 100:1 was chosen to aid in levelled dyeing. Response from the dyeing experiments is “appearance rating” which is categoric and measured subjectively and which was chosen to determine the levelness of the dyed samples. Similar ratings have been reported

previously. Ahmad and Tahir (1989) assessed the lustre of mercerized fabric samples in a subjective manner.

Ajayi *et al.* (1995) assessed the surface properties (roughness, flatness, etc.) of mercerized samples using a team of evaluators. Anderson and Whitcomb (2007) used DOE to optimize process parameters to reduce the number of bullets formed and improve on the taste of popcorn produced using a panel of Minnesotans. Solymanian *et al.* (2015) used panel of judges to grade samples in terms of levelness where the authors analyse the validity of the collected data by multi comparison procedure which determined whether the differences between pairs of means of desired ranks for samples were significantly different. In this study, attempt has been made to statistically analyse data from perceived levelness of fabric samples using ANOVA and diagnostic tools. The chemistry behind the colouristic effects produced from the two fabrics used as substrates and the dyeability of the fibres are discussed along with appearance rating (levelness).

Plate XXI shows a dyed BF (standard reference sample) where BFPWA remain undyed (white) because polyester fibres cannot be dyed with vat dyes under the same conditions as cellulosic fibres. The colouration effect is that of a "resist dyeing". A solid colouration was obtained on CF as shown in Plate XXII (standard reference sample) because the fabric consists of a single fibre (cellulose). "Resist dyeing" and "shadow dyeing" are the new fashion trend in the study area. A shadow effect produced from a BF, 40/60 polyester/cotton, is shown in Plate XVIIB (section 4.1.4.2). The sample shown in Plate XXI resembles a batik design obtained just by dyeing without the intricacy of designing the patterns. The yarns are deliberately weaved to produce such patterns when the fabric is dyed.

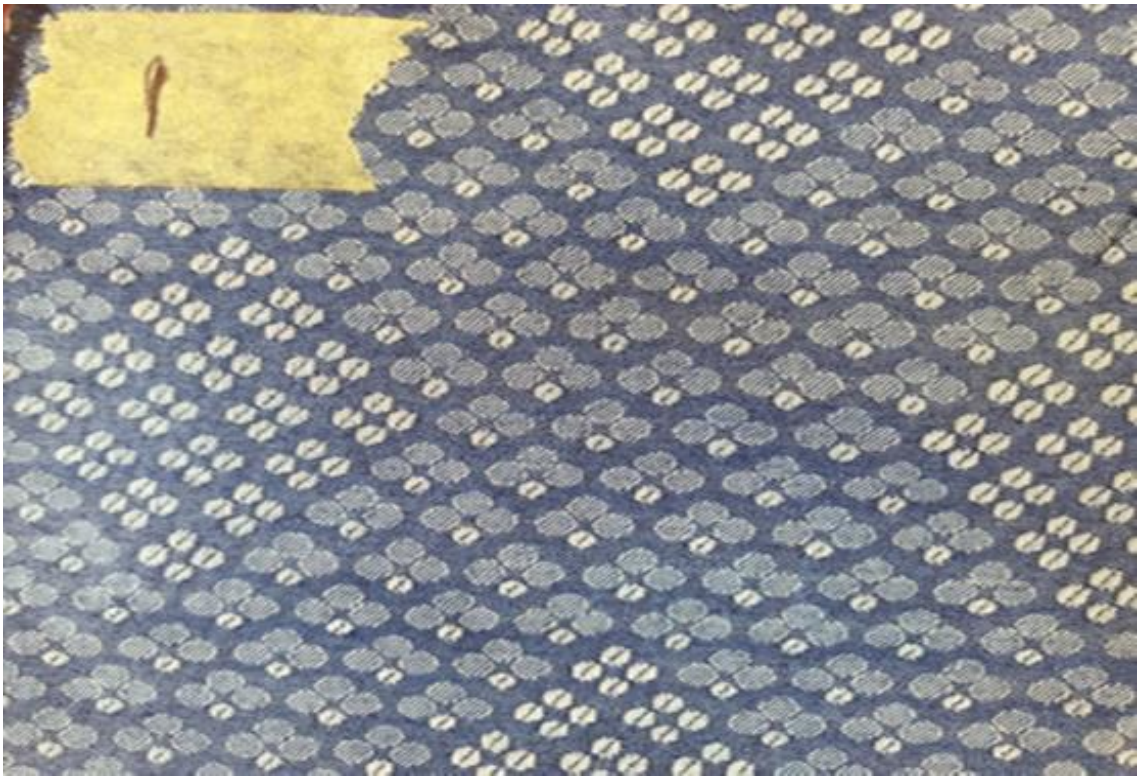


Plate XXI: Standard reference BF sample



Plate XXII: Standard reference CF sample



Plate XXIII: Unmercerized CF dyed by the standard method

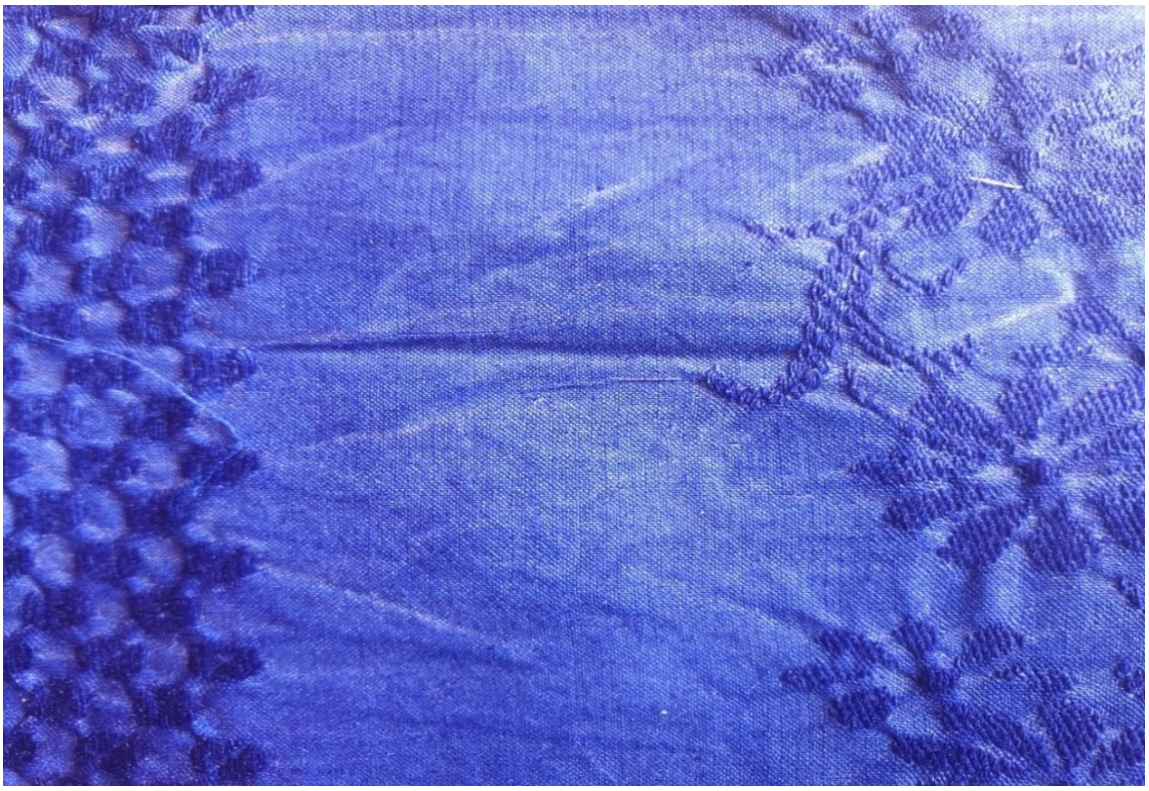


Plate XXIV: CF sample dyed by the wet-on-wet process

There are several colouration effects that can be applicable to blend of two fibres and the most difficult task is to create a solid colouring effect where both components are dyed as closely as possible (Borisova, 2018). Apart from union dyeing, different effects that can be obtained from dyeing of blends including "reserve or resist dyeing" where at least one of the components remains essentially undyed, i.e., almost white, and cross dyeing which is deliberately producing fibres of contrasting colours which may be strong differences in hue, brightness and/or depth such as tone-in-tone or "shadow" effect (Aspland, 1993). Different methods of producing "shadow" effect have been reported previously (Eltz and Maier, 1974; Ashraf *et al.,* 2014). Different types of dyes on different fibres will produce different colour depth and brightness, and the appearance of the dyed product is affected (Gao *et al.*, 2016).

The conditions under which blends can be dyed include the colouristic effect required, behaviour of different fibres in the blend towards different dyes as well as compatibility of dyes from different application categories with one another (Aspland, 1993). In order to satisfactorily dye blend, it is necessary to either modify the fibres, the dyes, or the process. In the case of cotton/polyester blend, two-bath-two-steps dyeing method has been developed where the cotton component is dyed with reactive, direct, or vat dyes and polyester component is dyed with disperse dyes (Oliveria *et al.,* 2017).

In another study, Chao *et al.* (1998) obtained leveled colouration on cotton/polyester blend using previously synthesized vat dyes of the anthraquinone type by a one-bath-two-steps process where polyester was dyed at 130 ^{o}C for 40 min. at pH 5.0 to 5.5 and the cotton component was dyed in aqueous solution of caustic soda, hydros, and sodium sulphate. Baig (2012) suggested that vat dyes are universal colourants as they may behave as either disperse

or acid dyes and therefore can dye synthetics. The author obtained good substantivity and fastness properties on polyester at pH 5.5 to 6.0 using 0.6-0.8 g/l caustic soda and 10 g/l hydros.

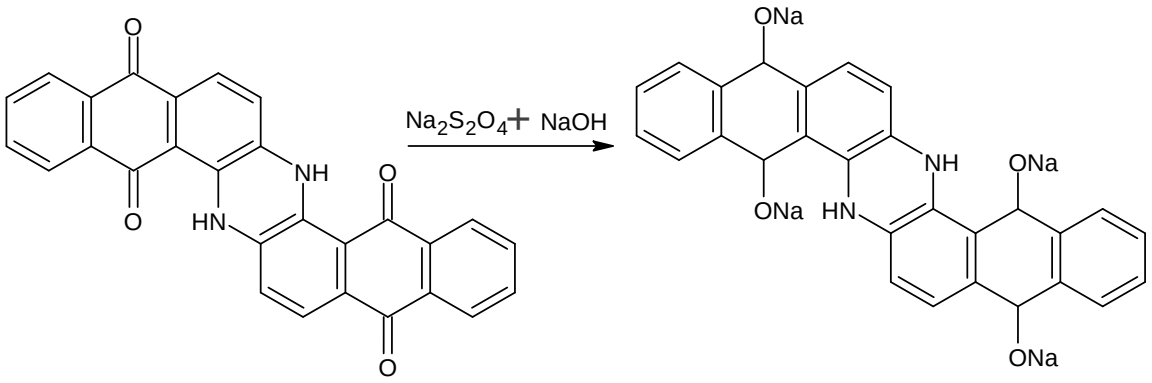
As shown in Plate XXII, mercerized CF dyed using the dry method resulted in dyeing with excellent levelling and uniformity of colour as well as depth of shade and with highly visible fabric design. This may be because vat dyes are amorphous on the fibre after adsorption and oxidation but form crystals on soaping hence only the lines due to the pattern of mercerized cellulose can be recognized (Valko, 1941). Sample in Plate XXII appears much better than that shown in Plate XXIII in terms of colour depth and visibility of fabric design. Mercerization results in increase in proportion of amorphous region and increased availability of hydroxyl groups which is directly related to the increase in moisture absorption, reactivity, and dye absorption (Wagaw and Chavan, 2012; Khalifa, 2017). The swelling of fibres causes the patterns on the fabric to contract and lead to greater dye absorption along the pattern. Vertical line in Plate XXII is 0.018±0.003 m in width while that in Plate XXIII (unmercerized) is 0.023±0.005 m which is a 22 % decrease with reference to the latter (from 5 measurements at different locations).

Mercerization converts fibres to cylindrical shape leading to the increase of the space between fibres so that dye molecules can easily penetrate into the fibres and increase colour depth (Elrys *et al.,* 2015). Vat dyes are not chemically bound to the fibres but are rather trapped between polymer chains that make up the fibres hence the dye molecule must be able to enter the space between polymer chains (Epp, 1995). Fibre channels in a swollen cellulose is between 20 and 40 A and also single molecules of vat dyes are in that order of diameter and

can therefore be able to enter the fibre if they don't agglomerate (Musschoff, 1957). Vat dyes exist as microcrystals on the crystalline micelles of cellulosic materials and affinity of the dyes depends on the extent of the non-polar molecular surface and it has been suggested that the ionized groups are only important for diffusion process (Daescu and Hadaruga, 2000).

The mean appearance rating of samples dyed by the dry and wet-on-wet method are, respectively, 86.07±2.1 % and 38.50±1.6 % (Table 4.24). The ratings are supported visually when samples in Plate XXII and XXIV are compared. As shown in Plate XXIV, the wet-on-wet process resulted in an unlevelled dyeing and low colour yield with white stripes spread on the fabric surface resulting in poor rating. The main reason for the unlevelness may be due to the high conc. of caustic soda embedded in the fibres after mercerization and then dyeing without intermittent washing and drying steps. In general, it is more difficult to produce level dyeing in practice with vat dyes than with other dye classes (Lee *et al.*, 2005).

Over-reduction increases as the conc. of caustic soda used is increased up to the point where it is such as to promote the crystallization of the leuco compound (Brassard, 1943). Equation 5.5 shows typical over-reduction of RSN where all the four keto (carbonyl) groups are reduced instead of two groups under ideal conditions. Carbonyl groups in vat dyes affect the substantivity, degree of adsorption, diffusion into the fibres, and colour uniformity (Sutlovic *et al.,* 2021). Over-reduction of vat dye leads to the formation of insoluble enolic and leuic compounds which may cause unevenness on the dyed material (Adeel *et al.,* 2018). In high alkali pH and the presence of large amounts of hydros, the hydros may dissolve the leuco vat dye which can represent the colour (Shim *et al.*, 2006) and appear as white stripes on the fabric as shown in Plate XXIV.



Equation 4.8: Over-reduction of RSN (Chakraborty, 2010)

Leuco vat anion may be compared to water soluble direct dye anions since it is the anion that is responsible for vat dyeing (Aspland, 1992b). The pH level of the dyebath solution in vat dyeing process is high by the presence of caustic soda that there should be an electrostatic repulsion force between anionic leuco vat dye and cellulose fibre which would show negative charge in the surface of the fibre in strong alkali solution (Kim *et al.* 2013). Large amounts of highly conc. caustic soda embedded on mercerized cellulose which would invariably go into the dyebath and saturate it with sodium ions, could have reduced the solubility of the leuco vat dye. Yoe and Edgar (1922) have similarly shown that the higher the caustic soda conc. in the dyebath, the lower the conc. of the reduced dye as hydroxyl ion favours the rate of solution while Na ions retard it.

Dye self-association (agglomeration) may be favoured by π-π interactions between aromatic regions in the dye molecules expediated by the screening of anionic charge on reduced dye by counterions (Na ions). The formation of leuco vat anion may be suppressed as a consequence of both the strong π-π interactions operating between aromatic regions in the neighbouring dye molecules and the screening of carboxylate ion by the Na^+ counterions. The dye molecules

within the dye aggregates may likely possess lower aqueous solubility than their monomolecular counterparts in the aqueous dyebath. As hydrophobic interaction will result in less water being available to the dye aggregates in the dyebath, the aggregates tend to coalesce and form particles that will constitute a dye dispersion within the aqueous bath (Ferus-Comelo, 2002).

Oschatz (1993) patented a process similar to the wet-on-wet dyeing method used in this study. According to the invention, mercerization and then dyeing of cellulose material with reactive dye was carried out without intermittent washing and drying. Dyes that can be applied according to the invention are those that can be used under alkaline treatment conditions without loss due to hydrolysis when they are applied and fixed on the goods. The alkali treatment can be carried out first followed by dyeing or dyeing can be carried out first before alkali treatment. According to the invention, alkali solution is applied to cellulosic substrate and then the substrate is allowed to dwell in the liquor for 3 to 30 sec. after which excess alkali is removed and then the dye is applied by padding.

The invention by Oschatz (1993) is similar to that of the dyeing experiments except for the padding technique (contrary to the exhaustion method with long liquors used in this study) as well as alkali treatment time and type of dye used. Also, similar but somehow different process has been reported by Wagaw and Chavan (2012). Cellulose material is treated with caustic soda, washed, and then dyed without the drying step. The authors suggested for the wet-on-wet dyeing to be carried out using the exhaust technique and not by padding because exchange of water from wet fabric will dilute the pad liquor. Based on the findings of this study, it is

suggested that the alkali treated material should be washed before the wet-on-wet dyeing process in accordance to the procedure outlined by Wagaw and Chavan (2012).

4.7.1 Model fitting and analysis of variance (ANOVA) for appearance rating

As shown in Table 4.25, the suggested model was "2FI Vs Linear" with insignificant lack of fit because the probability value of 0.1666 exceeds the threshold value of 0.05 (Table 4.26). The linear model selected exhibits low standard deviation, high coefficient of determination (92.25 %) and low PRESS. Values of "Prob>F" less than 0.05 will indicate that the model terms are significant. Caustic soda conc. (factor A), fabric type (factor C), dyeing method (factor D), AC and BD are significant model terms.

The predicted determination coefficient (Pred R^2=0.8753) is in reasonable agreement with the adjusted determination coefficient (Adj R^2=0.9049) which is also satisfactory to confirm the fitness of the model. "Adeq Precision" ratio of 22.562 indicates an adequate signal which implies that this model could be used to navigate the design space. The negative sign in front of the terms in the linear model shown in Equation 4.9 and Equations 4.10a to 4.10d indicates antagonistic effect whereas the positive sign shows synergistic effect.

Table 4.25: Model fitting for appearance rating

Sequential model sum of squares [Type I]						
Source	Sum of Squares	df	Mean Square	F-Value	P-Value>F	
Mean vs Total	3.2E+005	1	3.2E+5			
Block vs Mean	20.64	1	20.64			
Linear vs Block	17989.39	4	4497.35	18.01	<0.0001	
2FI vs Linear	**10121.77**	**6**	**1686.96**	**31.42**	**<0.0001**	**Suggested**
Quadratic vs 2FI	92.73	2	46.36	0.86	0.4313	
Cubic vs Quadratic	711.23	10	71.12	1.46	0.1998	Aliased

Residual	1558.24	32	48.70			
Total	3.54+005	56	6320.54			
			Lack of fit tests			
Source	Sum of Squares	df	Mean Square	F Value	P Value Prob > F	
Linear	11859.30	34	348.8	8.93	<0.0001	
2FI	**1737.54**	**28**	**62.05**	**1.59**	**0.1666**	**Suggested**
Quadratic	1644.81	26	63.26	1.62	0.1584	
Cubic	933.58	16	58.35	1.49	0.2152	Aliased
Pure Error	624.67	16	39.04			
			Model summary statistics			
Source	Standard Deviation	R squared	Adjusted R squared	Predicted R squared	PRESS	
Linear	15.80	0.5903	0.5576	0.4903	15532.42	
2FI	**7.33**	**0.9225**	**0.9049**	**0.8753**	**3800.01**	**Suggested**
Quadratic	7.35	0.9255	0.9042	0.8684	4010.67	
Cubic	6.98	0.9489	0.9137	0.8301	5176.24	Aliased

Table 4.26: Analysis of variance (ANOVA) test for significance (appearance rating)

Source	Sum of Squares	df	Mean Square	F Value	P Value Prob >F	
Block	20.64	1	20.64			
Model	**28111.15**	**10**	**2811.12**	**52.36**	**<0.0001**	**Significant**
A-NaOH conc.	333.25	1	333.25	6.21	0.0166	
B-Hydros conc.	36.06	1	36.06	0.67	0.4169	
C-Fabric	10532.57	1	10532.57	196.19	<0.0001	
D-Dyeing	7087.50	1	7087.50	132.02	<0.0001	
AB	203.06	1	203.06	3.78	0.0582	
AC	789.26	1	789.26	14.70	0.0004	
AD	87.25	1	789.26	1.63	0.2091	
BC	5.12	1	5.12	0.095	0.7589	
BD	236.98	1	236.98	4.41	0.0414	
CD	8800.07	1	8800.07	163.92	<0.0001	
Residual	2362.20	44	53.69			
Lack of Fit	**1737.54**	**28**	**62.05**	**1.59**	**0.1666**	**Not Significant**
Pure Error	624.67	16	39.04			
Cor Total	30494.00	55				
Std. Dev.	7.33			R-squared	0.9225	
Mean	78.00			Adj R-squared	0.9049	
C. V. %	9.64			Pred R-squared	0.8753	
PRESS	3800.01			Adeq Precisior	22.562	
Factor	Coefficient Estimate	df	Standard Error	95 % Confidence interval		VIF
				Low	High	
Intercept	76.00	1	0.98	74.03	77.97	
BLOCK 1	0.61	1				
BLOCK 2	-0.61					
A-NaOH conc.	-3.23	1	1.30	-5.84	-0.62	1.00

B-Hydros conc.	1.06	1	1.30	-1.55	3.67	1.00
C-Fabric	13.71	1	0.98	11.74	15.69	1.00
D-Dyeing	11.25	1	0.98	9.28	13.22	1.00
AB	-3.56	1	1.83	-7.25	0.13	1.00
AC	4.97	1	1.30	2.36	7.58	1.00
AD	1.65	1	1.30	-0.96	4.26	1.00
BC	0.40	1	1.30	-2.21	3.01	1.00
BD	2.72	1	1.30	0.11	5.33	1.00
CD	-12.54	1	0.98	-14.51	-10.56	1.00

Appearance rating =+76.00-3.23* A+1.06* B+13.71* C+11.25* D-3.56*A*B+4.97*A*C+1.65*A*D+0.4*B*C+2.72*B*D-12.54*C*D …..4.9

Appearance rating (100 % cotton/wet-on-wet) =+42.15+0.169* NaOH conc.+1.726* hydros conc.-0.143* NaOH conc.* hydros conc. …..4.10a

Appearance rating (blend/wet-on-wet) =+62.45+2.155* NaOH conc.+1.886* hydros conc.-0.143* NaOH conc.* hydros conc. …..4.10b

Appearance rating (100 % cotton/dry) =+63.486+0.830* NaOH conc.+2.814* hydros conc.-0.143* NaOH conc.* hydros conc. …..4.10c

Appearance rating (blend/dry) =+33.646+2.816* NaOH conc.+2.974* hydros conc.-0.143* NaOH conc.* hydros conc. …..4.10d

4.7.2 Diagnostics (appearance rating)

Diagnosis shown in Figures 4.83 to 4.86 indicated that there is no anomaly and therefore the model is statistically solid. Table 4.27 shows that most of the experimental values are in reasonable agreement with predicted values with the highest residuals observed in run order 9 and 47.

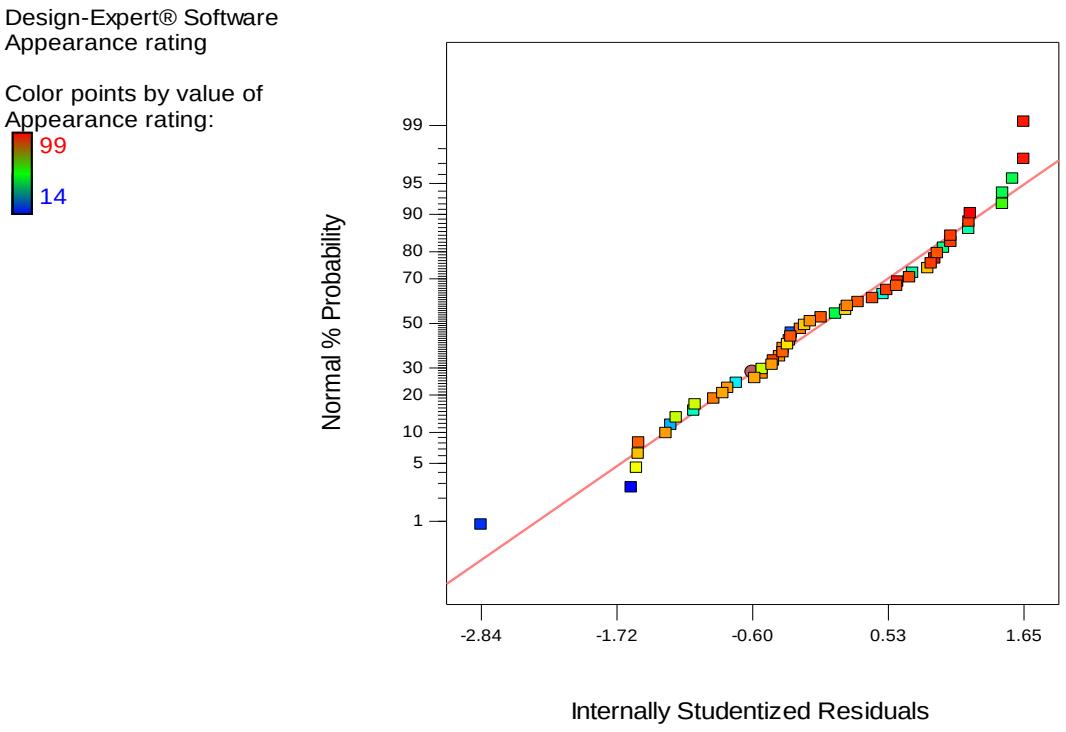


Figure 4.83: Normal probability plot of residuals

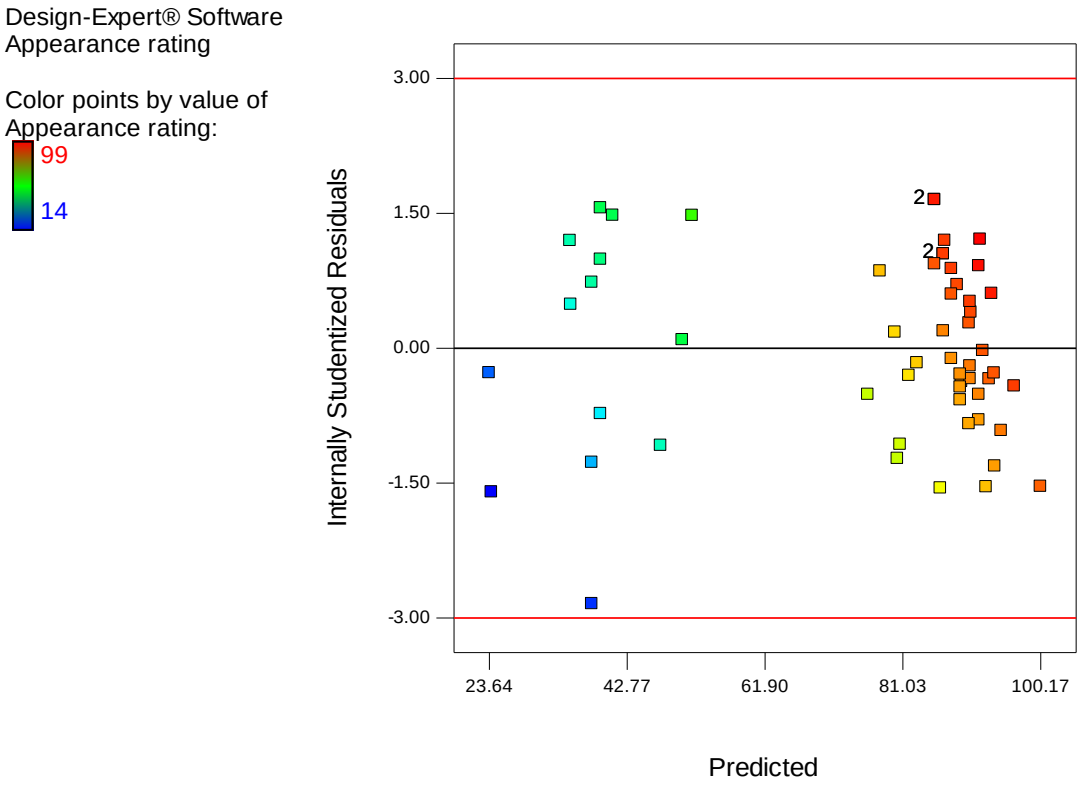


Figure 4.84: Studentized residuals versus predicted

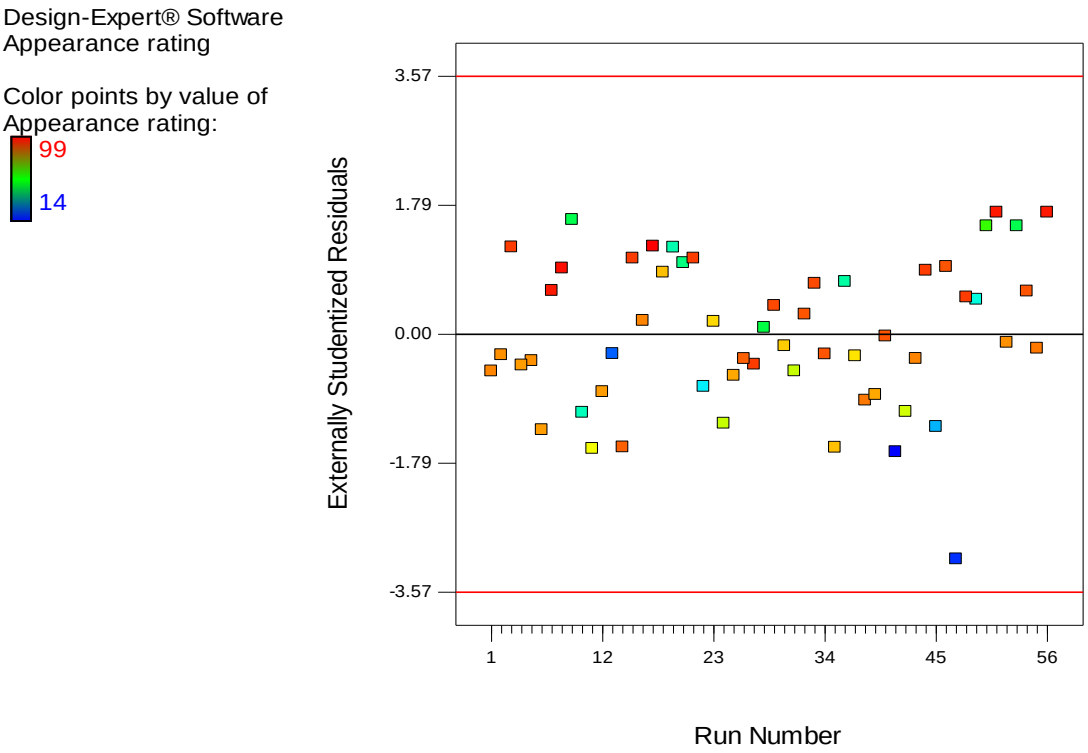


Figure 4.85: Externally studentized residuals

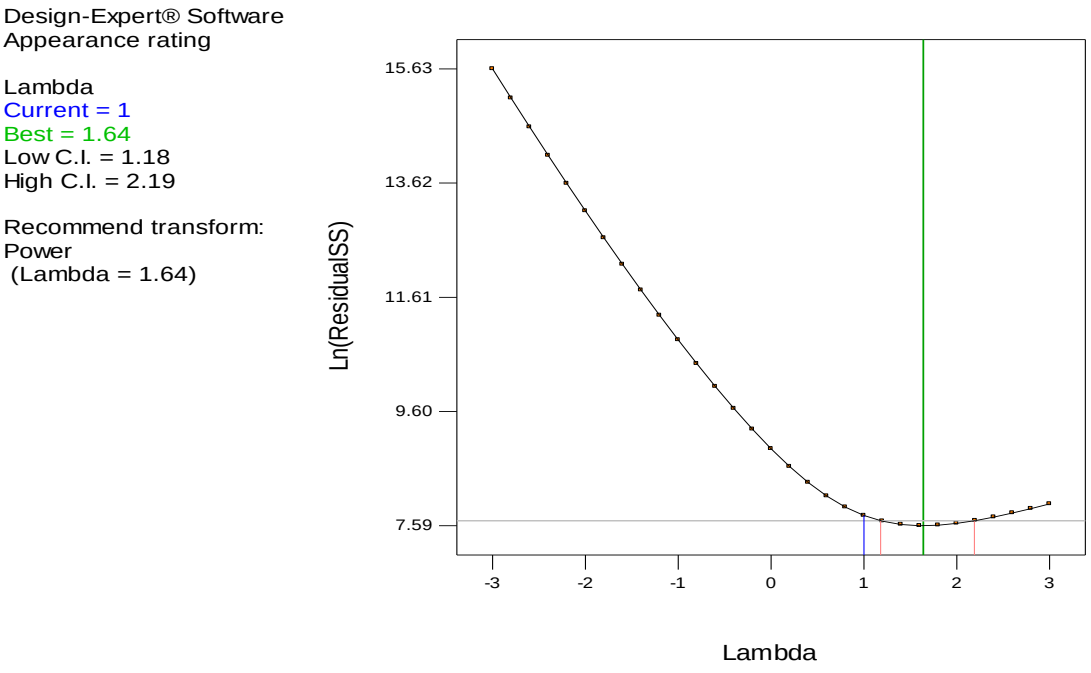


Figure 4.86: Box-Cox plot

Table 4.27: Diagnostics case statistics for appearance rating

SO	AV	PV	Res.	Lev.	ISR	ESR	IFVD	CD	RO
1	41.00	47.45	-6.45	0.339	-1.083	-1.085	-0.778	0.050	10
2	42.00	34.88	7.12	0.339	1.195	1.201	0.860	0.061	19
3	51.00	50.45	0.55	0.339	0.092	0.091	0.065	0.000	28
4	22.00	23.64	-1.64	0.339	-0.275	-0.272	-0.195	0.003	13
5	34.00	39.11	-5.11	0.089	-0.730	-0.726	-0.227	0.004	22
6	46.00	39.11	6.89	0.089	0.986	0.985	0.309	0.008	20
7	50.00	39.11	10.89	0.089	1.558	1.584	0.496	0.020	9
8	61.00	51.82	9.18	0.277	1.474	1.495	0.925	0.069	50
9	14.00	23.97	-9.97	0.277	-1.600	-1.630	-1.008	0.082	41
10	50.00	40.81	9.19	0.277	1.476	1.496	0.926	0.069	53
11	38.00	34.98	3.02	0.277	0.485	0.480	0.297	0.007	49
12	18.00	37.89	-19.89	0.089	-2.845	-3.113	-0.975	0.066	47
13	29.00	37.89	-8.89	0.089	-1.272	-1.281	-0.401	0.013	45
14	43.00	37.89	5.11	0.089	0.730	0.726	0.227	0.004	36
15	87.00	89.22	-2.22	0.339	-0.372	-0.368	-0.264	0.006	5
16	94.00	96.52	-2.52	0.339	-0.423	-0.419	-0.300	0.008	27
17	86.00	93.82	-7.82	0.339	-1.313	-1.325	-0.949	0.074	6
18	94.00	86.87	7.13	0.339	1.197	1.203	0.862	0.061	3
19	88.00	91.61	-3.61	0.089	-0.516	-0.512	-0.160	0.002	1
20	98.00	91.61	6.39	0.089	0.914	0.913	0.286	0.007	8
21	86.00	91.61	-5.61	0.089	-0.802	-0.799	-0.250	0.005	12
22	92.00	90.27	1.73	0.277	0.278	0.275	0.170	0.002	32
23	93.00	90.52	2.48	0.277	0.398	0.395	0.244	0.005	29
24	92.00	92.17	-0.17	0.277	-0.028	-0.028	-0.017	0.000	40
25	93.00	88.61	4.39	0.277	0.704	0.700	0.433	0.016	33
26	89.00	90.39	-1.39	0.089	-0.199	-0.197	-0.062	0.000	55
27	88.00	90.39	-2.39	0.089	-0.342	-0.339	-0.106	0.001	43
28	94.00	90.39	3.61	0.089	0.516	0.512	0.160	0.002	48
29	77.00	86.28	-9.28	0.339	-1.557	-1.584	-1.135	0.104	11
30	73.00	80.32	-7.32	0.339	-1.228	-1.236	-0.886	0.065	24
31	91.00	100.17	-9.17	0.339	-1.539	-1.564	-1.121	0.101	14
32	81.00	79.96	1.04	0.339	0.175	0.173	0.124	0.001	23
33	88.00	86.68	1.32	0.089	0.189	0.187	0.059	0.000	16
34	94.00	86.68	7.32	0.089	1.047	1.048	0.328	0.009	15
35	94.00	86.68	7.32	0.089	1.047	1.048	0.328	0.009	21
36	89.00	94.72	-5.72	0.277	-0.917	-0.916	-0.566	0.027	38
37	73.00	76.21	-3.21	0.277	-0.516	-0.511	-0.316	0.008	31
38	74.00	80.68	-6.68	0.277	-1.072	-1.074	-0.664	0.037	42
39	85.00	90.25	-5.25	0.277	-0.842	-0.839	-0.519	0.023	39
40	92.00	85.46	6.54	0.089	0.935	0.933	0.292	0.007	46

SO: Standard order, AV: Actual value, PV: Predicted value, Res: Residual, Lev: Leverage, ISR: Internally studentized residuals, ESR: Externally studentized residuals, IFVD: Influence on fitted values drifts, CD: Cooks distance, RO: Run order

4.7.3 Main and interaction effects

4.7.3.1 Main effects

Figures 4.87 to 4.93 show individual (main) effects. The warning sign still shows indicating that the factors are involved in an interaction and therefore not advisable to interpret the plots.

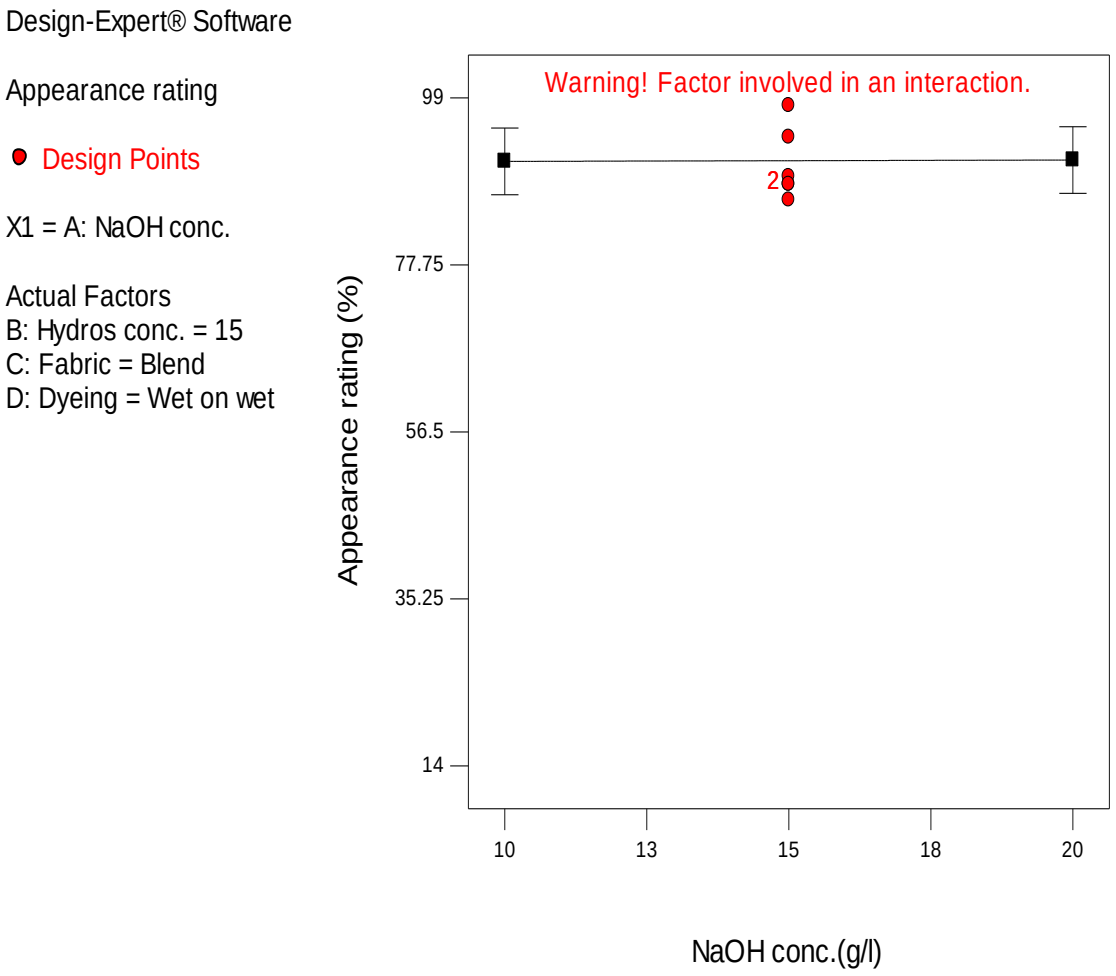


Figure 4.87: Effect of caustic soda conc. on appearance rating of BF

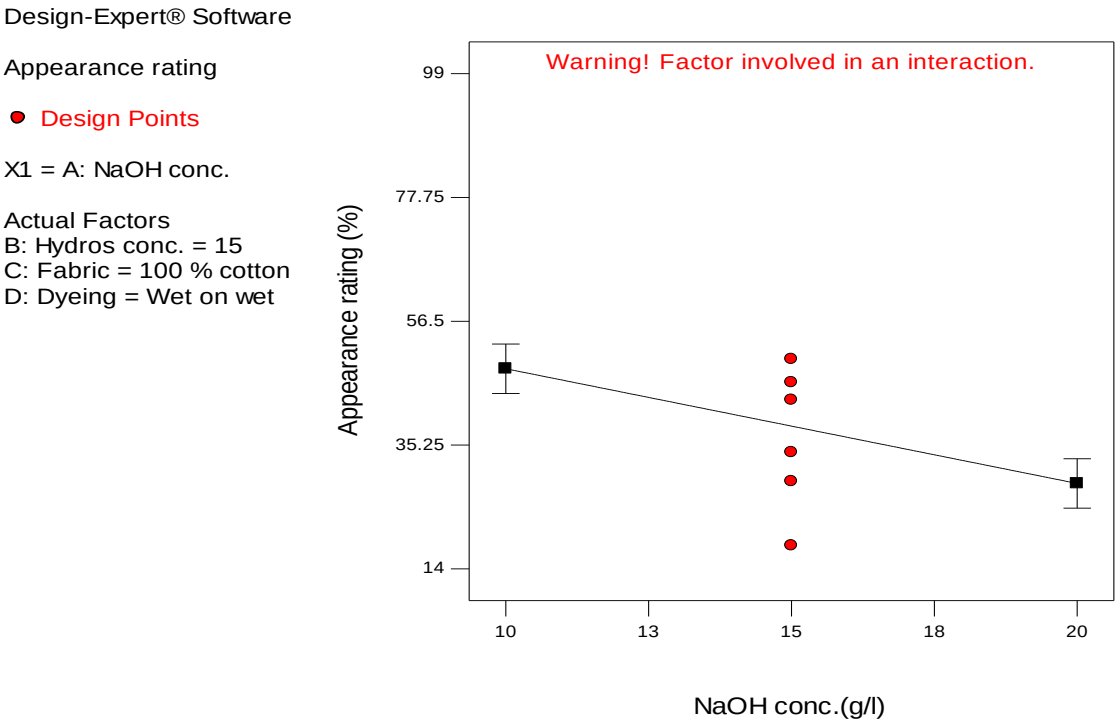


Figure 4.88: Effect of caustic soda conc. on appearance rating of CF

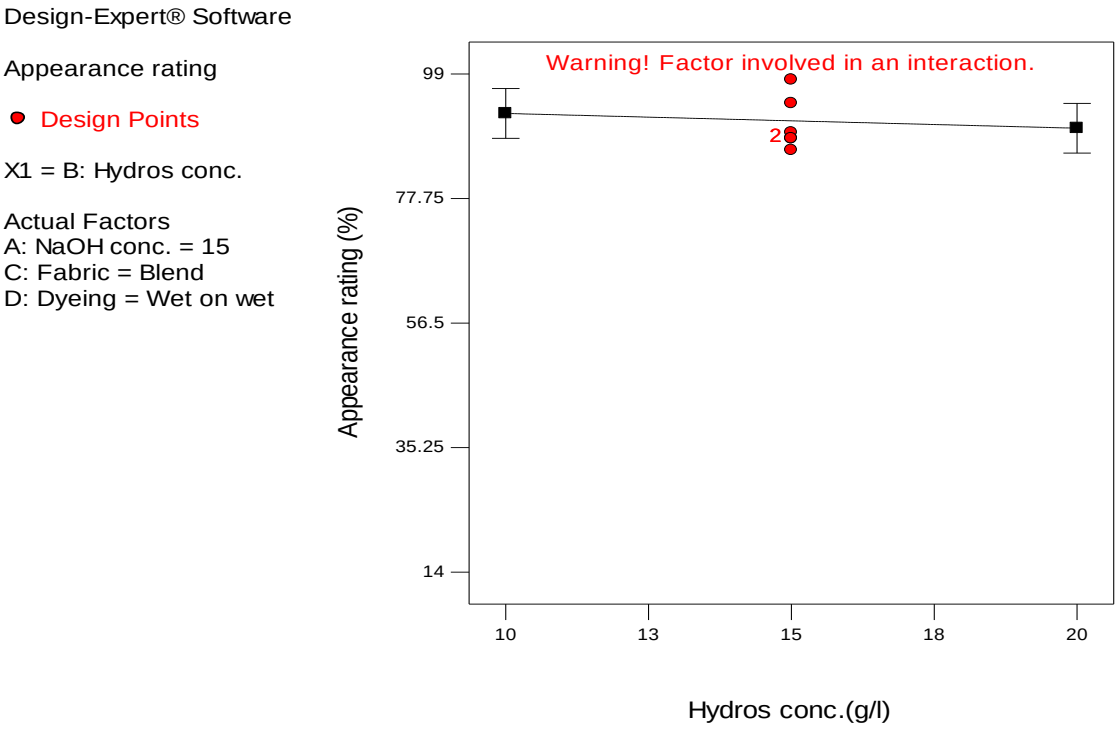


Figure 4.89: Effect of hydros conc. on appearance rating of BF

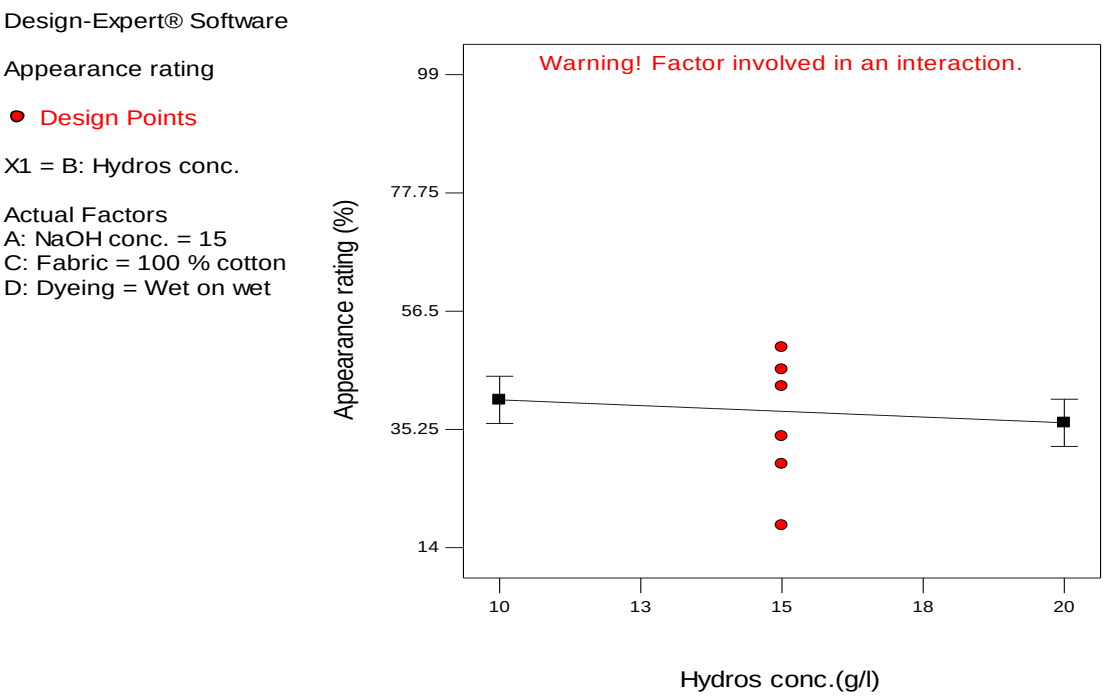


Figure 4.90: Effect of hydros concentration on appearance rating of CF

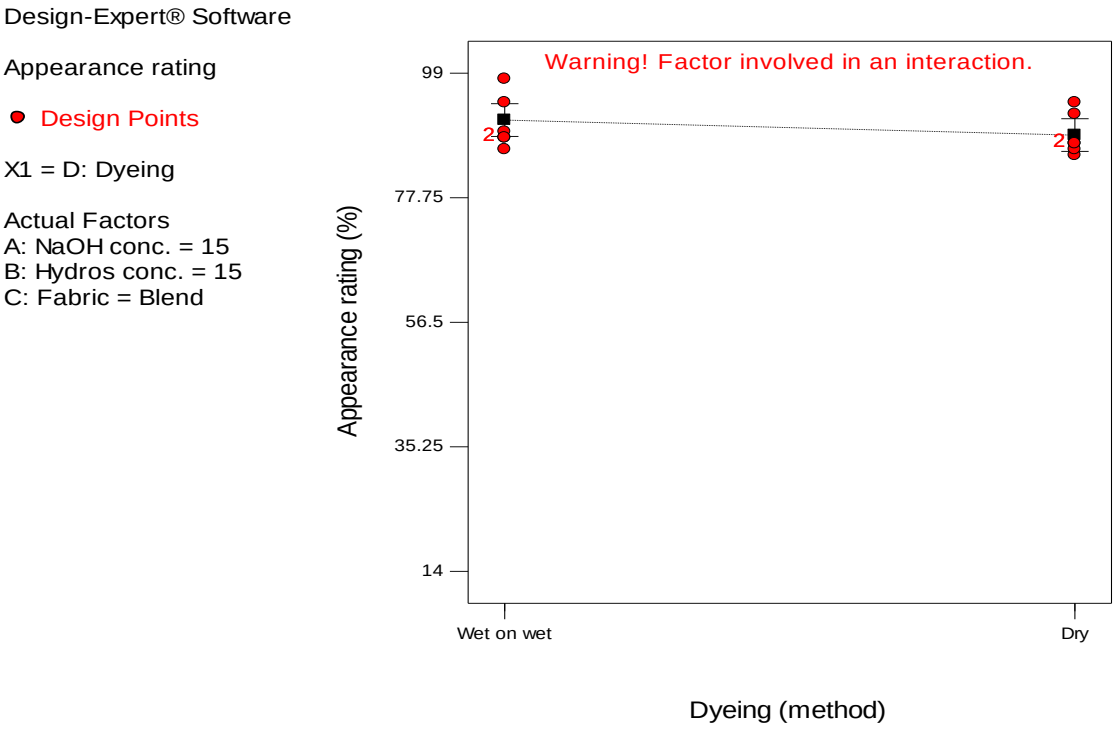


Figure 4.91: Effect of dyeing method on appearance rating of BF

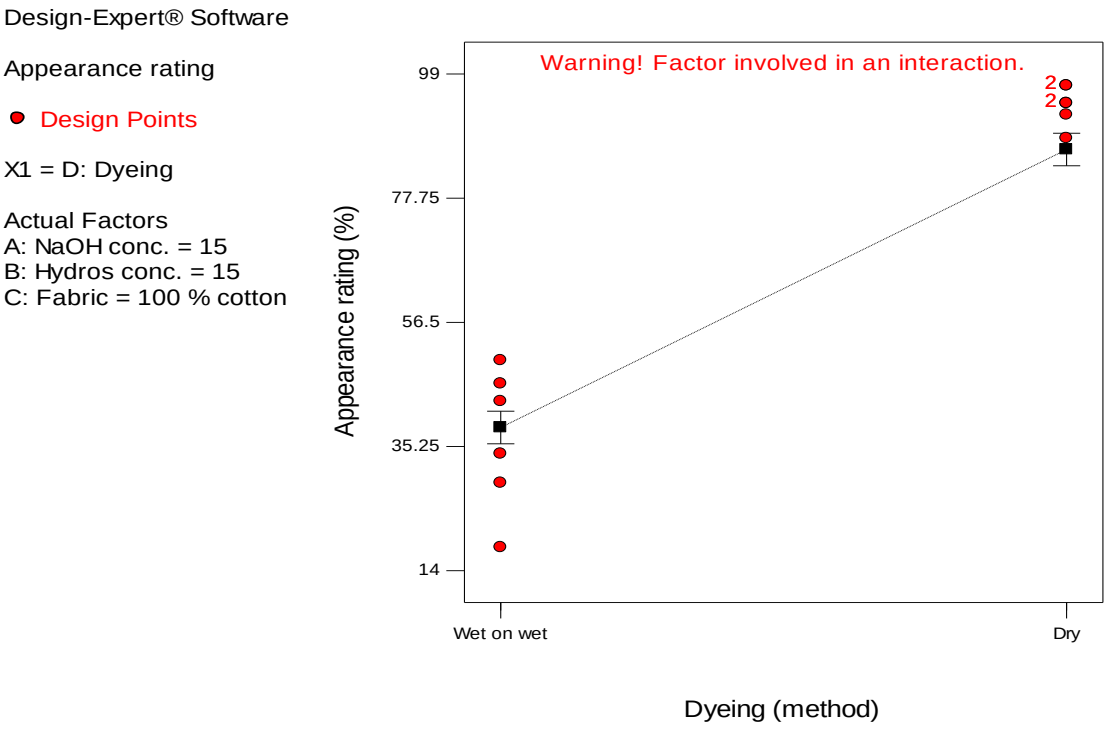


Figure 4.92: Effect of dyeing method on appearance rating of CF

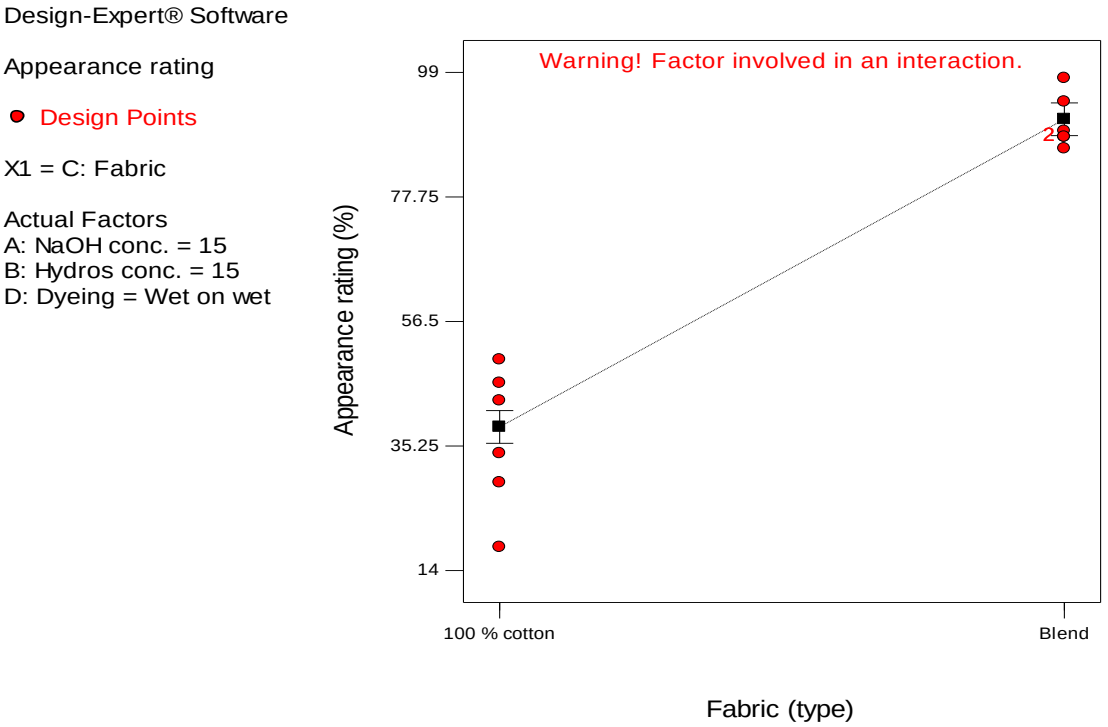


Figure 4.93: Appearance rating by fabric type

4.7.3.2 Interaction effects

ANOVA shown in Table 4.26 indicated that there is an interaction among factors that affected the appearance rating which include caustic soda conc. and hydros conc. (AB), caustic soda conc. and fabric type (AC), caustic soda conc. and dyeing method (AD), hydros conc. and fabric type (BC), hydros conc. and dyeing method (BD), as well as fabric type and dyeing method (CD).

Caustic soda and hydros conc.: Figure 4.94 shows that at high caustic soda conc., less quantity of hydros in needed to achieve better appearance on BF. As shown in Figure 4.95, high hydros conc. with high caustic soda conc. is bad for appearance in the wet-on-wet dyeing of CF. This combination is suggested as the likely cause of over-reduction of the dyes with consequent unlevelness and poor colour yield.

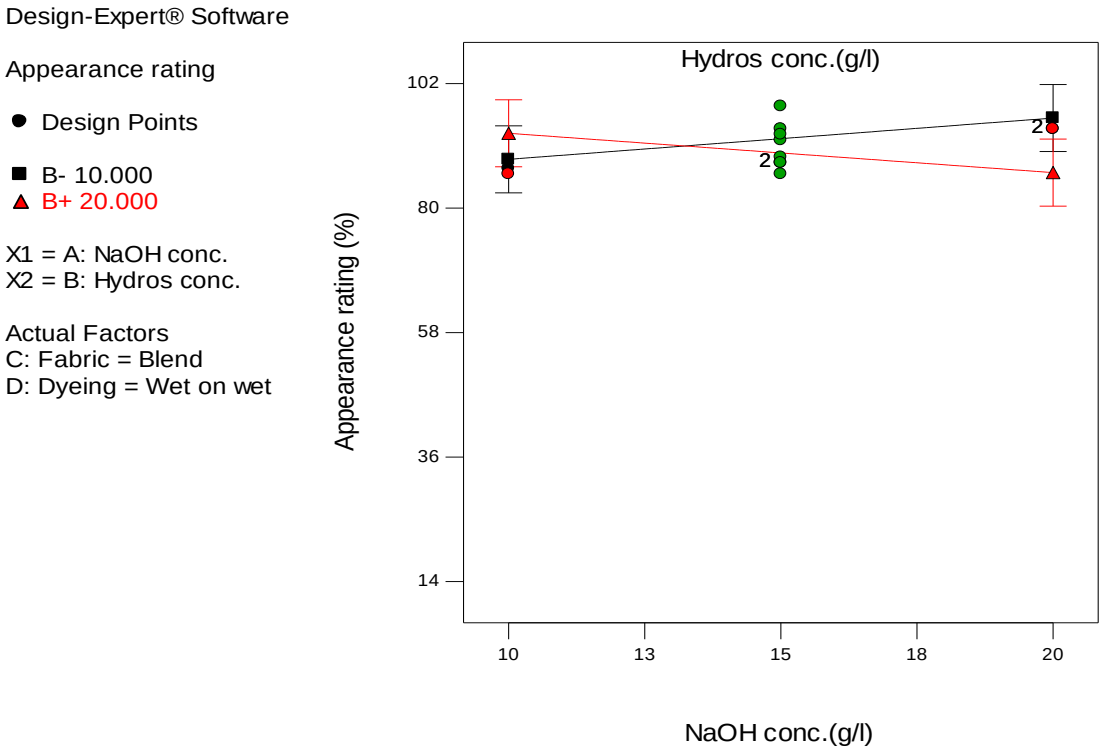


Figure 4.94: Interaction between caustic soda and hydros to affect the appearance of BF

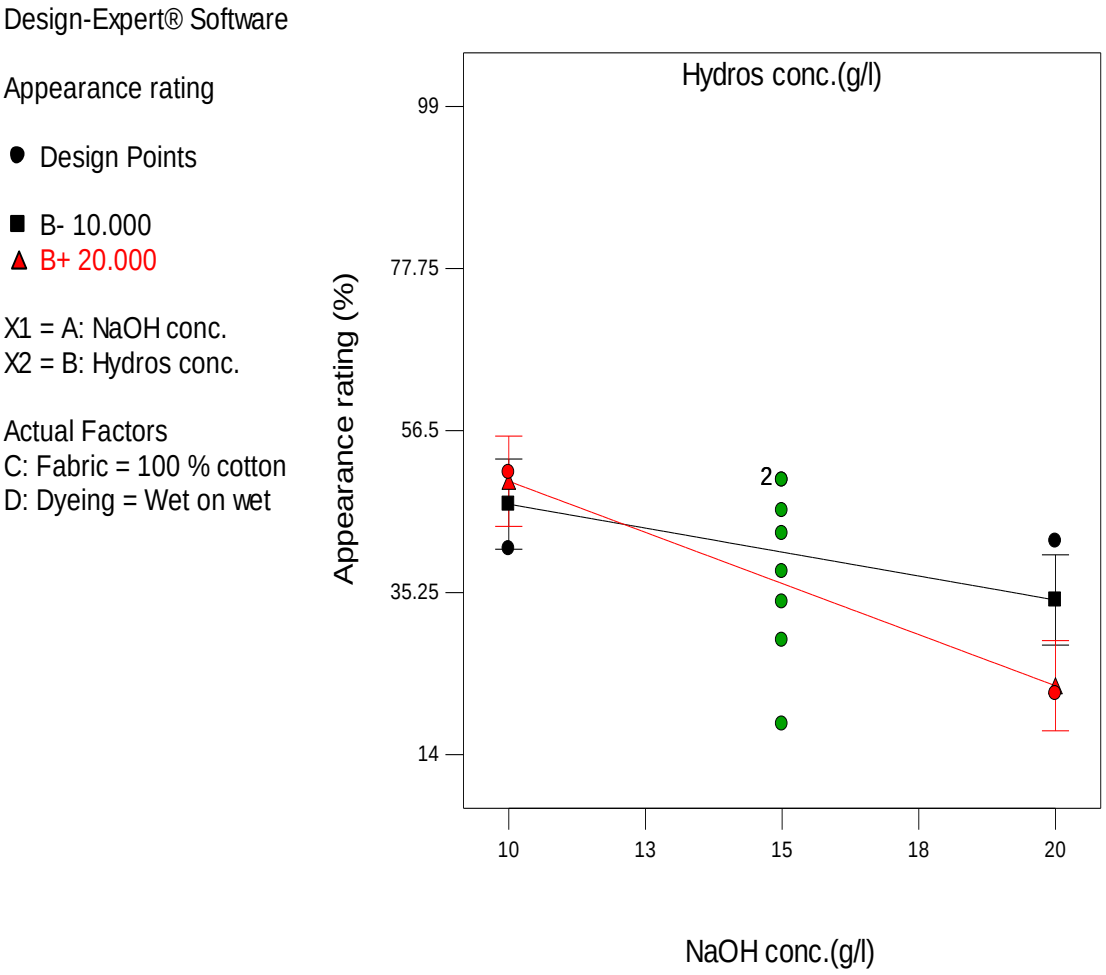


Figure 4.95: Interaction between caustic soda and hydros to affect the appearance of CF

Caustic soda conc. and dyeing method: Figure 4.96 shows that caustic soda conc. does not affect the appearance of BF for the wet-on-wet process. High caustic soda conc. is bad for appearance for the wet-on-wet dyeing of CF (Figure 4.97).

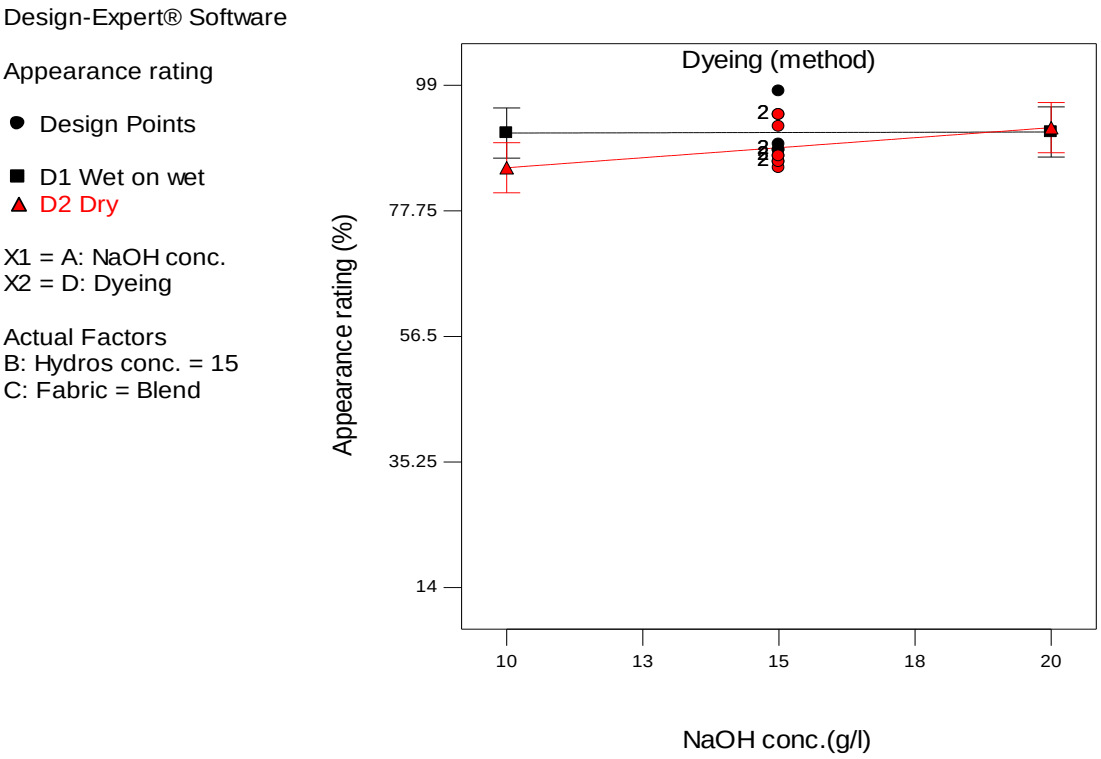


Figure 4.96: Interaction between caustic soda conc. and dyeing method to affect the appearance of BF

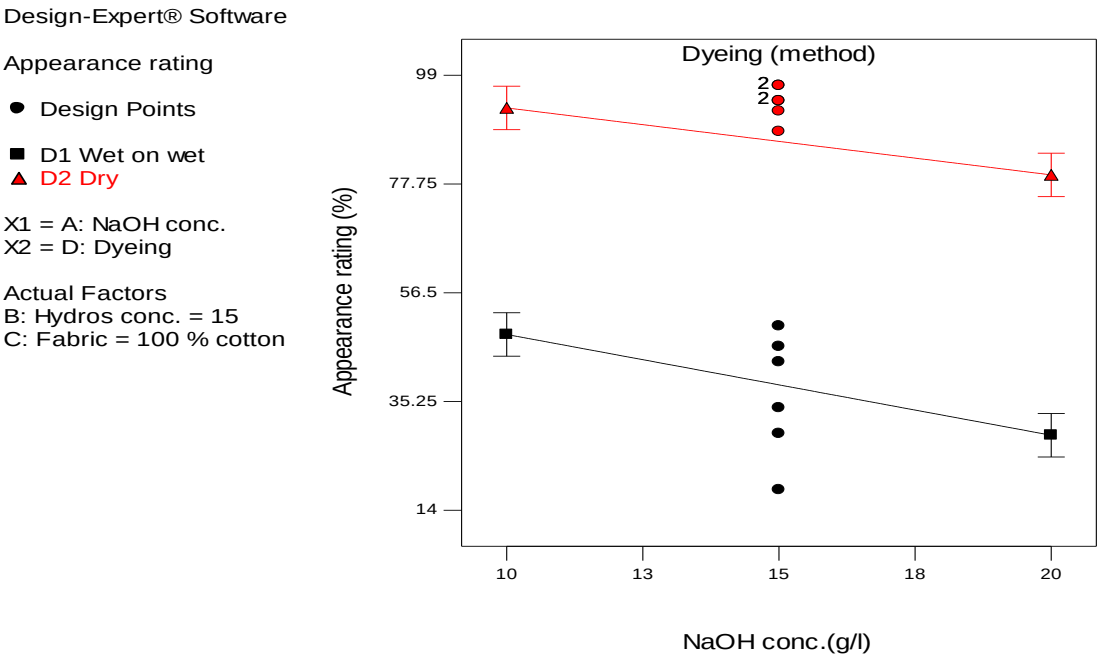


Figure 4.97: Interaction between caustic soda conc. and dyeing method to affect the appearance of CF

Conc. of hydros and dyeing method: Figure 4.98 shows that wet-on-wet dyeing of BF requires low hydros conc. for better appearance. The dry dyeing of CF, however, gave better appearance with high conc. of hydros as shown in Figure 4.99. This may be attributable to the fact that large quantity of hydros is needed to compensate for its loss due to oxidative decomposition of hydros as the dyebath is the open type with large LR.

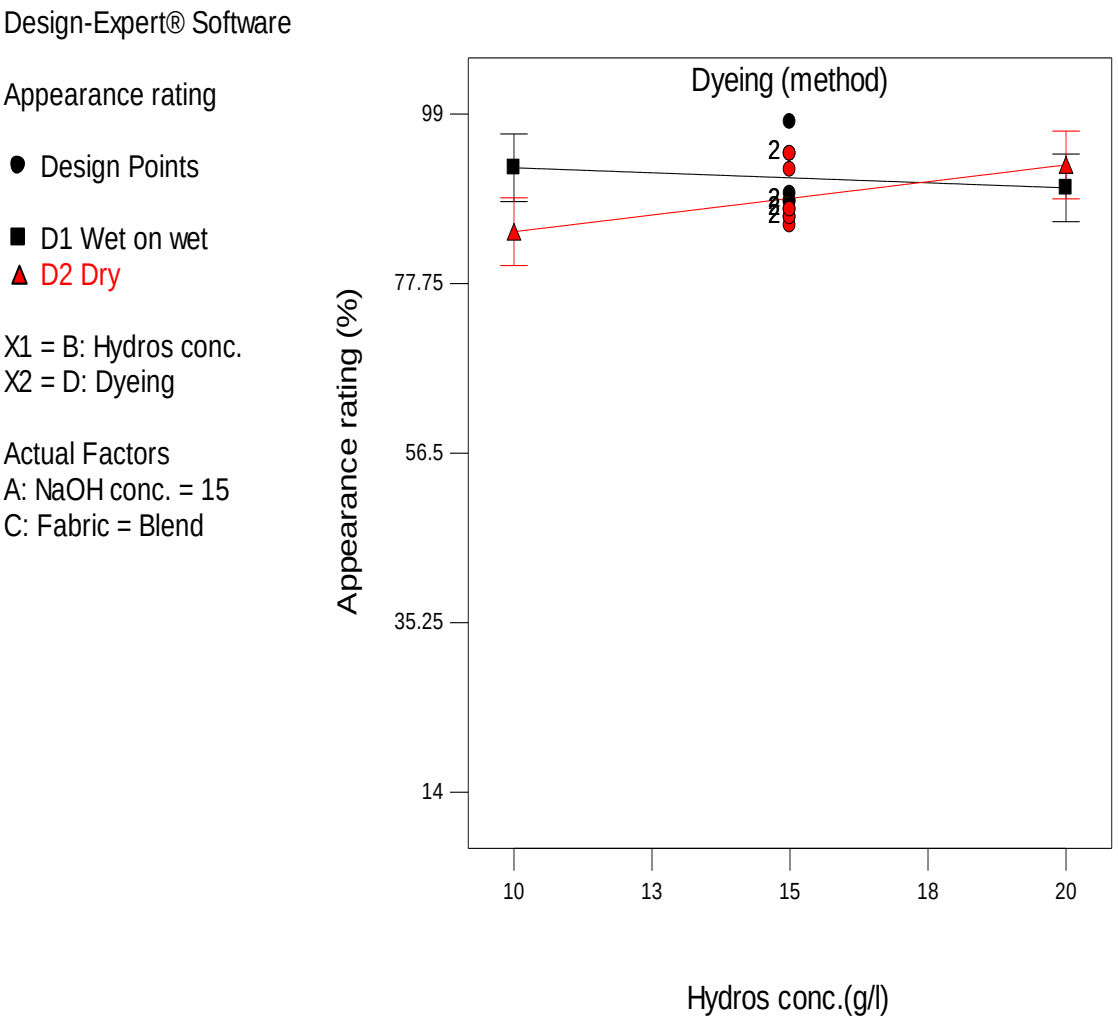


Figure 4.98: Interaction between hydros conc. and dyeing method to affect the appearance of BF

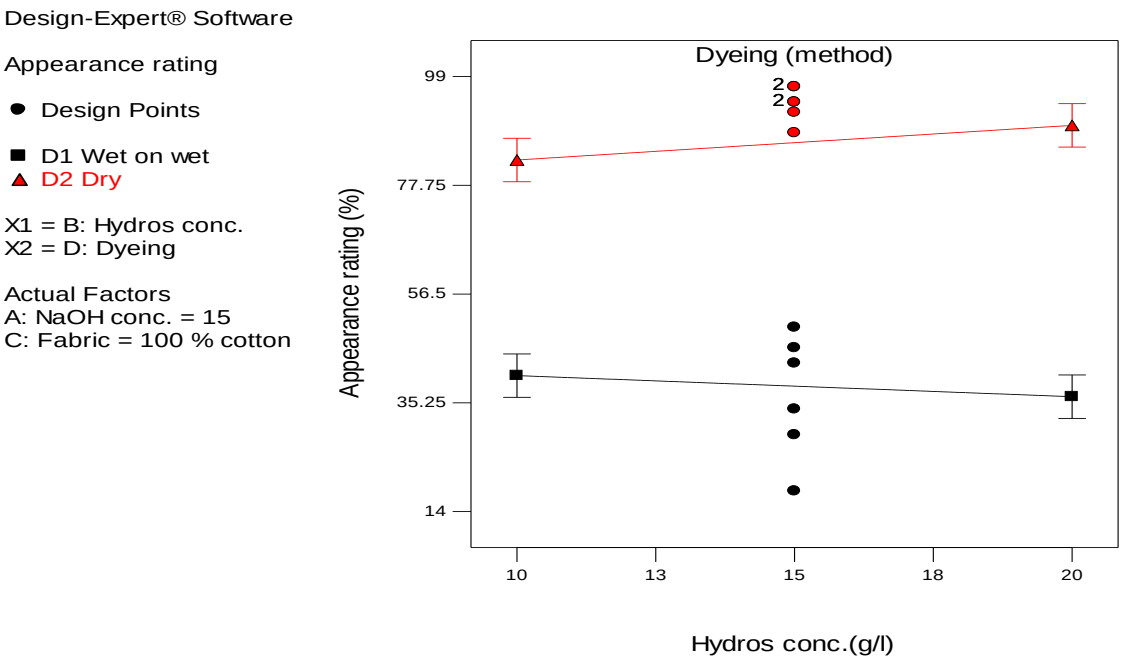


Figure 4.99: Interaction between hydros conc. and dyeing method to affect the appearance of CF

Caustic soda conc. and fabric type: As shown in Figure 4.100, the appearance of BF is the same for all conc. of caustic soda whereas CF appear better with lower caustic soda conc.

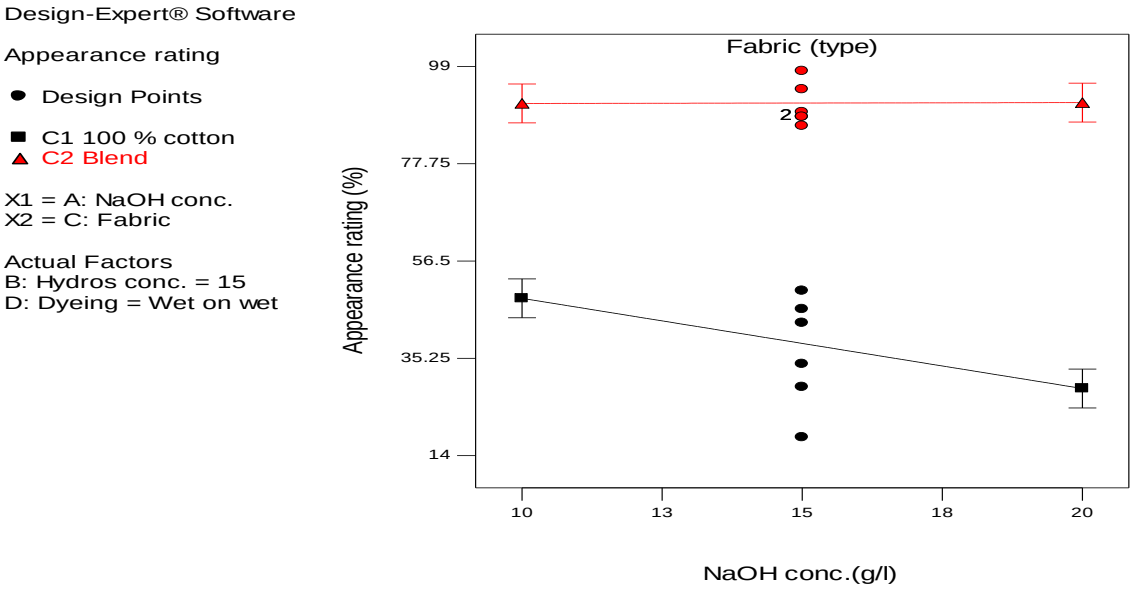


Figure 4.100: Interaction between caustic soda conc. and fabric type to affect the appearance rating of BF and CF

Conc. of hydros and fabric type: The appearance of CF is rated low with high concentration of hydros while BF has high rating with at all concentrations of hydros (Figure 4.101).

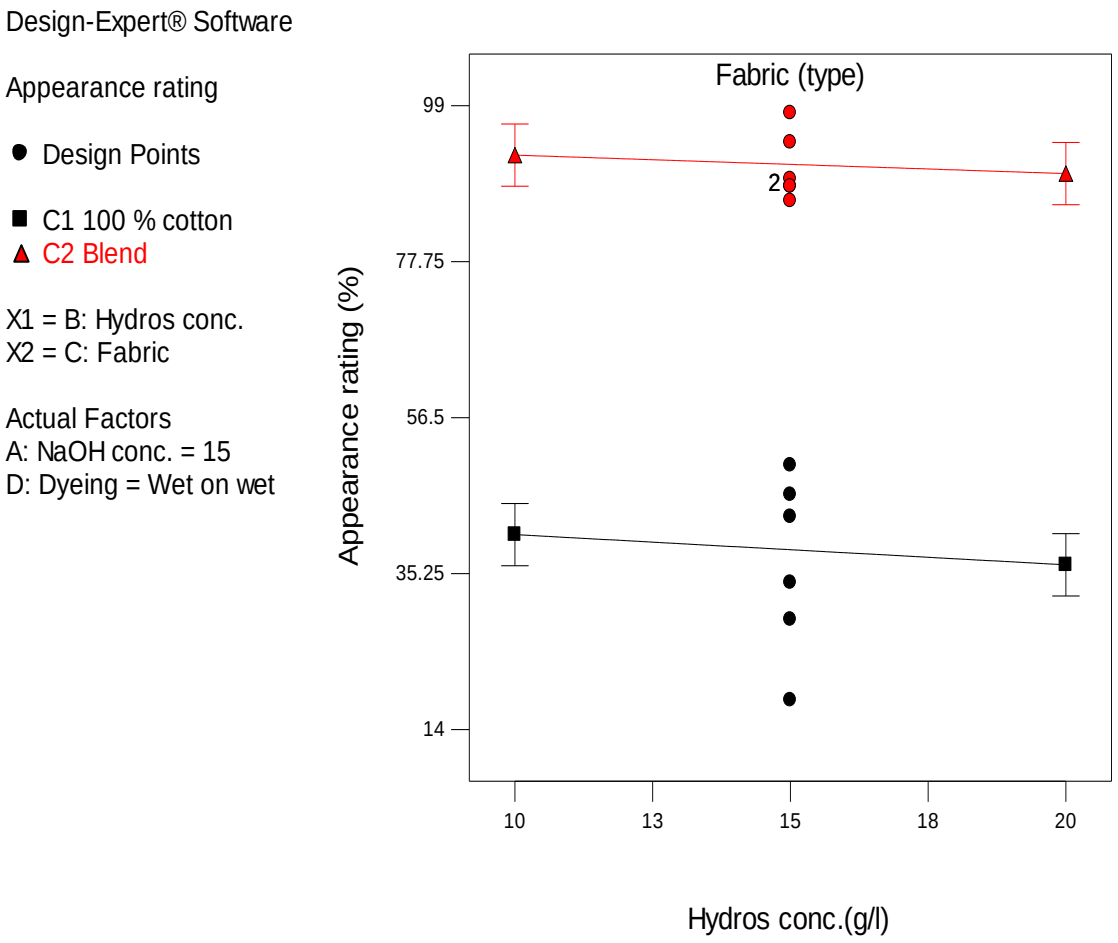


Figure 4.101: Interaction between hydros conc. and fabric type to affect the appearance of BF and CF

Fabric type and dyeing method: Figure 4.102 shows that dry dyeing method is good for appearance of both CF and BF whereas the wet-on-wet method is bad for the rating of CF.

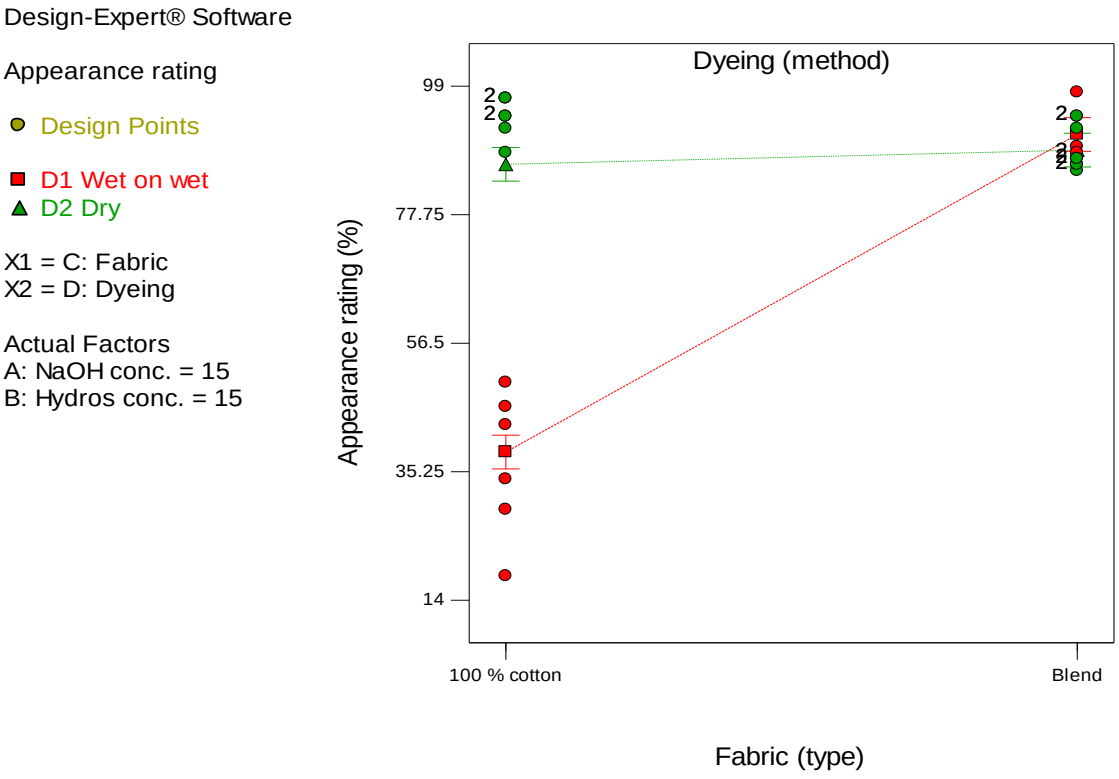


Figure 4.102: Interaction between fabric type and dyeing method to affect the appearance of BF and CF

4.7.4 Tensile strength of dyed fabrics

Tensile strength has not been included as a response in the CCD of the dyeing experiment because it cannot be fit by any model in mercerization experiments. However, it has been established that dye-fibre interactions are accompanied by changes in the mechanical properties of the fibres (Ugbolue and Aula, 1980). CF Samples were selected from the dyeing experiments which include samples from run number 10, 11, 13, and 23 based on dyeing method employed, conc. of caustic soda and hydros used for dyeing as well as whether the material undergo finishing operation or not. As shown in Table 4.28, samples 10 and 11 were both dyed using 10 g/l each of caustic soda and hydros by the wet-on-wet and dry methods, respectively (wet/UF-10 and dry/UF-11, respectively). Samples 13 and 23 were dyed using 20

g/l each of caustic soda and hydros also dyed by the wet-on-wet and dry methods, respectively, (wet/UF-13 and dry/UF-23, respectively).

Table 4.28: Tensile strength of dyed and finished fabrics

Sample	NaOH conc. (g/l)	Hydros conc. (g/l)	Dyeing/ Finishing	Tensile strength±SD (N)		Average tensile strength (N)
				warp	weft	
10	10	10	Wet/UF	173.14±23.41	76.43±14.26	124.79
10	10	10	Wet/F	128.11±18.21	46.84±13.68	87.48
11	10	10	Dry/UF	181.21±28.73	87.02±20.63	134.12
11	10	10	Dry/F	139.17±13.68	51.74±18.59	95.46
13	20	20	Wet /UF	178.94±48.58	68.14±16.32	123.54
13	20	20	Wet/F	130.72±26.41	42.83±11.96	86.78
23	20	20	Dry/UF	190.28±36.25	84.51±32.48	137.40
23	20	20	Dry/F	135.72±25.37	54.38±12.80	95.05
UMD	20	20	Dry/UF	140.74±18.36	48.47±13.27	108.12
UMD	20	20	Dry/F	135.93±22.62	34.18±10.25	82.06
UMUD	-	-	-	147.15±41.70	59.39±19.60	103.27

Wet: wet-on-wet method, Dry: dry dyeing method, UF: Unfinished, F: Finished, UMD: Unmercerized dyed, UMUD: Unmercerized undyed

In order to determine the effect of finishing operation on the dyed materials, the four selected samples were divided into two equal halves with one half of each subjected to a beating operation shown in Plate V (section 3.2.8.3) using a force of 53.51 N. The samples were labelled wet/F-10, dry/F-11, wet/F-13, and dry/F-23. Dry/UF-UMD sample, dyed by the dry

method using 20 g/l each of caustic soda and hydros resulted in strength value of 108.12 N which is about 4.7 % higher than that of UMUD sample with a strength value of 103.27 N **(**Table 4.16, section 4.6.2**).** This increase may be due to the nature of vat dyes where the dyes are converted to insoluble pigments within the fibre by oxidation and soaping aftertreatment which reorient the pigments and associate them into more crystalline form. Elrys *et al.* (2015) gave similar suggestion for increase in breaking load of mercerized yarn due to vat dyeing.

Dry/F-UMD sample has an inferior strength when compared to Dry/UF-UMD and the former also has lower values than that of UMUD sample. This may be attributed to the weakening and breaking of yarns during the beating operation. This suggestion holds when all finished and unfinished samples are compared irrespective of the dyeing method employed (wet-on-wet or dry). When the strengths of wet/UF-10 and dry/UF-11 samples are compared, the latter has higher values than the former with about 7.5 % increase. Similarly, the strength value of dry/UF-23 is about 11.2 % higher than that of wet/UF-13 sample. The results clearly indicate that the wet-on-wet dyed samples have inferior strength which can be ascribed to the formation of oxycellulose during the dyeing process. Montazer and Sadighi (2006) attributed reduction of tensile strength of mercerized yarn to cotton weakness caused by the production of oxycellulose.

Results showed that samples dyed with 20 g/l each of caustic soda and hydros generally have lower strength values than those dyed with 10 g/l each of caustic soda and hydros. Similarly, Landolt (1949) measured lower strength values of yarns with increasing caustic soda conc. in vat dyebath formulation. Strength values of all selected samples which are previously mercerized before dyeing are higher than that of UMD and the UMUD samples. Since

mercerization using 201 g/l at 85 ^{o}C for 3 min. resulted in strength value of 137.93 N (Table 4.16, section 4.6.2) and the selected samples were treated under nearly similar conditions before they are dyed, it is indicative that the dyeing process caused little changes in strength. Ugbolue and Aula (1980) showed that covalent bond formed between Procion reactive dye and cotton fibre led to noticeable changes in the mechanical properties of the fibre where higher dye absorption resulted in low specific stress of the tested yarns. The authors attributed the decrease in specific stress to the breaking of internal structural elements.

4.7.5 Optimization of dyeing parameters using desirability function

A single response method was applied for optimization of combinations of four factors (two numeric and two categoric) namely caustic soda conc., hydros conc., fabric type, and dyeing method. The response was appearance rating (levelness). The criterion was set as follows: “in range” caustic soda concentration (8-22 g/l), “in range” hydros concentration (8-22 g/l), “in range” fabric type (low level for CF and high level for BF), “in range” dyeing method (low level for wet-on-wet and high level for dry method), “maximize” appearance rating (levelness).

By seeking response changes from one hundred and twenty starting points for four combinations of categoric factor levels (fabric type and dyeing method), two solutions each for BF and CF were selected (from twenty-seven solutions) on the basis of wet-on-wet and dry dyeing method and the one that has relatively lower caustic soda concentration and higher hydros concentrations. The solutions were also chosen not by having high desirability only but from factor combinations that will provide better levelness (dyeing quality).

The dot on each ramp shown in Figures 4.103 and 4.104 for the wet-on-wet process (for BF and CF, respectively) and Figures 4.105 and 4.106 for dry dyeing method (for BF and CF, respectively) reflects the factor setting or response prediction for that solution. The height of the dot shows how desirable it is. Figures 4.103 and 4.104 show that wet-on-wet dyeing using 10g/l caustic soda conc. and 20 g/l hydros conc. will result in 93.21 % appearance rating for BF and 49.85 % for CF with respective desirabilities of 0.932 and 0.422. Figures 4.105 and 4.106 indicated that dry dyeing using 10g/l caustic soda conc. and 20 g/l hydros conc. will result in 92.78 % appearance rating for BF and 99.17 % for CF with desirabilities of 0.927 and 1.000, respectively.

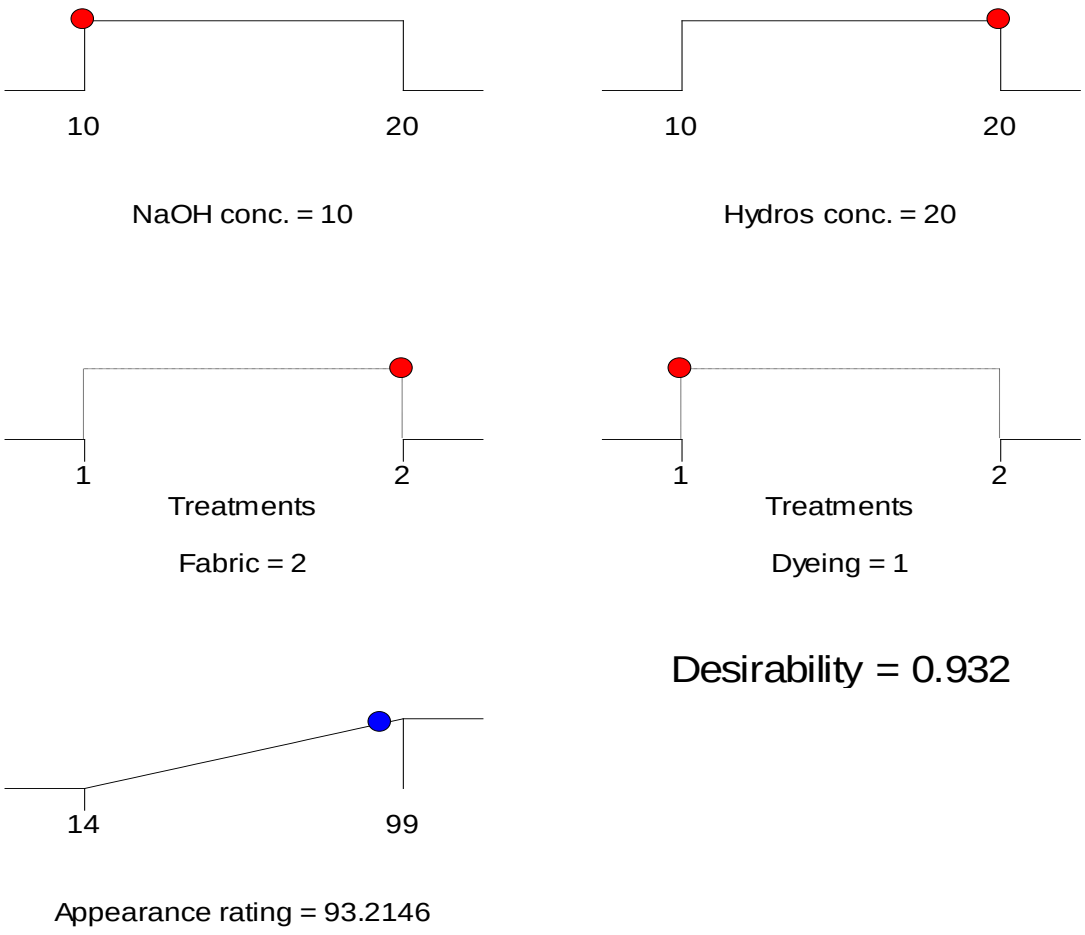


Figure 4.103: Ramp of optimal conditions for wet-on-wet dyeing of BF

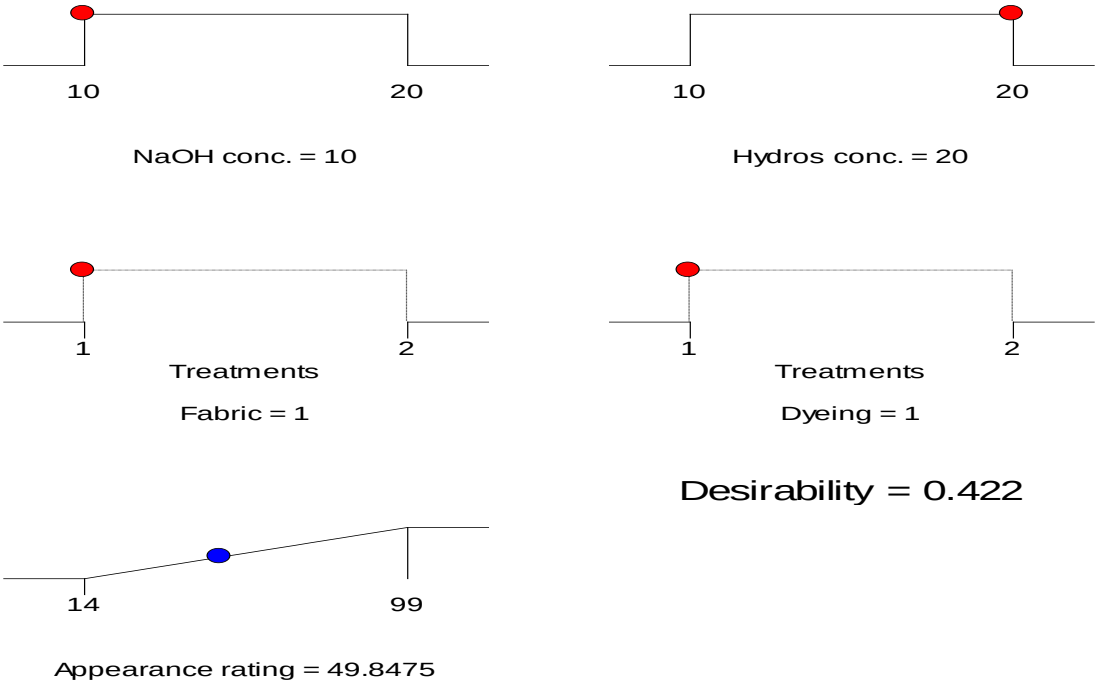


Figure 4.104: Ramp of optimal conditions for wet-on-wet dyeing of CF

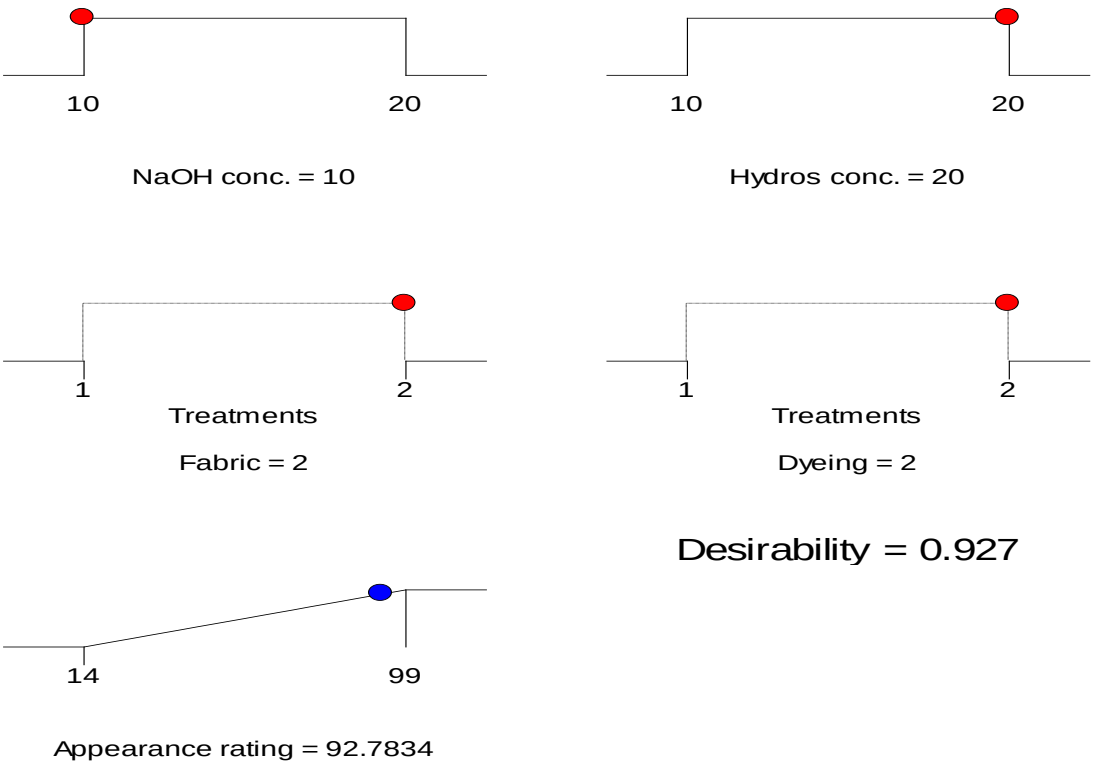


Figure 4.105: Ramp of optimal conditions for dry dyeing of BF

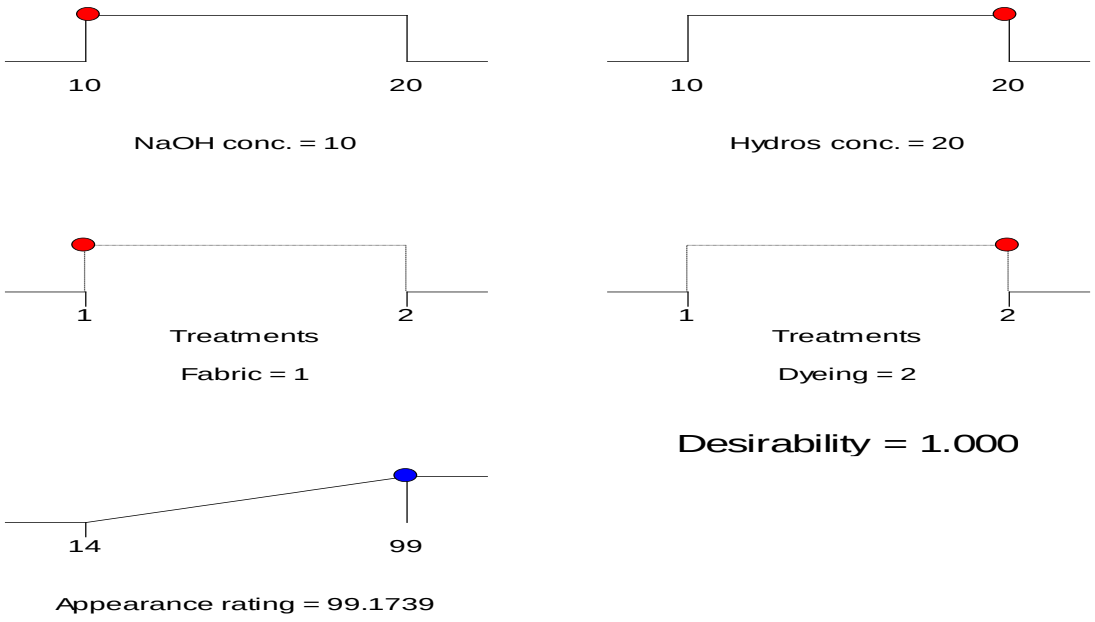


Figure 4.106: Ramp of optimal conditions for dry dyeing of CF

Figures 4.107 to 4.110 show histograms depicting individual and combined desirabilities (for BF and CF, respectively) using the wet-on-wet and dry dyeing methods in that order. Histogram shows how well each variable satisfied the criteria where values near one are good.

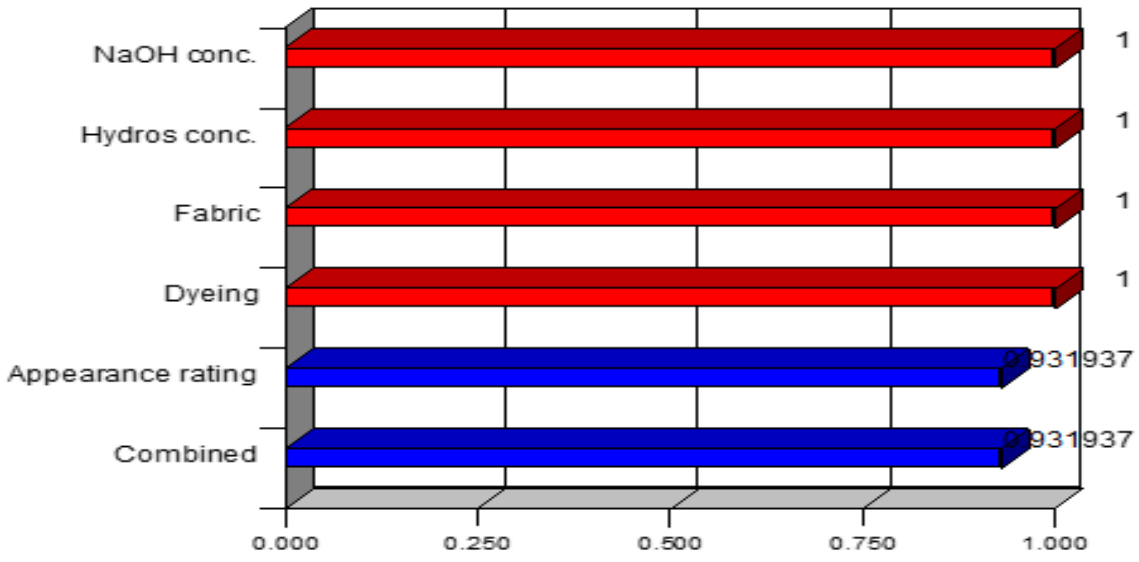


Figure 4.107: Histogram of individual and combined desirabilities for wet-on-wet dyeing of BF

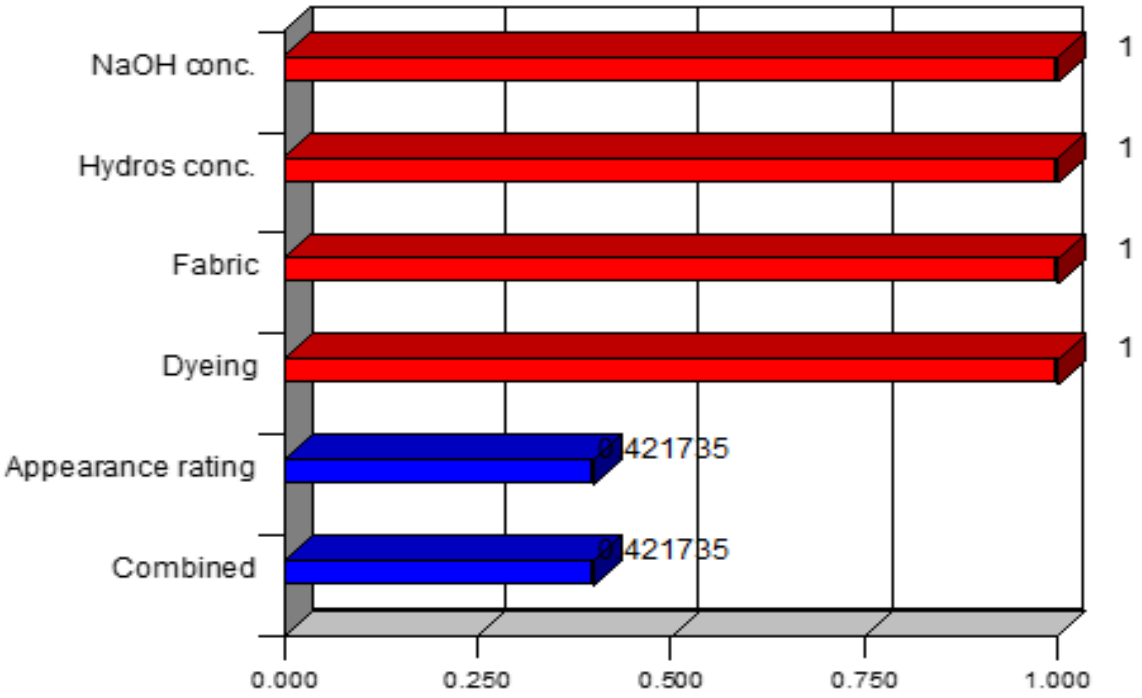


Figure 4.108: Histogram of individual and combined desirabilities for wet-on-wet dyeing of CF

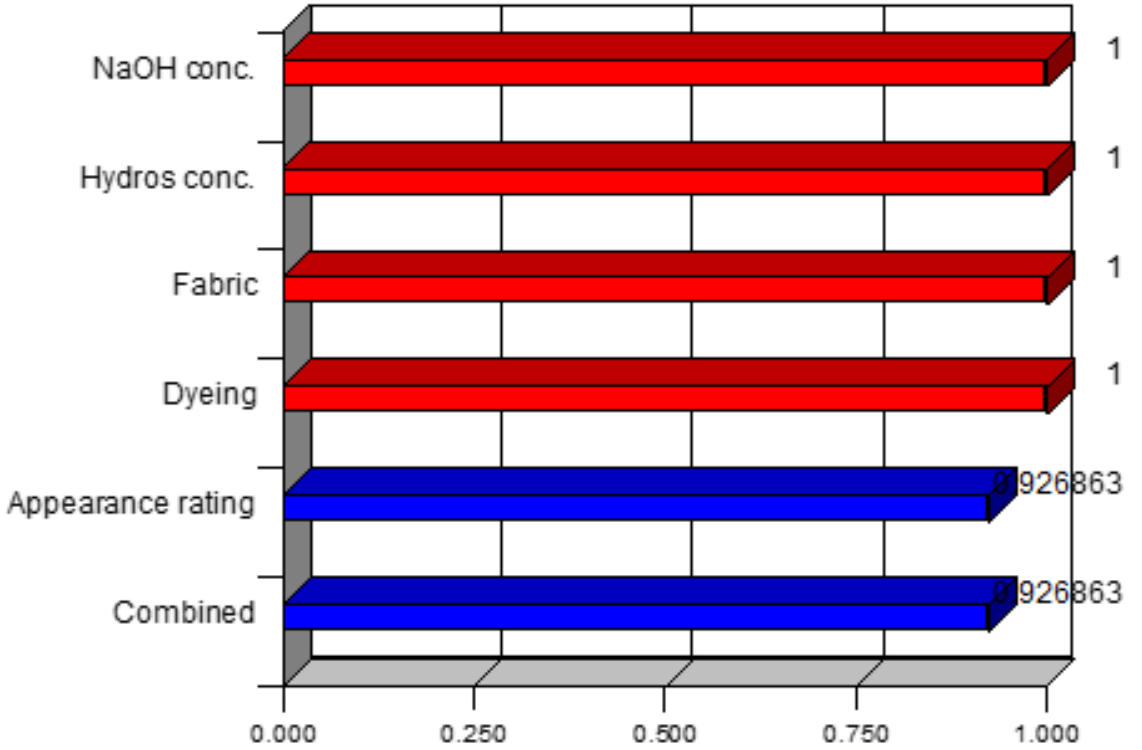


Figure 4.109: Histogram of individual and combined desirabilities for dry dyeing of BF

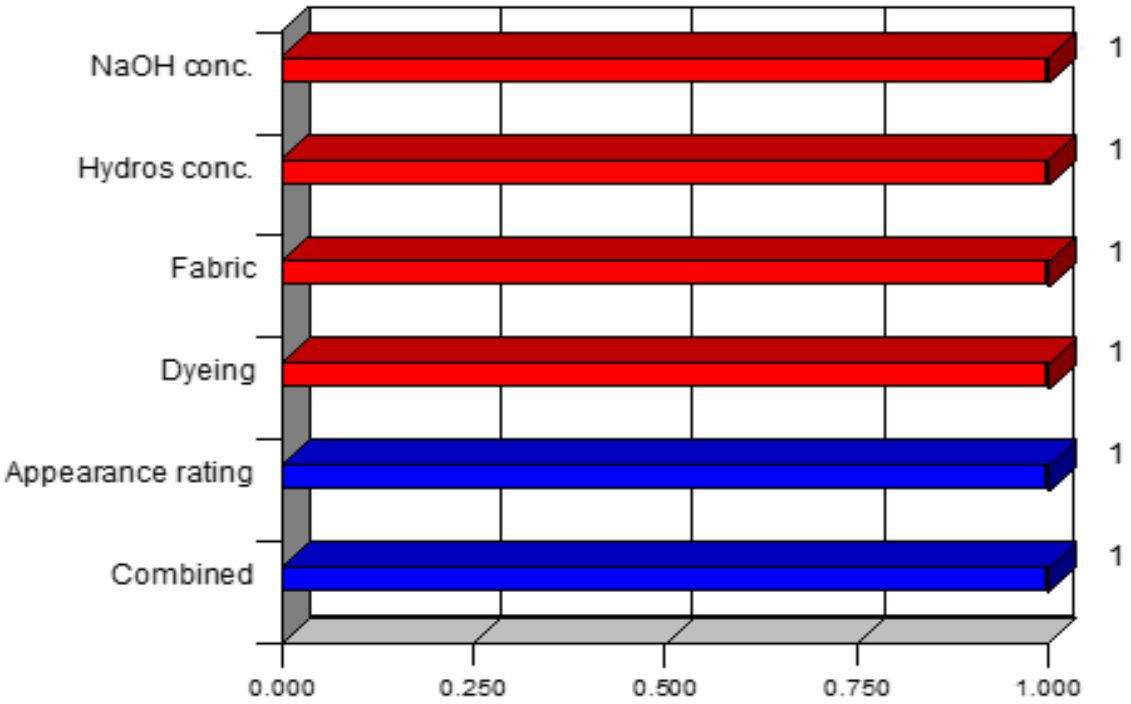


Figure 4.110: Histogram of individual and combined desirabilities for dry dyeing of CF

Caustic soda conc. of 10 g/l may reduce unlevelness due to wet-on-wet dyeing of CF, reduce effluent load, as well as dyeing cost (the dyers use an average of 21.43 g/l caustic soda). Conc. of hydros (20 g/l) may be necessary to compensate for loss due to oxidative decomposition (open bath and long liquor). The optimum conditions predicted were checked. Levelness for the wet-on-wet dyeing was 92.9±0.5 % and 50.12±0.9 % (respectively for BF and CF) while the rating for dry dyeing was 91.6±0.7 % and 98.8±1.1 % (respectively for BF and CF) for 5 replications. Small errors between these values indicated that the values obtained were in good agreement with the values predicted from the models. Figures 4.111 and 4.112 show contour plots for levelness prediction for the wet-on-wet dyeing method while Figures 4.113 and 4.113 show contour plots for levelness prediction using the dry method, respectively, for BF and CF.

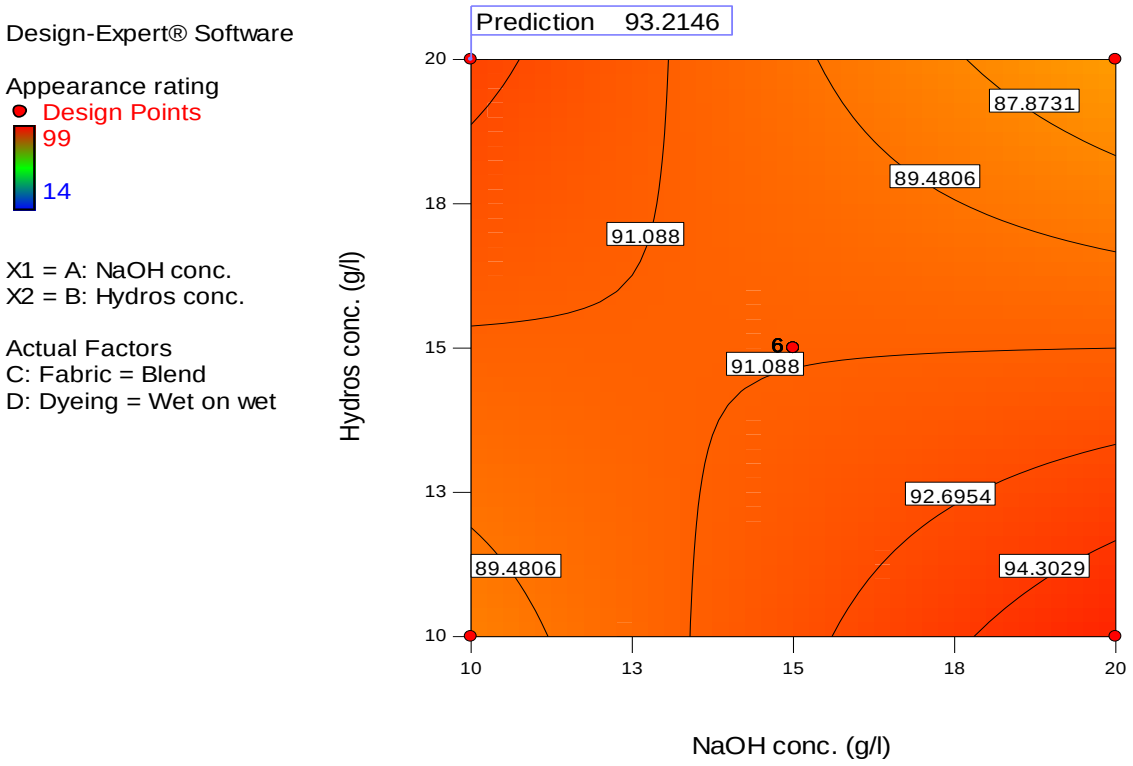


Figure 4.111: Contour plot for appearance rating prediction on BF dyed by wet-on-wet method

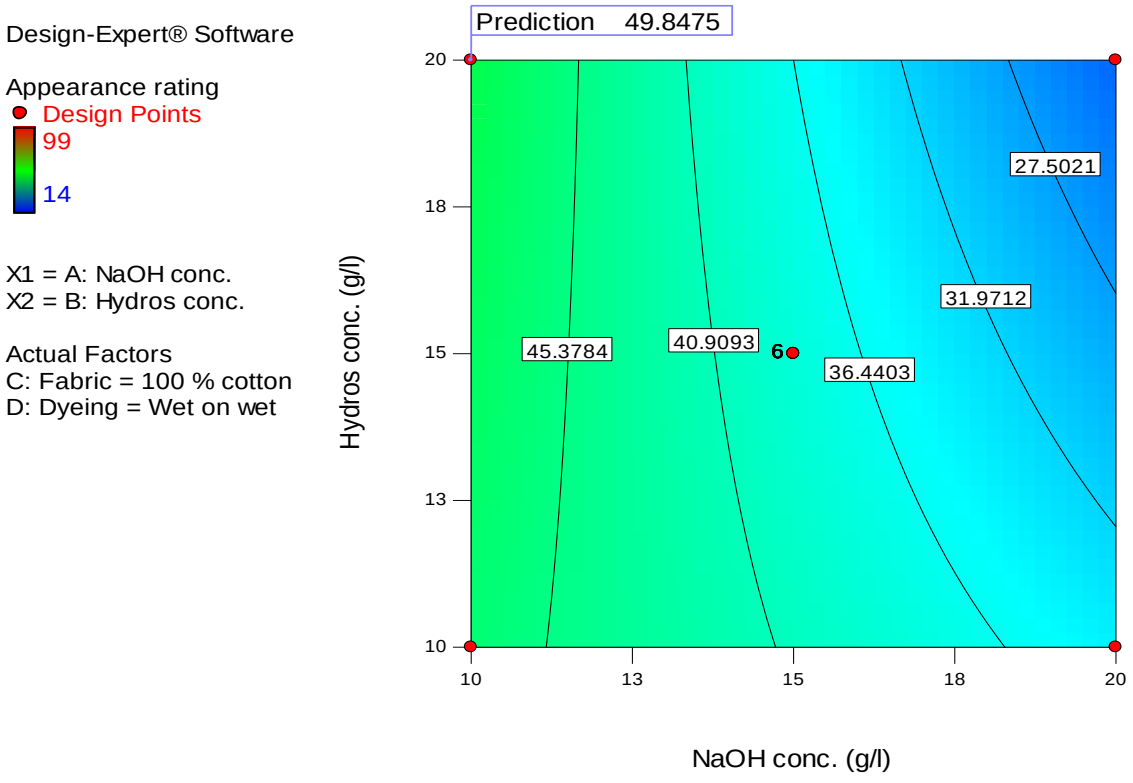


Figure 4.112: Contour plot for appearance rating prediction on CF dyed by wet-on-wet method

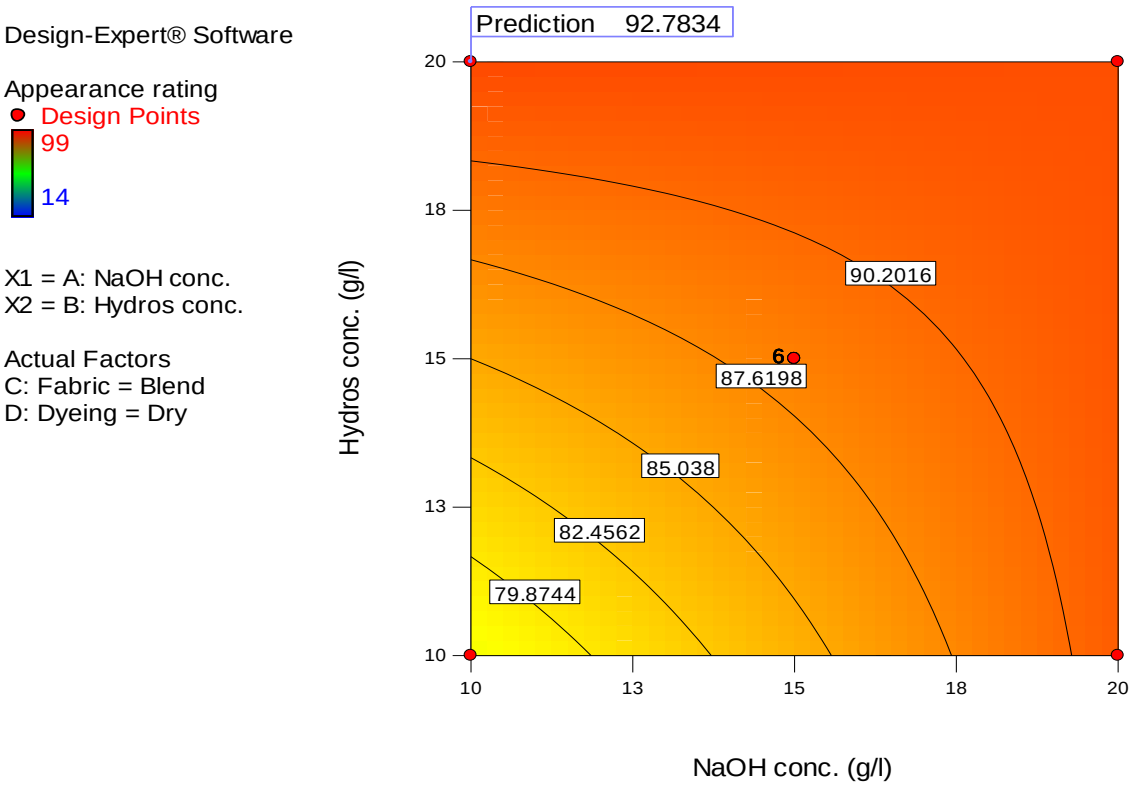


Figure 4.113: Contour plot for appearance rating prediction on BF dyed by dry method

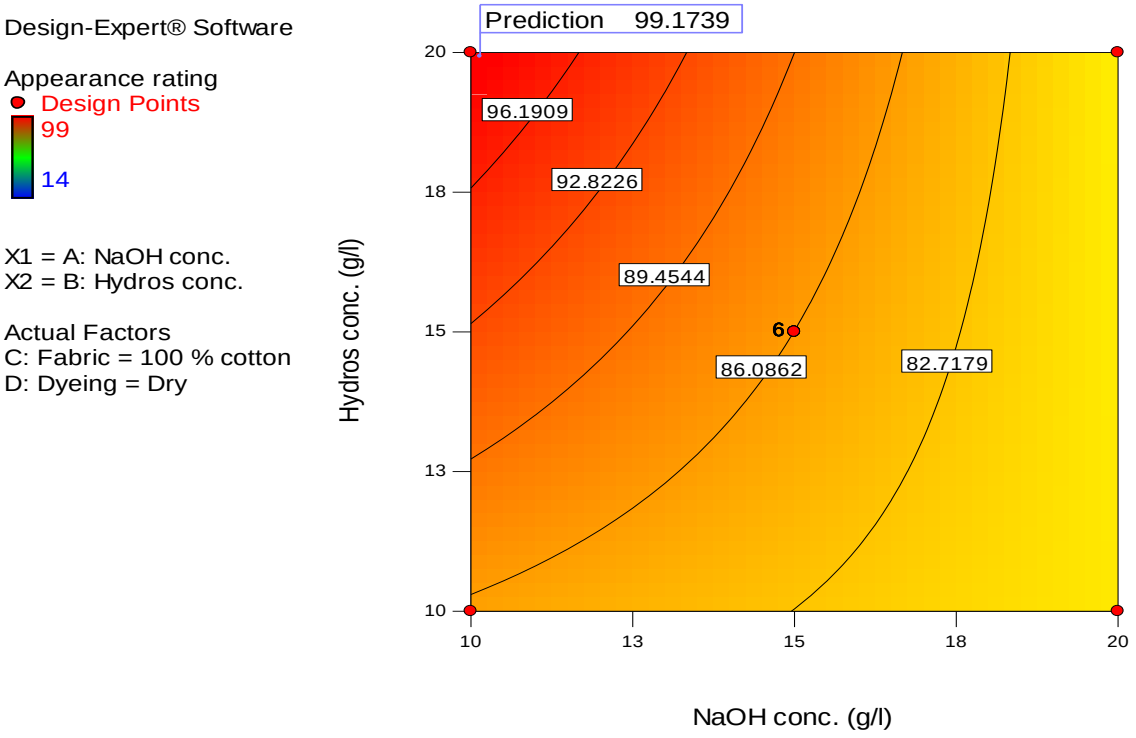


Figure 4.114: Contour plot for appearance rating prediction on CF dyed by dry method

4.7.6 Fastness test results

Fastness ratings of samples from occupational dyers and dyeing experiments to light, wash, and perspiration are shown in Tables 4.29 and 4.30, respectively. Vat dyes are well known for their excellent all-round fastness to washing, light and chlorine bleaching. The wash fastness of vat dyes is rarely rated less than 4-5 in a scale of 5 while the light fastness give rating of about 5-6 and 7-8 in a scale of 8 for light and heavy shades, respectively (Aspland, 1997). Vat dyes have coplanar and multiring system that contribute in strengthening van der Waals forces between the dye and the substrate which is the main reason why they offer better colour fastness than reactive dyes (Khatri *et al.*, 2017).

Table 4.29: Fastness ratings of samples from occupational dyers to light, washing and perspiration

Sample	Light fastness	Wash fastness		Perspiration			
		Colour change	Staining	Acid		Alkaline	
				Colour change	Staining	Colour change	Staining
DAS	6	4	4	4	4	4	4
DBS	4	3	4	4	4	3	4
DCS	5	3	3	3	4	4	4
DDS	4	3	4	4	4	4	4
DES	6	3	3	3	4	3	3
DFS	6	4	4	2	3	3	3
DGS	6	3	4	3	4	3	4
DHS	7	5	4	4	3	4	4
DIS	6	4	4	4	3	4	4
DJS	5	4	3	3	4	2	3
DKS	5	4	3	4	3	3	3
DLS	5	3	4	4	3	2	3
DMS	6	3	4	2	4	4	3
DNS	4	4	3	2	3	4	3
DOS	4	3	3	4	4	4	4
DPS	5	3	4	4	4	3	3
DQS	4	3	4	3	4	2	4
DRS	6	4	3	4	3	3	4

Grey scale ratings for wash fastness: 5-Excellent, 4-Good, 3-Fair, 2-Poor, 1-Very poor. Grey scale ratings for staining: 1-Much change, 2- Considerable change, 3-Noteceable change, 4-Slight change, 5-Negligible change. Grey scale for light fastness test: 1-Very poor, 2-Poor, 3-Moderate, 4-Faily good, 5-Good, 6-Very good, 7-Excellent, 8-Outstanding

Table 4.30: Fastness ratings of samples from the dyeing experiments to light, washing and perspiration

Sample	Light fastness	Wash fastness		Perspiration			
		Colour change	Staining	Acid		Alkaline	
				Colour change	Staining	Colour change	Staining
1	7	5	5	5	5	5	5
2	7	5	5	5	5	5	5
3	7	5	5	5	5	5	5
4	7	5	5	5	5	5	5
5	7	5	5	5	5	5	5
6	7	5	5	5	5	5	5
7	7	5	5	5	5	5	5
8	7	5	5	5	5	5	5
9	7	5	5	5	5	5	5
10	7	5	5	5	5	5	5
11	7	5	5	5	5	5	5
12	7	5	5	5	5	5	5
13	7	5	5	5	5	5	5
14	7	5	5	5	5	5	5
15	7	5	5	5	5	5	5
16	7	5	5	5	5	5	5
17	7	5	5	5	5	5	5
18	7	5	5	5	5	5	5
19	7	5	5	5	5	5	5
20	7	5	5	5	5	5	5
21	7	5	5	5	5	5	5
22	7	5	5	5	5	5	5
23	7	5	5	5	5	5	5
24	7	5	5	5	5	5	5
25	7	5	5	5	5	5	5
26	7	5	5	5	5	5	5
27	7	5	5	5	5	5	5
28	7	5	5	5	5	5	5
29	7	5	5	5	5	5	5
30	7	5	5	5	5	5	5
31	7	5	5	5	5	5	5
32	7	5	5	5	5	5	5
33	7	5	5	5	5	5	5
34	7	5	5	5	5	5	5
35	7	5	5	5	5	5	5
36	7	5	5	5	5	5	5
37	7	5	5	5	5	5	5
38	7	5	5	5	5	5	5
39	7	5	5	5	5	5	5
40	7	5	5	5	5	5	5
41	7	5	5	5	5	5	5
42	7	5	5	5	5	5	5

43	7	5	5	5	5	5	5
44	7	5	5	5	5	5	5
45	7	5	5	5	5	5	5
46	7	5	5	5	5	5	5
47	7	5	5	5	5	5	5
48	7	5	5	5	5	5	5
49	7	5	5	5	5	5	5
50	7	5	5	5	5	5	5
51	7	5	5	5	5	5	5
52	7	5	5	5	5	5	5
53	7	5	5	5	5	5	5
54	7	5	5	5	5	5	5
55	7	5	5	5	5	5	5
56	7	5	5	5	5	5	5

Grey scale ratings for wash fastness: 5-Excellent, 4-Good, 3-Fair, 2-Poor, 1-Very poor. Grey scale ratings for staining: 1-Much change, 2- Considerable change, 3-Noteceable change, 4-Slight change, 5-Negligible change. Grey scale for light fastness test: 1-Very poor, 2-Poor, 3-Moderate, 4-Faily good, 5-Good, 6-Very good, 7-Excellent, 8-Outstanding

4.7.6.1 Light fastness

All samples received from the dyers showed very good to fairly good fastness to light except for sample from dyehouse H (DHS) which exhibit an excellent light fastness. All the samples from the dyeing experiments showed excellent light fastness. Light fastness of dyes depends primarily on the photosensitivity and secondarily on the ease of photo-oxidation (Hihara *et al.,* 2002). Dyes of maximum light fastness (7-8) belong mainly to structures of all which contain imino (-NH-) ring. Polynuclear vat dyes containing nitrogen bearing ring such as Indanthrones are capable of withdrawing the action of light as in RSN (Fox, 1948).

Fibres with large aggregates of dye are more light-fast since a smaller surface area of the dye is exposed to air and light. Light fastness of a dyed fibre is usually increased by increase in dye conc., source, intensity of illumination, temp., and humidity (Christea and Vilarem, 2006). The soaping stage in vat dyeing, however, increase the association of vat dye particles resulting in the formation of submicroscopic crystals of the dye within the fibre thus presenting minimum surface area to the invading light (Fox, 1948). Excellent light fastness recorded may

be ascribed to the lack of strongly polar constituents such as donor and acceptor groups found in other dye classes. The planar structure of the dye could be another reason for the excellent light fastness because it is easy for the dyes to aggregate (Kim *et al.,* 2013).

4.7.6.2 Wash fastness

Apart from one sample that has excellent rating (sample DHS), all the dyed materials from the occupational dyers (Table 4.29) exhibited fair to good ratings for colour change. Ratings for staining also vary between slight change to noticeable change. All the dyed materials from the dyeing experiments showed excellent wash fastness and have negligible change in staining. Excellent wash fastness recorded may be ascribed to the water insolubility of vat dyes where the dyes are physically retained in the fibre through hydrogen bond and van der Waals forces. High fastness to severe washing is dependent on absence of sodium salt forming groups such as -OH, -ONa and difficulty of reduction of the dye to the sodium salt of its leuco compound (Fox, 1948).

4.7.6.3 Fastness to perspiration

Fading of dyed cloth under the arm fit and at the back in between the shoulders where the material comes in contact with sweat is very common in the study area. Samples from the dyers generally have fair to good fastness to acidic perspiration except for DFS, DMS, and DNS (with poor colour change rating) and also fair to good fastness to alkali perspiration except for samples DJS, DLS, and DQS (with poor colour change). All the samples exhibited slight to noticeable change in staining test. Samples from the dyeing experiments showed excellent fastness to acidic perspiration and excellent alkali fastness. All the experimental samples exhibited negligible change in staining test.

CHAPTER 5

5.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary

Questionnaire survey revealed that most of the dyers were of youthful age from Gwale and Fagge Local Government Areas with majority being natives. Most of them have learnt the art of dyeing by apprenticeship and their work experience ranged from five to thirty-one years (mean = 11.76±4.7). Close to one half of the dyers earn more than the minimum wage of civil servants in Nigeria. All of them are engaged in plain dyeing of cotton fabric and its blend as well as redyeing of faded articles. The dyers work as informal groups where the dyehouses are mostly not more than 91 m away from residential houses and 72 percent of the dyers discharge wastewaters into open drain. Raw-materials used by the dyers include synthetic vat dyes, caustic soda, hydros and woven fabrics all imported from China where their availability has greatly reduced and their cost has multiplied about five times within five years period.

The result obtained showed that the order of concentrations of heavy metals detected in caustic soda and hydros are, respectively, Na>Fe>Zn>Cu>Ni>Cr>Cd>Mn and Na>Fe>Ni>Cu>Cr>Zn>Mn. The order of mean concentrations of heavy metals in dyes is Na>Fe>Cr>Mn>Zn>Ni>Cu>Cd>Pb and with the exception of Na which has not been listed, the values for all the metals were found to be far below ETAD heavy metals limits for dyes. COD in effluent was found to be about four times higher than the BOD and also contains high amounts of lead and sodium. Groundwater investigated contain high levels of TDS, low concentration of DO (DO is vital to aquatic life), and heavy metal concentrations above the limits set by SON and WHO for drinking water quality.

Results show that the dyers use an estimated liquor ratio of 40:1, few seconds of vatting time, and accomplish dyeing in less than 10 min. They use an average temperature of 76±4 ^{o}C with 21.43±3.46 g/l and 18.99±2.05 g/l caustic soda and hydros concentrations, respectively, in the dyeing of 10 percent shade of fabric. The optimized mercerization conditions were found to be 250 g/l caustic soda concentration, 85 ^{o}C and 3 min. treatment time. Under optimized conditions, the elongation of mercerized samples increased by about 51.62 and 120.85 percent, respectively, for BF and CF when compared to the original unmercerized samples. Shrinkage, however, has reduced by about 19.50 percent for BF and 17.30 percent for CF when compared to the mean average shrinkage of mercerized samples from the dyeing experiments. The tensile strength of all mercerized samples is higher than that of the untreated sample except for BF samples mercerized using high caustic soda conc., and/or high temperature, and/or long treatment time which caused alkali hydrolysis of polyester component of the blend with subsequent loss of strength.

The mean appearance rating (levelness) of samples dyed by the dry and wet-on-wet method are, respectively, 86.07±2.1 and 38.50±1.6 percent. The optimized dyeing conditions were found to be 10g/l caustic soda and 20 g/l hydros using the dry method which resulted in 92.78 percent levelness for BF and 99.17 percent for CF with desirabilities of 0.927 and 1.000, respectively. All selected dyed materials have higher tensile strength than the original untreated sample except for samples that were subjected to local calendering (beating operation). Samples from the occupational dyers exhibited very good to fairly good fastness to light, fair to good ratings for colour change, and ratings for staining varying between slight change to noticeable change. Samples from the dyers generally have fair to good fastness to acidic and alkali perspiration with slight to noticeable change in staining test. Samples from

the dyeing experiment showed excellent fastness to light and washing, have negligible change in staining, have excellent fastness to acidic and alkali perspiration, and exhibited negligible change in staining test.

5.2 Conclusion

The dyeing occupation is lucrative and employs huge labour and therefore has propensity to alleviate poverty which is a serious problem in the region. Redyeing of faded garment and denim jeans, jackets, caps, and fashion accessories/household items such as shoes, bags, towels, etc., are needed on daily basis and it may not be convenient getting such services in a textile industry for bureaucratic reasons hence the relevance of the occupational dyers. The dyeing enterprises, by their nature, may find it difficult to get any support given to entrepreneurs because they are unrecognised by the government. The increase in cost of dyes and auxiliaries, rise in cost and scarcity of white undyed fabrics, and importation of coloured textiles could be linked to Chinese competitive advantage, with the dyeing rate drastically reducing, gradually rendering the dyers jobless.

Concentration of metals found in dyes and auxiliaries may not pose immediate environmental concern but their accumulation at the dumping site could be a threat since dyes and metals are recalcitrant and stay for a long time without decomposing. The dye powders, however, are safe to use based on their metal content. Based on the physico-chemical parameters determined, the effluent was found to be non-biodegradable. Lead concentration is far above FEPA limits which is alarming especially because the effluent must have seeped into the ground and affected groundwater quality in the neighbourhood. Based on some physico-

chemical parameters and heavy metals measured, groundwater within 100 m radius from the dyehouses is not suitable for drinking and irrigation.

Vatting for few sec. and dyeing within 10 min. has significantly reduced time compared to at least one hour used industrially. The high temperature used (70 ^{o}C) may be disadvantageous as it may increase the tendency of over-reduction. The quantity of caustic soda (about 21 g/l) and hydros (about 18 g/l) used may be adequate since previous studies have suggested the use of 20 g/l each. Mercerization within 3 min. using 250 g/l caustic soda saves both time and cost and at the same time solved the problem of excessive shrinkage of fabric reported by the occupational dyers.

The wet-on-wet dyeing method results in unlevelness caused by over-reduction due to excess caustic soda embedded in the fibres after mercerization and then dyeing without intermittent washing and drying steps. Dyeing with 10 g/l caustic soda saves cost and also produce a well leveled material (>99 percent) when the dry method is used. Use of 20 g/l hydros may be necessary to compensate for loss due to oxidative decomposition. The tensile strength improves after mercerization and then reduces after dyeing and calendering. The beating operation breaks/weakens the fibres resulting in significant reduction in tensile strength. Fastness ratings of samples from the dyeing experiments are much better than those of samples dyed by the occupational dyers which may be due to soaping of the former samples.

5.3 Recommendations

It is recommended that the dyers should be encouraged to become formal in order to gain from numerous Federal Governments' incentive towards entrepreneurship development. Kano State

Government in its part should visit the dyehouses identified in this study so as to come up with policies and intervention strategies that will sustain the venture since it has propensity to employ huge labour. The study suggests creating and implementing effective policies that will ban importation of coloured textiles especially from China, subsidize the cost of dyes and chemicals, revive textile industries, and tackle Boko-Haram insurgency and banditry which threaten businesses in the study area.

Based on the potential environmental impacts identified, the study recommends that the dyehouses should be relocated to industrial areas of the state where their activities can be closely monitored. Stringent environmental laws should be created and existing ones to be enforced with regards to waste management. To mitigate harmful effects of dyes and auxiliaries, the dyers should be encouraged to revert to the use of eco-friendly natural indigo dyes which are usually grown in the state and most of the dyers already have the technical know-how being formally traditional indigo dye workers. The natural dyes will be less polluting for sustainable development.

In order to improve on the dyeing processes, it is recommended for related Departments in Academic Institutions to collaborate with the dyehouses in terms of research/innovation and to encourage placement of students under Students Industrial Work Experience Scheme (SIWES). Furthermore, government should incorporate dyeing in the entrepreneurship courses introduced into the Nigerian educational system for students to acquire innovations in dyeing and management skills. The dyers in their part should endeavour to soap dyed materials in order to improve fastness properties and also to stop beating operation which results in loss of

strength. To avoid unlevelness, it is suggested that the mercerized fabrics should be washed to neutral pH before wet-on-wet dyeing.

The dyer's blood sample should be subjected to complete blood count to ascertain the effects of the dyeing activity on human health. Oral toxicity of the dye effluent should be assessed through animal study. Blood of residents drinking the water samples in the study area should be examined so that medical experts can proffer solutions in the event that there is anomaly due to the water consumption. Further study should include determination of chronic daily intake and chance of cancer risk through water ingestion and dermal contact as well as dermal contact with dye effluent. Potential health risk due to inhalation exposure to caustic soda, hydros and the dye powders should be investigated by animal studies.

More heavy metals including mercury and arsenic which are more commonly used as catalysts in vat dye synthesis should be investigated in effluent and groundwater samples so that actual sources of the heavy metals and correlation among them in groundwater could be identified using factor analysis. Small-scale effluent treatment plant should be developed for use in the dyehouses which could at least decolourize the effluent and remove heavy metals. Heavy metal content of dyed materials should be investigated as the extraction of heavy metals from fabrics by perspiration is a main source of human contact.

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APPENDICES

APPENDIX A

Questionnaire used in the study

SURVEY ON VAT DYEING IN KANO METROPOLIS			
PART A: Demographic/socio-economic characteristics			
S/No.		RESPONSE	CODE
1a	Gender	1. Male 2. Female	
1b	Marital status	1. Married 2. Single 3. Divorced 4. Widowed	
1c	Age (years)		
1d	Local Government Area		
1e	State of origin		
1f	Nationality		
1g	Educational qualification (only one option)	1. Primary education 2. Secondary education 3. Tertiary education 4. Qur'anic education 5. No education	
1h	Is dyeing your primary occupation?	1. Yes 2. No	
1i	What else do you do to earn a living?		
1j	For how long have you been practicing dyeing? (years)		
1k	What is your job specification in the enterprise/group? (Only one option)	1. Colour mixing 2. Dyeing 3. Rinsing 4. Starching	

		5. Marketing		
1l	Where did you learn how to dye cloth? (Only one option)	1. Trial and error 2. Observation 3. Apprentice 4. Long standing tradition in the family 5. Formal training		
1m	How much is your monthly income from the enterprise/group?	1. ₦1,000-₦20,000 2. ₦21,000-₦40,000 3. ₦41,000-₦60,000 4. ₦61,000-₦80,000 5. ₦81,000-₦100,000 6. Over ₦100,000		
PART B: Management of the dyeing enterprises				
2a	What is the type of the enterprise/group? (Only one option)	1. It is a formal enterprise-sole owner 2. It is an informal enterprise-sole owner 3. It is a formal enterprise, various owners 4. It is an informal enterprise, various owners 5. It is a co-operative 6. It is of other type (specify)		
2b	Is the enterprise/group a member of any formal/informal group/association?	1. Yes 2. No		
2c	Is (are) there benefit (s) of being a member of the formal/informal group/association?	1. Yes 2. No		
2d	How many are you in the enterprise/group? (Only one option)	1. 1-10 2. 11-20 3. 21-30 4. 31-40 5. 41-50 6. Over 50		
2e	Where is the location of the enterprise/group? (Only one option)	1. It is located in the house of owner/group member 2. It is located in the neighborhood 3. It is located in another place (specify)		
PART C: Operations of the dyeing enterprises				
3a	Services offered by the enterprise/group (multiple options)	**Yes**	**No**	
	1. Dyeing of cotton fabric			

	2. Dyeing of other type of fabric 3. Redyeing of faded garment 4. Tie and dye 5. Batik work 6. Other services (specify)			
3b	Tools/equipment the enterprise/group use for dyeing (multiple options)	**Yes**	**No**	
	1. Plastic bowl 2. Drum 3. Stirrer (specify type) 4. Bucket 5. Other tools/equipment (specify)			
3c	Source (s) of power that the enterprise/group uses in production (multiple options)	**Yes**	**No**	
	1. Electric heater 2. Gas 3. Fire wood 4. Other power sources (specify)			
3d	Source (s) of water used by the enterprise/group (multiple options)	**Yes**	**No**	
	1. The enterprise/group use water from borehole 2. The enterprise/group use water from hand dug well			

	3. The enterprise/group use water from tap 4. The enterprise/group use water purchased from water vendors 5. The enterprise/group use water from other sources (specify)			
3e	Inputs/raw-material that the enterprise/group usually employ (multiple options)	**Yes**	**No**	
	1. Dye 2. Sodium dithionite (hydros) 3. Caustic soda 4. Starch 5. Sodium chloride 6. Other inputs/raw-material (specify)			
3f	Source (s) of inputs/raw-material for the work of the enterprise/group (multiple options)	**Yes**	**No**	
	1. Purchase from retailers 2. Purchase from wholesalers 3. Purchase from other sources (specify)			
3g	How frequently does the enterprise/group operate? (Only one option)	1. 1-2 times in a week 2. 3-4 times in a week 3. 5-6 times in a week		

		4. Daily 5. On demand		
3h	Is there any period that the enterprise/group becomes more engaged?	1. Yes 2. No		
3i	The occasion (s) that the enterprise/group becomes more engaged (multiple options)	**Yes**	**No**	
	1. Muslims' festivity (Karamar Sallah) period 2. Muslims' festivity (Babbar Sallah) period 3. Christmas period 4. Muslims' festivity (Maulud) period 5. Other festivity periods (specify)			
3j	Clients of the services offered by the enterprise/group (multiple options)	**Yes**	**No**	
	1. Customers living in the neighborhood 2. Customers from other states 3. Customers from other countries 4. Vendors from cloth market 5. Other customers (specify)			
3k	The manner (s) in which the enterprise/group measure the quantity of dye/auxiliaries (multiple options)	**Yes**	**No**	

	1. Use of weighing balance 2. Rough estimate 3. Spoon measurement 4. Other means of measurement (specify)			
PART D: Step by step dyeing processes				
4a	Dyeing sequence, the enterprise/group usually employ (multiple options)	**Yes**	**No**	
	1. Mixing the dye, caustic soda and hydros, immersing the fabric, rinsing the material after dyeing, oxidation, starching and drying 2. Mixing the dye, caustic soda and hydros, immersing the fabric, rinsing the material after dyeing, starching, oxidation and drying 3. Mixing the dye and caustic soda, immersing the fabric, adding hydros, rinsing the material after dyeing, oxidation, starching and drying 4. Mixing the dye and caustic soda, immersing the fabric, adding hydros, rinsing the material after dyeing, starching, oxidation and drying 5. Other dyeing sequence			
4b	Way (s) in which the enterprise/group achieves level dyeing (multiple options)	**Yes**	**No**	
	1. Continues movement of the fabric/garment in the dyebath 2. Proper control of goods to liquor ratio			

	3. Steeping the fabric/garment before dyeing 4. Reducing the dyebath temperature for light shade 5. Other means (specify)			
4c	Manner (s) in which the enterprise/group achieves desired colour shade (multiple options)	**Yes**	**No**	
	1. Adding appropriate dye to the dyebath until the desired shade develops 2. Mixing the colour (s) and testing until the desired shade is obtained 3. Consulting a more experienced dyer 4. Other means (specify)			
4d	Treatment (s) carried out by the enterprise/group before dyeing (multiple options)	**Yes**	**No**	
	1. Desizing 2. Scouring 3. Bleaching 4. Other treatments (specify)			
4e	How long does it take to immerse the material after preparation of the dyebath? (Only one option)	1. Few seconds 2. 1-2 minutes 3. 3-4 minutes 4. 5 minutes and above		
4f	How long does it take to finish dyeing from the time a material is immersed into the dyebath? (Only one option)	1. 1-3 minutes 2. 4-6 minutes 3. 7-9 minutes 4. 10-12 minutes 5. 12 minutes and above		

4g	Treatment (s) carried out by the enterprise/group after dyeing (multiple options)	**Yes**	**No**	
	1. Oxidation 2. Soaping 3. Acidification 4. Other treatments (specify)			
PART E: Challenges and prospects				
5a	Challenges usually faced by the enterprise/group (multiple options)	**Yes**	**No**	
	1. Limited capital 2. Poor infrastructure 3. Training problems 4. Low patronage 5. High cost of production 6. Occupational hazard 7. Variability in cost of services 8. Insecurity 9. Decline in local fabric production 10. Competition with imported textiles 11. Credit owed by cloth vendors			
5b	Has there been any period that the vat dyeing occupation was more lucrative?	1. Yes 2. No		
5c	When is the period that the vat dyeing occupation was more lucrative? (Only one option)	1. 1 year ago 2. 2 years ago 3. 3 years ago		

		4. 4 years ago 5. 5 years ago 6. Over 5 years ago		
5d	Reason (s) why the vat dyeing occupation was more lucrative as at that period (multiple options)	**Yes**	**No**	
	1. Inputs/raw-material were cheap 2. The economy was better hence more customers 3. There was little or no competition with foreign dyed materials 4. There was better working environment 5. There was availability of cheap white (un-dyed) materials in the market 6. Other reasons (specify)			
5e	During the period that the vat dyeing occupation was more lucrative, what quantity of materials did you dye weekly? (Only one option)	1. 1-4000 yards 2. 4001-8000 yards 3. 8001-12000 yards 4. 12001-16000 yards 5. 16001-20000 yards 6. Over 20000 yards		
5f	Is the vat dyeing occupation still lucrative at present time?	1. Yes **2.** No		
5g	Reason (s) why the vat dyeing occupation is no longer lucrative (multiple options)	**Yes**	**No**	
	1. Inputs/raw-material are expensive 2. Poor economy and therefore less customers 3. There is serious competition with foreign dyed materials 4. Poor working environment			

	5. Scarcity of cheap white (un-dyed) material in the market 6. Other reasons (specify)			
5h	Do you believe that it is only government that can help revive the vat dyeing occupation?	**1. Yes** **2. No**		
5i	Way (s) in which the government can help revive the vat dyeing occupation (multiple options)	**Yes**	**No**	
	1. Stop importation of coloured textiles 2. Improve the economy for people to have more purchasing power 3. Provide sites for the occupational dyers within the community 4. Construct many dyeing units in all the industrial areas of Kano Metropolis 5. Subsidize the prices of dyes/auxiliaries 6. Revive textile industries which can provide material for the work of the occupational dyers 7. Other ways (specify)			
5j	What is the approximate quantity of material that you dye weekly at present time? (Only one option)	1. 1-400 yards 2. 401-800 yards 3. 801-1200 yards 4. 1201-1600 yards 5. 1601-2000 yards **6.** Over 2000 yards		
5k	With the current situation, do you think that the vat dyeing occupation will survive?	**1. Yes** **2. No**		
5l	Consequence (s) of the vat dyeing occupation collapsing (multiple options)	**Yes**	**No**	

	1. Thousands of youths will be out of the business of dyeing, calendaring and selling of chemicals 2. Dyed materials, which are every day attire, will be expensive since they will be mostly imported 3. Other consequences (specify)			
PART F: Perception on chemical toxicity				
6a	Has a public health worker, for any reason, ever visited the enterprise/group?	1. Yes 2. No		
6b	Reason (s) why a public health worker visited the enterprise/group (multiple options)	**Yes**	**No**	
	1. To advice the dyers on how to protect their bodies from toxic chemicals 2. To enlighten the dyers on the importance of going to hospital when sick 3. Other reasons (specify)			
6c	The dyeing activity exposes you to toxic chemicals	1. Yes 2. No		
6d	Way (s) that chemicals enter the body (multiple options)	**Yes**	**No**	
	1. Through breathing 2. Through ingestion 3. Through contact with spills and splashes 4. Through other means (specify)			
6e	Do you use personal protective equipment?	1. Yes 2. No		
6f	Protective equipment you normally use (multiple options)	**Yes**	**No**	
	1. Protective hand gloves			

	2. Protective boots 3. Nose guard 4. Face mask with eye glass 5. Polyethene skirt 6. Other protective equipment (specify)			
6g	**How frequently do you engage in protective behaviour? (Only one option)**	1. Often 2. Some times 3. Rarely 4. Never		
6h	**Are you confident with the outcome of protective behaviour?**	**1. Yes** 2. **No**		
6i	**How frequently do you visit hospital? (Only one option)**	1. Often 2. Some times 3. Rarely 4. Never		
6j	**Which of the following symptoms have you ever had? (Multiple options)**	**Yes**	**No**	
	1. Coughing 2. Chest pain 3. Shortness of breath 4. Abdominal pain 5. Nausea 6. Vomiting			

PART G: Waste management and perception on potential environmental impacts						
7a	Has an environmental officer, for any reason, ever visited the enterprise/group?	**1. Yes** 2. **No**				
7b	Reason (s) why an environmental officer visited the enterprise/group (multiple options)	**Yes**		**No**		
	1. To ensure that dye effluent is properly discharged 2. To advice the dyers on how to keep the environment clean **3.** Other reasons (specify)					
7c	Way (s) in which the enterprise/group discharges its waste water (multiple options)	**Yes**		**No**		
	1. Through open drain 2. Through dumping on the ground 3. Into sewage system 4. Through another disposal means (specify)					
7d	How far is the next available house from the location of the enterprise/group? (Only one option)	1. 1-30ft 2. 31-40ft 3. 41-50ft 4. Above 50ft				
7e	Level of agreement on the following views related waste water discharged by the enterprise/group	**SA**	**A**	**D**	**SD**	
	1. The waste water discharged by the enterprise/group seep into the ground 2. The waste water discharged by the enterprise/group goes straight to a treatment plant					

	3. The waste water disposal unit is highly coloured 4. Vat dye effluent can kill plants and aquatic animals 5. The waste water discharged by the enterprise/group does not smell					

APPENDIX B

Demographic/socio-economic characteristics of the dyers investigated

Personal characteristics	Frequency (%), n= 226
Age group	
10-20	16 (7.1)
21-40	193 (85.4)
41-60	16 (7.1)
61-80	1 (0.4)
Sex	
Male	207 (91.6)
Female	19 (8.4)
Marital status	
Married	109 (48.2)
Single	115 (50.9)
Divorced	1 (0.4)
widowed	1 (0.4)
Level of education	
Primary education	30 (13.3)
Secondary education	132 (58.4)
Tertiary education	53 (23.5)
Qur'anic education	11 (4.9)
Local government area	

Fagge	42 (18.6)
Gwale	85 (37.6)
Kano municipal	31 (13.7)
Nassarawa	6 (2.7)
Ungogo	12 (5.3)
Dala	20 (8.8)
Tarauni	8 (3.5)
Kumbotso	22 (9.7)
State of origin	
Kano state indigenes	215 (95.1)
Non-indigenes	11 (4.9)
Nationality	
Nigerians	217 (96)
Malians	3 (1.3)
Gambians	6 (2.7)
Job specification	
Colour mixing	61 (27)
Dyeing	90 (39.8)
Starching/Rinsing/Drying	39 (17.3)
Marketing	36 (15.9)
Job learning method	
Trial and error	16 (7.1)
Observation	57 (25.2)

Apprentice	142 (62.8)
Long standing tradition in the family	9 (4)
Formal training	2 (0.9)
Years of experience	
1-10 years	119 (52.7)
11-20 years	102 (45.1)
21-30 years	4 (1.8)
31-40 years	1 (0.4)
Additional source of income	
None	96 (42.5)
Calendering	22 (9.7)
Tailoring	21 (9.3)
Trading/Cloth vending	57 (25.2)
Civil service	9 (4)
Others	19 (8.4)
Monthly income from the dyeing job	
₦1,000-₦20,000	122 (54)
₦21,000-₦40,000	48 (21.2)
₦41,000-₦60,000	13 (5.8)
₦61,000-₦80,000	16 (7.1)
₦81,000-₦100,000	6 (3.1)
Above ₦100,000	20 (8.8)

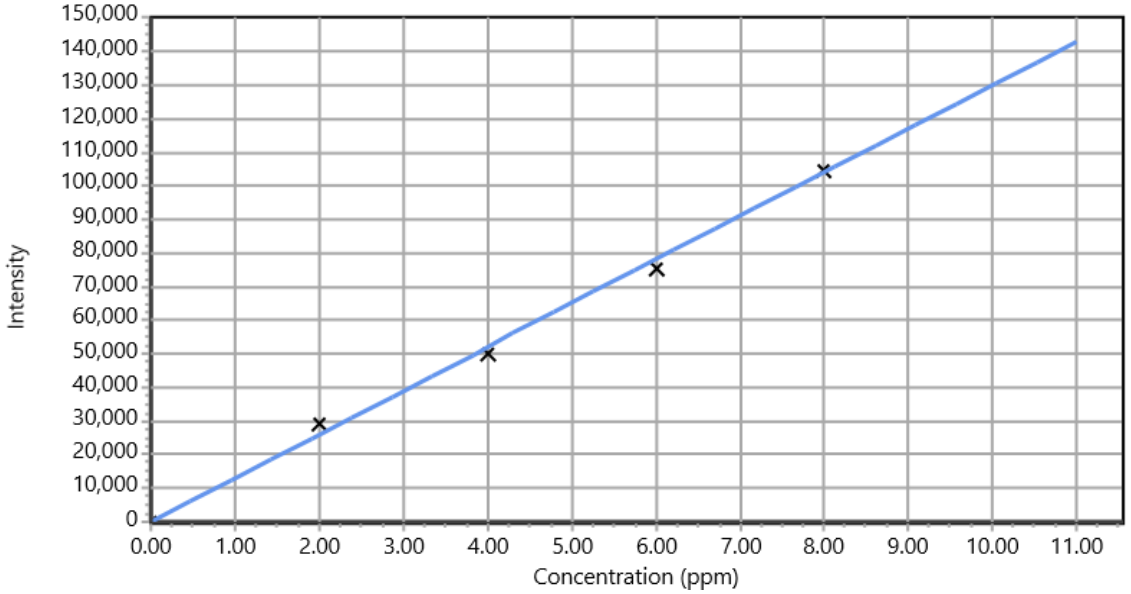
APPENDIX C

Coordinates of the dyehouses visited

Dyehouses	Longitude	Latitude	Local government area
DA	11°58.128’	008° 31.901’	Tarauni
DB	11°58.947’	008° 30.862’	Gwale
DC	11°59.655’	008° 30.696’	Gwale
DD	12°00.182’	008° 31.392’	Kano Municipal
DE	12°02.630’	008° 29.085’	Fagge
DF	12°02.698’	008° 29.230’	Fagge
DG	12°00.040’	008° 31.559’	Kano Municipal
DH	11°58.324’	008° 31.951’	Kano Municipal
DI	11°59.598’	008° 30.184’	Gwale
DJ	11°59.825’	008° 29.857’	Dala
DK	11°59.967’	008° 30.210’	Dala
DL	11°59.683’	008° 30.047’	Dala
DM	12°01.162’	008° 27.131’	Ungogo
DN	11°59.628’	008° 28.341’	Gwale
DO	11°59.216’	008° 28.148’	Gwale
DP	11°56.640’	008° 34.169’	Kumbotso
DQ	11°58.065’	008° 34.810’	Nassarawa
DR	11°58.050’	008° 32.186’	Tarauni
DS	11°57.809’	008° 32.100’	Tarauni
DT	11°56.737’	008° 28.167’	Gwale

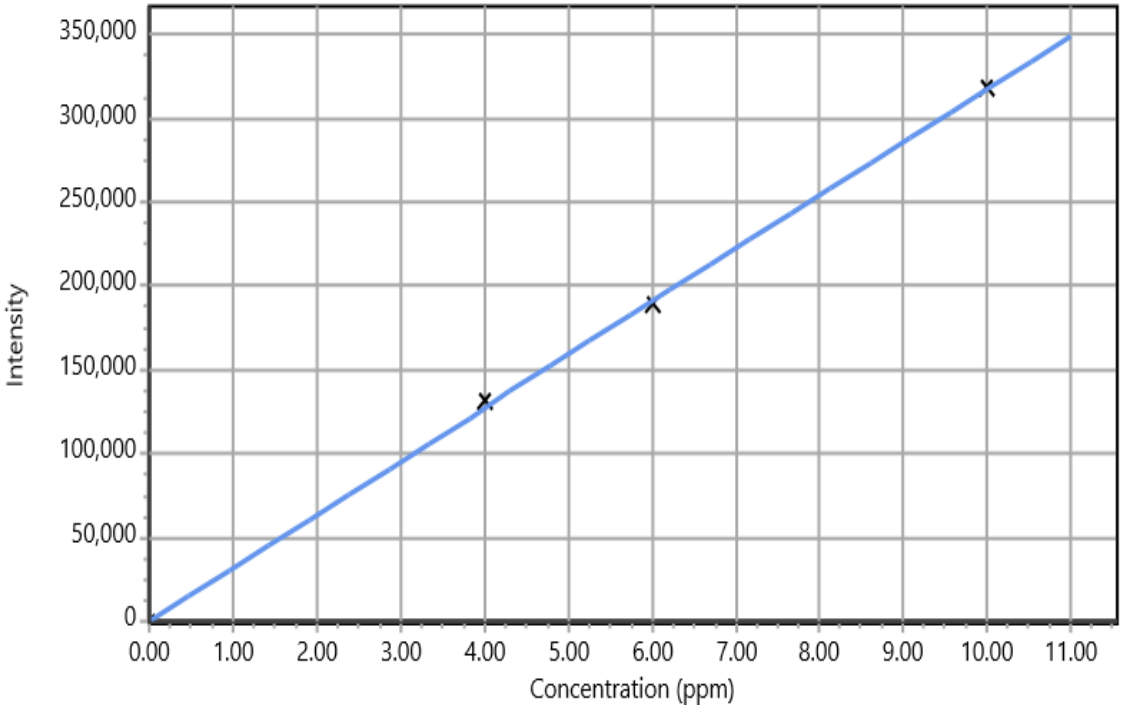
APPENDIX D

Calibration curves for the determination of metal concentrations



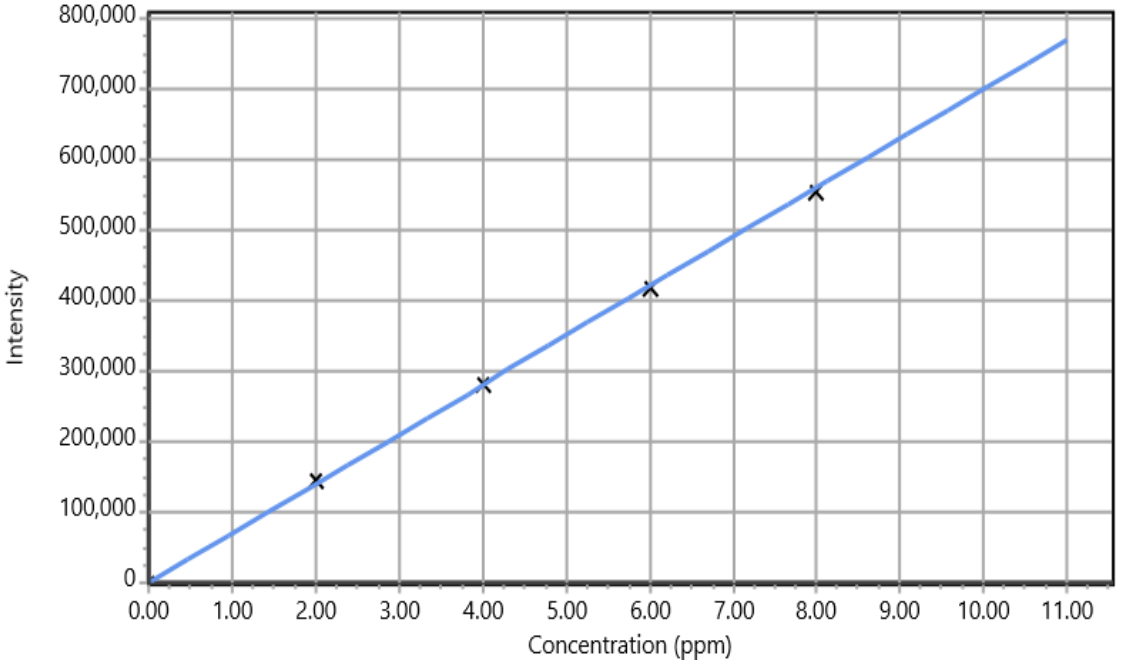
R^2= 0.99848, Intensity=13006.01119729*Conce+17.41042404

Figure D1: Calibration curve for sodium in hydros and caustic soda



R^2= 0.99981, Intensity= 31768.35527533*Conc+0.89475167

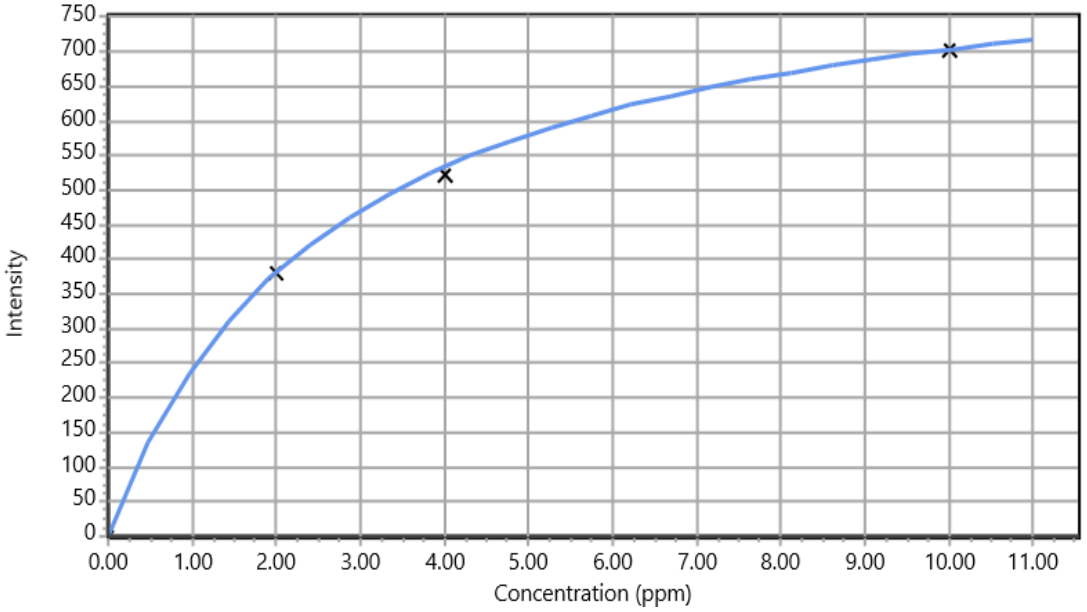
Figure D2: Calibration curve for cadmium in hydros and caustic soda



Correlation coefficient: 0.99995

Intensity: 70154.61971659*Concentration+0.14427202

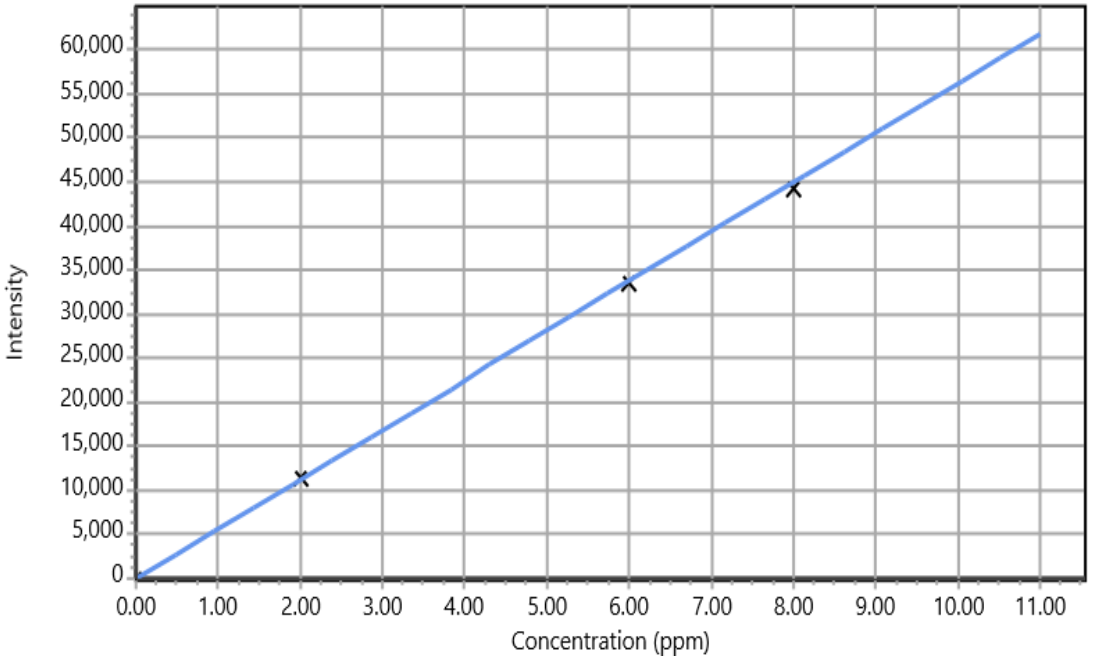
Figure D3: Calibration curve for chromium (425.433nm) in hydros and caustic soda



Correlation coefficient: 0.99969,

Intensity=(332.64855759*Concentration+0.20947861)/(1+0.37292341*Concentration)

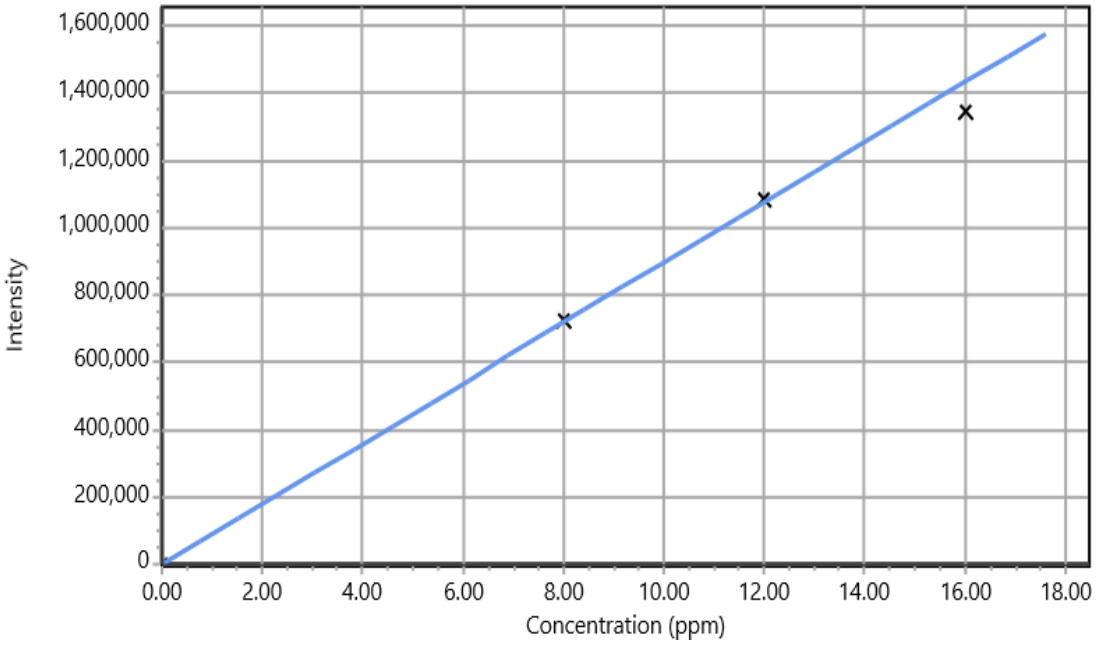
Figure D4: Calibration curve for iron (371.993nm) in hydros and caustic soda



Correlation coefficient: 0.99995

Intensity: 5621.76390269*Concentration+0.77278544

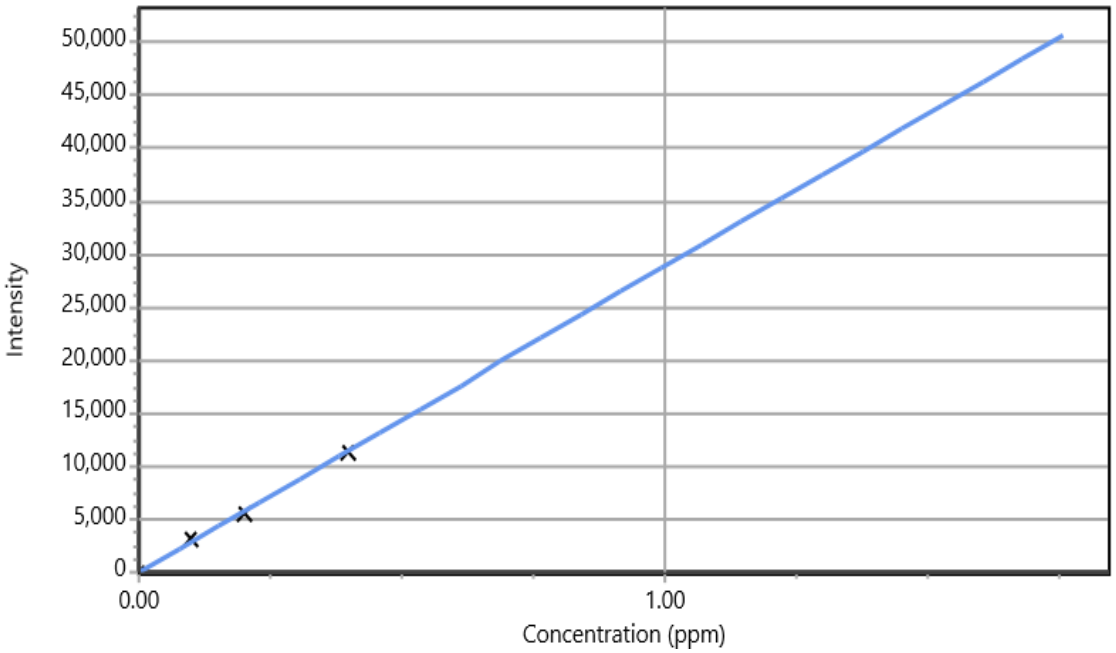
Figure D5: Calibration curve for lead (405.781nm) in hydros and caustic soda



Correlation coefficient: 0.99815

Intensity: 89669.82882529*Concentration+0.01276351

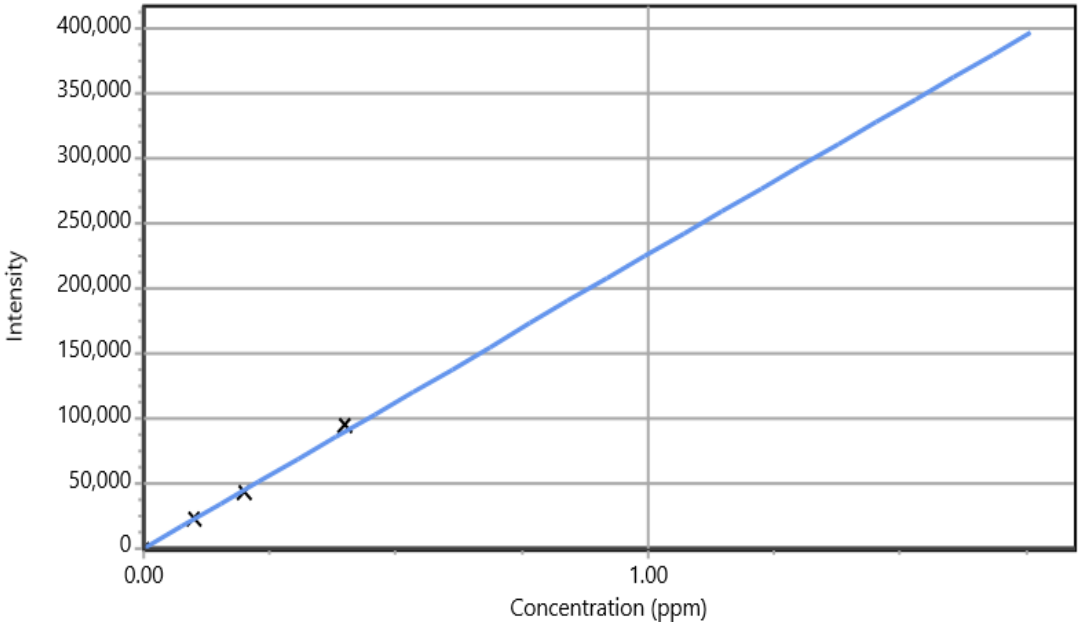
Figure D6: Calibration curve for manganese (403.076nm) in hydros and caustic soda



Correlation coefficient: 0.99924

Intensity: 28809.89727294*Concentration+13.88312039

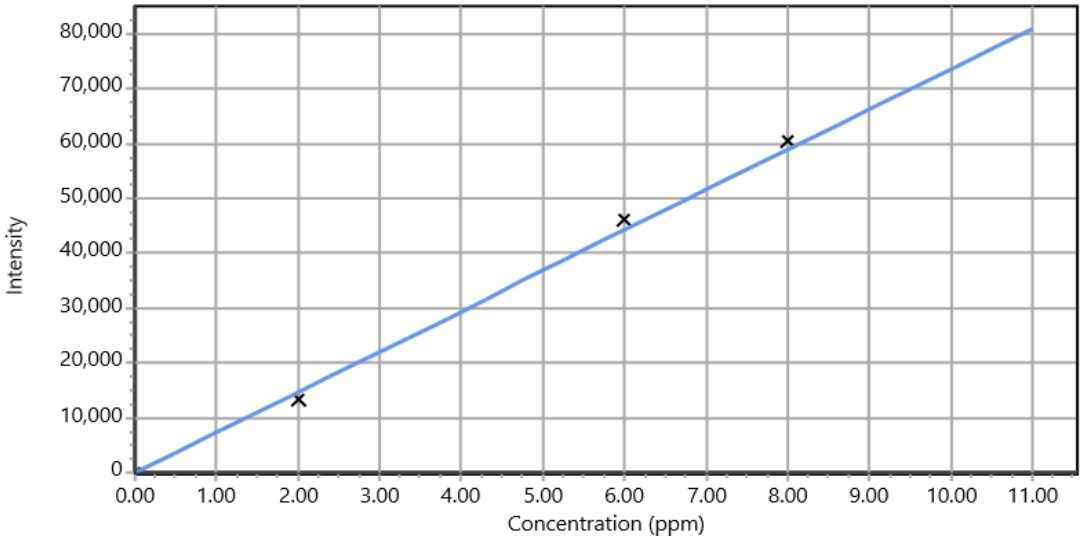
Figure D7: Calibration curve for zinc (213.857nm) in hydros and caustic soda



Correlation coefficient: 0.99916

Intensity: 225937.37091348*Concentration-155.08932447

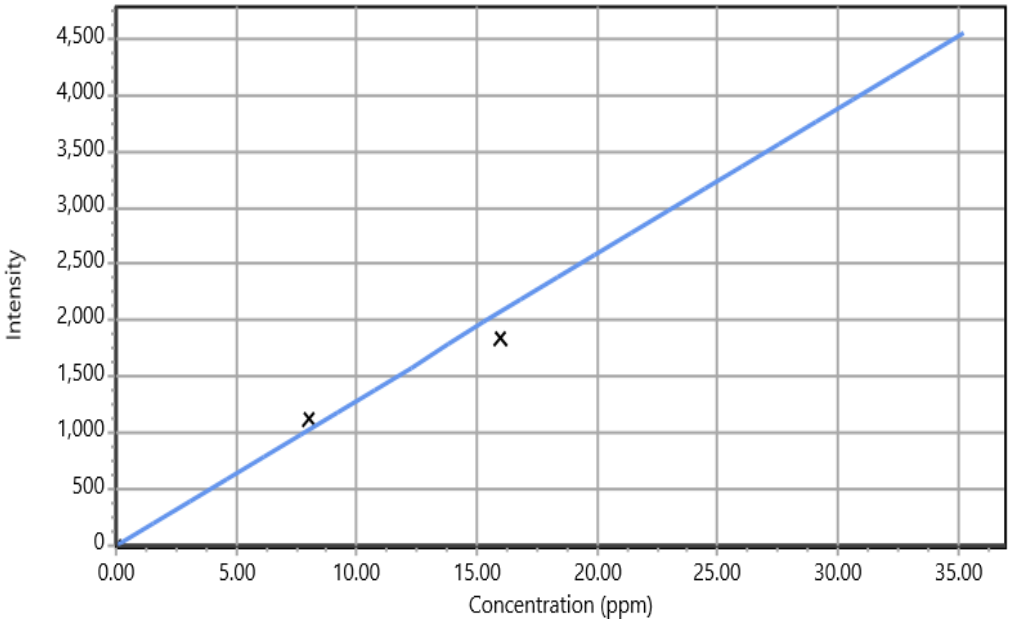
Figure D8: Calibration curve for cupper (324.754nm) in hydros and caustic soda



Correlation coefficient: 0.99932

Intensity: 7362.70412760*Concentration-17.33699153

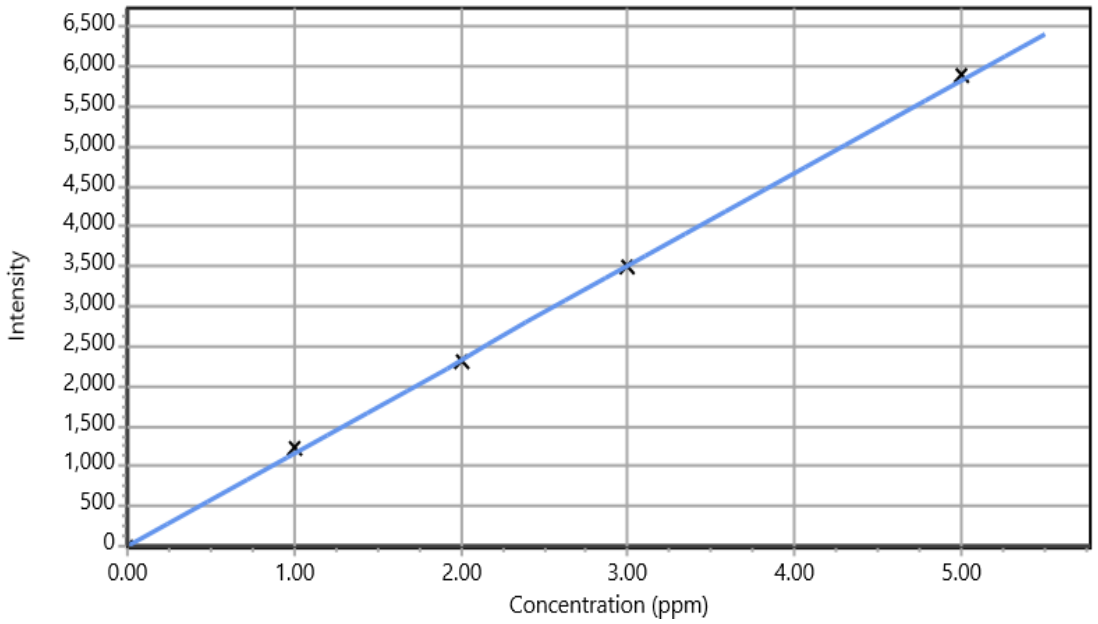
Figure D9: Calibration curve for nickel (352.454nm) in hydros and caustic soda



Correlation coefficient= 0.99209

Intensity= 129.45220777*Concentration-0.00000

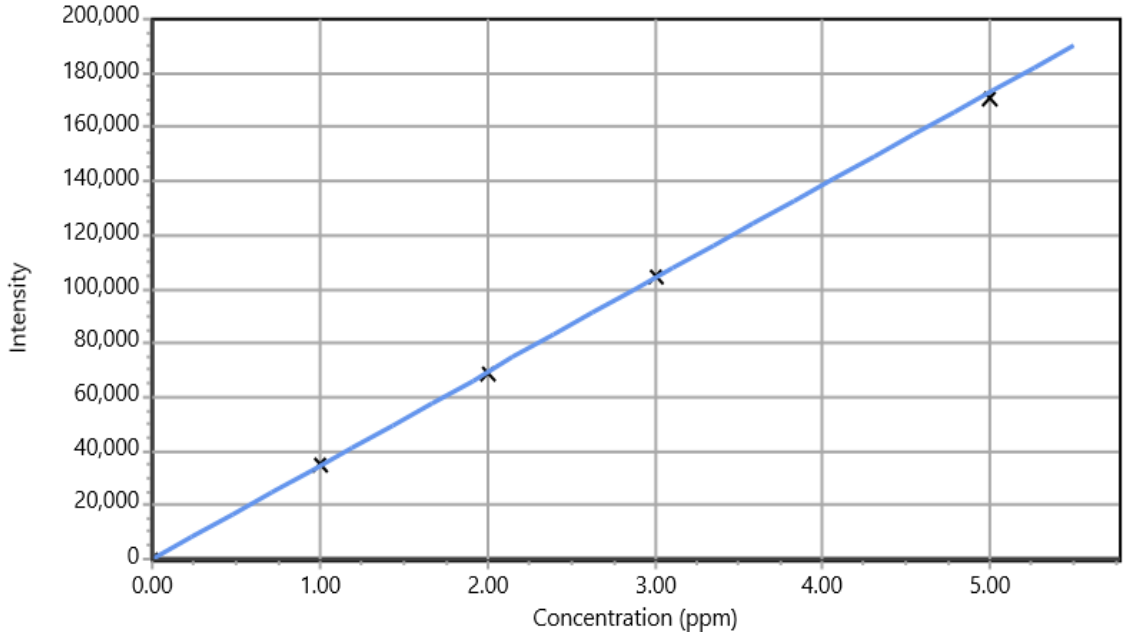
Figure D10: Calibration curve for sodium (568.820nm) in dye powders



Correlation coefficient= 0.99985

Intensity= 1166.13449403*Concentration+2.01715434

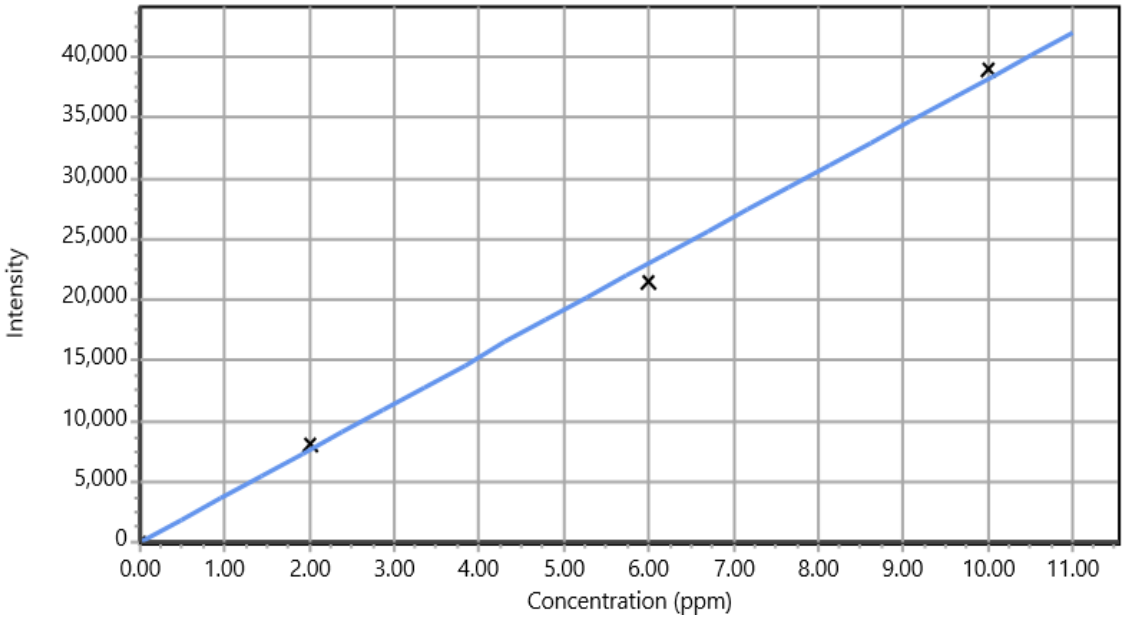
Figure D11: Calibration curve for cadmium (361.051nm) in dye powders



Correlation coefficient= 0.99988

Intensity= 34646.53504354*Concentration+0.02524991

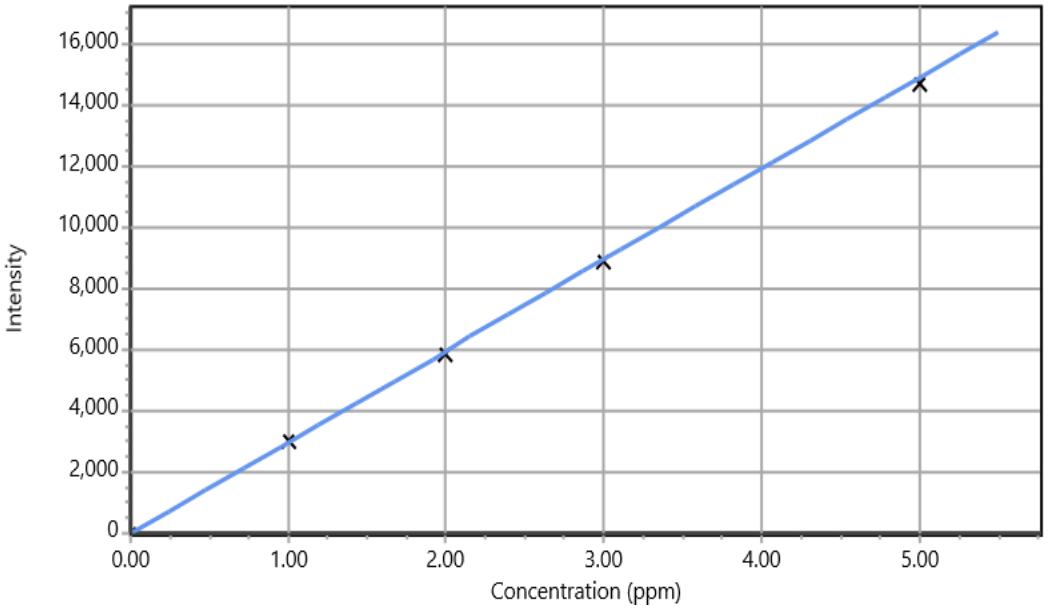
Figure D12: Calibration curve for chromium (425.433nm) in dye powders



Correlation coefficient= 0.99847

Intensity= 3821.70968730*Concentration+1.02534495

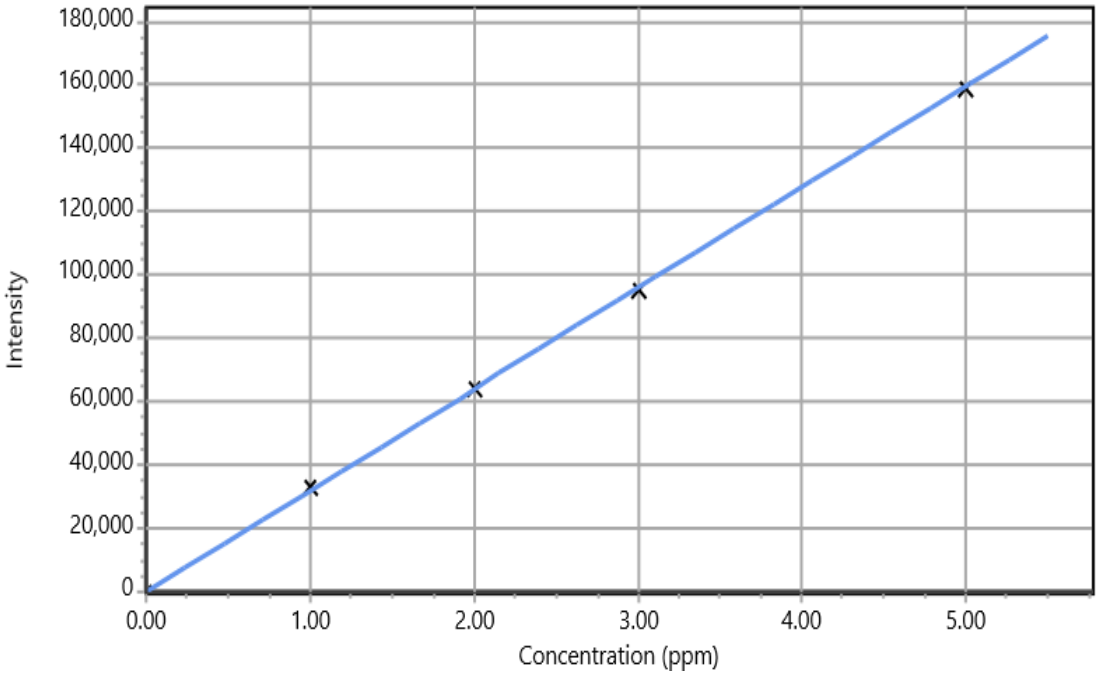
Figure D13: Calibration curve for iron (373.713nm) in dye powders



Correlation coefficient= 0.99997

Intensity= 2987.41638467*Concentration+0.0279721

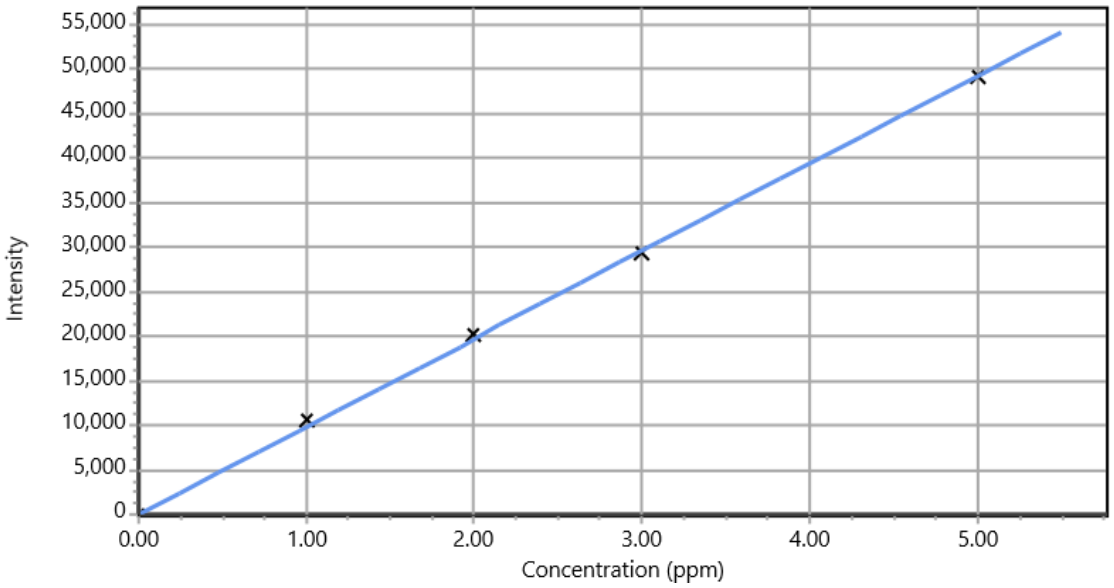
Figure D14: Calibration curve for lead (405.781nm) in dye powders



Correlation coefficient= 0.99997

Intensity= 31950.93111750*Concentration+0.03066989

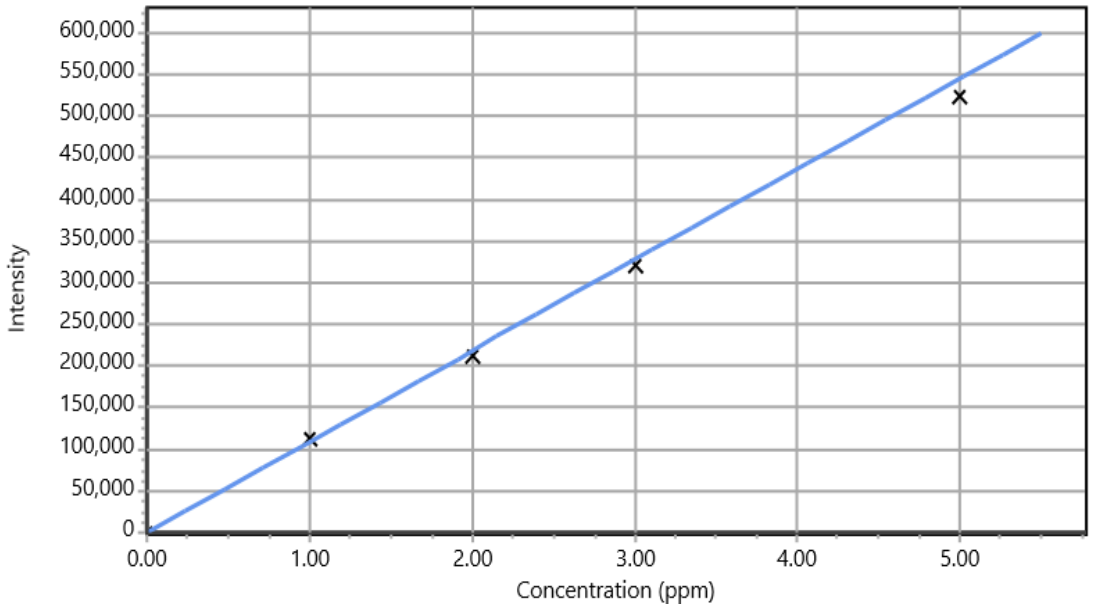
Figure D15: Calibration curve for manganese (403.076nm) in dye powders



Correlation coefficient= 0.99982

Intensity= 9853.54648562*Concentration+2.70826691

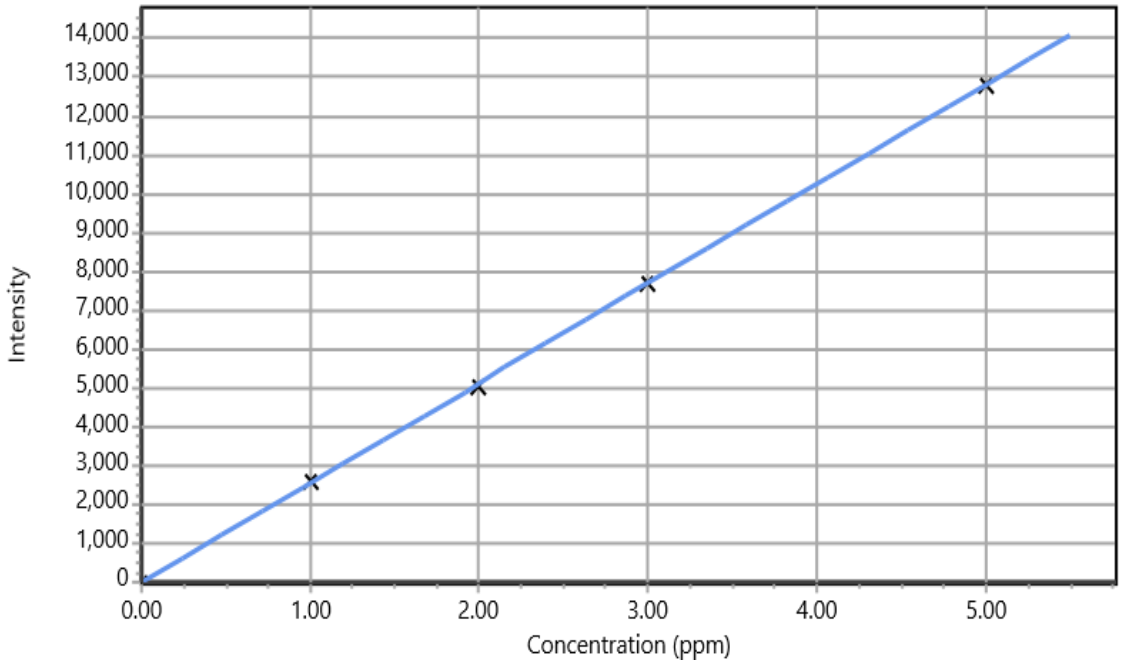
Figure D16: Calibration curve for zinc (213.857nm) in dye powders



Correlation coefficient= 0.99979

Intensity= 109126.79760270*Concentration+2.412941

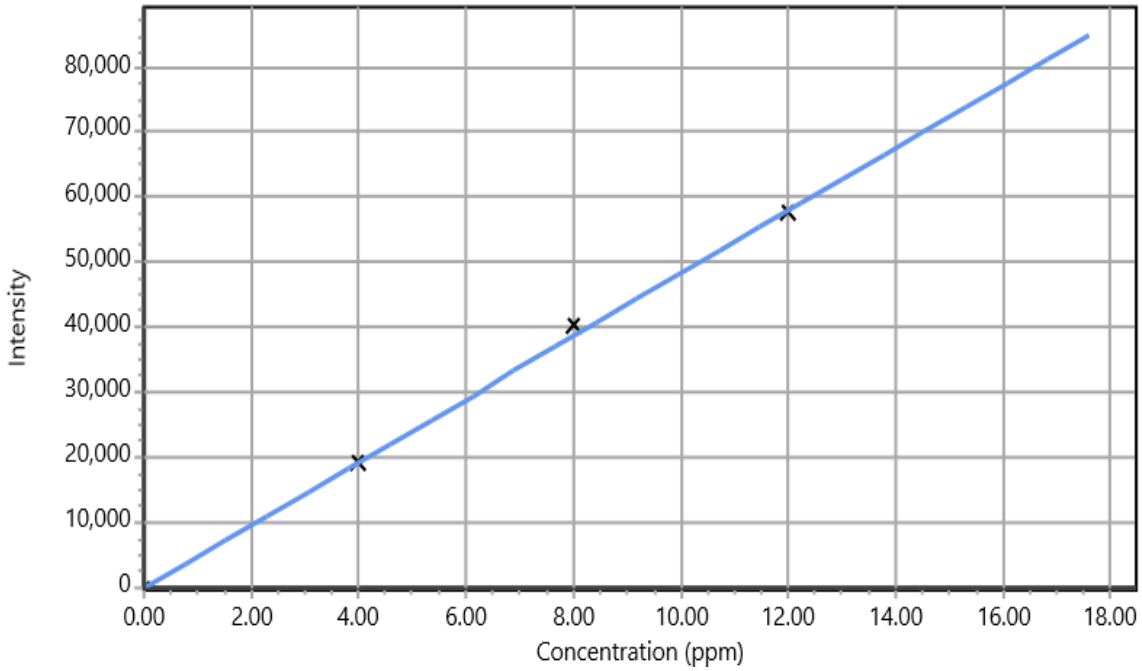
Figure D17: Calibration curve for cupper (324.754nm) in dye powders



Correlation coefficient= 0.99994

Intensity= 2562.90413849*Concentration+0.31939102

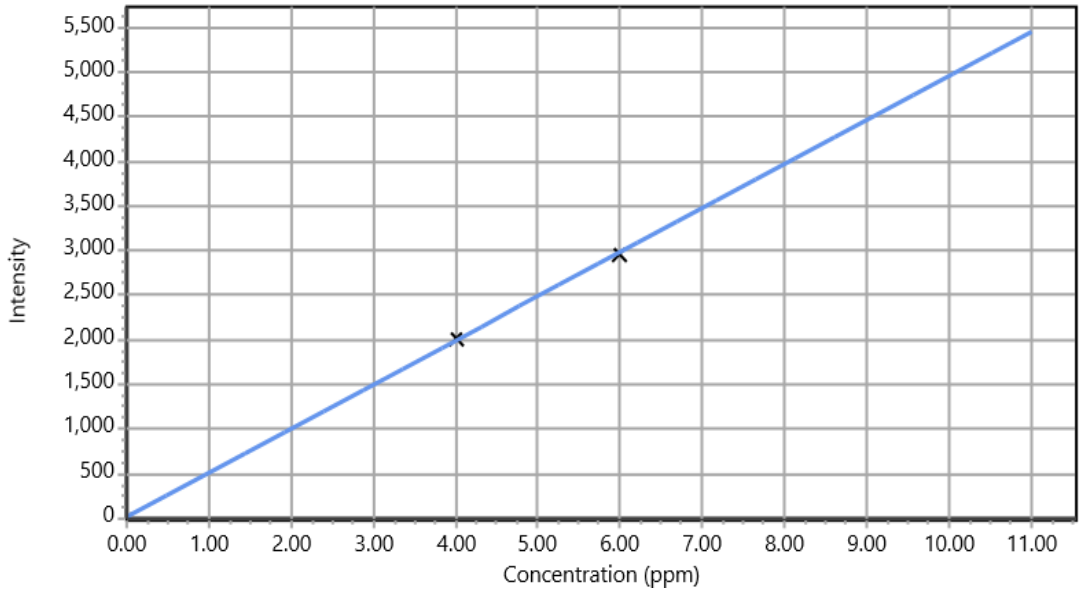
Figure D18: Calibration curve for nickel (231.096nm) in dye powders



Correlation coefficient= 0.99924

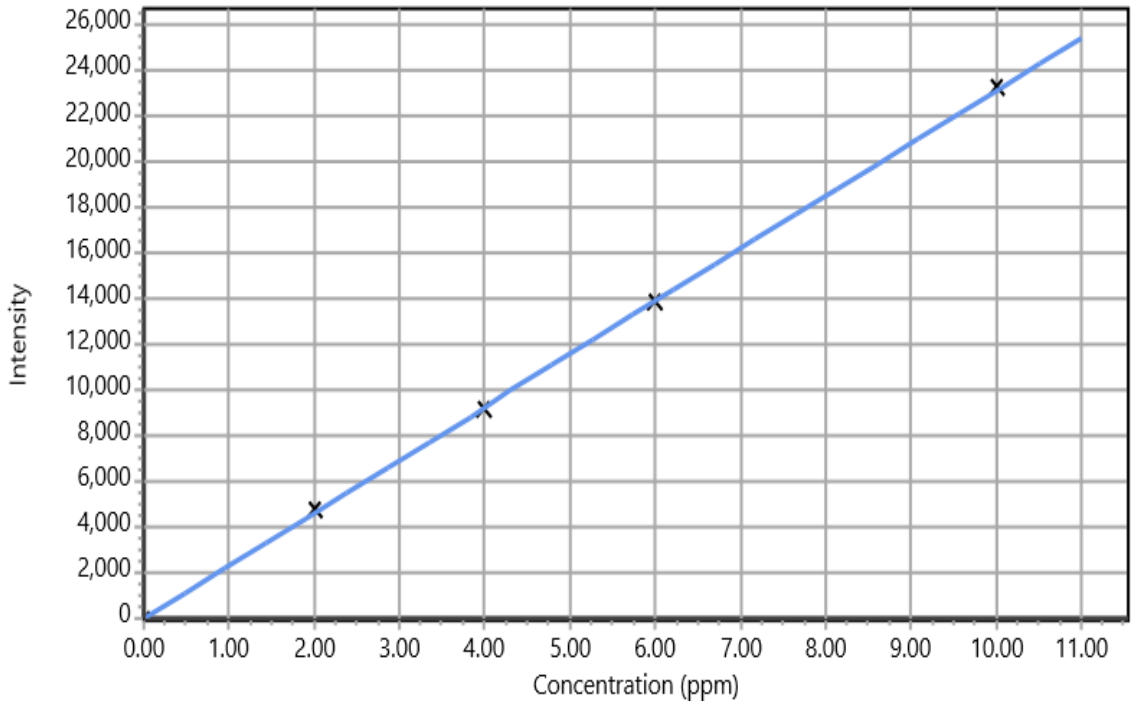
Intensity= 4826.96216922*Concentration+0.82960184

Figure D19: Calibration curve for nickel (352.454nm) in water and effluent samples



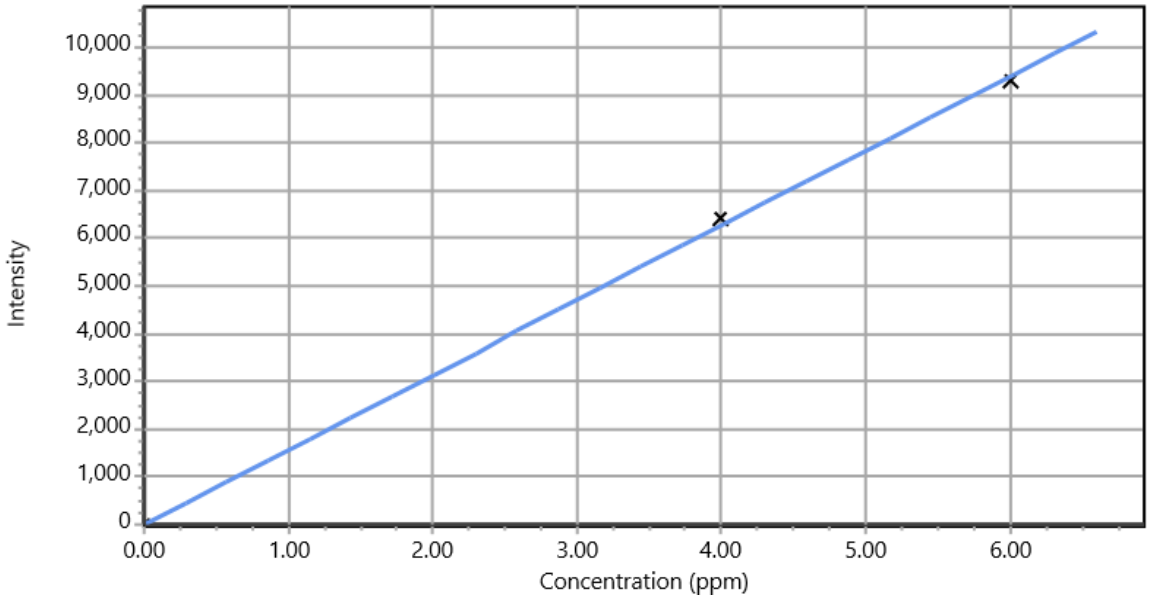
Correlation coefficient= 0.99983, Intensity= 494.70197317*Concentration+12.61508908

Figure D20: Calibration curve for lead (405.781nm) in water and effluent samples



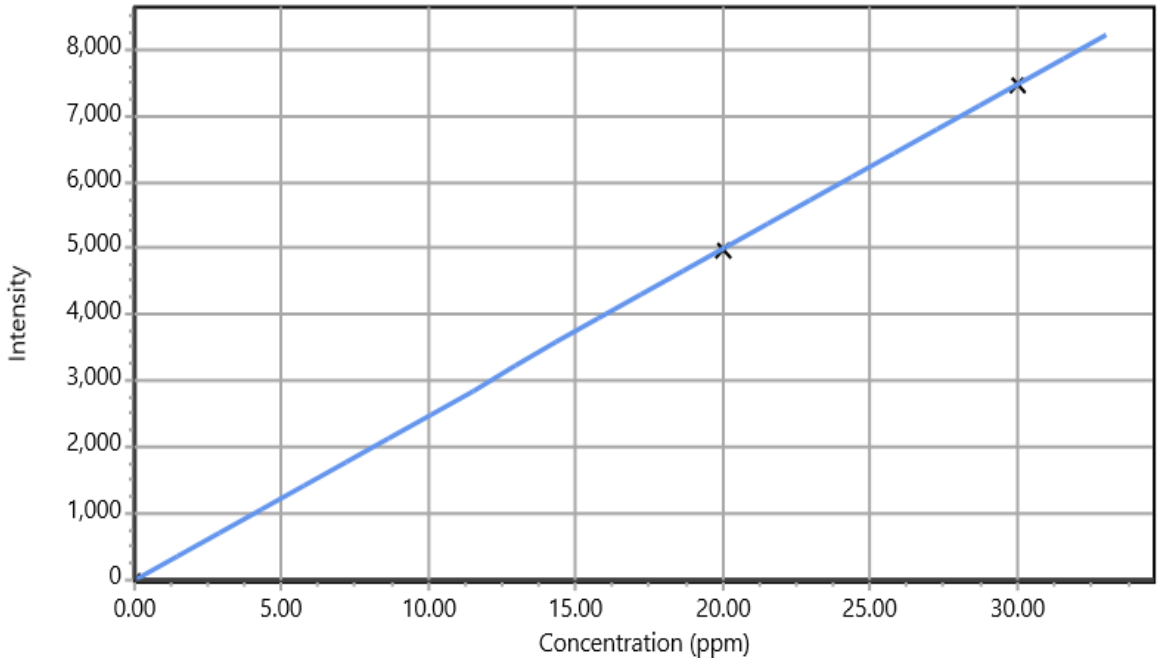
Correlation coefficient= 0.99996, Intensity= 2315.13652820*Concentration+5.36406583

Figure D21: Calibration curve for chromium (425.433nm) in water and effluent samples



Correlation coefficient= 0.99960, Intensity= 1565.81245270*Concentration+0.46552719

Figure D22: Calibration curve for iron (371.993nm) in water and effluent samples



Correlation coefficient= 1.00000, Intensity= 249.33861741*Concentration-0.04825557

Figure D23: Calibration curve for sodium (568.820nm) in water and effluent samples

APPENDIX E

Physico-chemical parameters and heavy metals in effluent samples

Table E1: Physico-chemical parameters and heavy metals in VR1 effluent samples

Parameter (Units)	**Samples ID**						**Mean± SD**
	DA	DB	DC	DD	DE	DF	
pH	11.64±0.07	11.47±0.03	11.65±0.06	11.54±0.06	11.61±0.11	11.53±0.06	11.57±0.07
Colour	607.44±2.35	915.52±4.60	599.44±2.55	750.22±7.00	527.92±2.52	493.45±2.79	649±157.68
DO	1.44±0.02	1.49±0.01	1.42±0.03	1.62±0.02	1.41±0.01	1.56±0.01	1.49±0.08
BOD	369.80±1.56	366.84±1.84	308.59±1.35	486.22±4.39	388.76±1.58	338.97±3.35	376.53±60.58
COD	1448.13±10.8	2211.67±6.11	1307.07±7.14	1233.33±6.25	2102.55±8.54	1406.70±7.08	1618.24±425.53
Cond.	2111.33±4.16	2012.00±12	2110.67±14.1	2048.00±14.0	2057.33±23	2142.86±21.2	2080.37±49.06
TDS	3813.20±16.1	4262.43±21.9	4323.06±16.3	3732.69±19.4	4842.30±28.7	4461.06±23.01	4239.12±414.38
Sulphate	59.16±2.47	54.22±1.32	60.22±1.67	37.24±1.35	61.13±1.61	47.05±2.45	53.17±9.39
Sodium	ND	914.17±18.5	1208.97±38.3	1085.71±77.5	ND	1234.36±8.31	740.53±584.7
Iron	0.20±0.05	0.94±0.02	0.25±0.06	1.01±0.07	0.95±0.01	1.01±0.02	0.73±0.39
Nickel	0.15±0.02	0.16±0.01	0.09±1.7E-17	0.16±0.00	0.14±0.01	0.09±0.01	0.13±0.03
Chromium	0.06±0.01	0.06±0.01	0.06±0.01	0.76±0.52	0.04±0.01	0.03±0.00	0.17±0.29
Lead	0.98±0.39	2.22±0.08	0.15±0.09	0.72±0.90	2.77±0.07	2.54±0.02	1.56±1.08

pH: no units, Colour: pt-co, Cond.: µs/cm, All other parameters: mg/l

Table E2: Physico-chemical parameters and heavy metals in RSN effluent samples

Parameters (Units)	**Samples ID**						**Mean± SD**
	DG	DH	DI	DJ	DK	DL	
pH	11.47±0.07	11.44±0.06	11.73±0.06	11.65±0.06	11.65±0.05	11.56±0.07	11.58±0.01
Colour	478.02±3.31	632.72±4.56	579.54±3.01	408.42±2.89	425.19±3.13	808.43±3.36	555.39±151.8
DO	1.58±0.01	1.32±0.01	1.34±0.01	1.57±0.01	1.54±0.02	1.45±0.02	1.46±0.12
BOD	377.88±2.12	418.77±1.10	478.22±2.11	364.21±0.94	419.93±3.42	460.50±2.04	419.92±44.54
COD	1414.09±7.4	1386.77±10	1303.60±4.8	1209.41±6.1	1971.16±16	2110.97±4.4	1566±377.45
Cond.	2203.61±11.3	2014.65±15.9	1976.07±17	2147.18±22	2136.11±15.6	1978.71±10.9	2076.06±98.16
TDS	4939.45±31	3962.51±26	3194.39±24	3427.08±21	4898.40±43.50	4822.66±30.33	4207.41±785.75
Sulphate	47.73±1.09	64.04±2.14	63.46±2.26	47.66±2.28	49.22±1.88	59.20±2.20	55.22±7.88
Sodium	1275.29±62.4	ND	ND	ND	1228.25±12.9	872.89±69.67	562.74±631.96
Iron	0.84±0.04	0.99±1.4E-16	0.98±0.02	0.11±0.01	1.01±0.01	1.03±0.01	0.83±0.36
Nickel	0.10±0.01	0.19±0.01	0.15±0.01	0.14±0.01	0.12±0.03	0.08±0.01	0.13±0.04
Chromium	0.03±0.01	0.03±0.01	0.03±0.01	0.1±0.01	0.04±0.01	0.04±0.01	0.05±0.03
Lead	2.44±0.01	2.31±0.06	3.22±0.19	0.75±0.27	3.67±0.03	3.45±0.13	2.64±1.08

pH: no units, Colour: pt-co, Cond.: µs/cm, All other parameters: mg/l

Table E3: Physico-chemical parameters and heavy metals in VRR effluent samples

Parameters (Units)	**Samples ID**						**Mean±SD**
	DM	DN	DO	DP	DQ	DR	
pH	11.35±0.05	11.45±0.04	11.35±0.06	11.15±0.05	11.27±0.03	11.55±0.05	11.36±0.14
Colour	619.06±2.85	734.92±5.12	604.13±3.22	585.54±2.26	721.03±5.82	609.79±4.88	645.75±64.78
DO	1.53±0.02	1.45±0.01	1.38±0.01	1.46±0.01	1.56±0.01	1.67±0.01	1.51±0.10
BOD	480.11±2.45	384.26±3.81	397.09±3.08	474.31±2.08	310.68±2.48	479.51±3.47	420.99±69.07
COD	1304.30±8.5	1387.02±9.8	1421.12±4.4	1222.02±9.04	1950.77±3.8	1515.04±7.7	1466.71±257
Cond.	2412.65±13	2516.33±21.5	2316.8±9.85	2066.11±19.35	2385.36±15.6	2023.83±10.2	2286.85±198.5
TDS	4977.73±48.7	3935.05±25.7	4748.14±33.9	4944.03±32.16	5073.01±27.4	4861.61±41.2	4756.59±417
Sulphate	52.14±2.65	54.18±1.17	61.93±1.82	56.51±0.68	48.65±1.55	33.97±1.09	51.23±9.55
Sodium	1325.27±16	1376.66±23	1330.95±48	1142.31±191	1304.33±36	1121.88±90	1266.9±107.25
Iron	0.70±0.70	1.04±1.04	1.03±1.03	1.26±1.26	0.99±0.99	1.02±1.02	1.01±0.18
Nickel	0.14±0.01	0.09±0.01	0.16±0.01	0.13±0.01	0.16±0.01	0.14±0.02	0.14±0.02
Chromium	0.48±0.50	0.09±0.01	0.03±0.01	0.47±0.03	0.04±0.01	0.03±0.02	0.19±0.22
Lead	1.41±0.06	3.92±0.09	3.76±0.02	2.01±0.07	3.71±0.28	4.03±0.07	3.14±1.13

pH: no units, Colour: pt-co, Cond.: µs/cm, All other parameters: mg/l

APPENDIX F

Physico-chemical parameters and heavy metals in groundwater samples

Parameter (unit)	**Samples ID**											
	WA	WB	WC	WD	WE	WF	WG	WH	WI	WJ	WK	WL
pH	5.6±0.03	6.1±0.1	7.2±0.06	6.7±0.06	6.4±0.04	6.0±0.08	6.8±0.12	6.4±0.04	6.1±0.04	6.7±0.08	6.7±0.07	6.8±0.06
Temperature	31±0.58	32±0.58	32±0.76	31±0.58	33±0.50	30±0.50	31±0.58	30±0.68	32±0.24	30±0.68	31±1.00	30±0.74
DO	4.15±0.02	4.86±0.03	3.10±0.02	4.72±0.04	3.96±0.03	4.54±0.05	5.37±0.03	4.67±0.04	3.72±0.01	3.11±0.02	2.95±0.02	3.41±0.03
BOD	1.16±0.01	0.94±0.01	2.28±0.02	1.97±0.01	0.70±0.01	1.70±0.01	2.16±0.02	1.62±0.02	0.96±0.01	1.22±0.01	2.12±0.01	1.04±0.01
Cond.	980.31±5.02	1010.34±2.65	1093.15±6.06	1179.15±9.66	1210.06±6.41	931.14±8.97	944.05±3.83	995.69±3.30	1327.78±7.91	983.27±4.94	1359.17±7.83	1333.00±7.37
TDS	971.82±5.03	1048.96±2.73	1202.96±6.28	339.58±2.85	1015.32±5.15	18.95±0.15	1667.52±9.14	96.42±0.71	717.68±1.98	646.35±3.40	1126.96±5.76	582.08±3.40
Sulphate	20.72±3.18	16.59±1.25	24.30±2.34	19.14±1.16	21.13±1.55	20.79±2.55	15.41±2.06	19.57±1.17	21.11±1.37	24.26±1.20	24.25±1.50	22.12±1.35
Sodium	558.33±62.79	773.41±127.96	887.38±58.37	1000.07±26.30	979.34±25.69	744.00±165.75	ND	804.10±152.03	1130.02±16.70	659.67±104.29	1116.24±65.85	1052.44±71.13
Iron	0.87±0.01	0.85±0.02	0.93±0.02	1.91±0.01	0.85±0.01	0.90±0.01	0.87±0.00	1.09±0.02	3.95±0.06	0.84±0.01	0.87±0.01	0.81±0.01
Nickel	0.103±0.01	0.100±1.7E-17	0.097±0.01	0.107±0.01	0.100±1.7E-17	0.097±0.01	0.100±1.7E-17	0.100±1.177E-17	0.103±0.01	0.100±1.7E-17	0.103±0.01	0.137±0.01

Chromium	0.05±8.5E-18	0.07±0.00	0.05±0.01	0.08±0.01	0.08±0.05	0.06±0.00	0.05±0.01	0.15±0.02	0.17±0.01	0.05±0.01	0.05±0.01	0.05±8.5E-18
Lead	2.23±0.02	2.20±0.02	2.27±0.03	2.26±0.03	2.22±0.02	2.31±0.01	2.33±0.03	2.37±0.01	2.32±0.02	2.29±0.04	2.29±0.01	2.17±0.01

pH: no units, Temperature: oC, Conductivity: µs/cm, All other parameters: mg/l

APPENDIX G

Load elongation curves for the determination of tensile strength and elongation

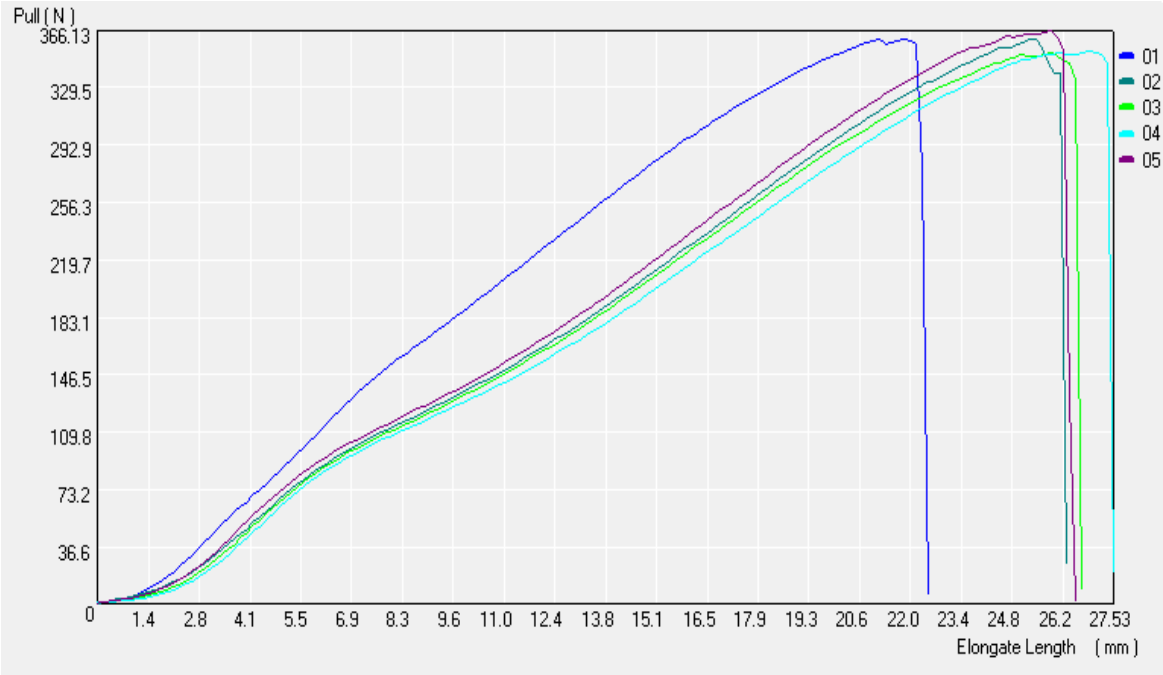


Figure G1: Load elongation curve for Unmercerized BF in warp direction

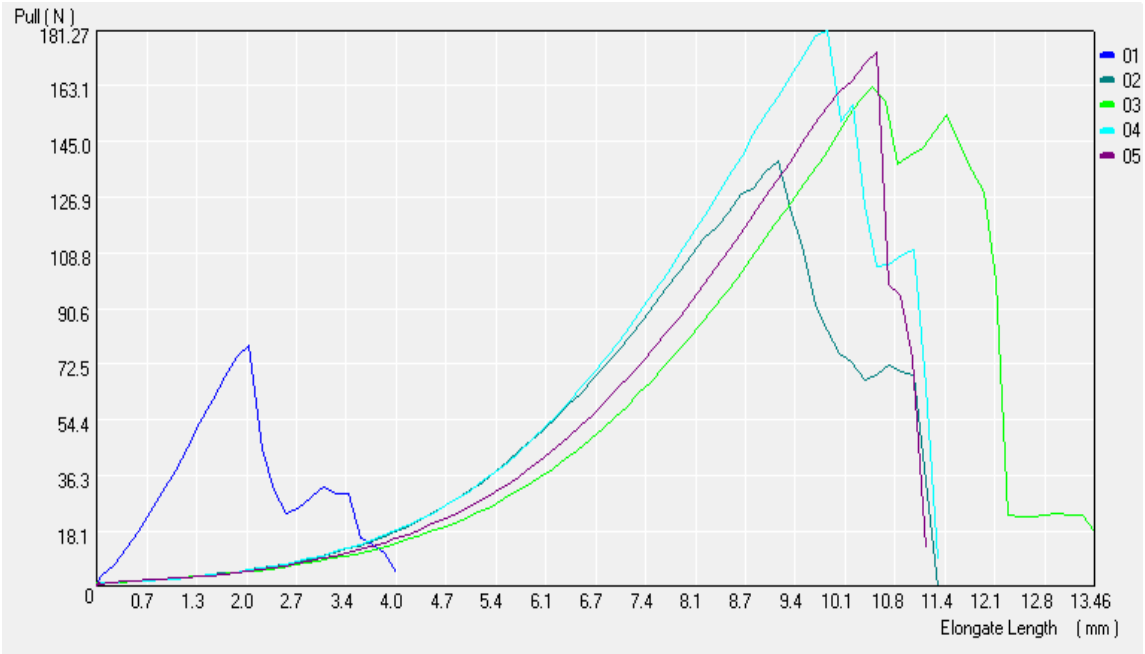


Figure G2: Load elongation curve for Unmercerized CF in warp direction

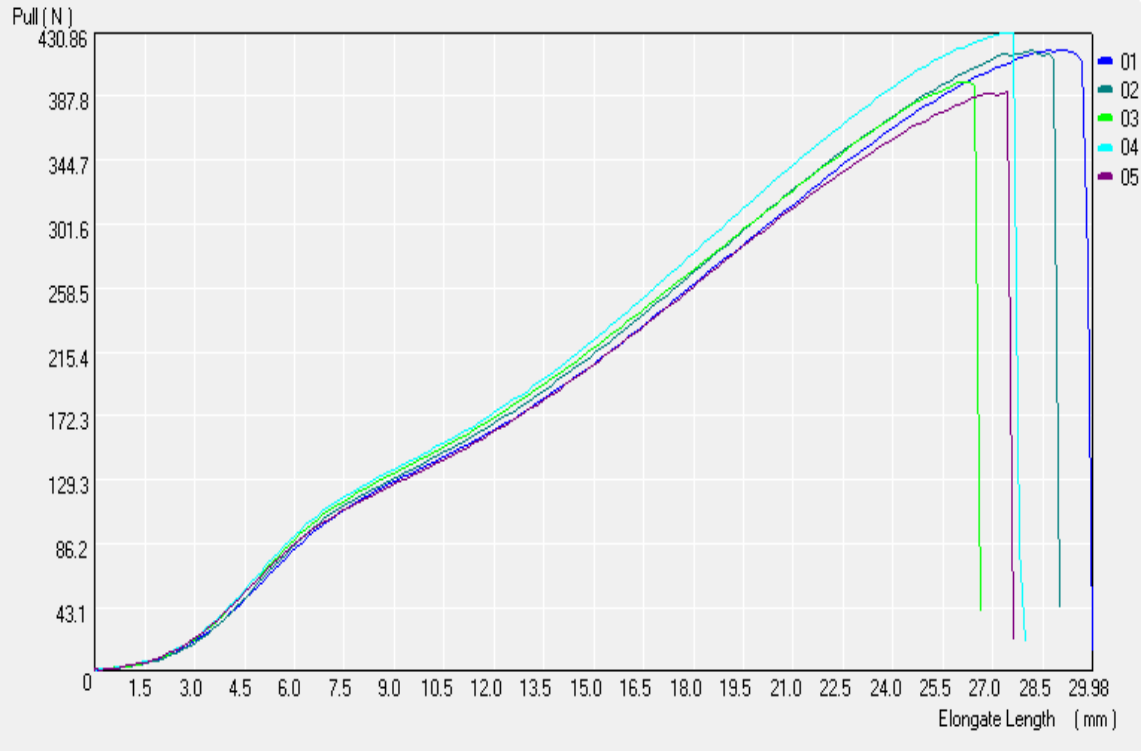


Figure G3: Load elongation curve for sample from run number 1 in warp direction

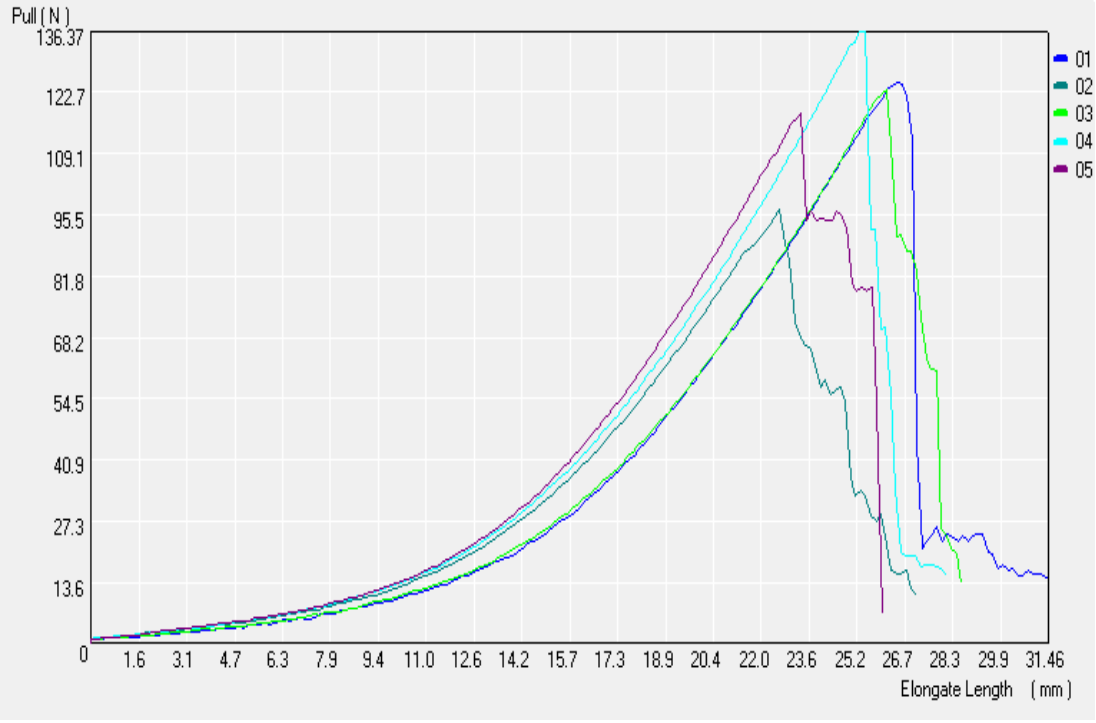


Figure G4: Load elongation curve for sample from run number 1 in weft direction

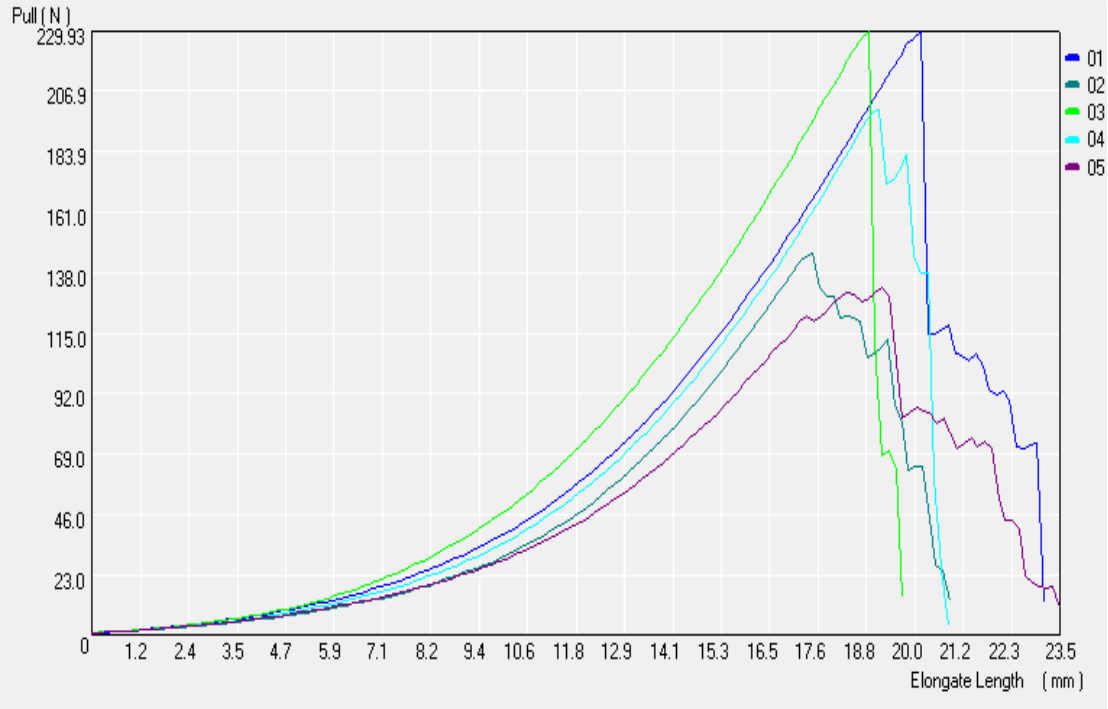


Figure G5: Load elongation curve for sample from run number 2 in warp direction

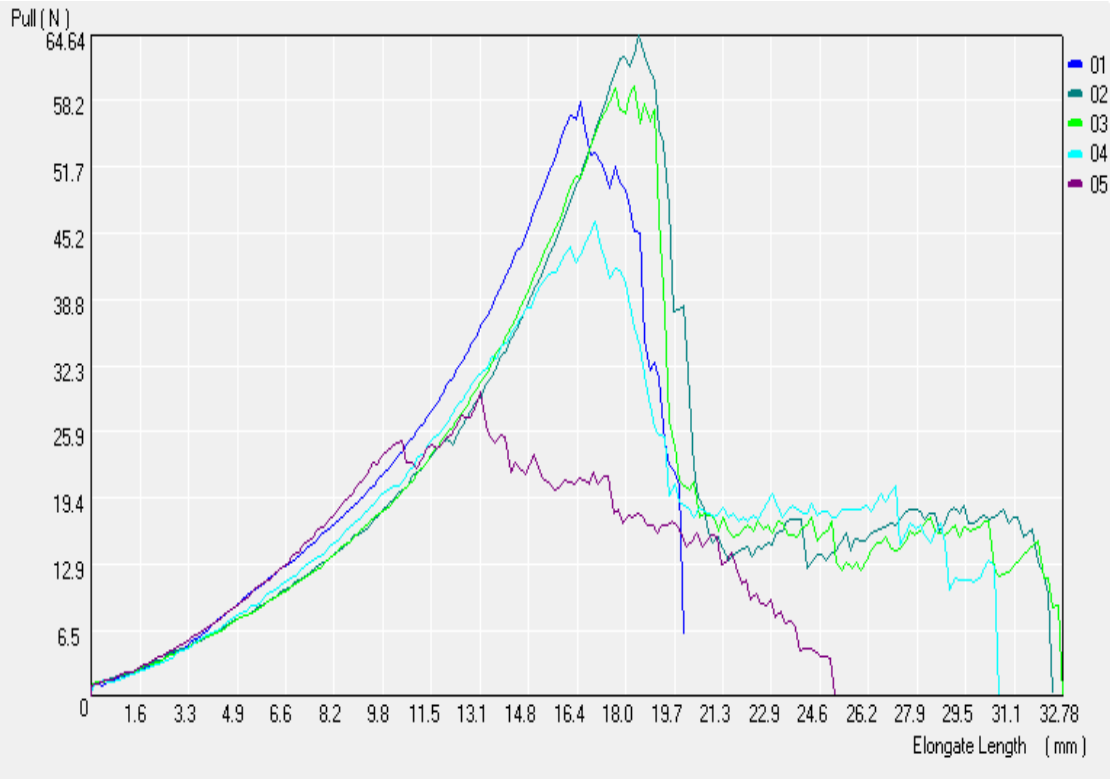


Figure G6: Load elongation curve for sample from run number 2 in weft direction

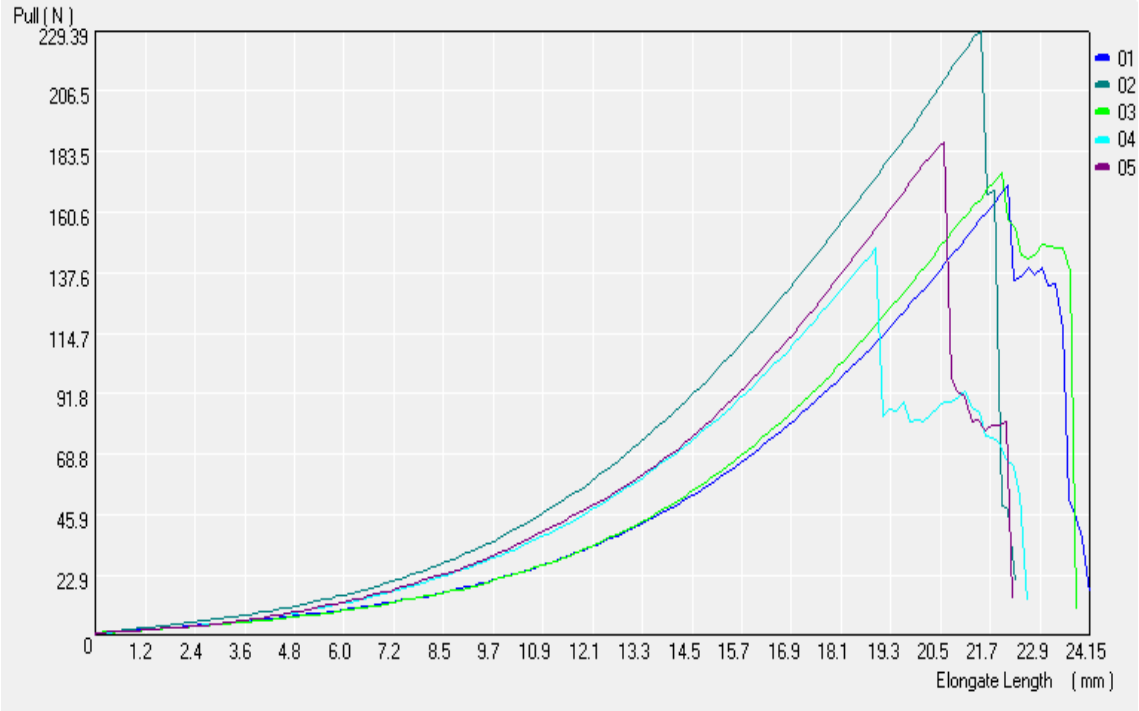


Figure G7: Load elongation curve for sample from run number 3 in warp direction

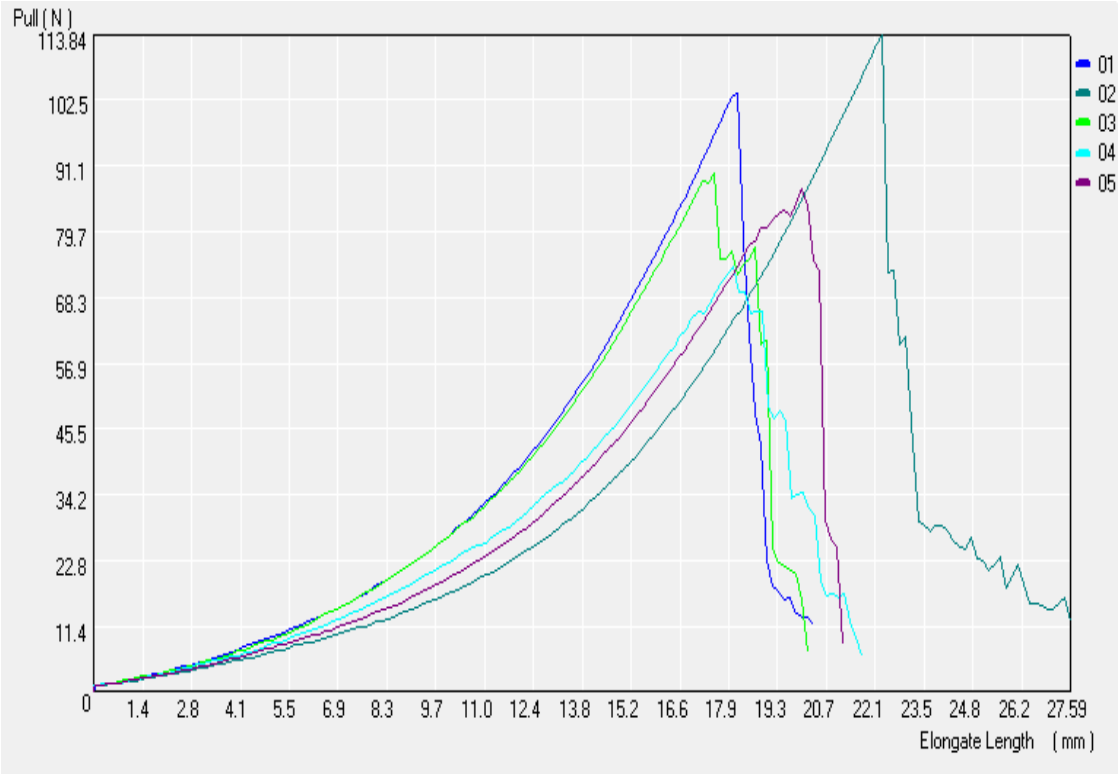


Figure G8: Load elongation curve for sample from run number 3 in weft direction

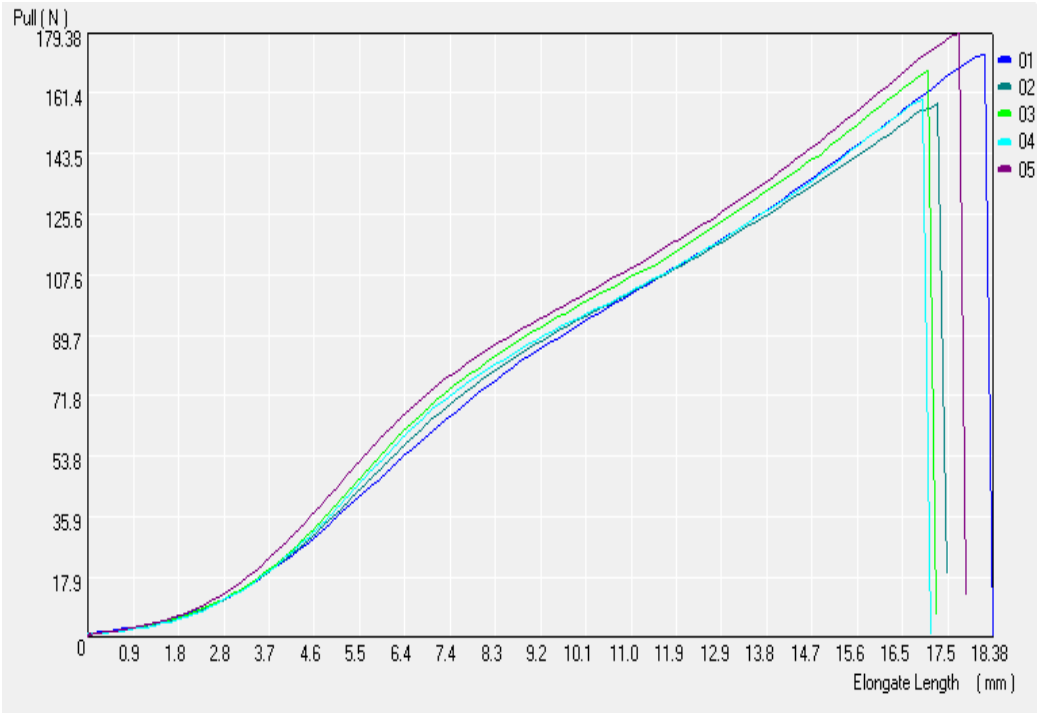


Figure G9: Load elongation curve for sample from run number 4 in warp direction

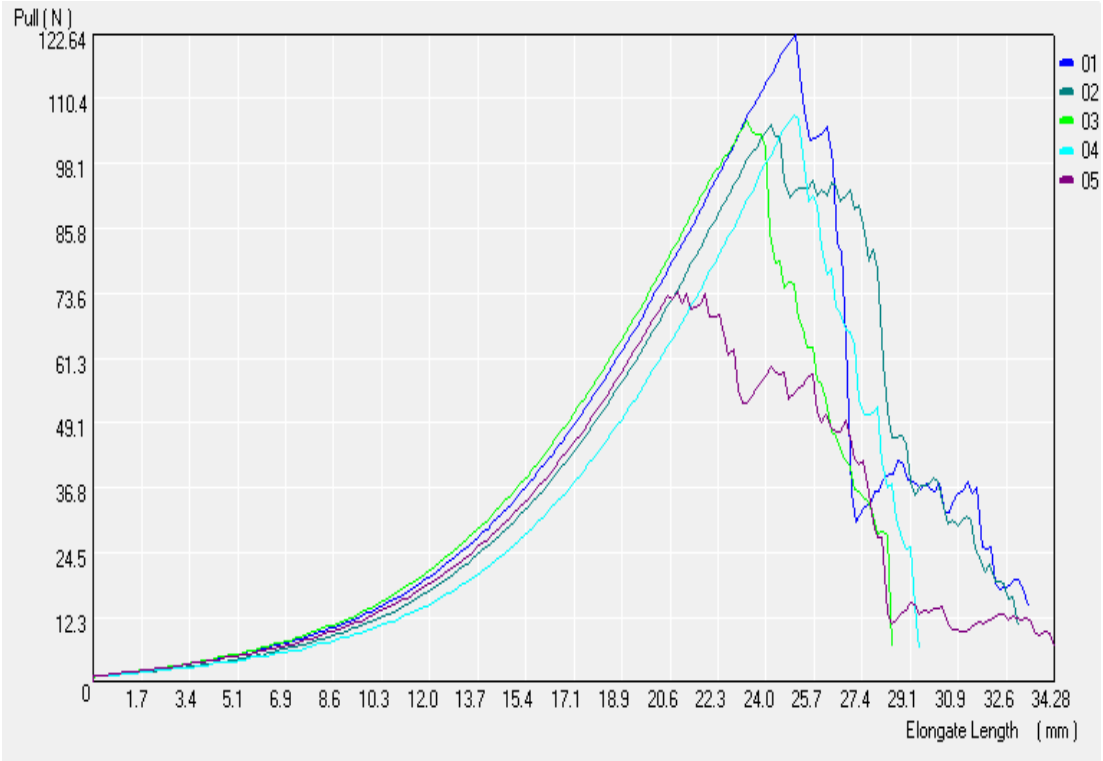


Figure G10: Load elongation curve for sample from run number 4 in weft direction

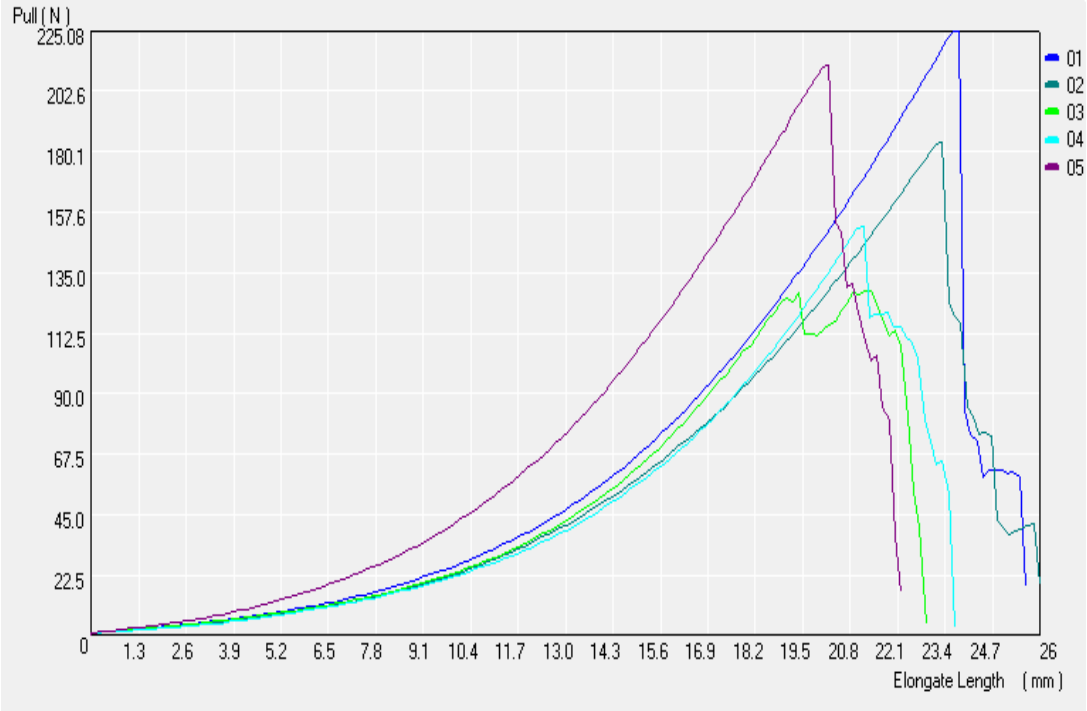


Figure G11: Load elongation curve for sample from run number 5 in warp direction

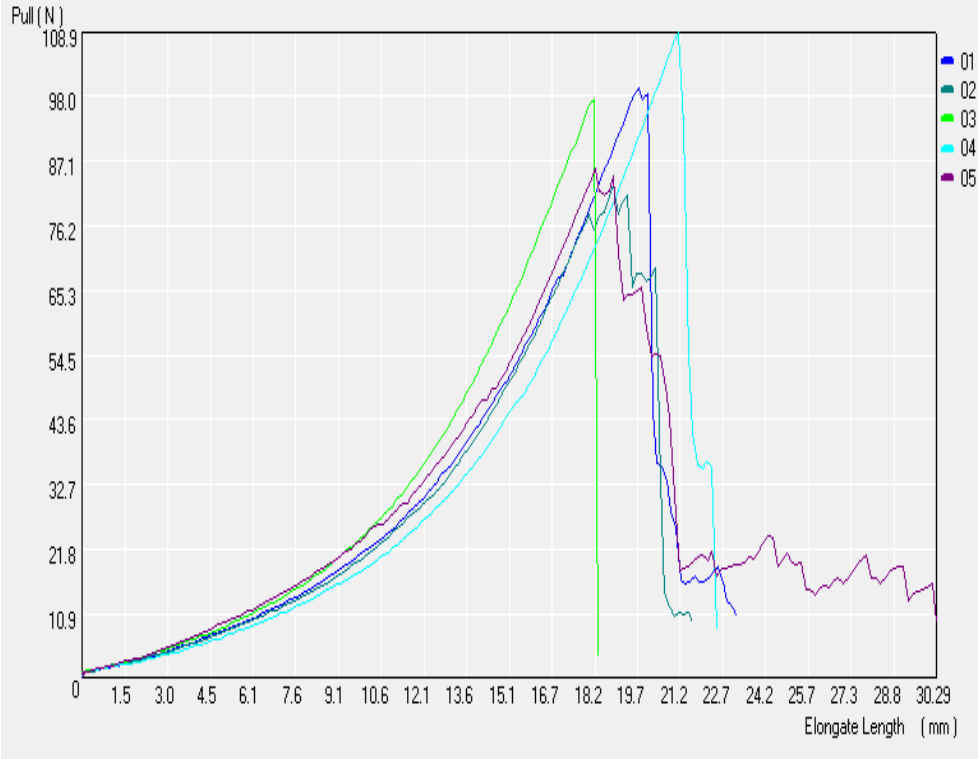


Figure G12: Load elongation curve for sample from run number 5 in weft direction

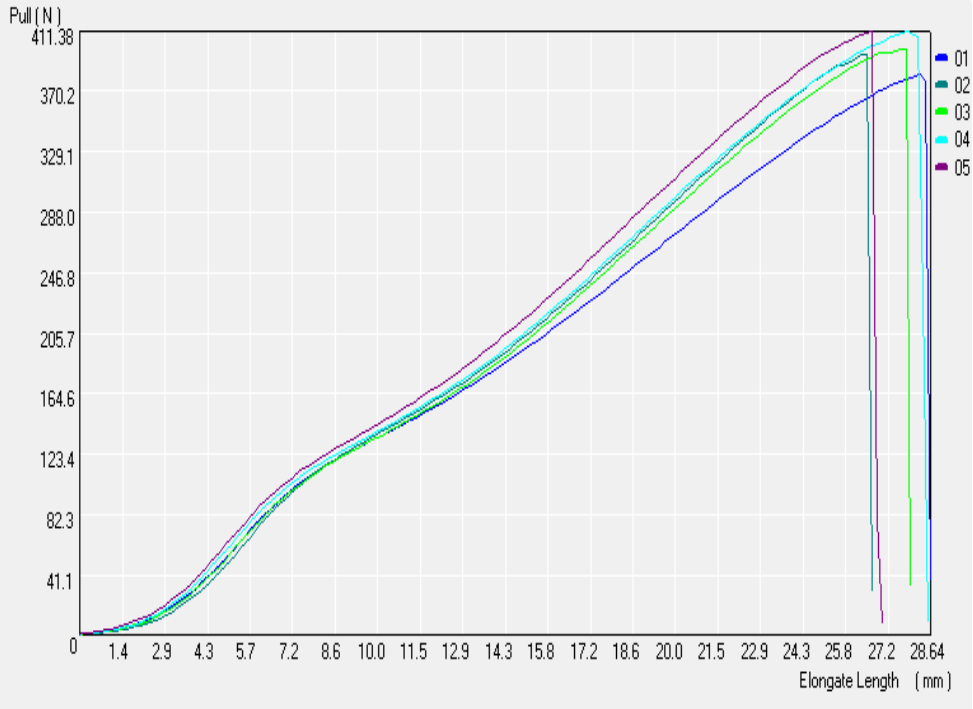


Figure G13: Load elongation curve for sample from run number 6 in warp direction

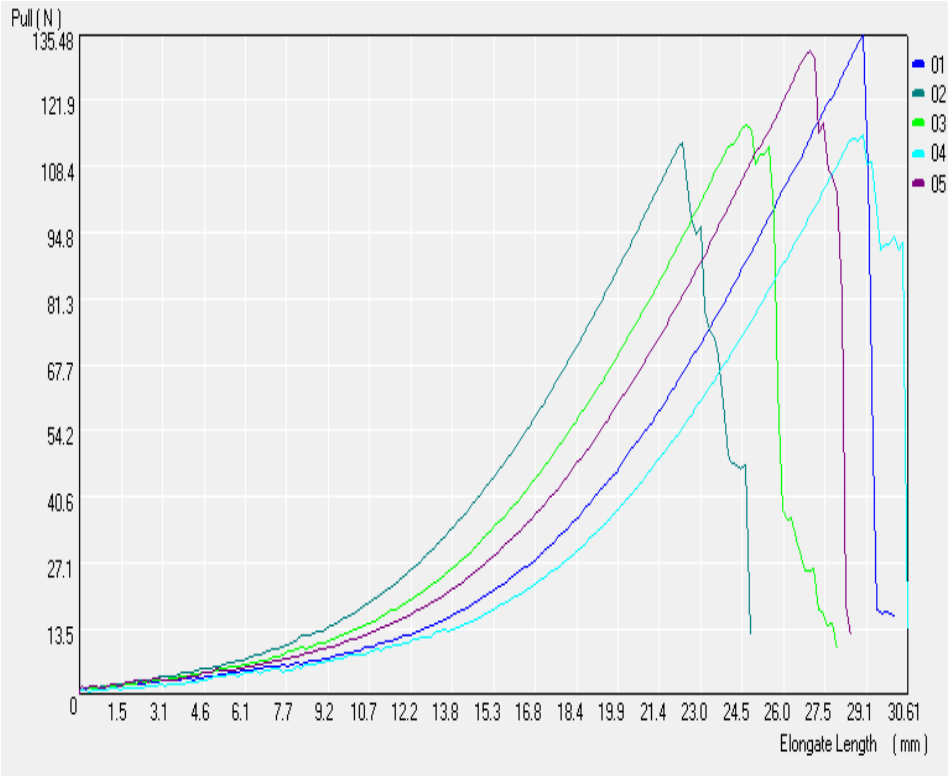


Figure G14: Load elongation curve for sample from run number 6 in weft direction

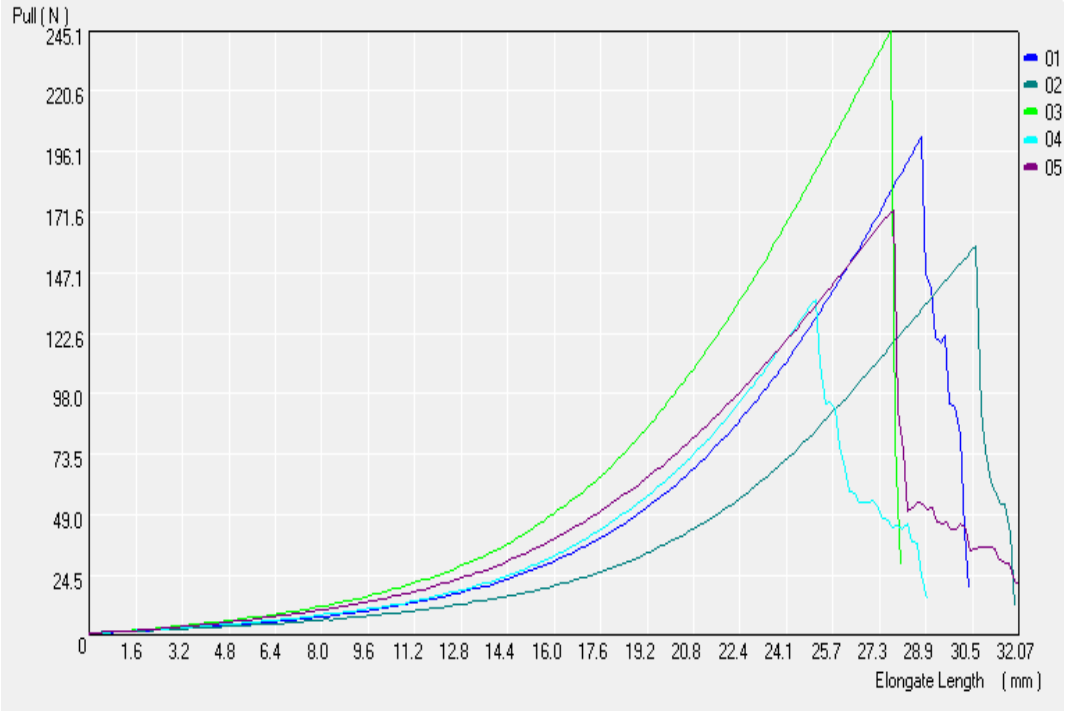


Figure G15: Load elongation curve for sample from run number 7 in warp direction

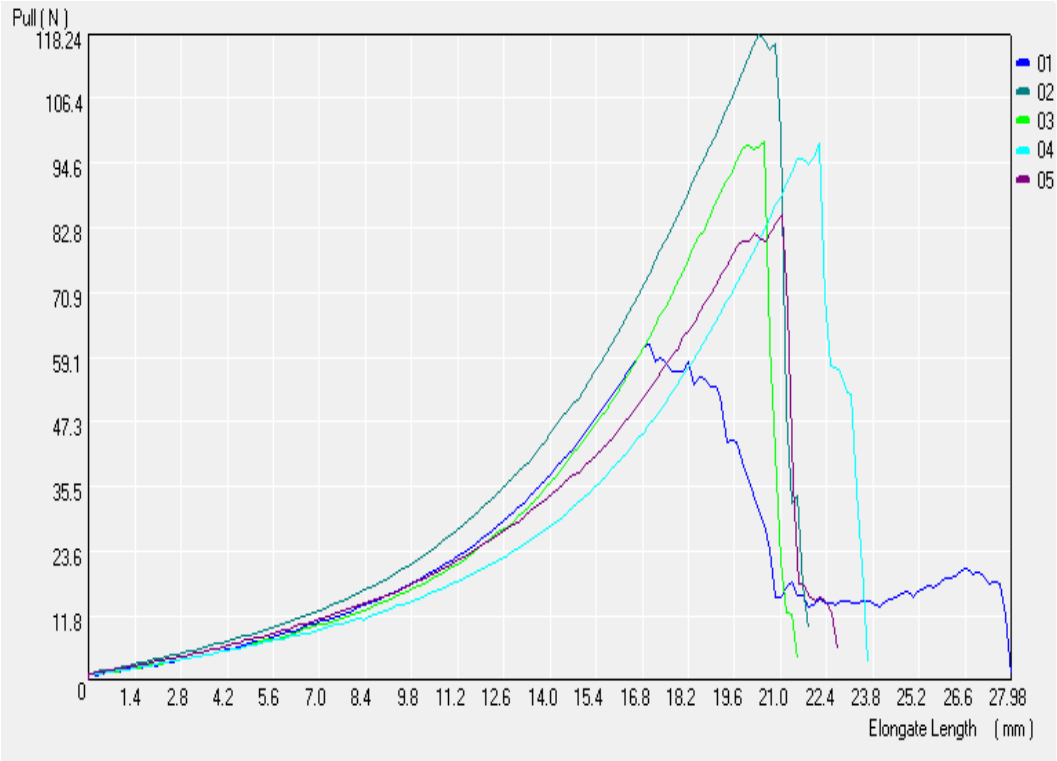


Figure G16: Load elongation curve for sample from run number 7 in weft direction

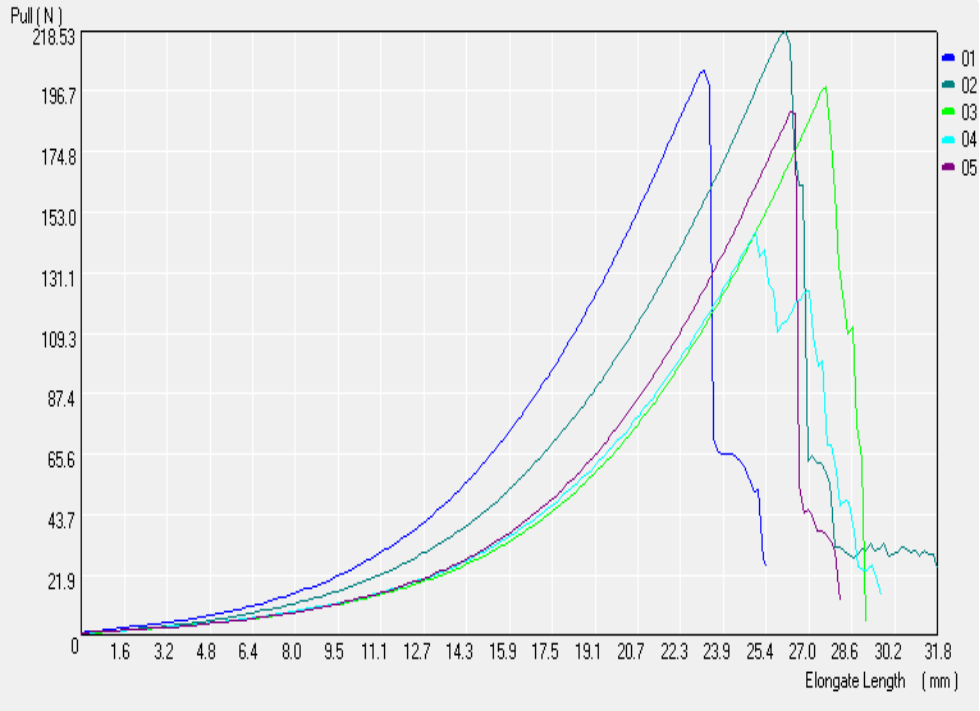


Figure G17: Load elongation curve for sample from run number 8 in warp direction

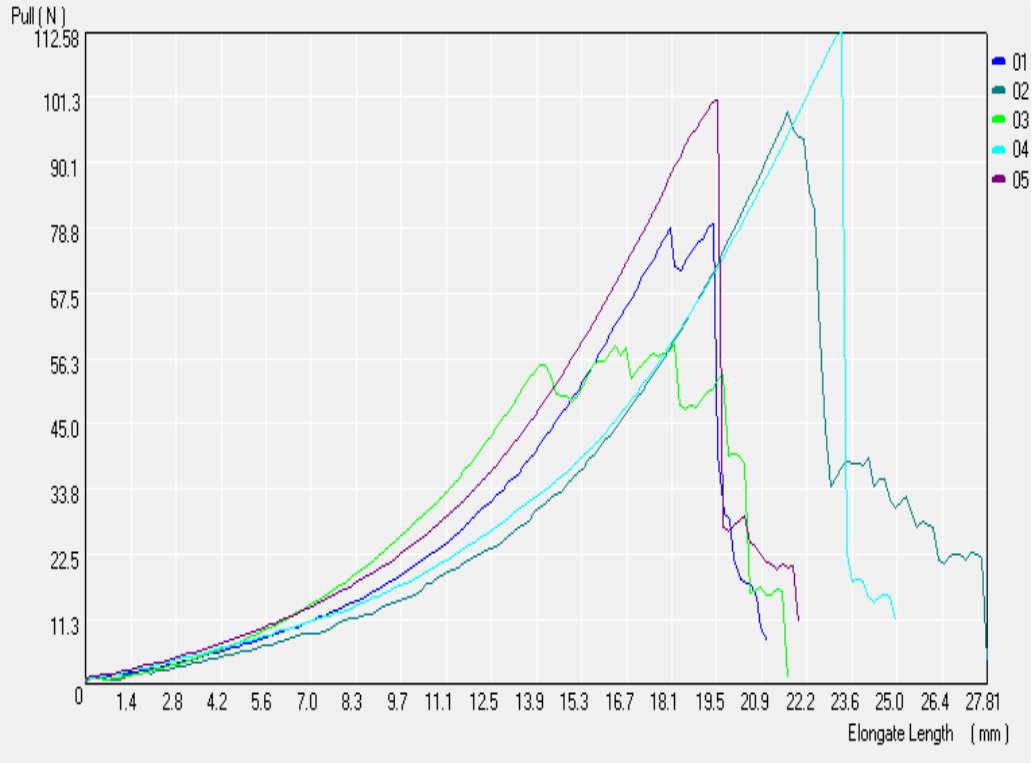


Figure G18: Load elongation curve for sample from run number 8 in weft direction

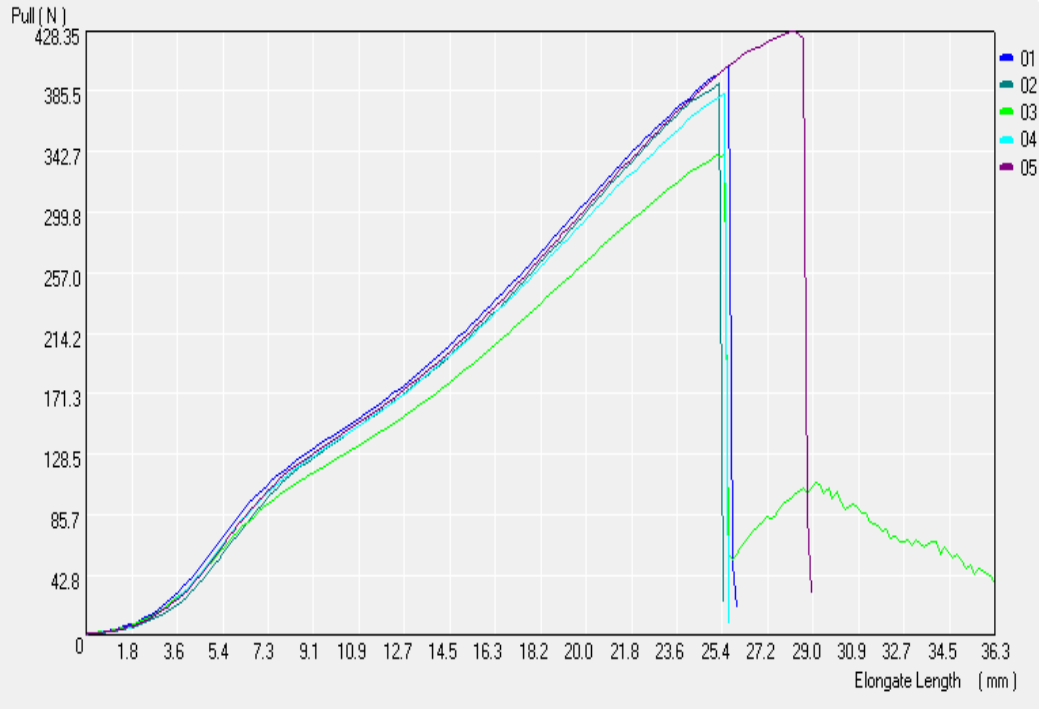


Figure G19: Load elongation curve for sample from run number 9 in warp direction

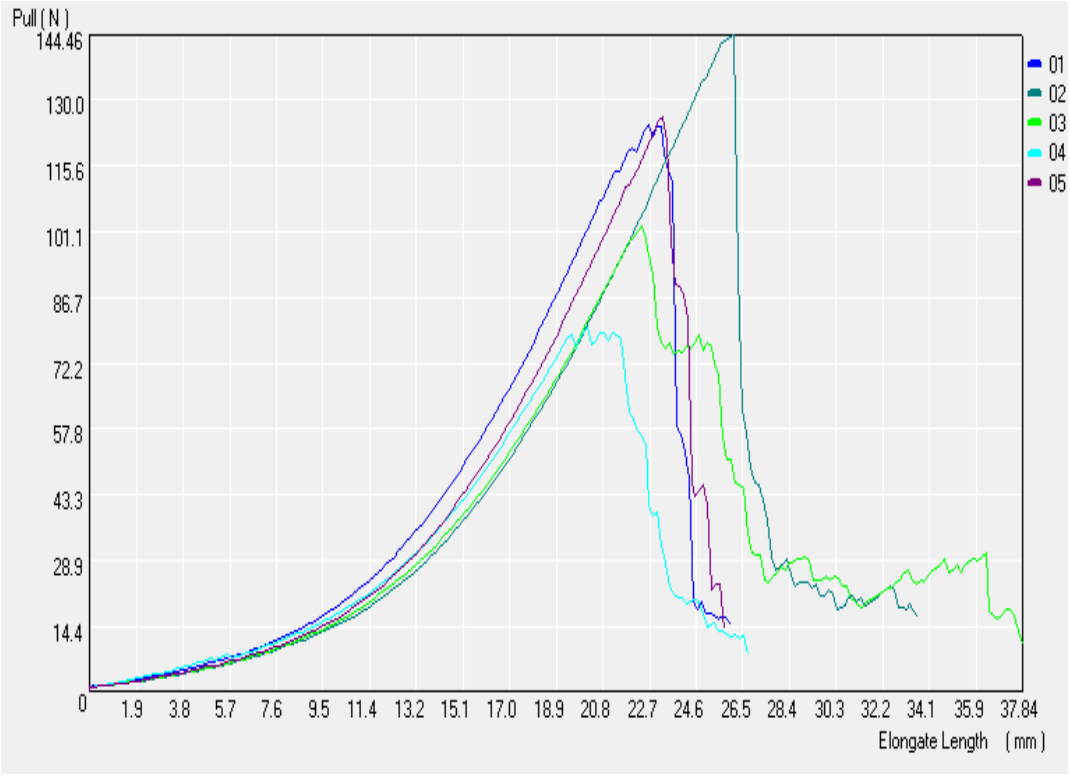


Figure G20: Load elongation curve for sample from run number 9 in weft direction

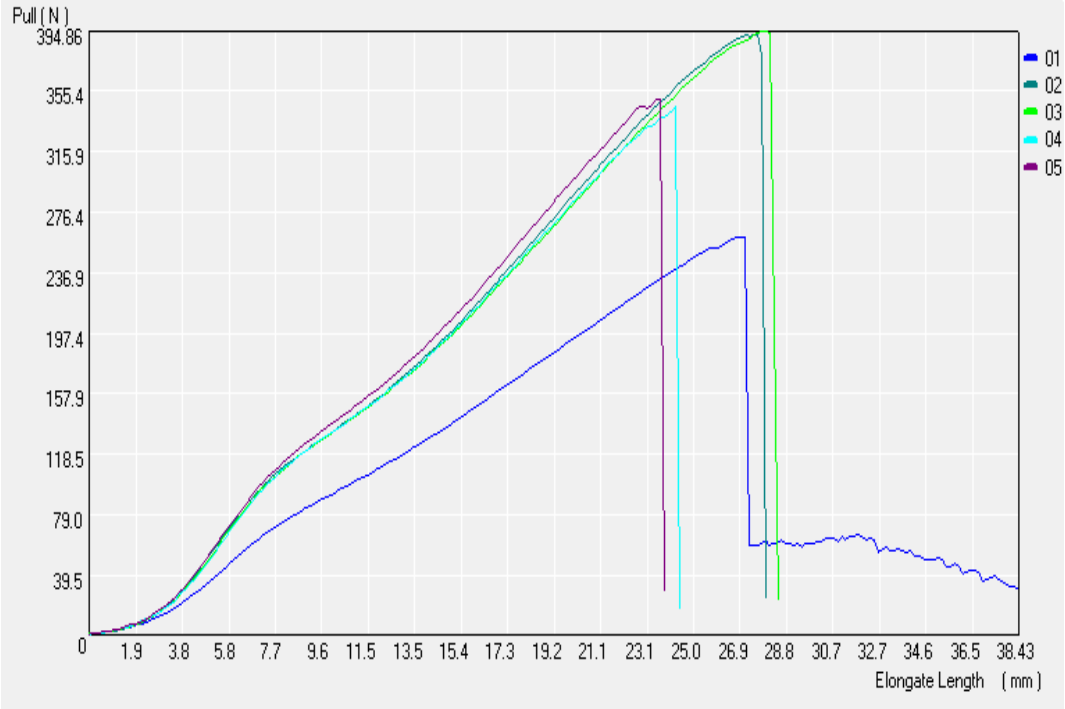


Figure G21: Load elongation curve for sample from run number 10 in warp direction

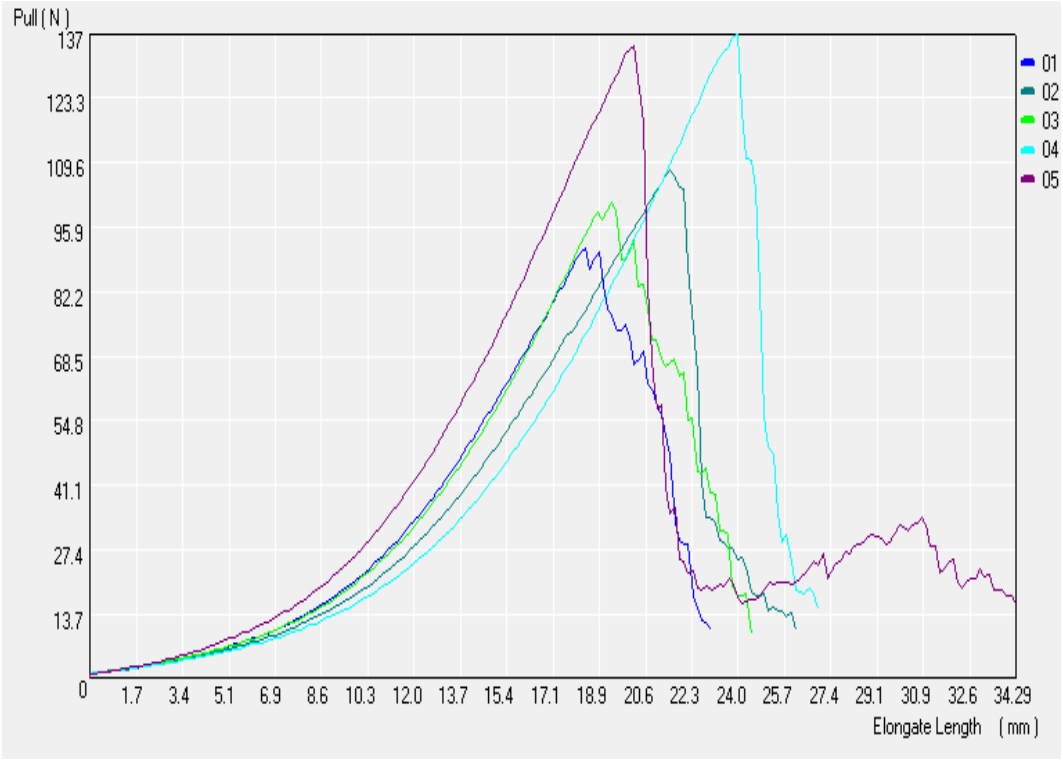


Figure G22: Load elongation curve for sample from run number 10 in weft direction

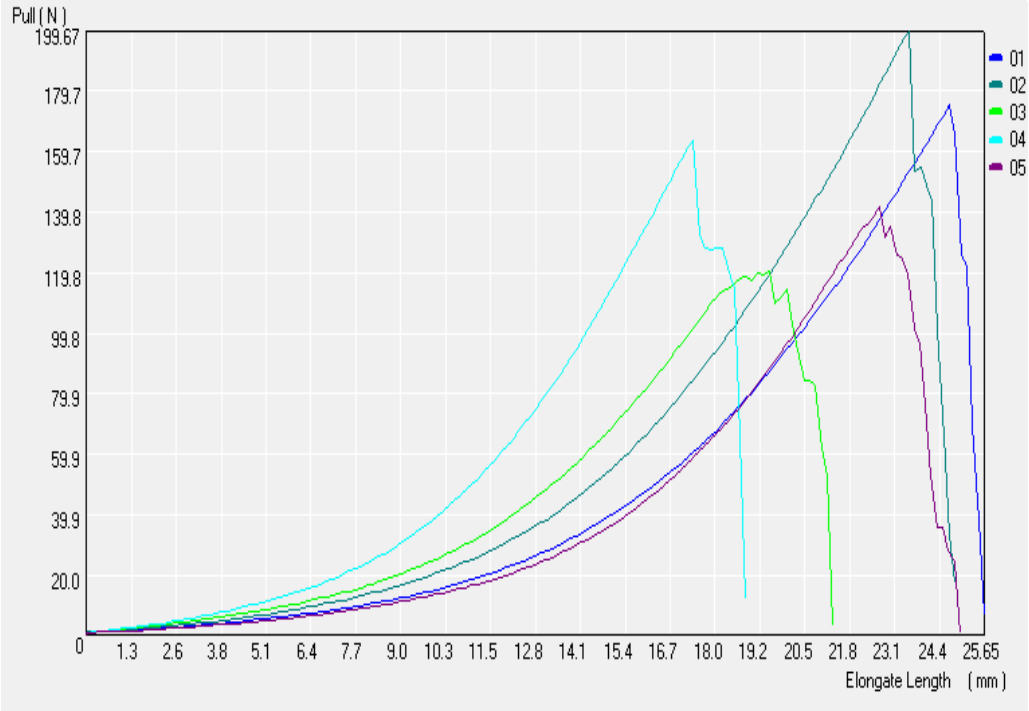


Figure G23: Load elongation curve for sample from run number 11 in warp direction

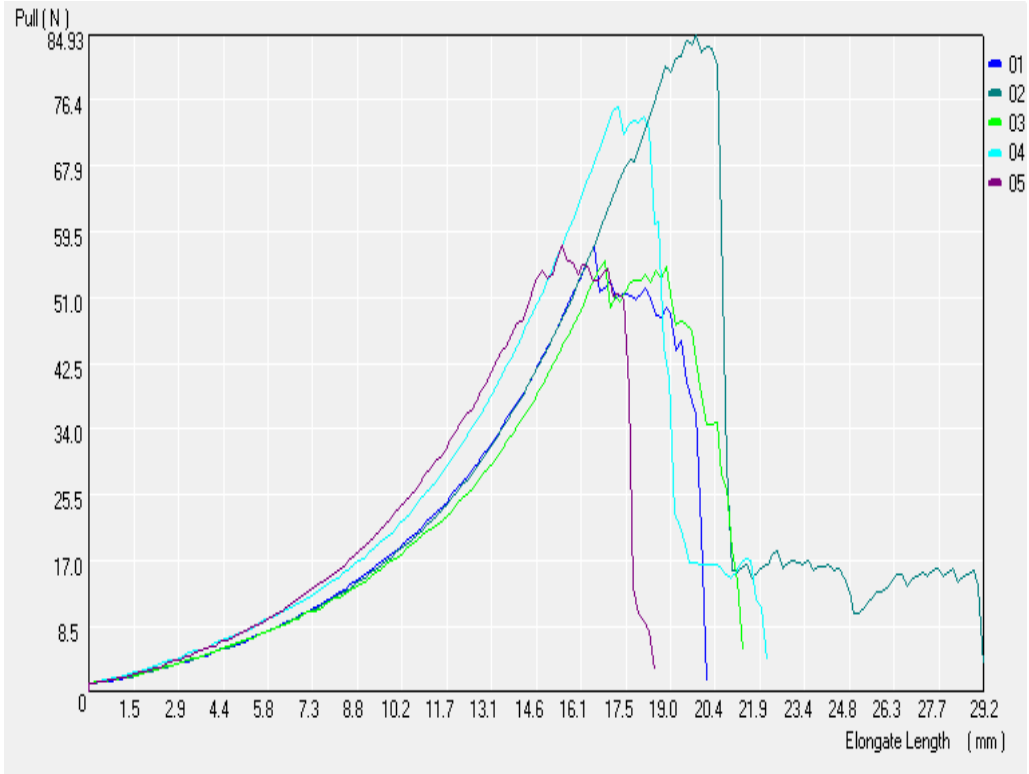


Figure G24: Load elongation curve for sample from run number 11 in weft direction

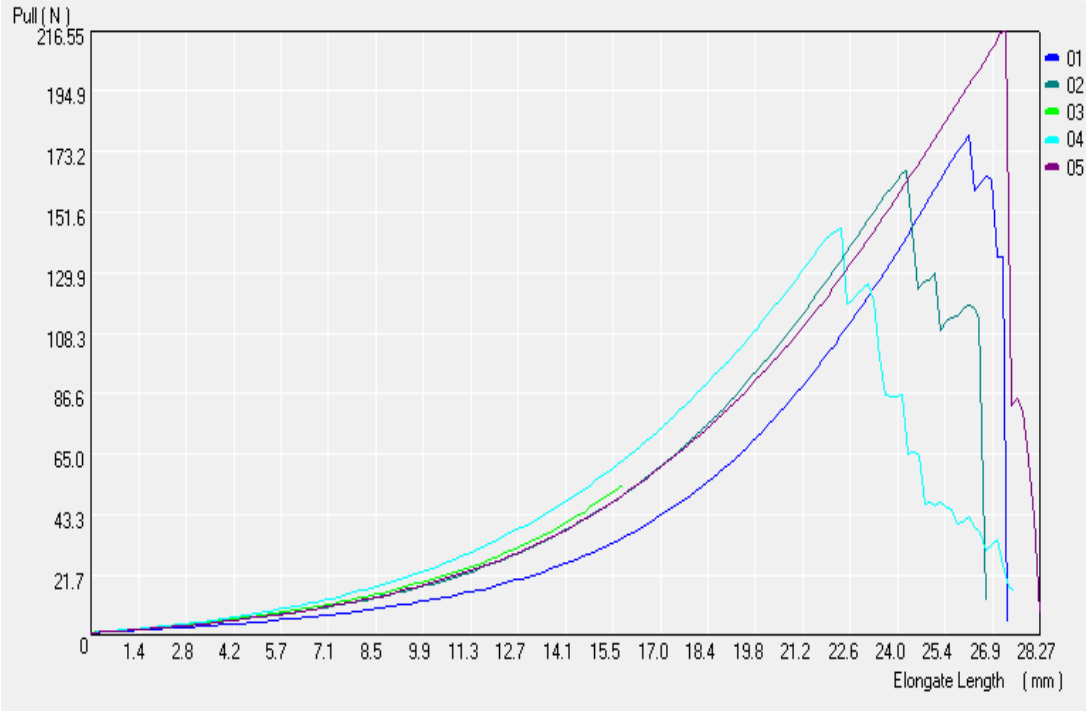


Figure G25: Load elongation curve for sample from run number 12 in warp direction

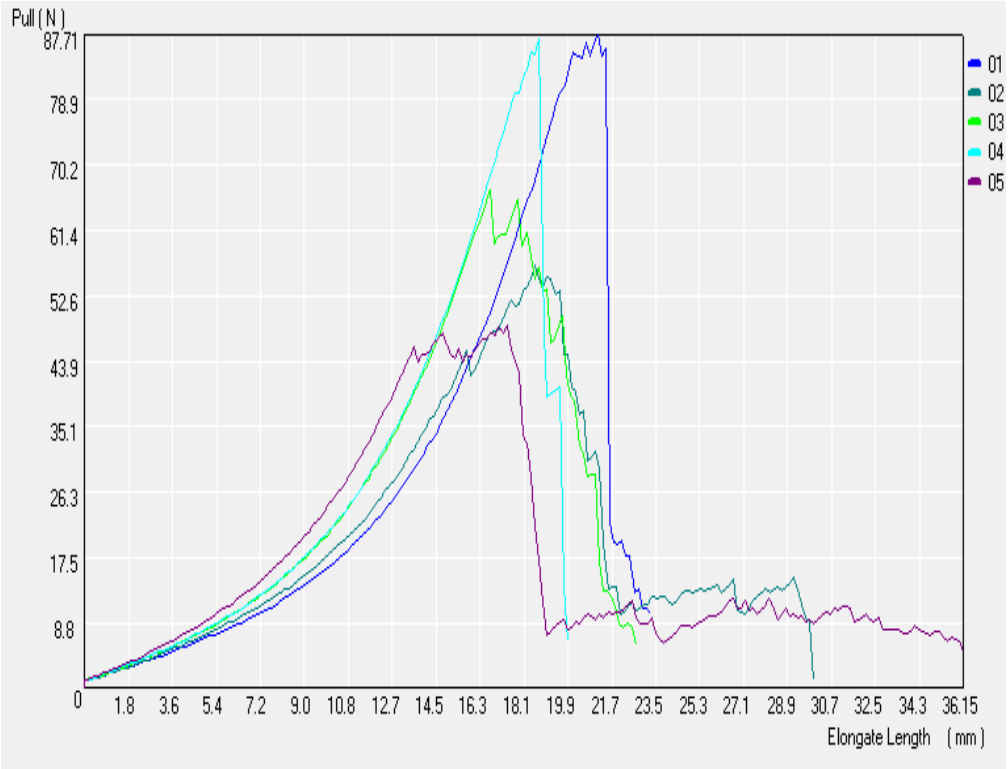


Figure G26: Load elongation curve for sample from run number 12 in weft direction

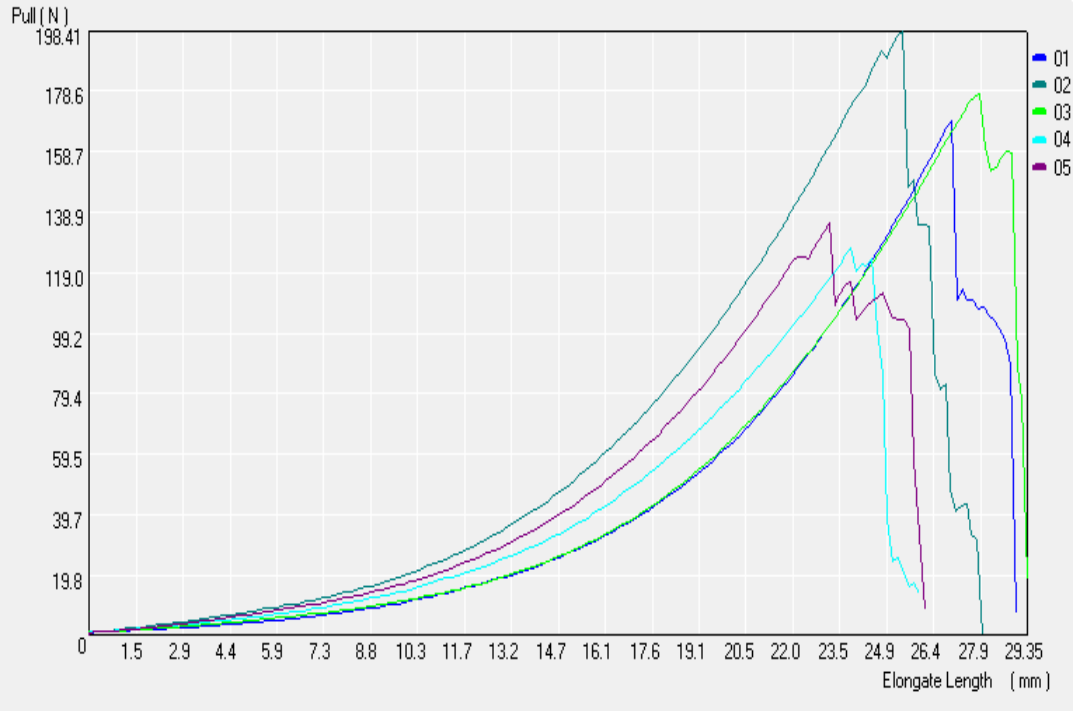


Figure G27: Load elongation curve for sample from run number 13 in warp direction

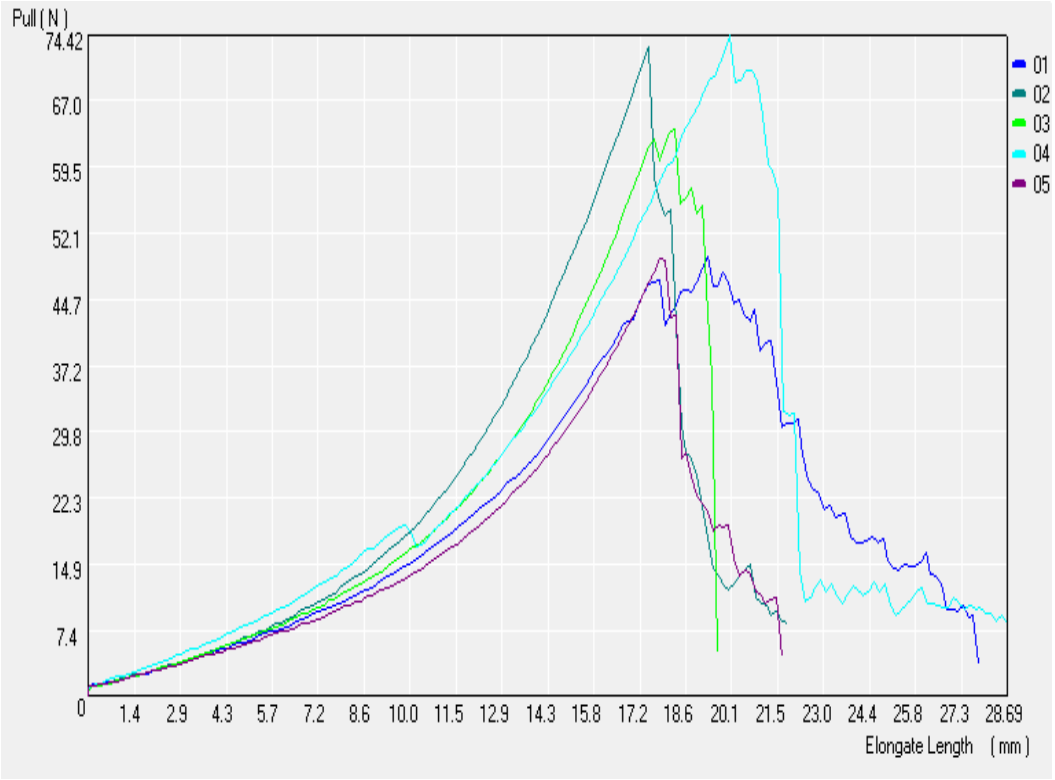


Figure G28: Load elongation curve for sample from run number 13 in weft direction

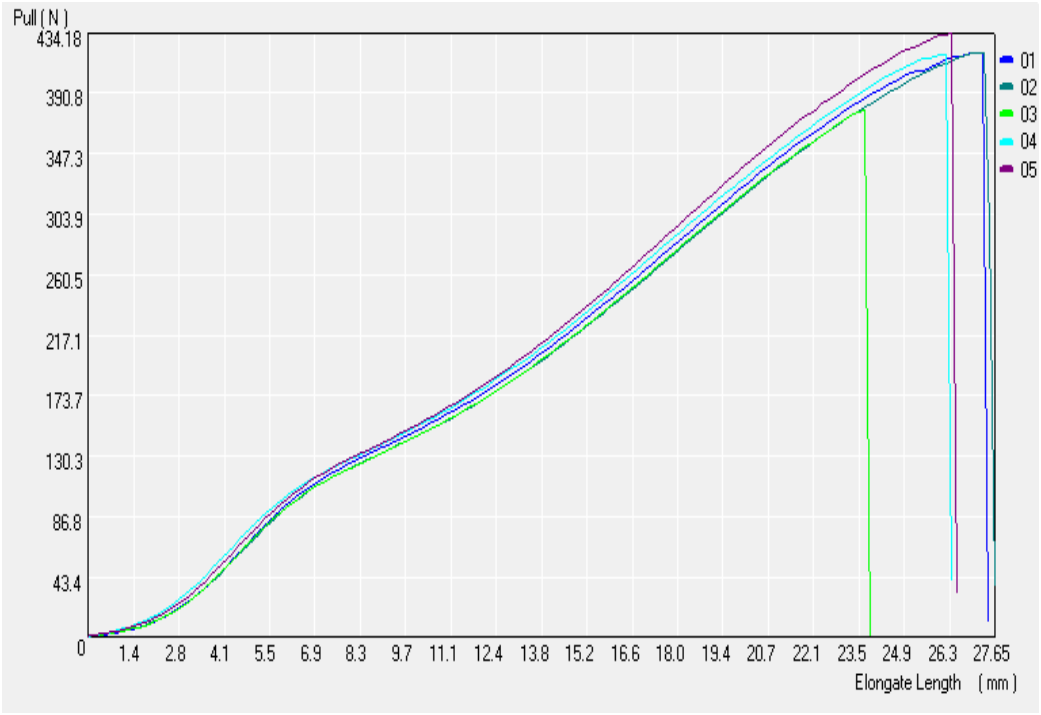


Figure G29: Load elongation curve for sample from run number 14 in warp direction

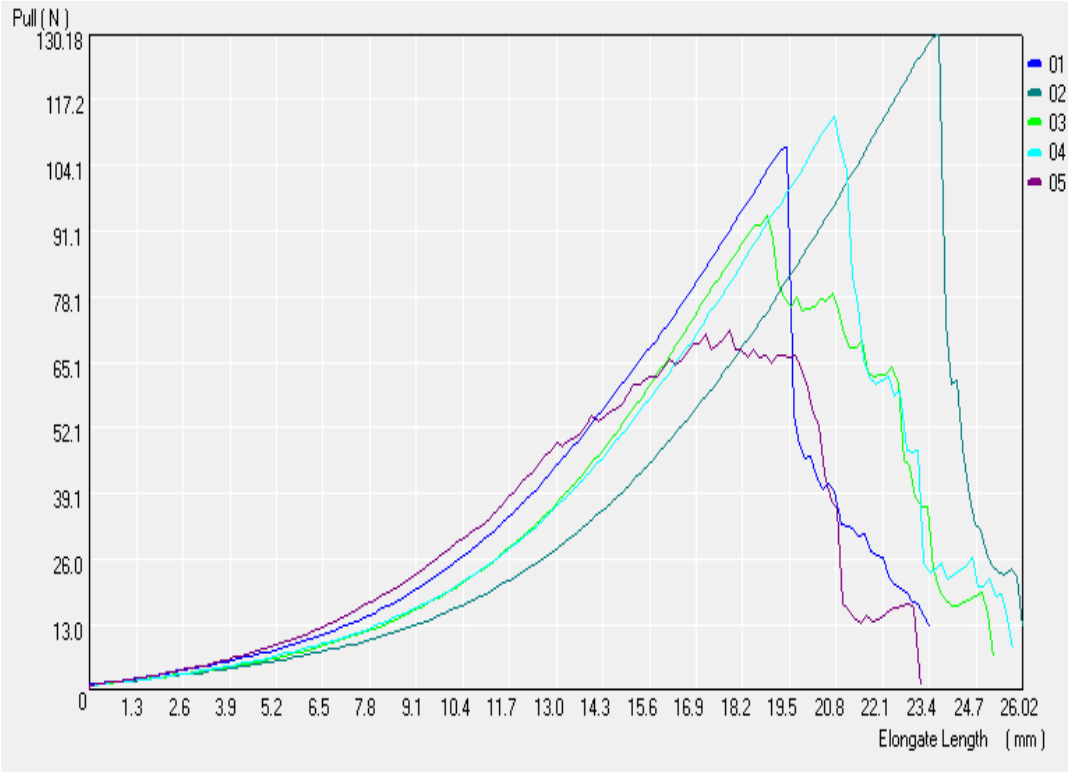


Figure G30: Load elongation curve for sample from run number 14 in weft direction

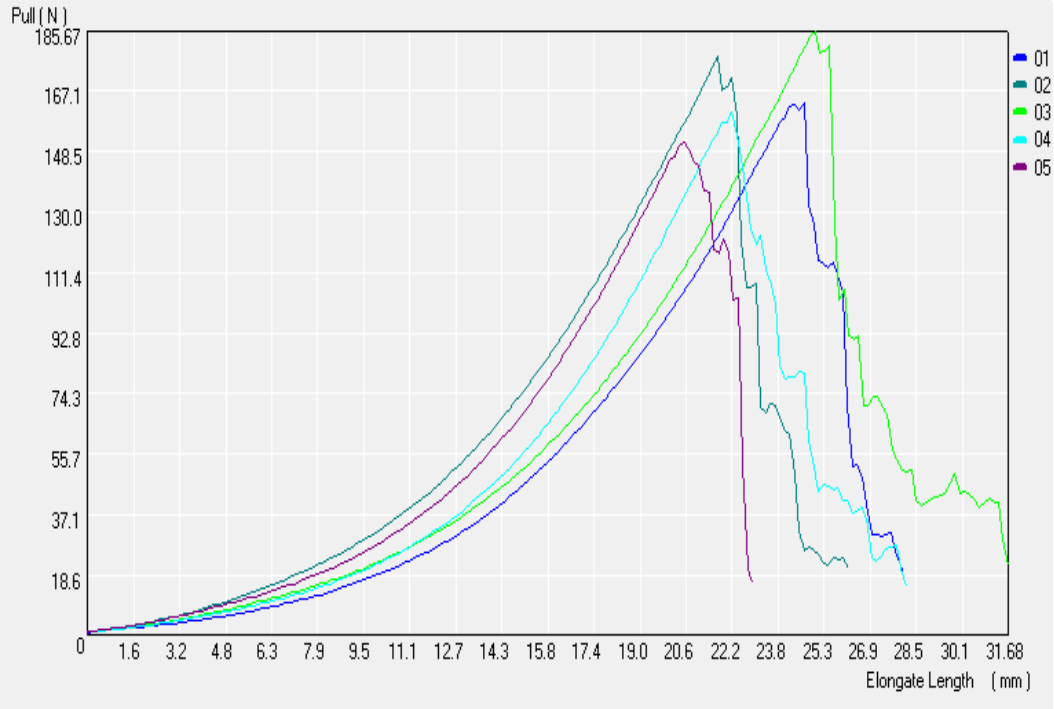


Figure G31: Load elongation curve for sample from run number 15 in warp direction

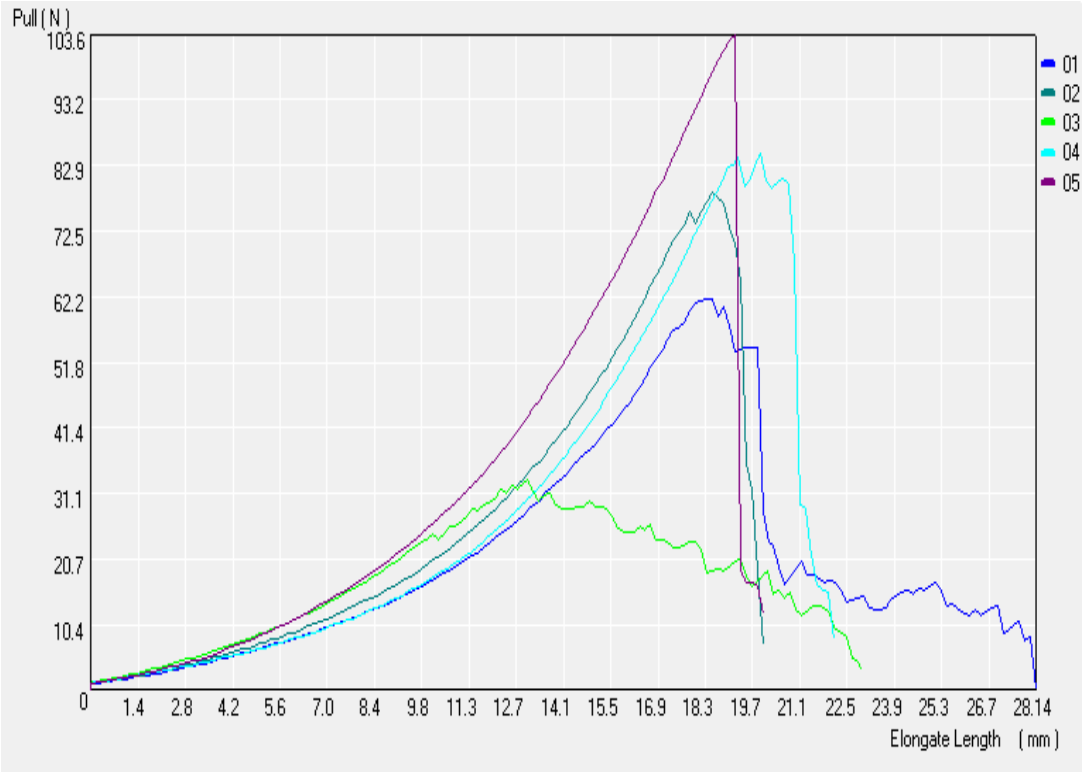


Figure G32: Load elongation curve for sample from run number 15 in weft direction

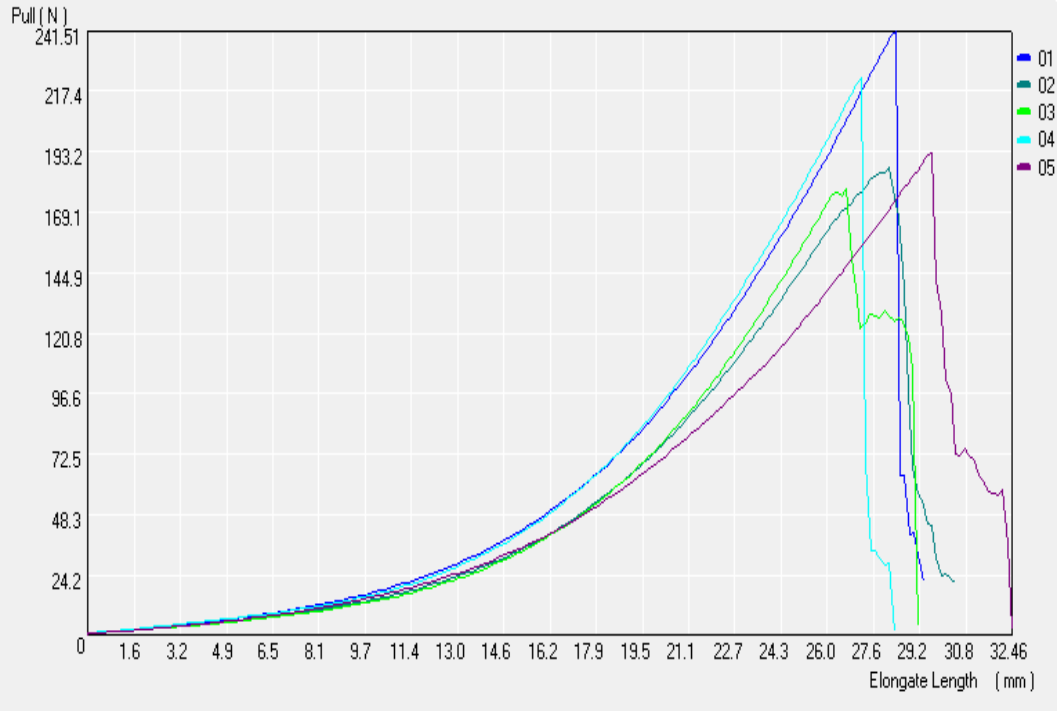


Figure G33: Load elongation curve for sample from run number 16 in warp direction

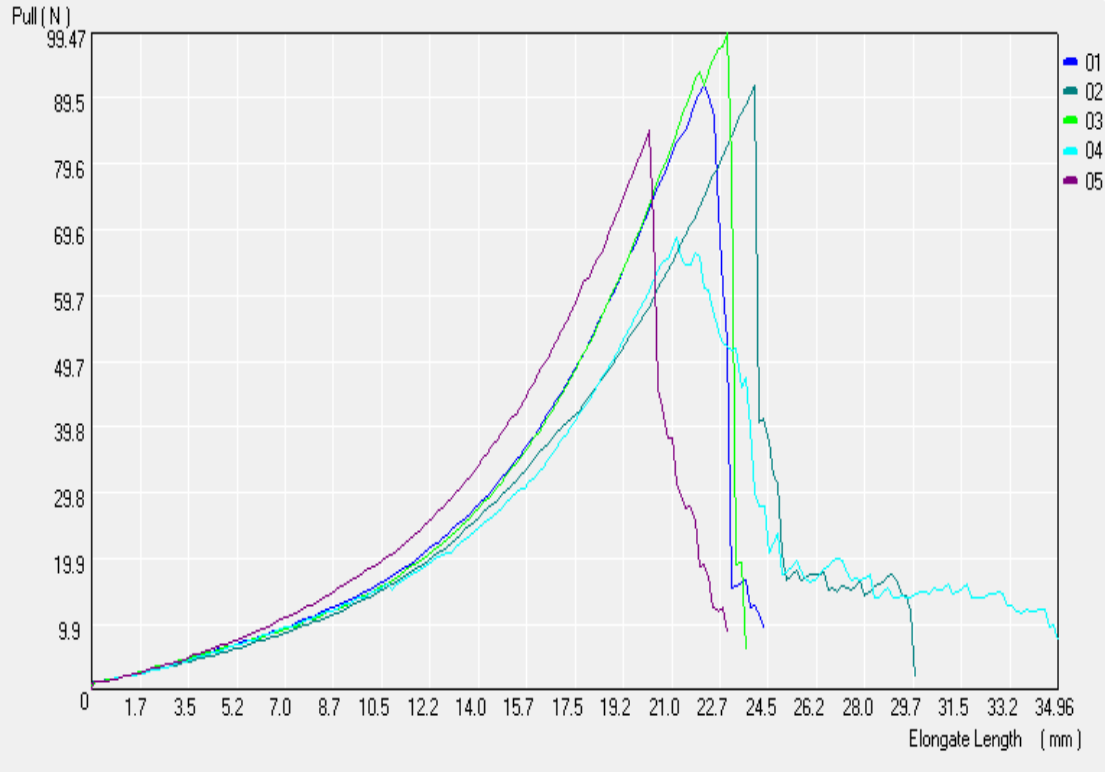


Figure G34: Load elongation curve for sample from run number 16 in weft direction

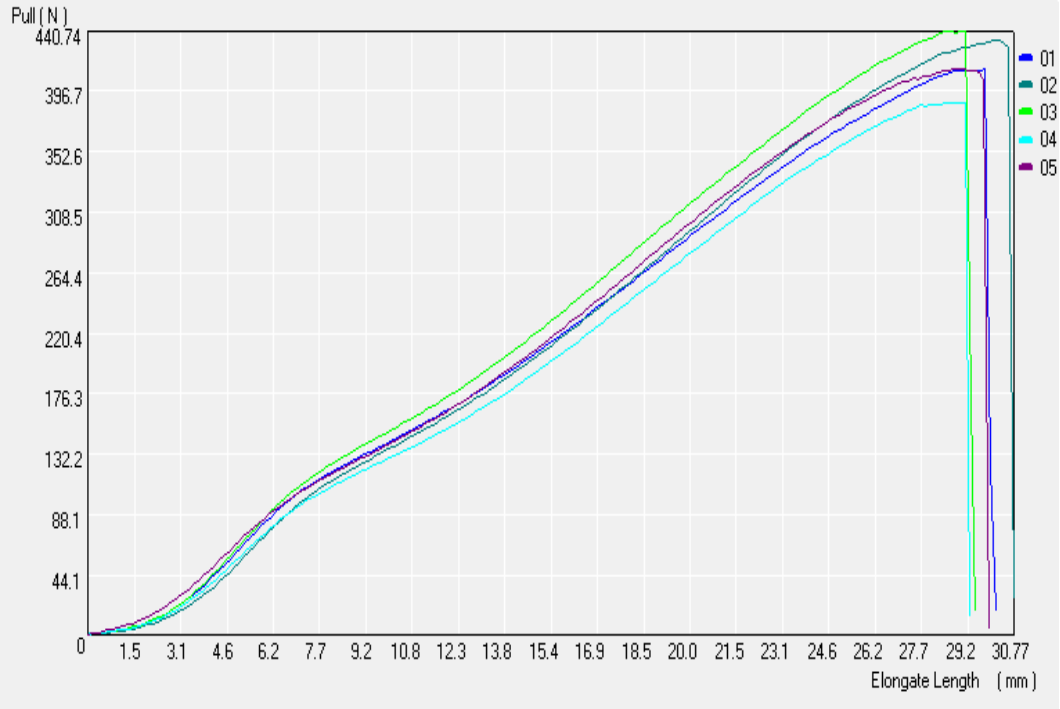


Figure G35: Load elongation curve for sample from run number 17 in warp direction

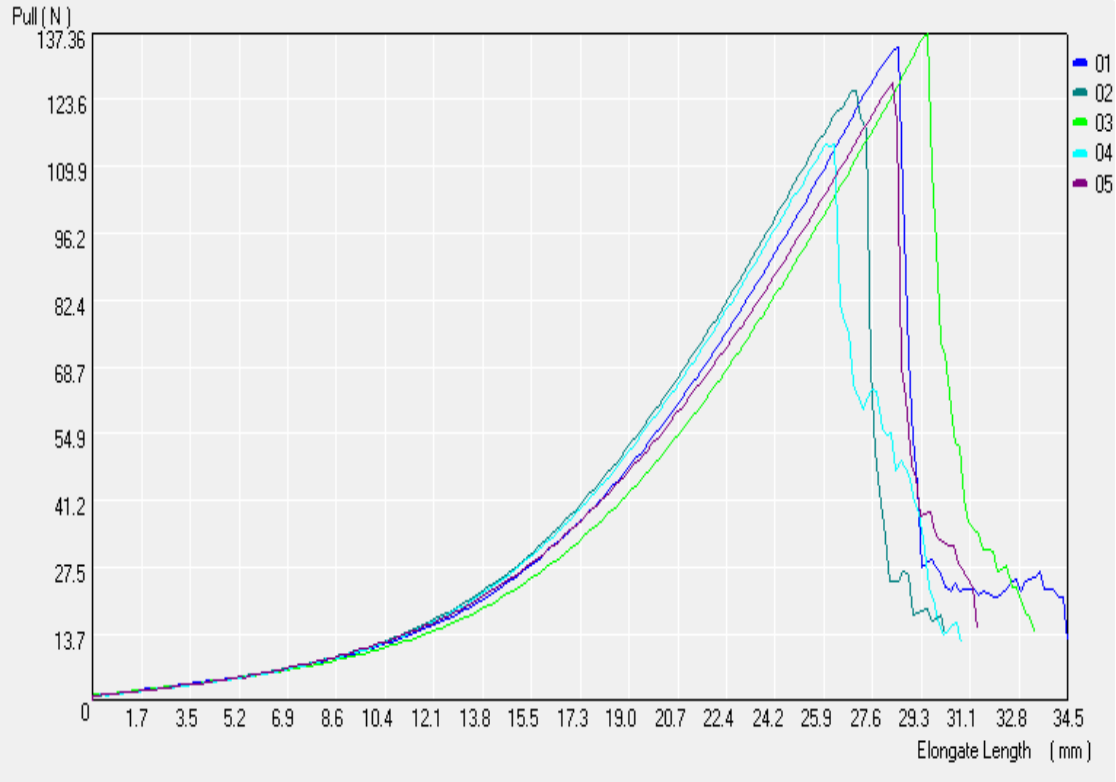


Figure G36: Load elongation curve for sample from run number 17 in weft direction

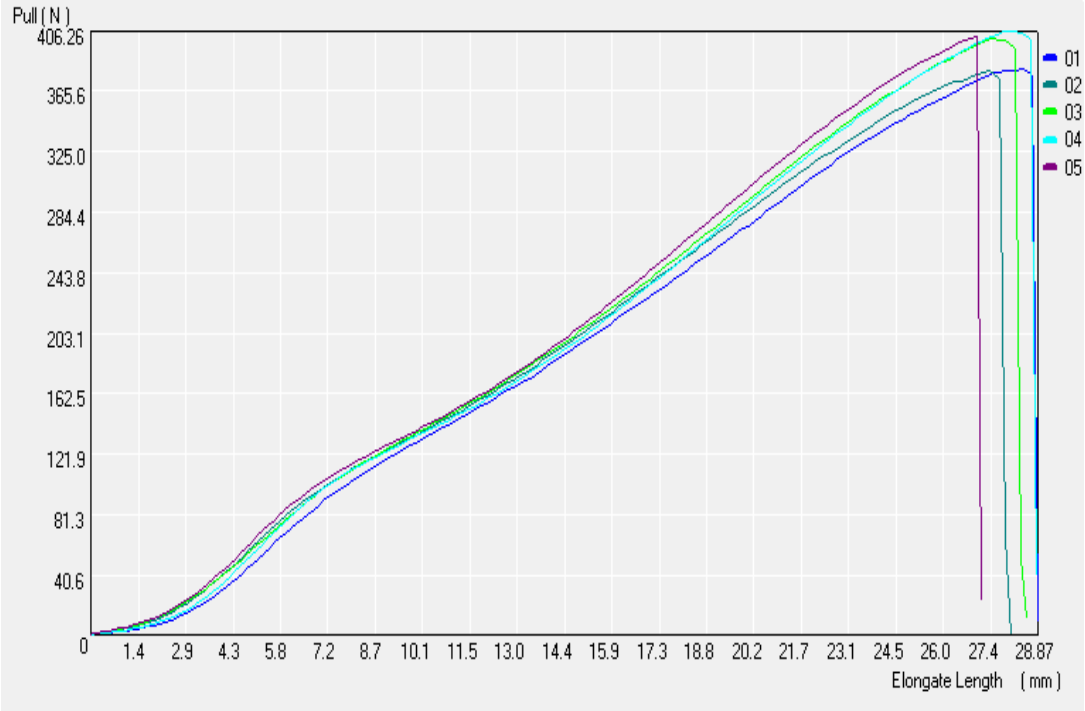


Figure G37: Load elongation curve for sample from run number 18 in warp direction

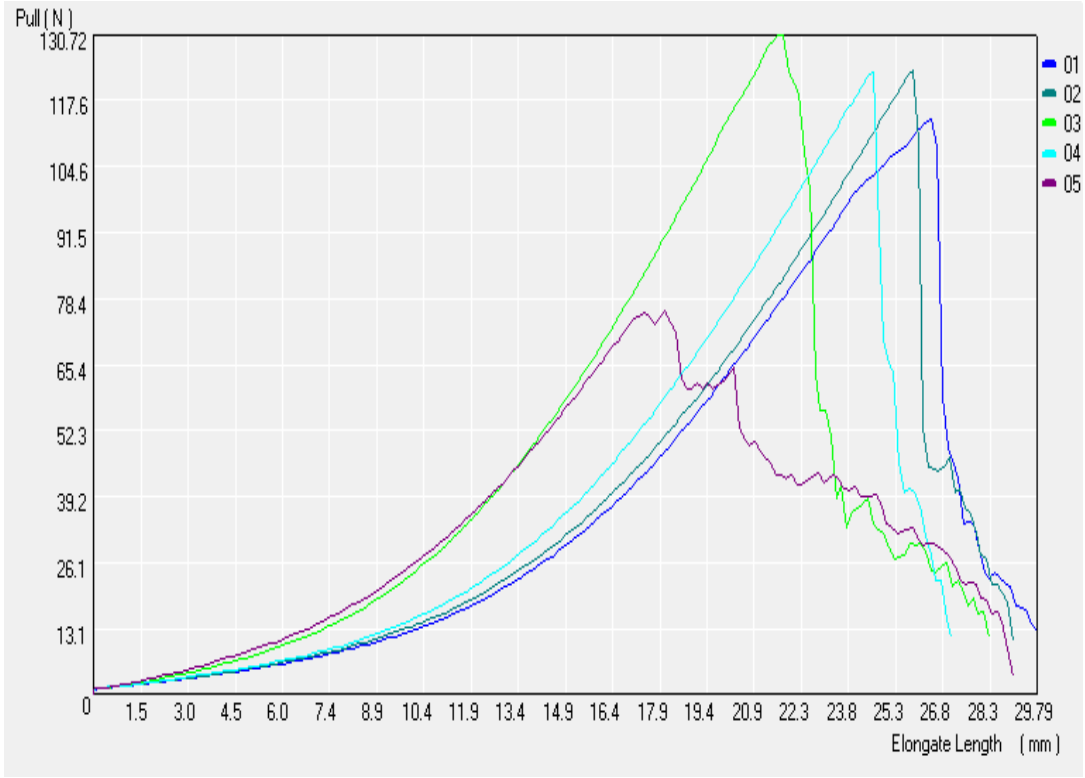


Figure G38: Load elongation curve for sample from run number 18 in weft direction

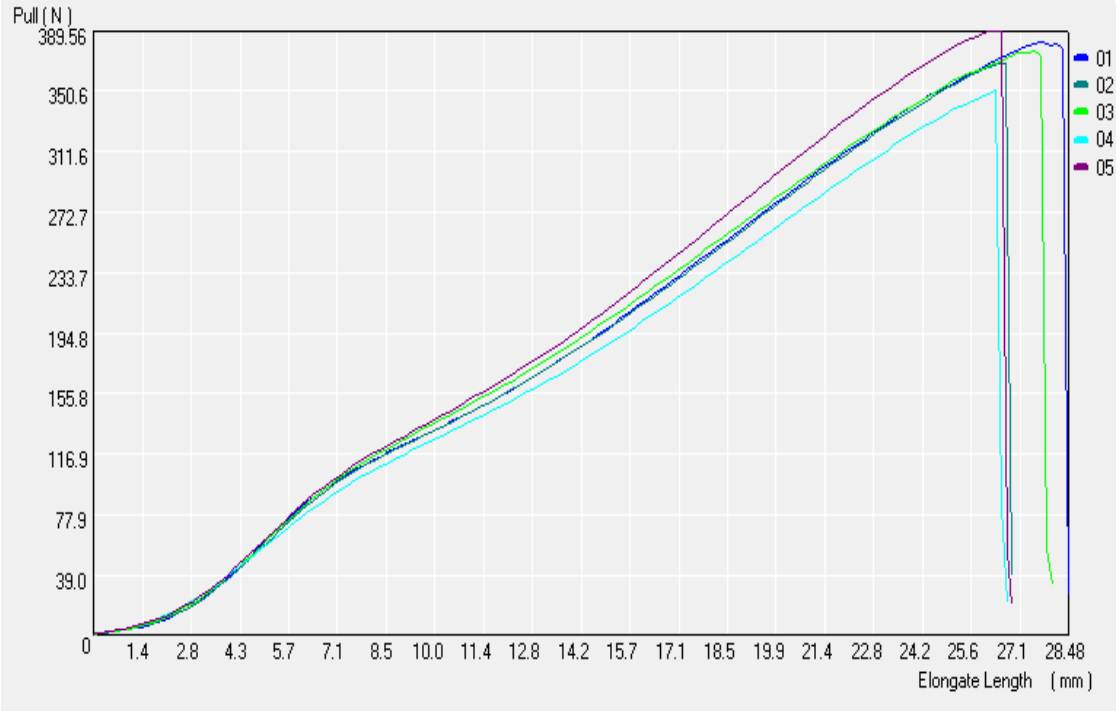


Figure G39: Load elongation curve for sample from run number 19 in warp direction

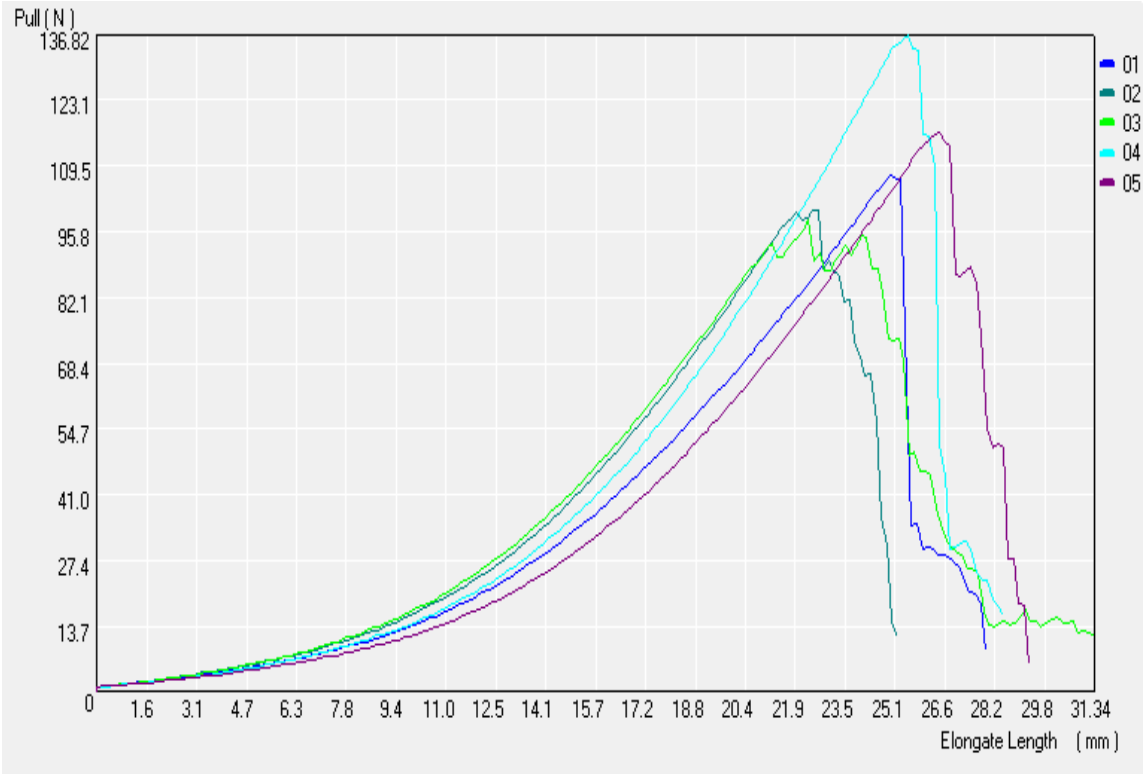


Figure G40: Load elongation curve for sample from run number 19 in weft direction

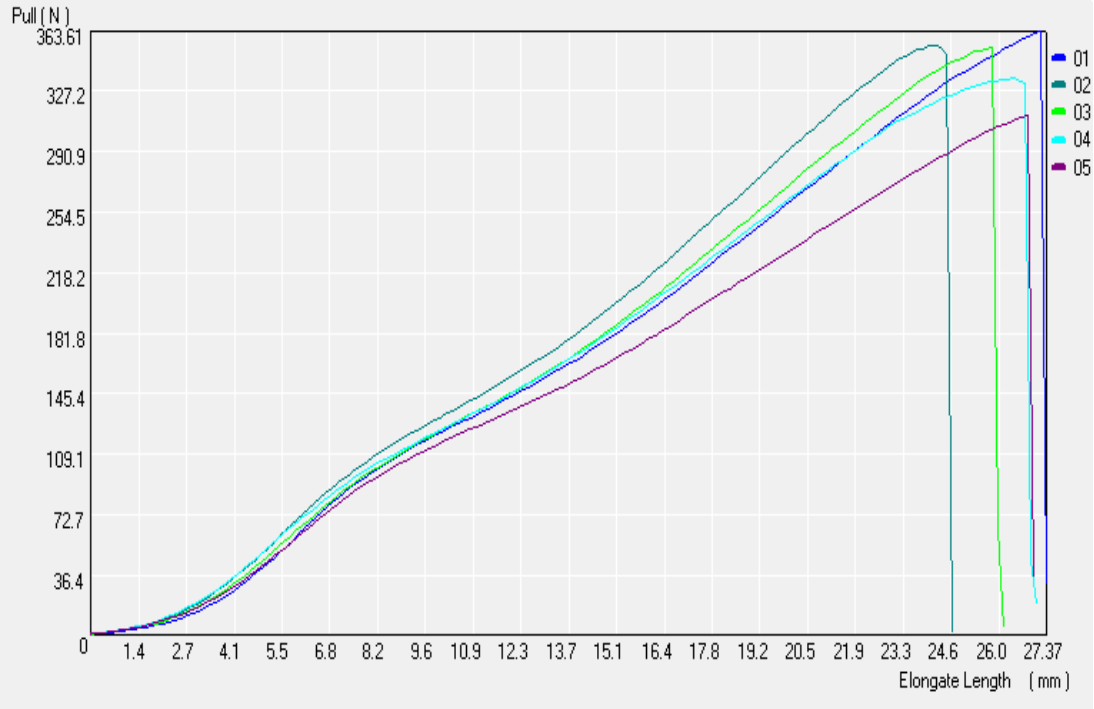


Figure G41: Load elongation curve for sample from run number 20 in warp direction

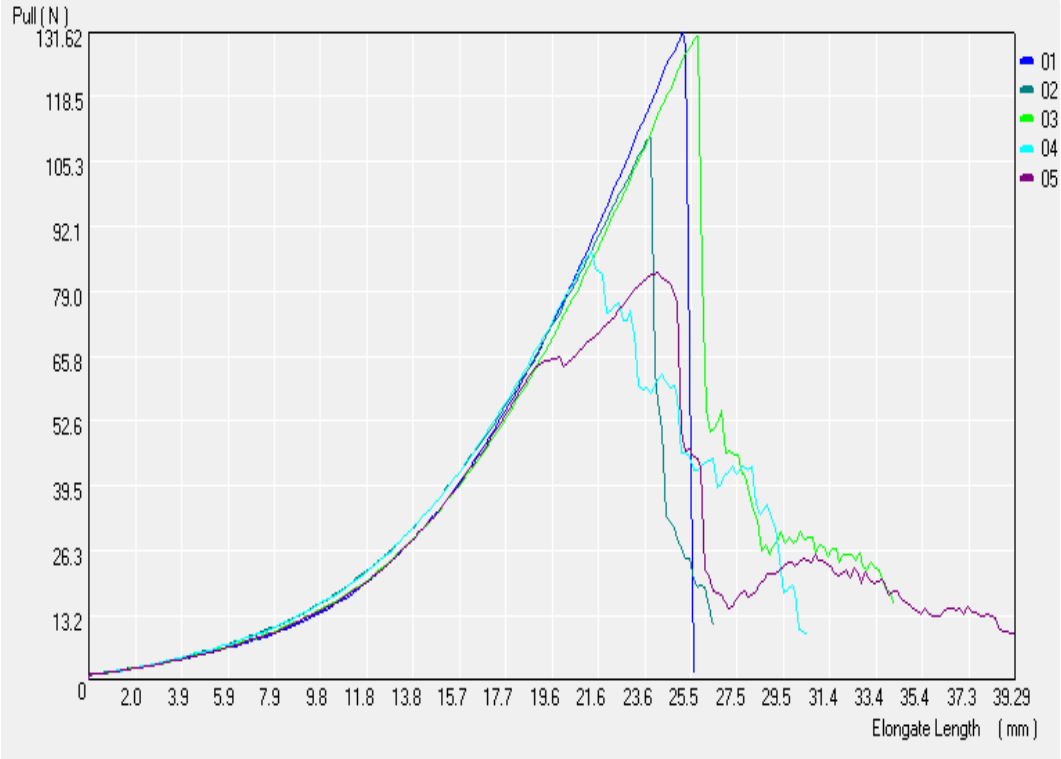


Figure G42: Load elongation curve for sample from run number 20 in weft direction

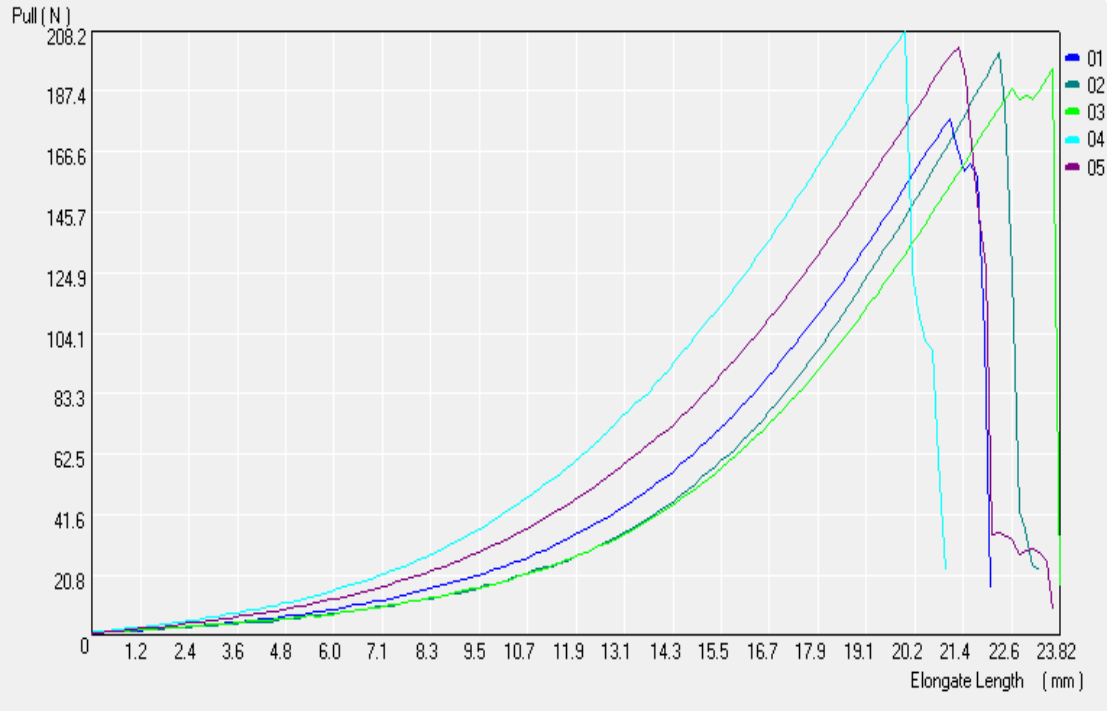


Figure G43: Load elongation curve for sample from run number 21 in warp direction

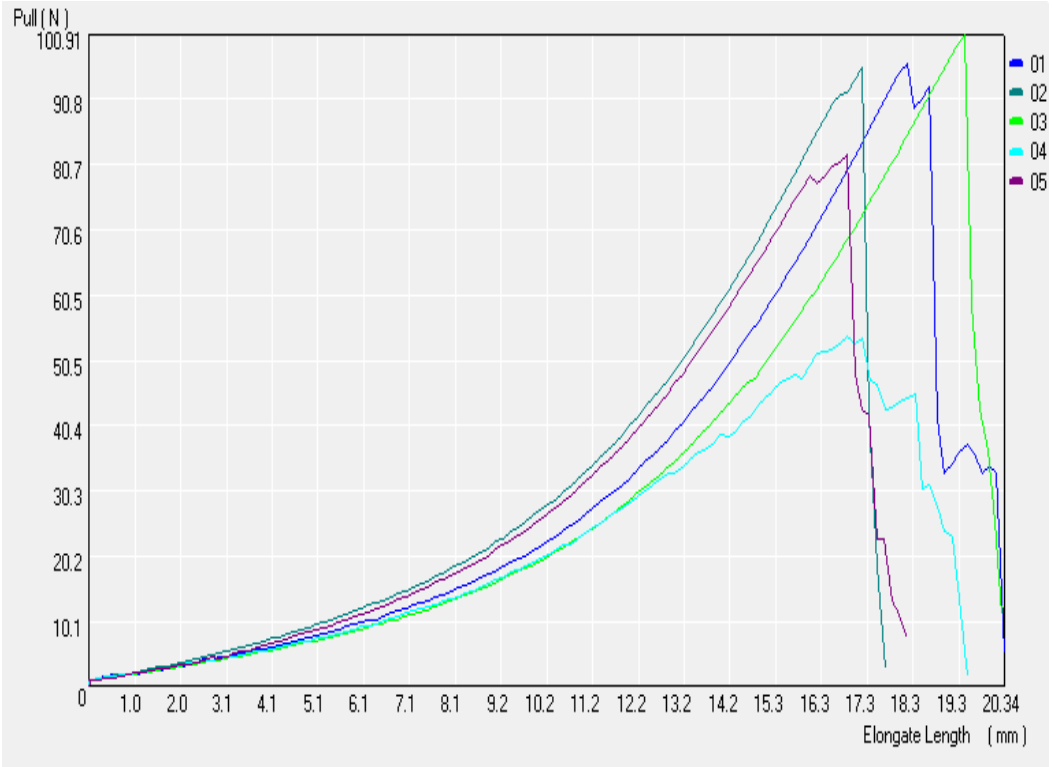


Figure G44: Load elongation curve for sample from run number 21 in weft direction

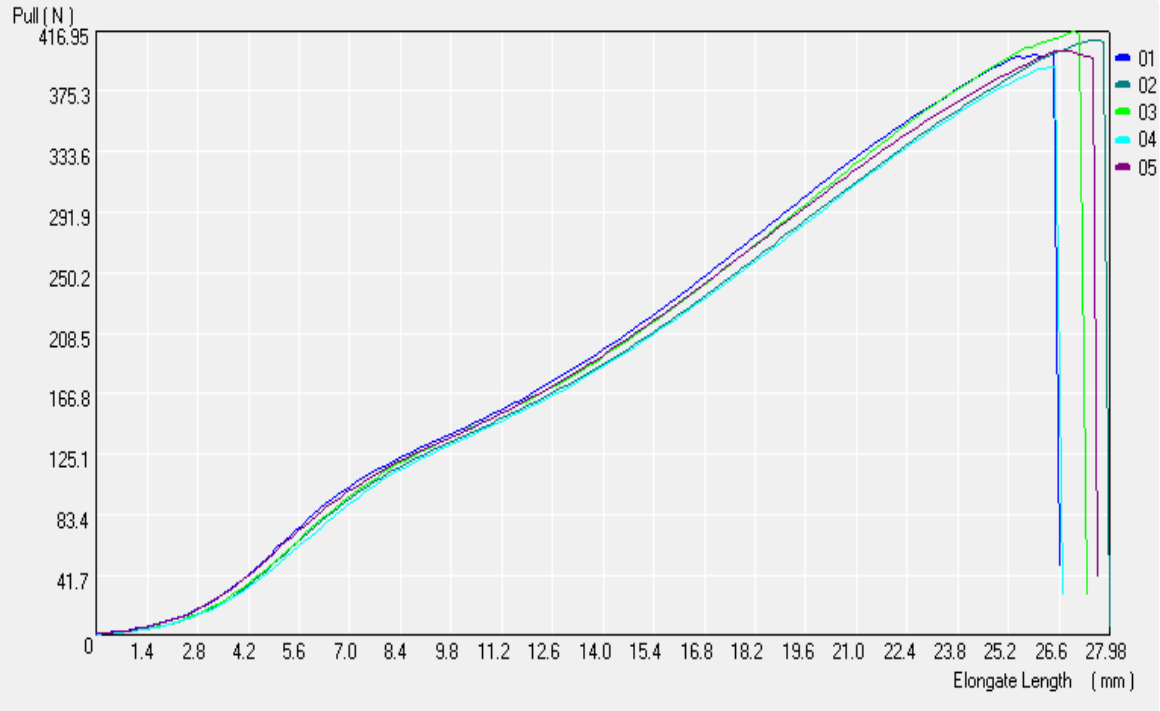


Figure G45: Load elongation curve for sample from run number 22 in warp direction

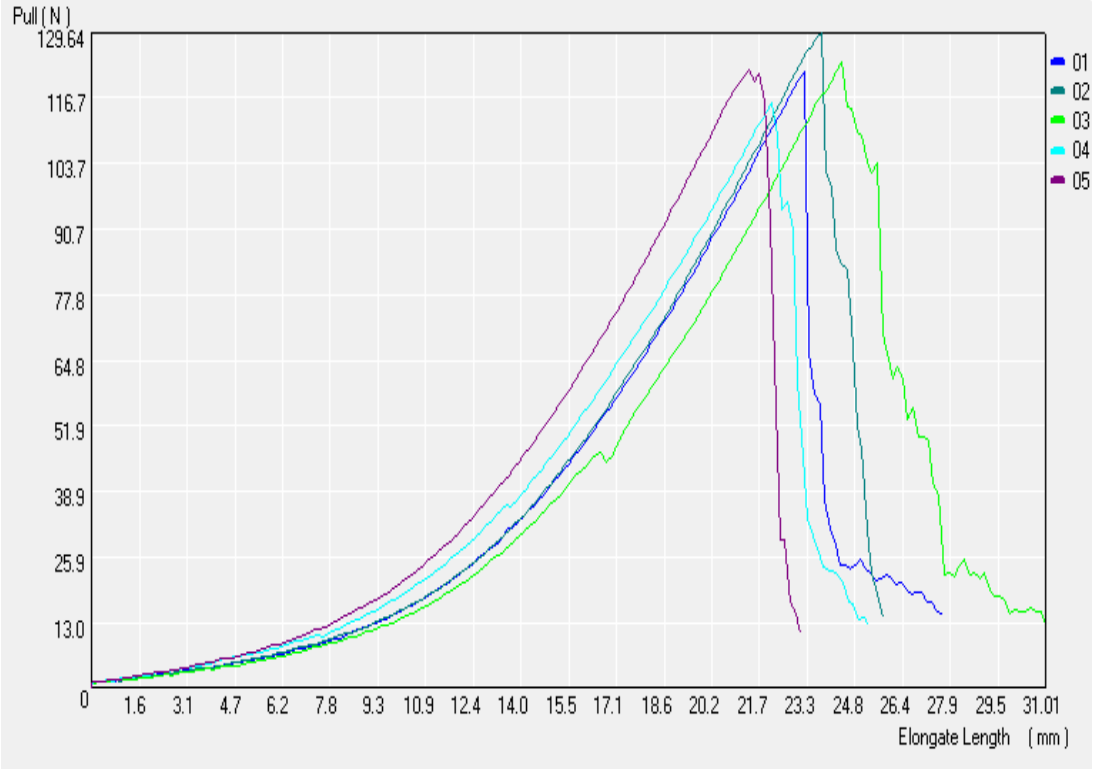


Figure G46: Load elongation curve for sample from run number 22 in weft direction

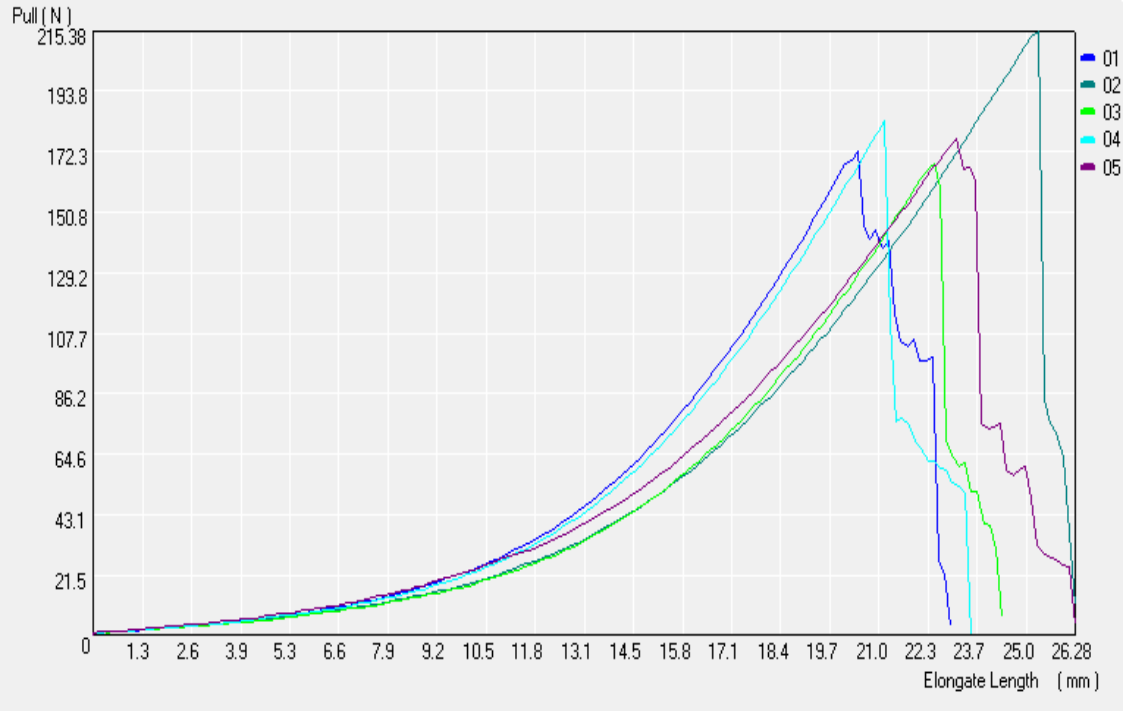


Figure G47: Load elongation curve for sample from run number 23 in warp direction

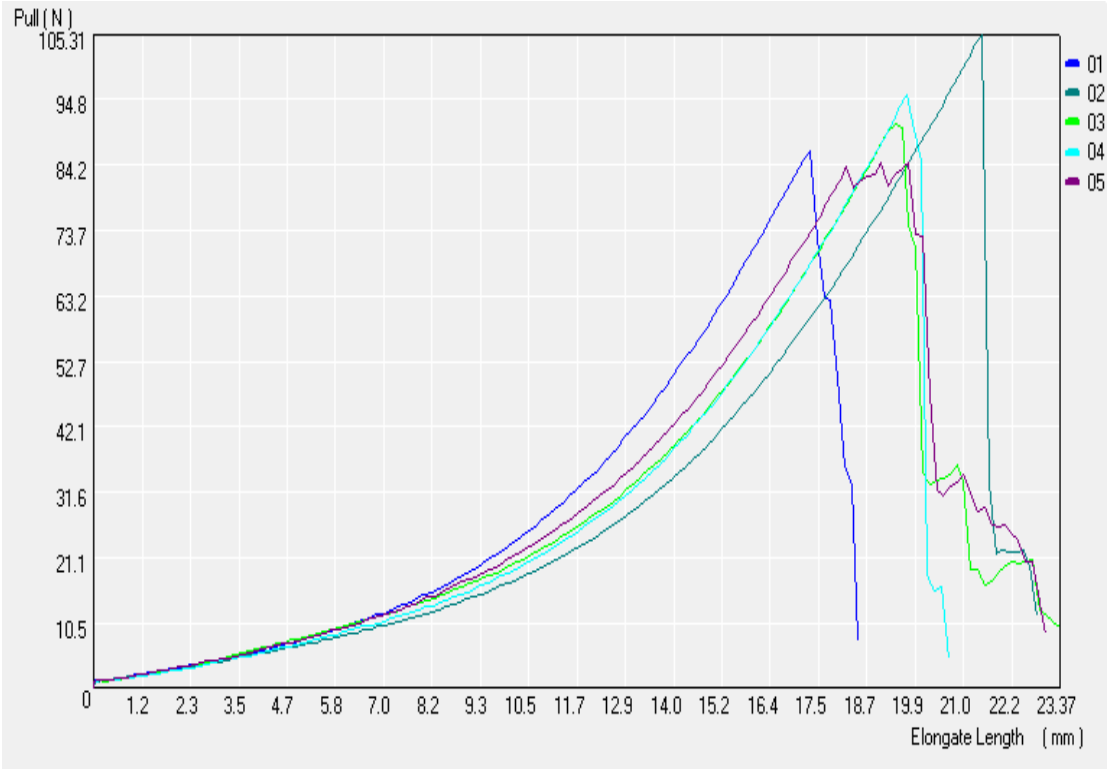


Figure G48: Load elongation curve for sample from run number 23 in weft direction

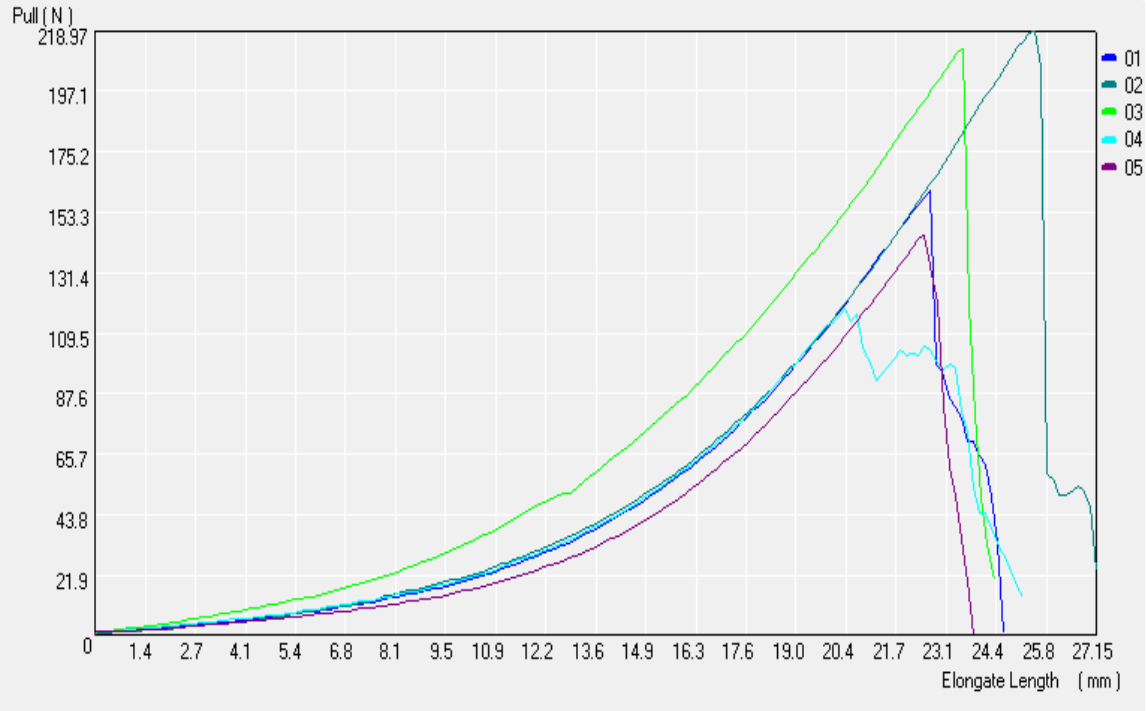


Figure G49: Load elongation curve for sample from run number 24 in warp direction

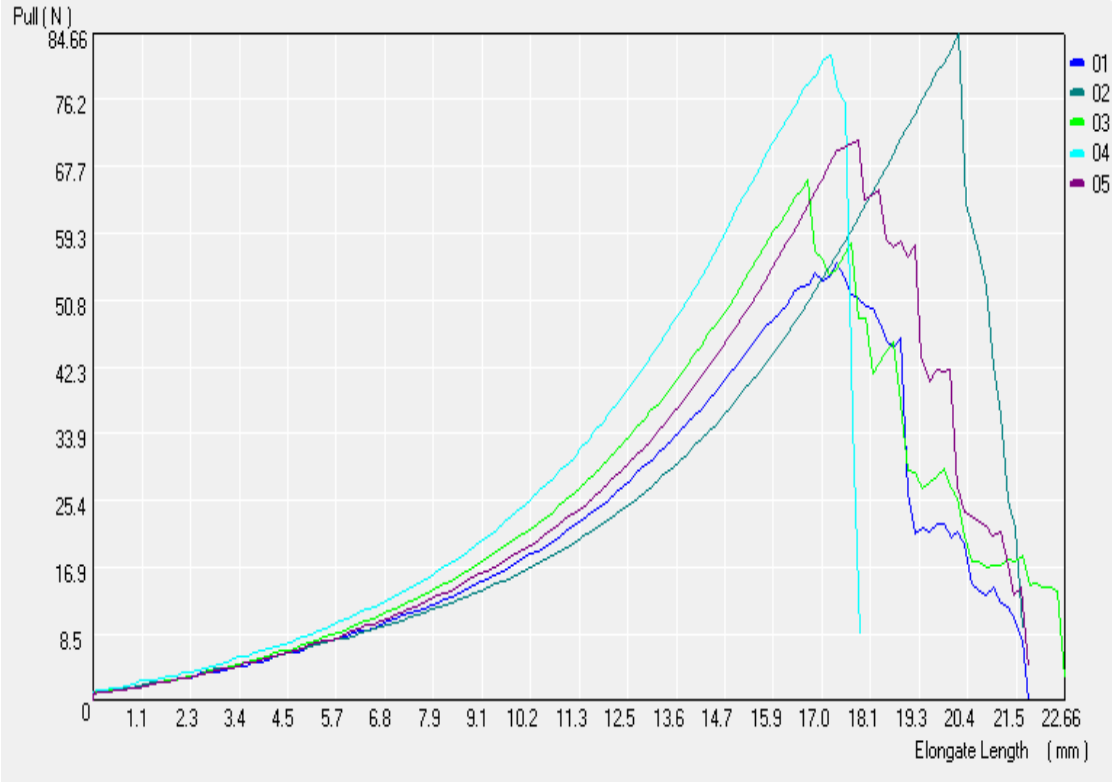


Figure G50: Load elongation curve for sample from run number 24 in weft direction

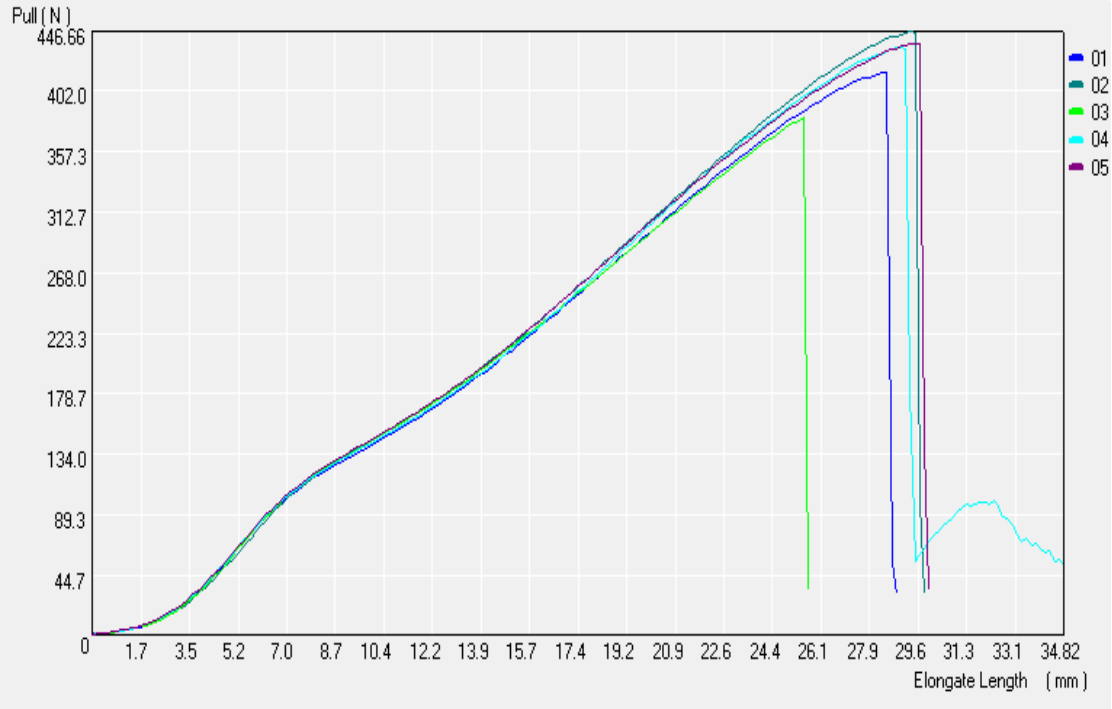


Figure G51: Load elongation curve for sample from run number 25 in warp direction

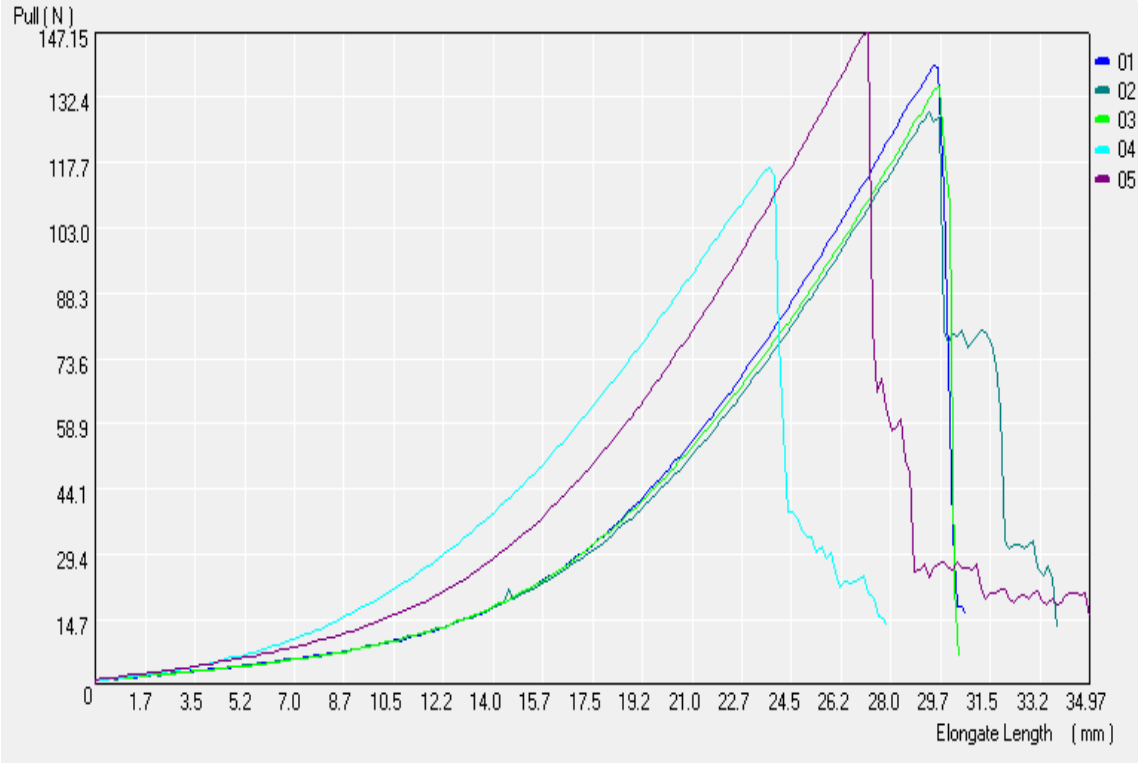


Figure G52: Load elongation curve for sample from run number 25 in weft direction

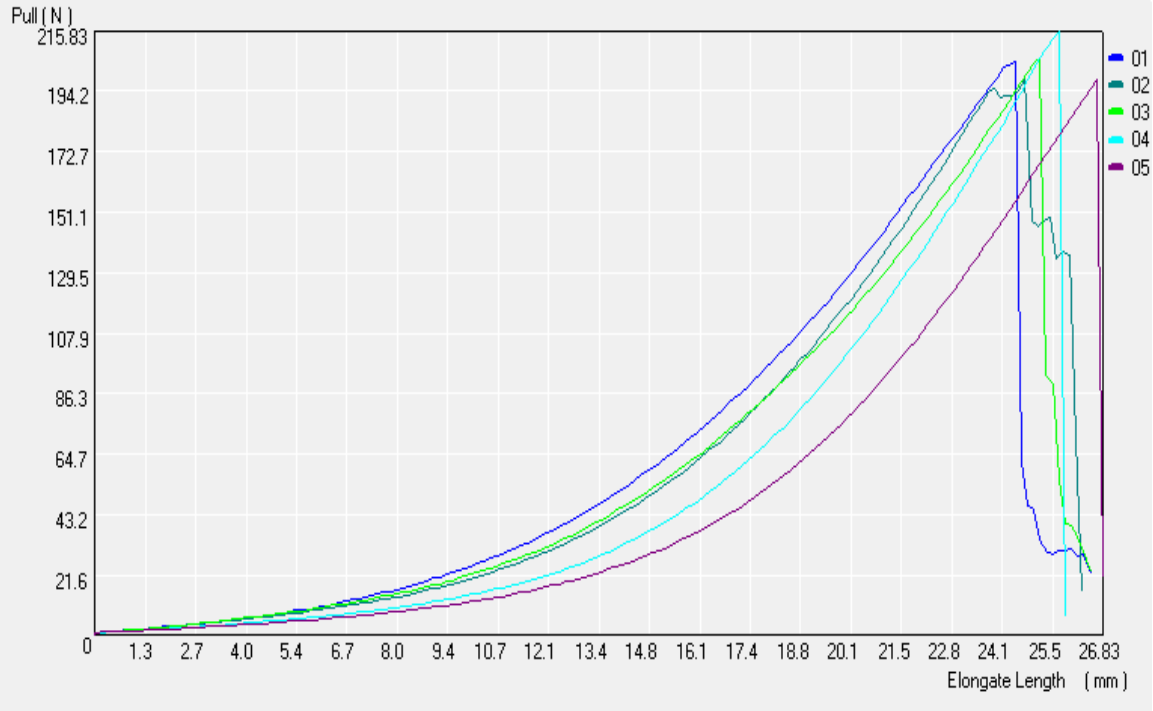


Figure G53: Load elongation curve for sample from run number 26 in warp direction

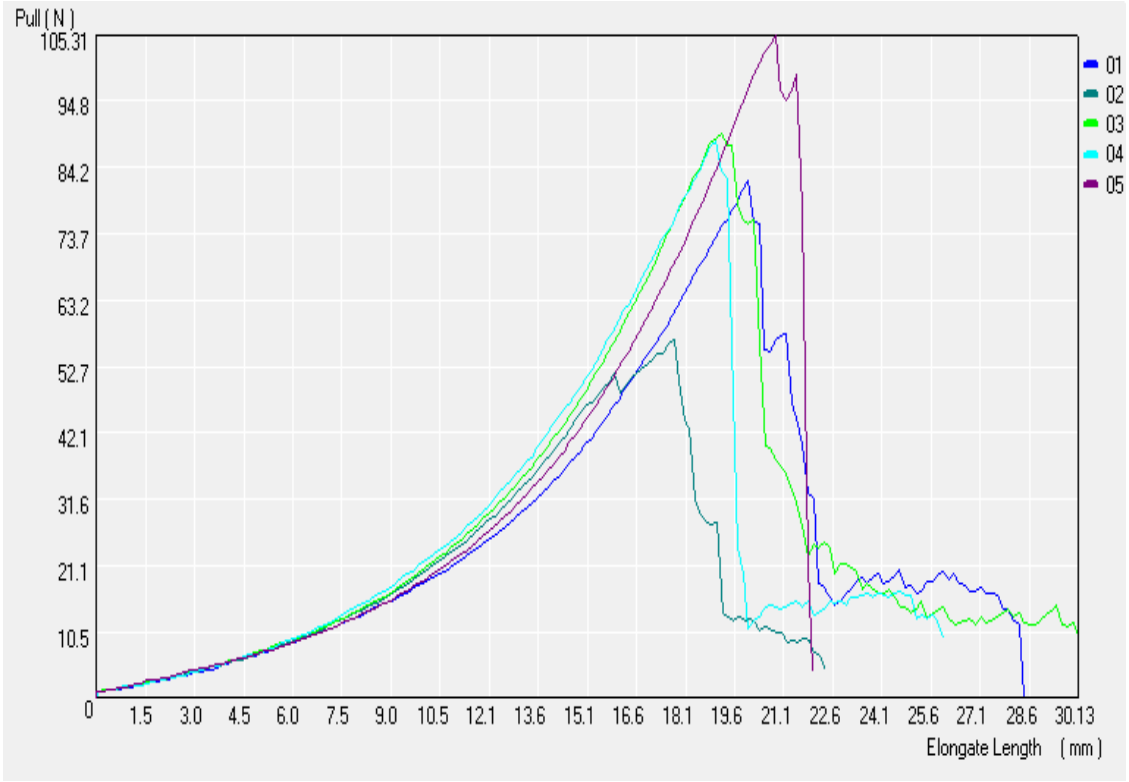


Figure G54: Load elongation curve for sample from run number 26 in weft direction

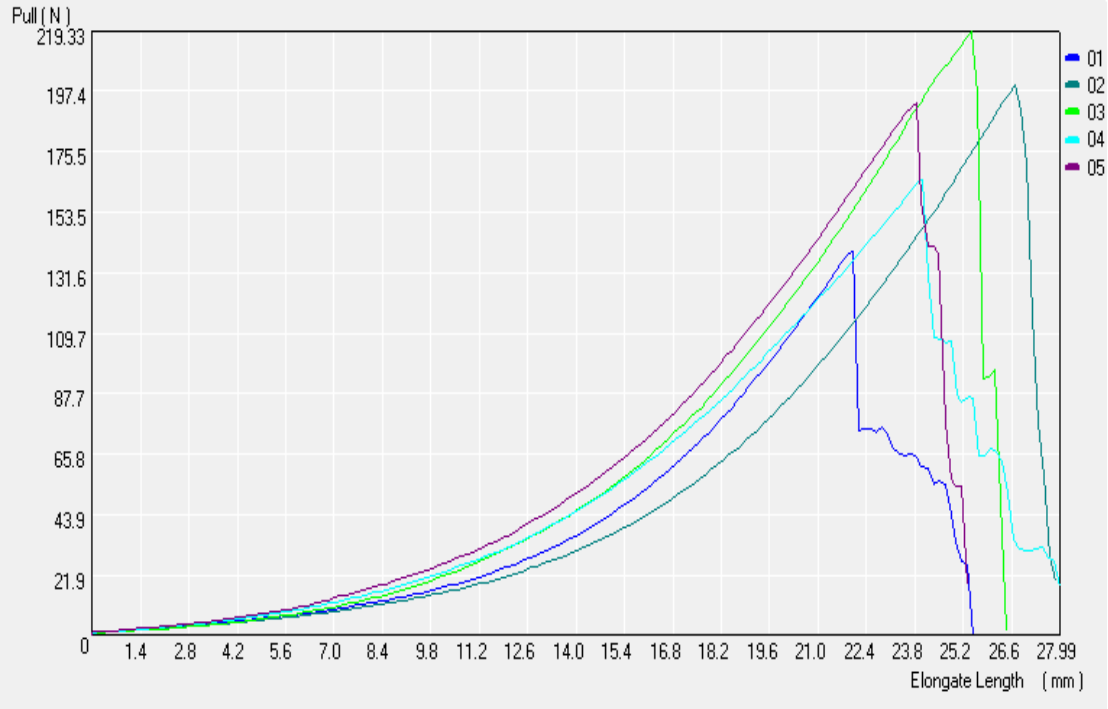


Figure G55: Load elongation curve for sample from run number 27 in warp direction

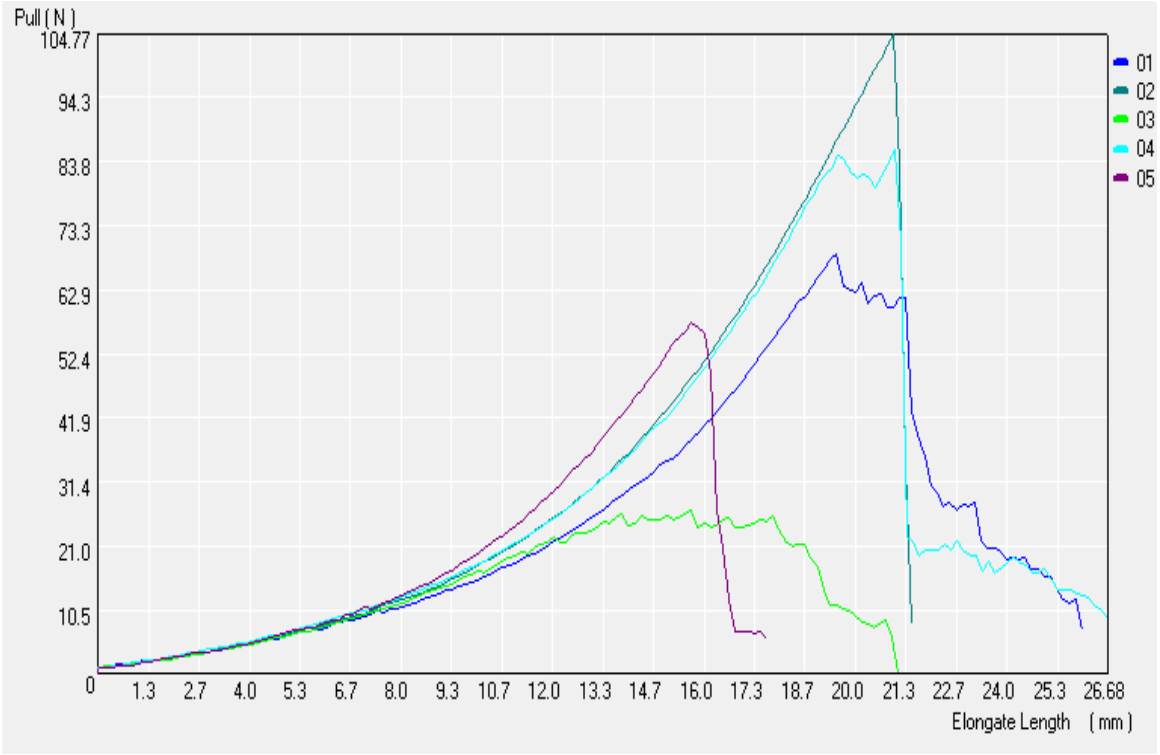


Figure G56: Load elongation curve for sample from run number 27 in weft direction

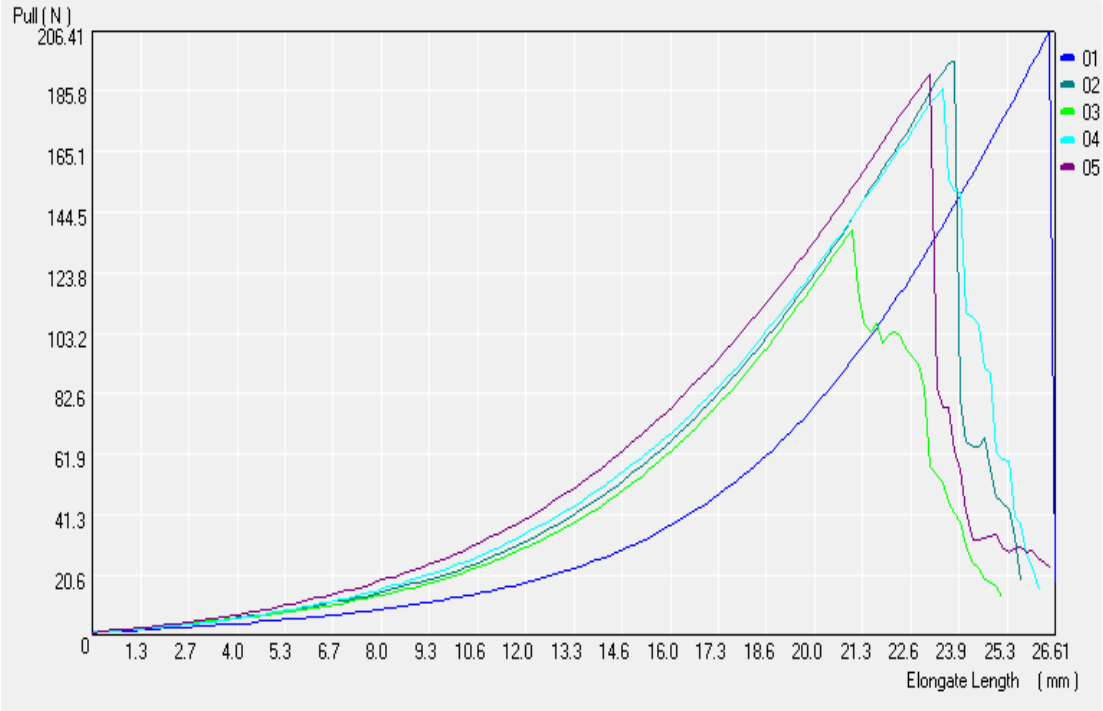


Figure G57: Load elongation curve for sample from run number 28 in warp direction

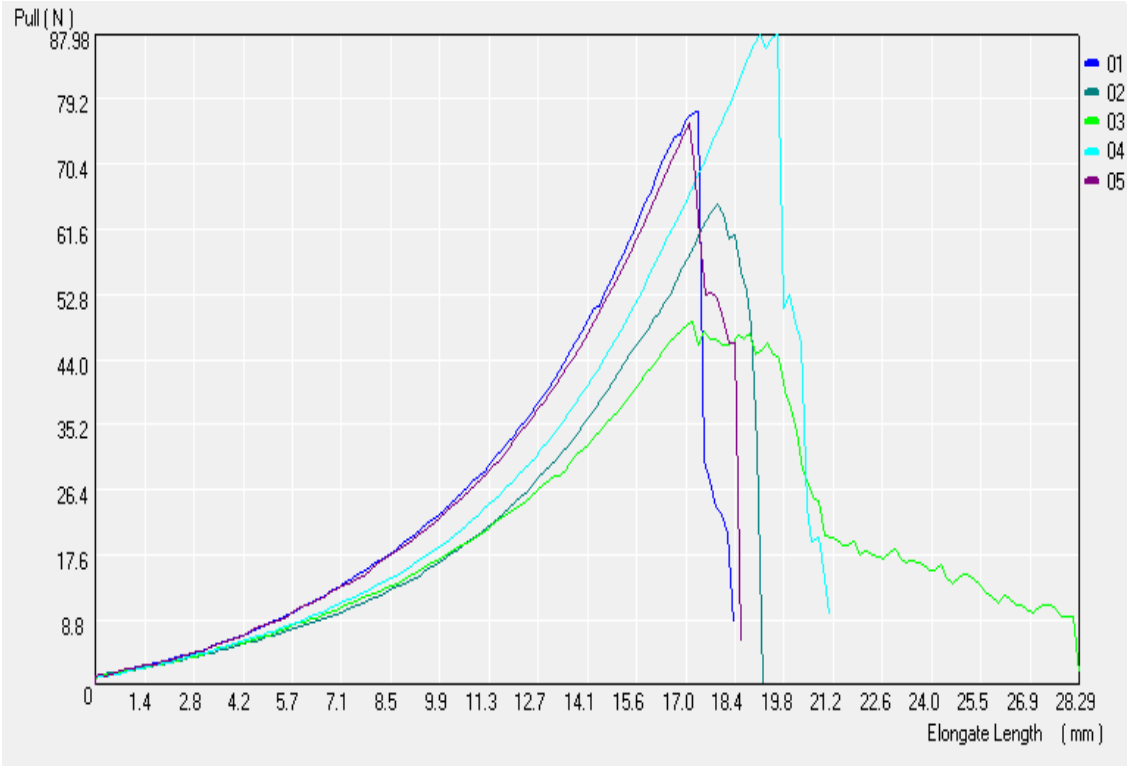


Figure G58: Load elongation curve for sample from run number 28 in weft direction

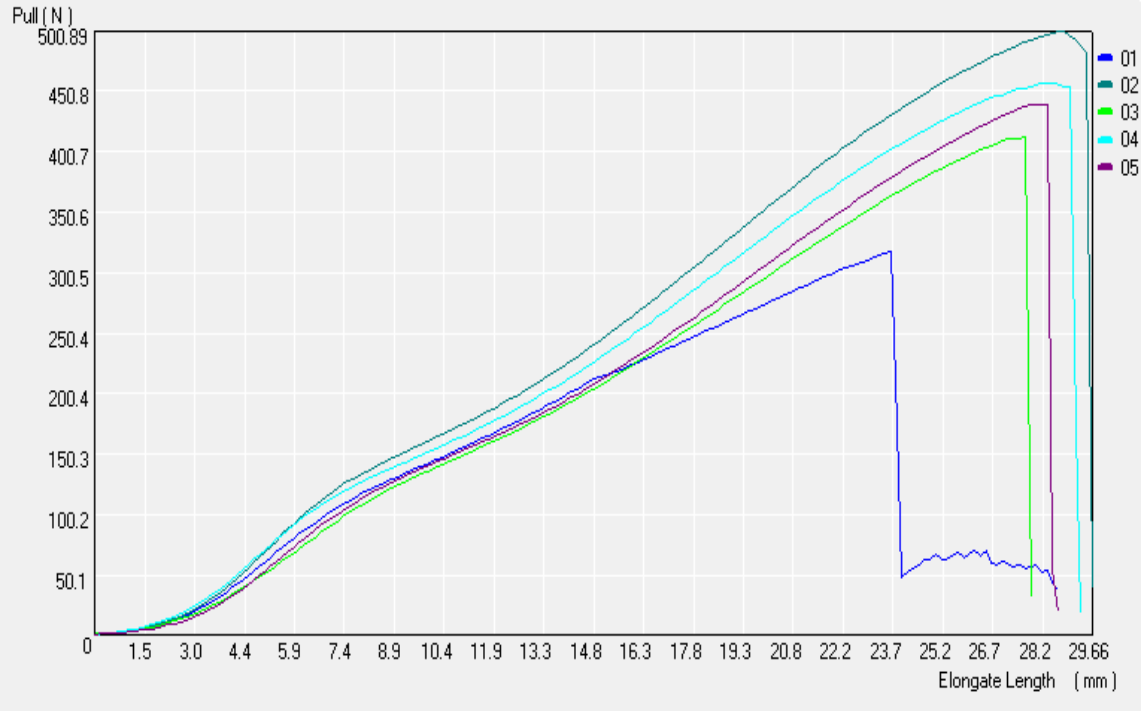


Figure G59: Load elongation curve for sample from run number 29 in warp direction

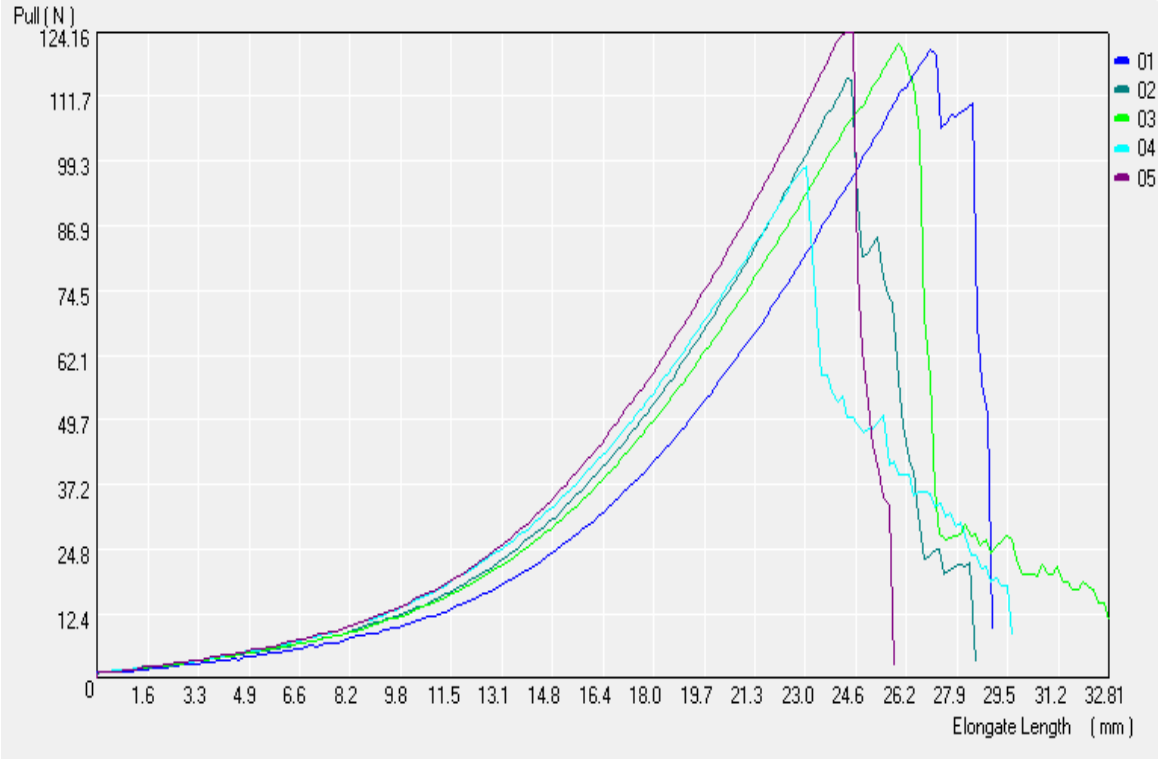


Figure G60: Load elongation curve for sample from run number 29 in weft direction

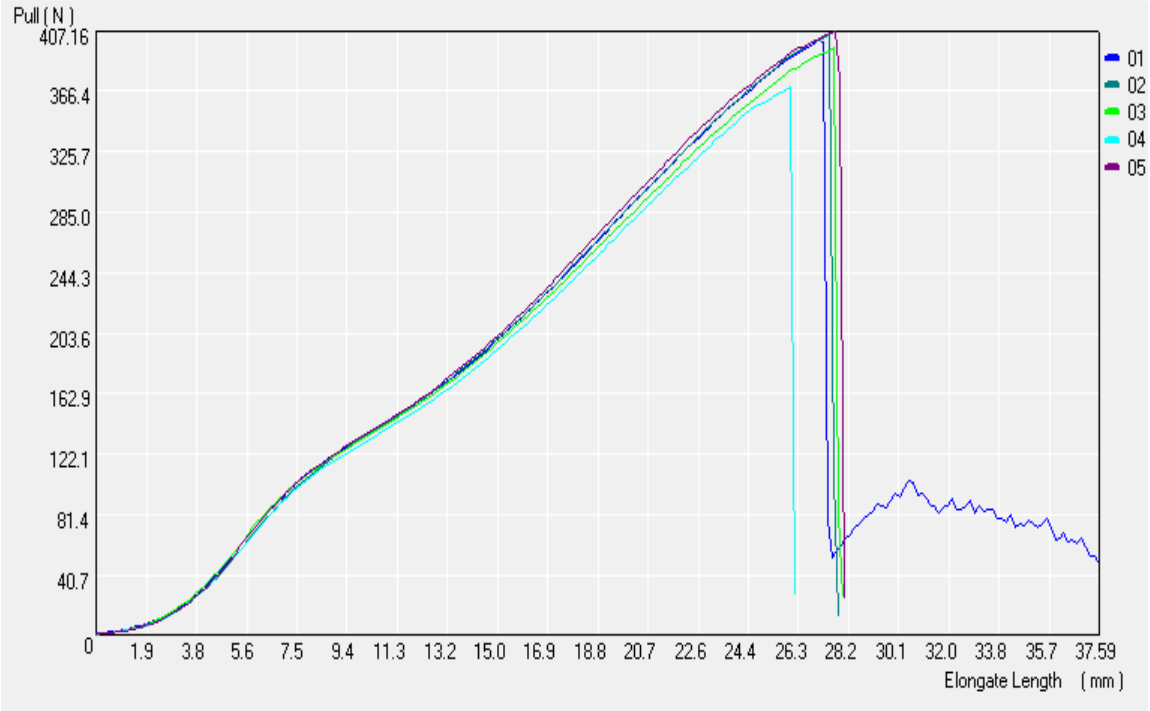


Figure G61: Load elongation curve for sample from run number 30 in warp direction

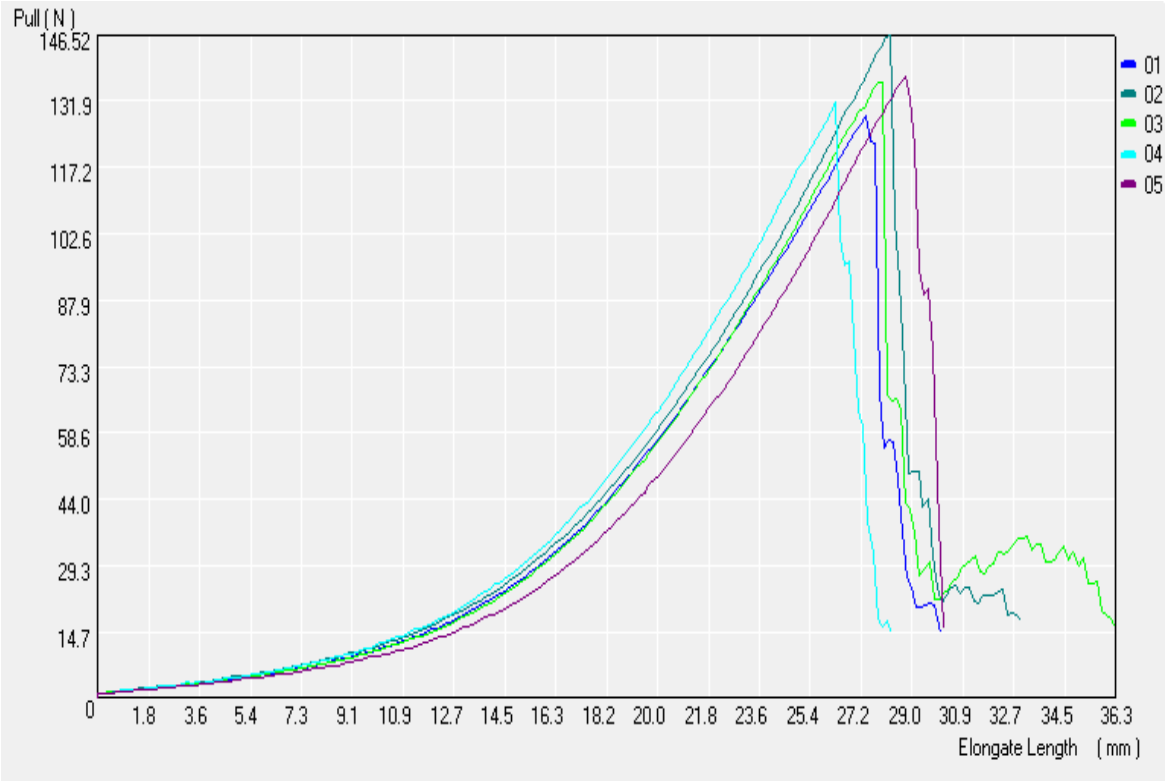


Figure G62: Load elongation curve for sample from run number 30 in weft direction

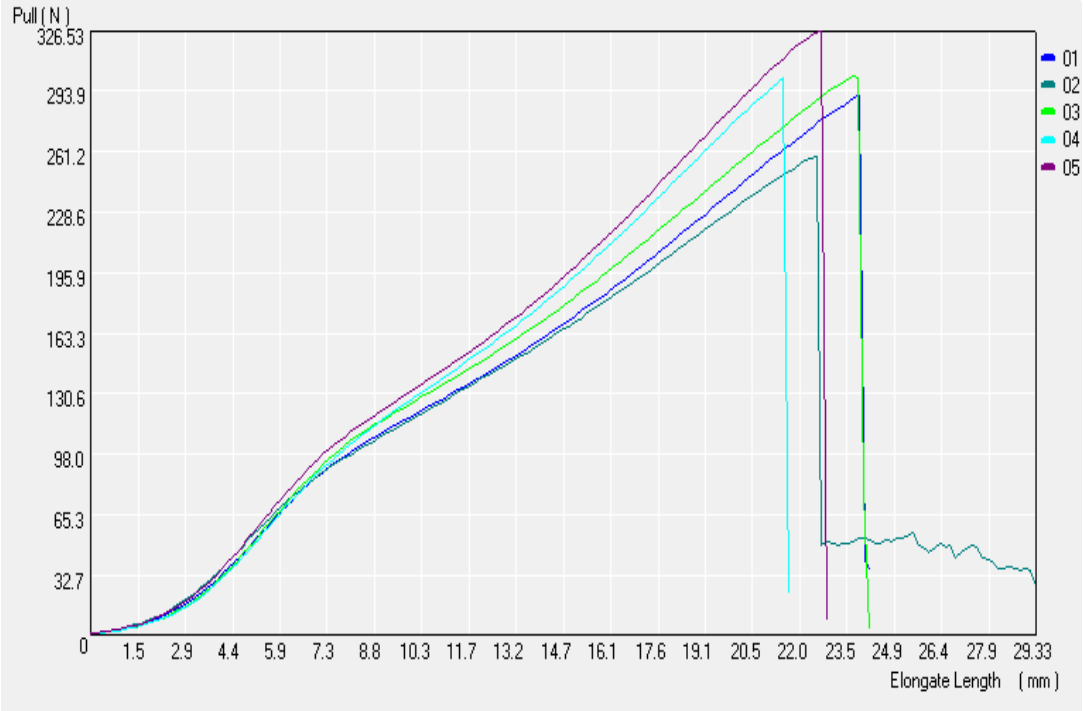


Figure G63: Load elongation curve for sample from run number 31 in warp direction

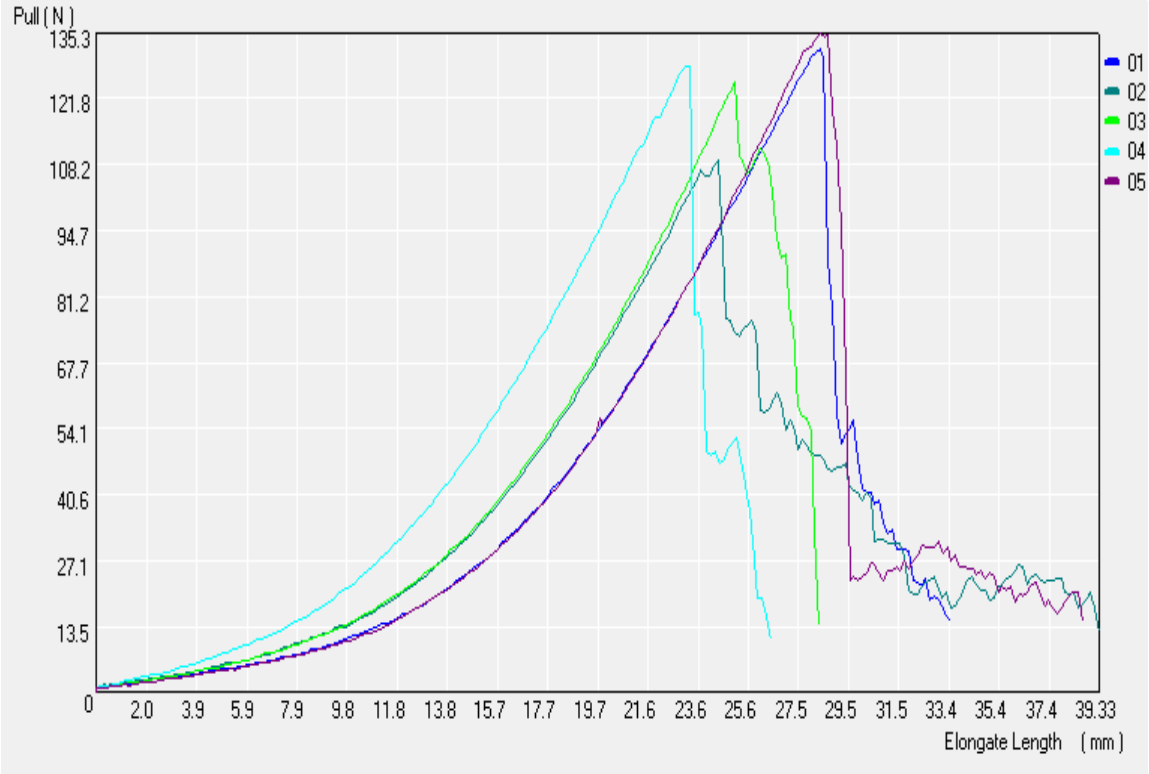


Figure G64: Load elongation curve for sample from run number 31 in weft direction

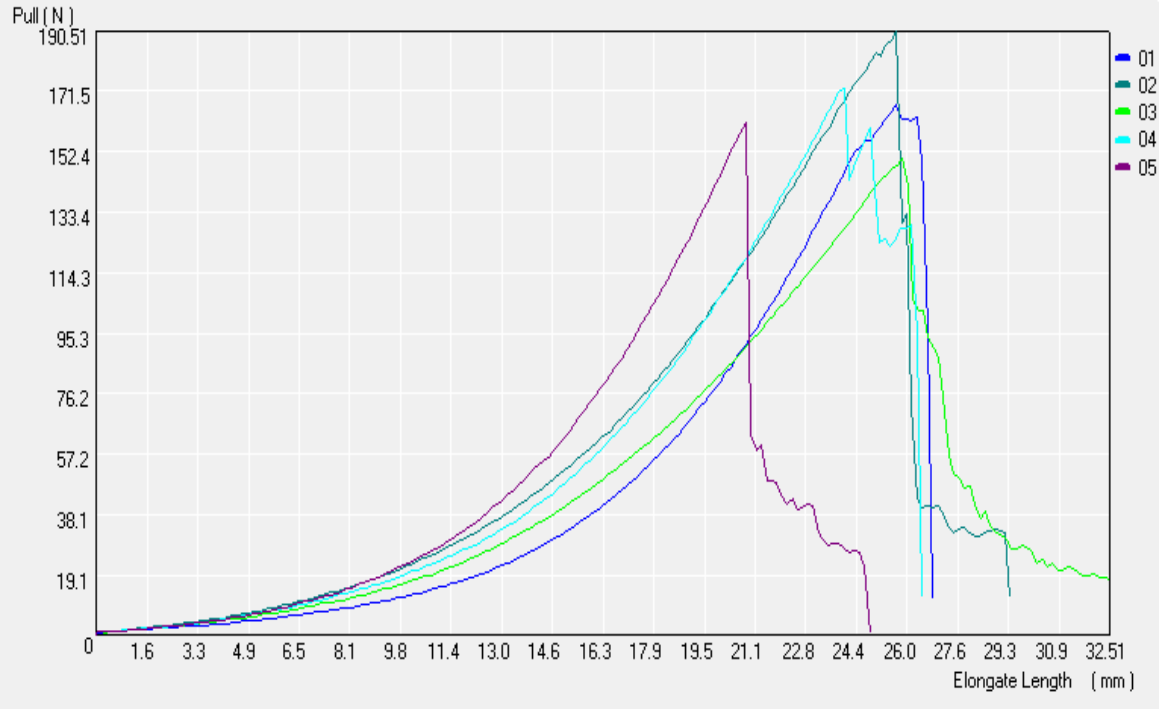


Figure G65: Load elongation curve for sample from run number 32 in warp direction

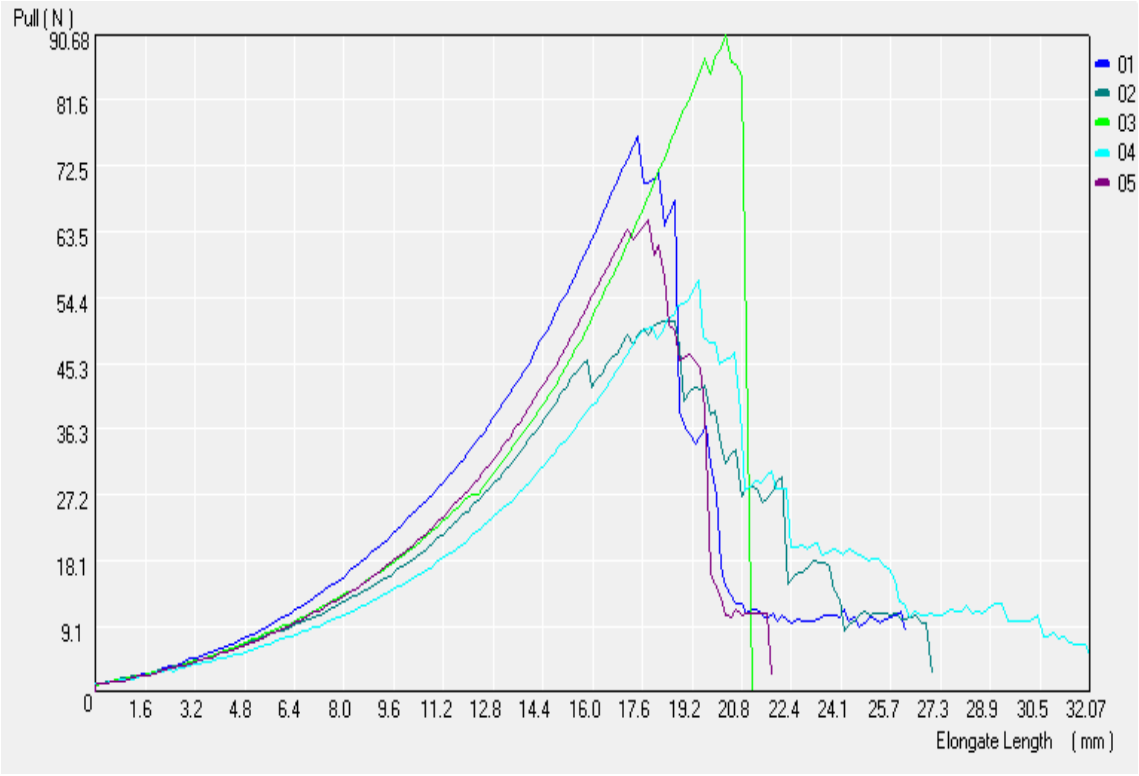


Figure G66: Load elongation curve for sample from run number 32 in weft direction

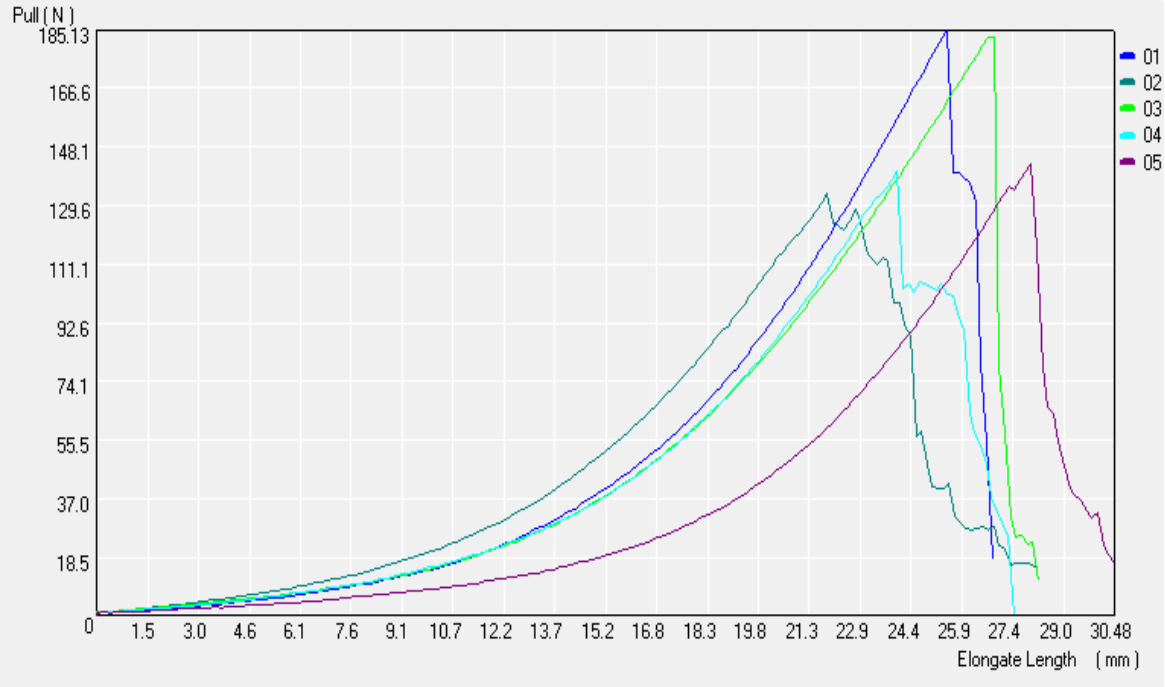


Figure G67: Load elongation curve for sample from run number 33 in warp direction

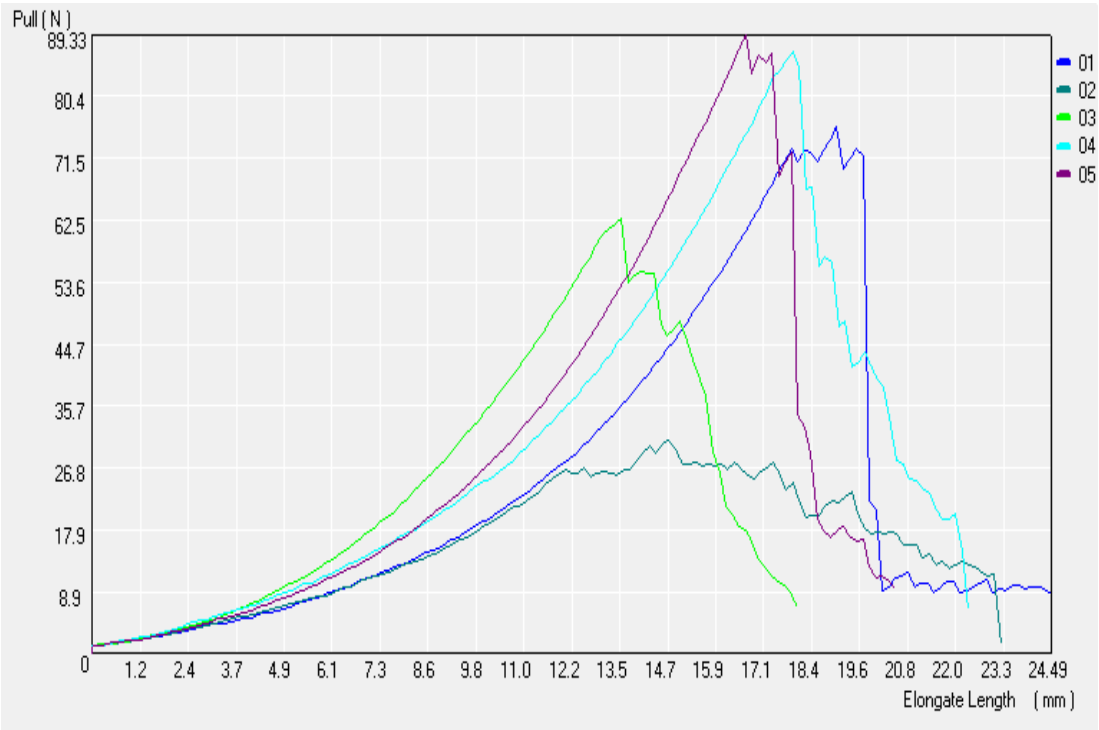


Figure G68: Load elongation curve for sample from run number 33 in weft direction

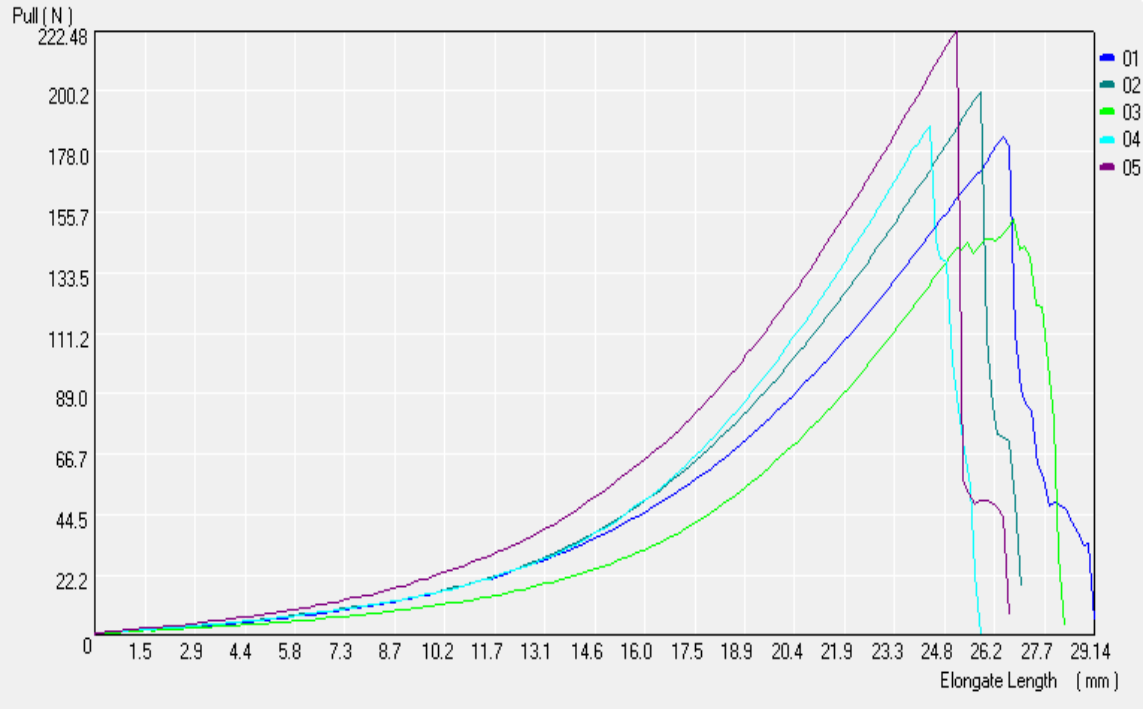


Figure G69: Load elongation curve for sample from run number 34 in warp direction

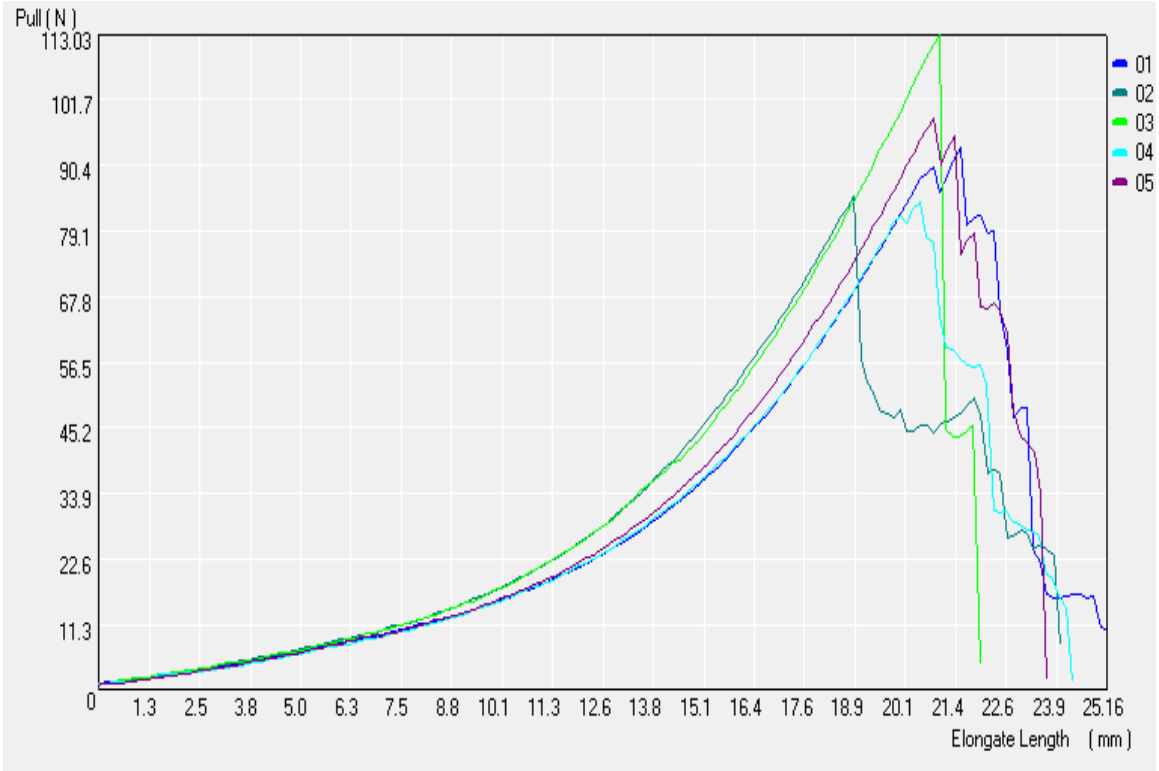


Figure G70: Load elongation curve for sample from run number 34 in weft direction

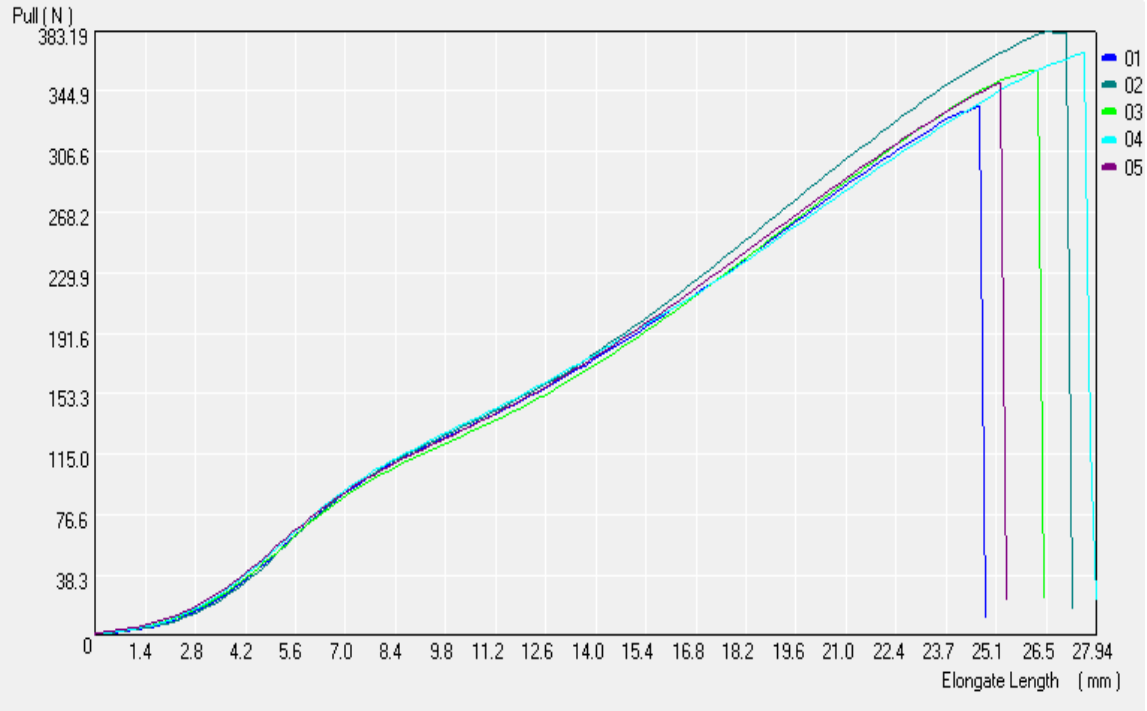


Figure G71: Load elongation curve for sample from run number 35 in warp direction

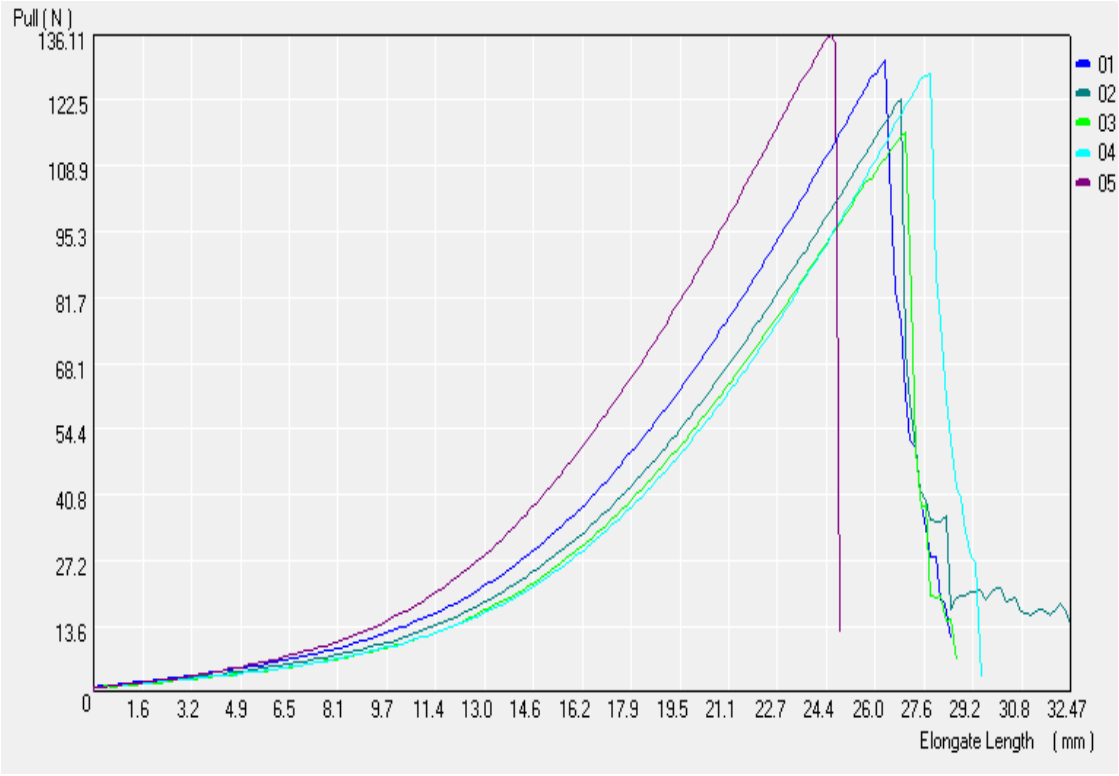


Figure G72: Load elongation curve for sample from run number 35 in weft direction

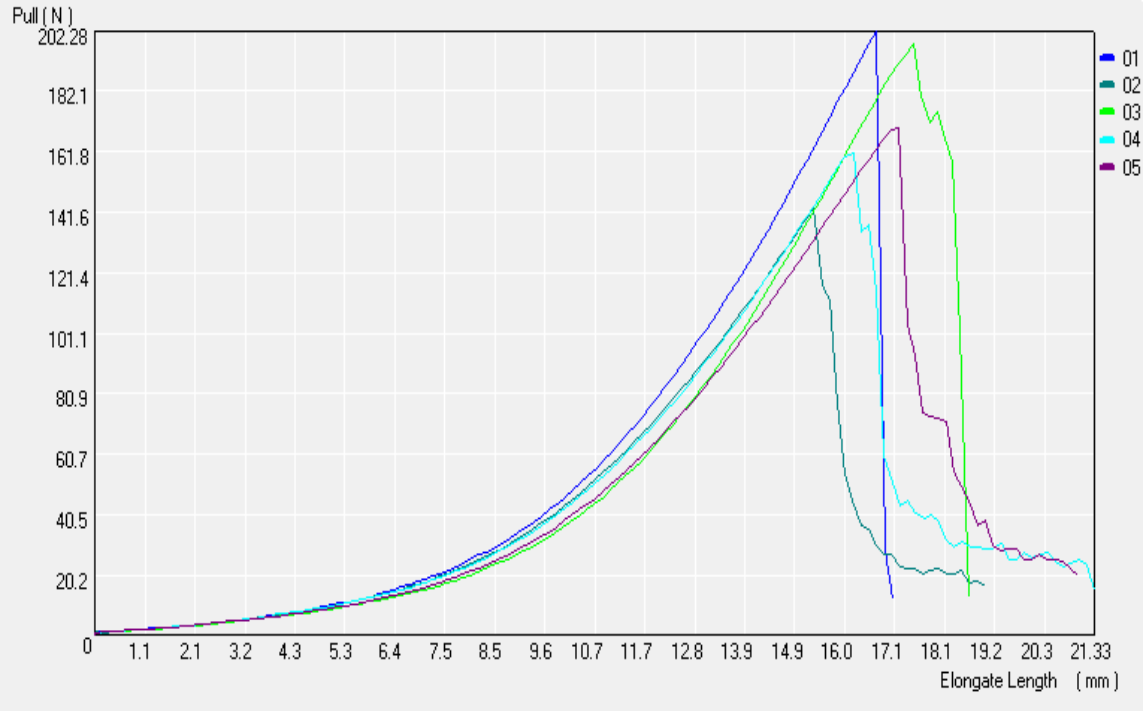


Figure G73: Load elongation curve for sample from run number 36 in warp direction

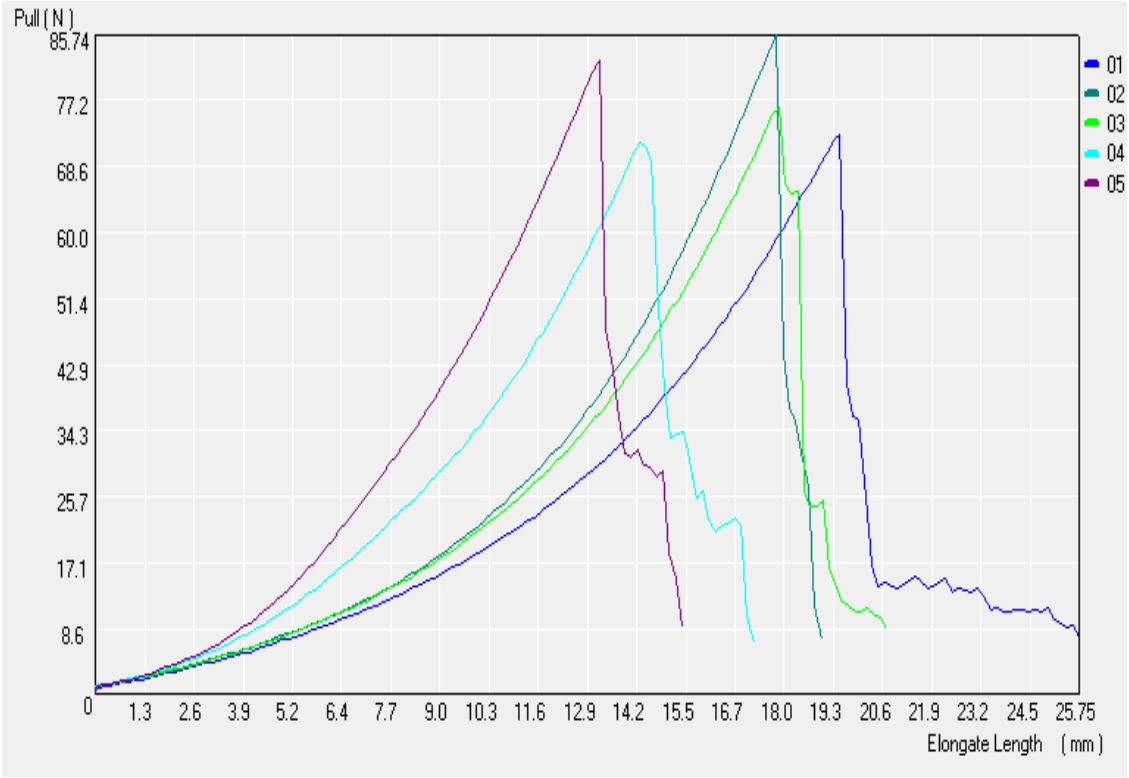


Figure G74: Load elongation curve for sample from run number 36 in weft direction

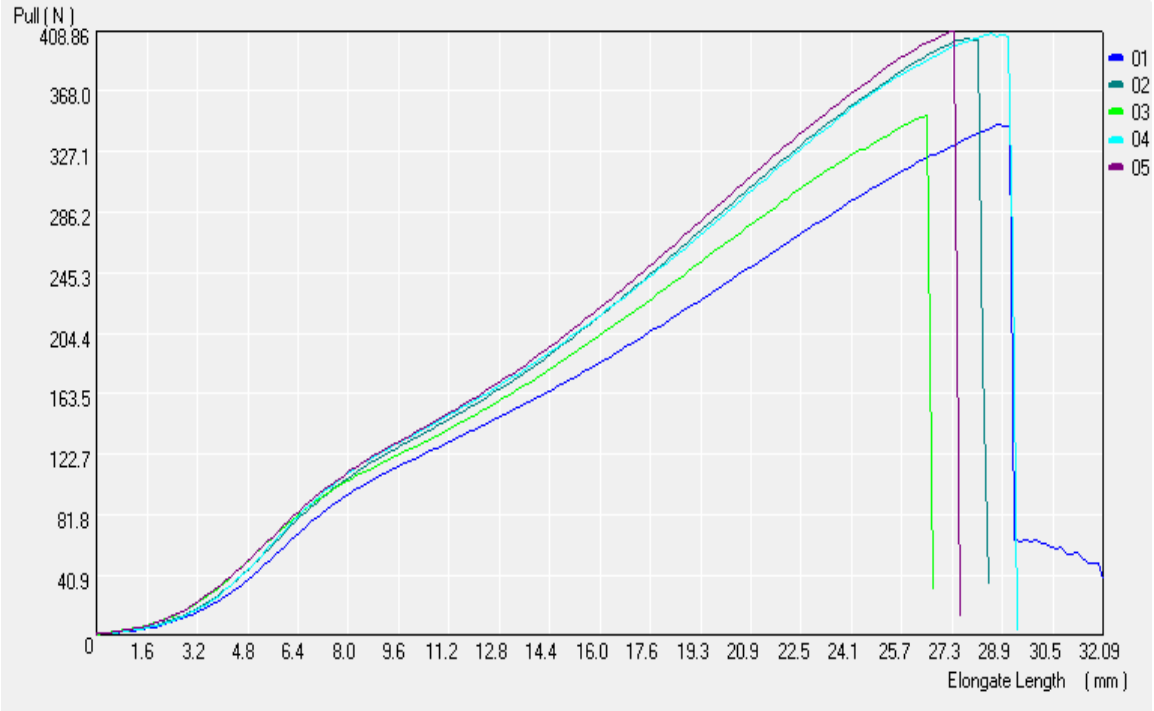


Figure G75: Load elongation curve for sample from run number 37 in warp direction

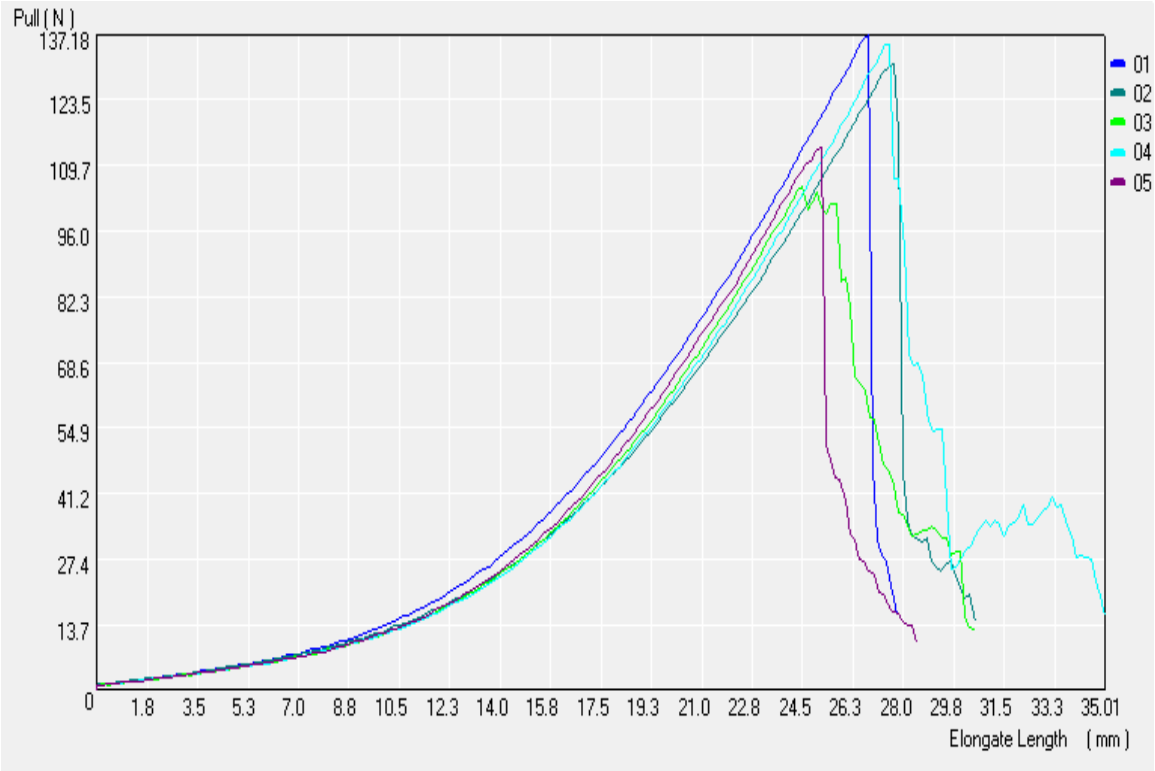


Figure G76: Load elongation curve for sample from run number 37 in weft direction

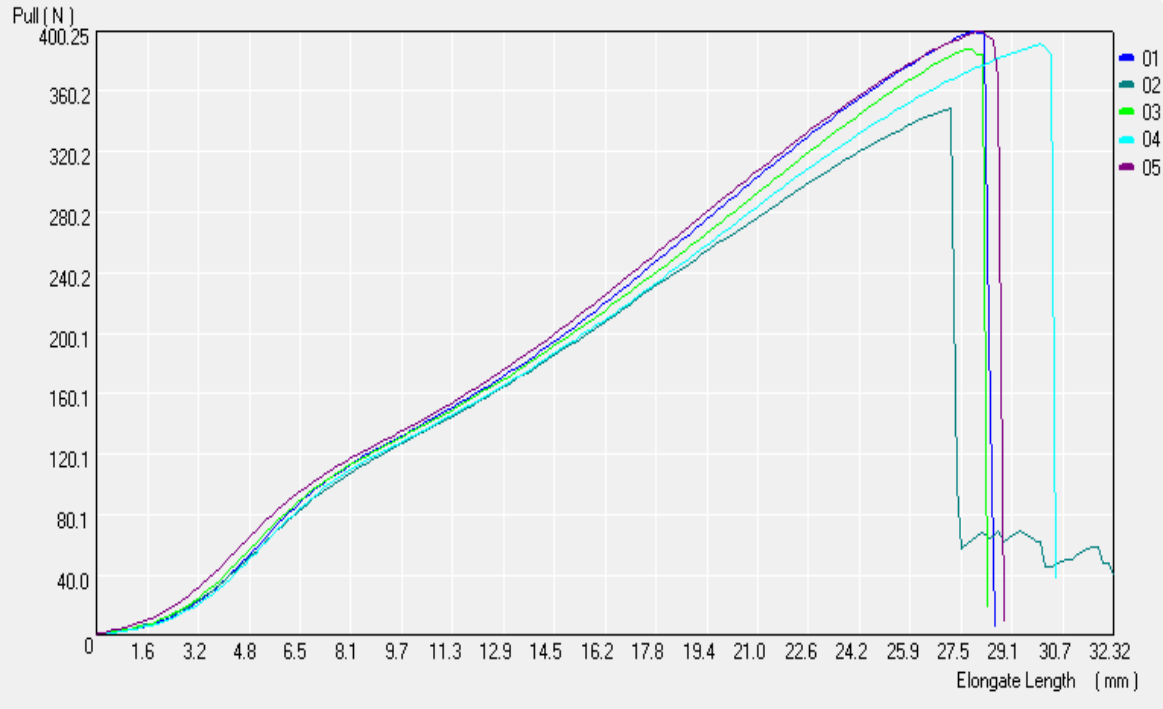


Figure G77: Load elongation curve for sample from run number 38 in warp direction

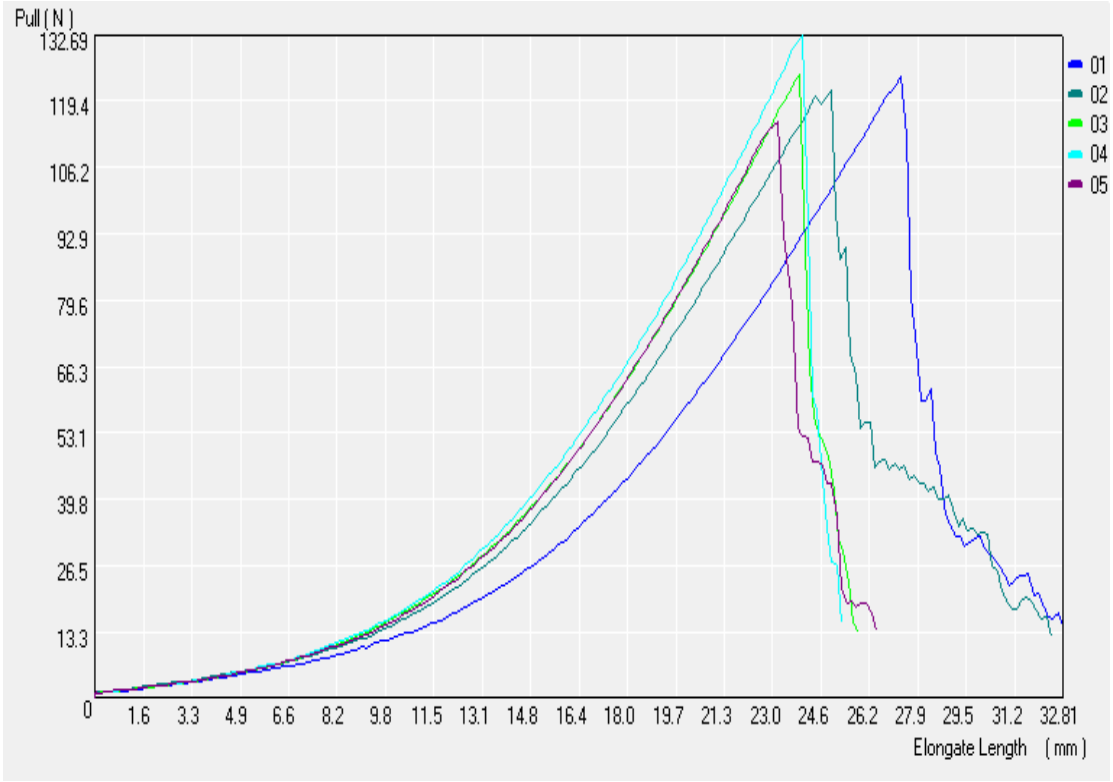


Figure G78: Load elongation curve for sample from run number 38 in weft direction

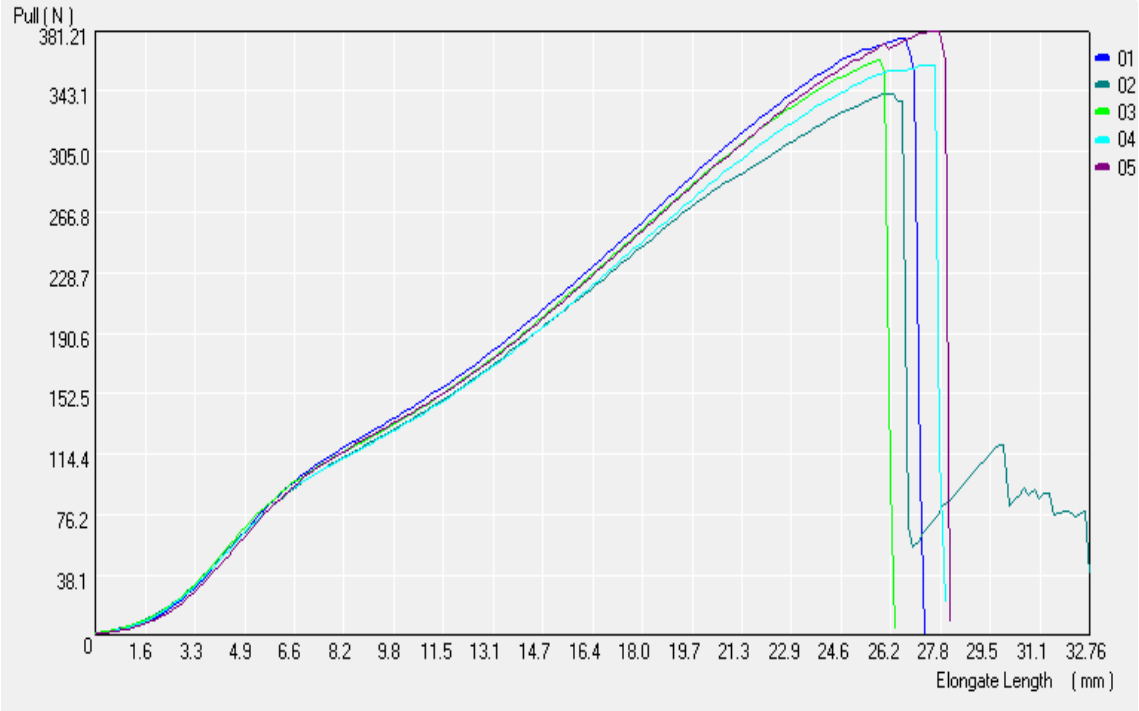


Figure G79: Load elongation curve for sample from run number 39 in warp direction

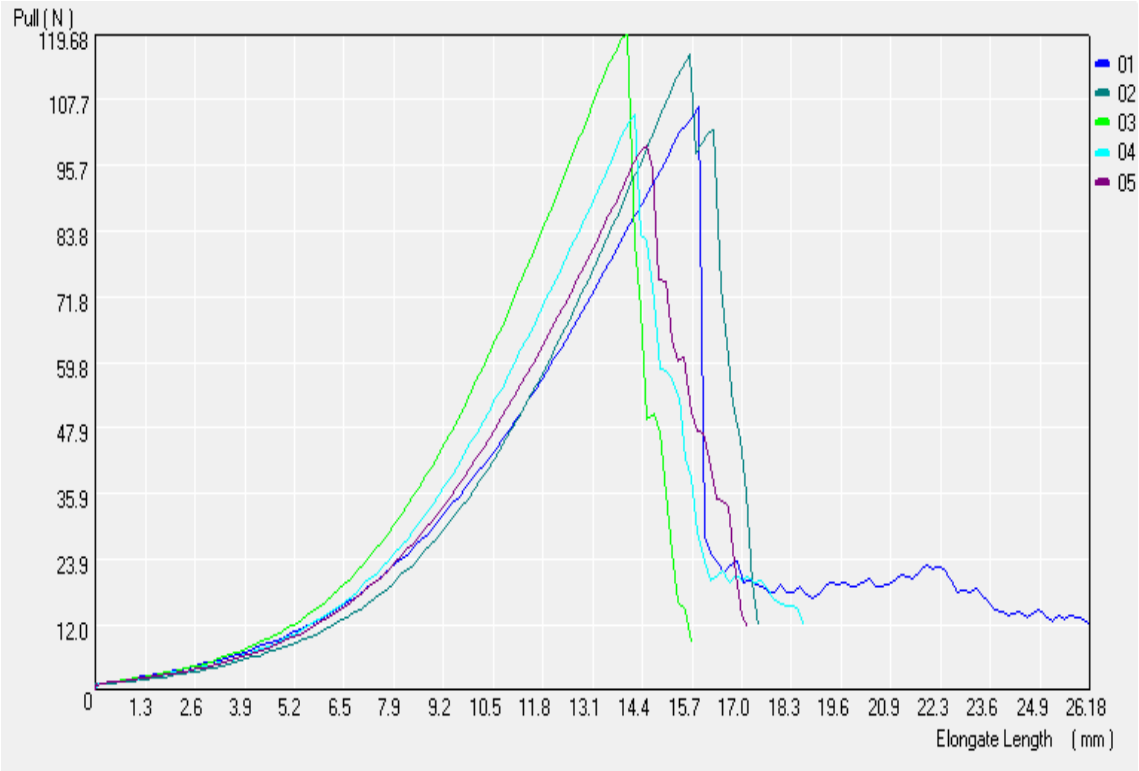


Figure G80: Load elongation curve for sample from run number 39 in weft direction

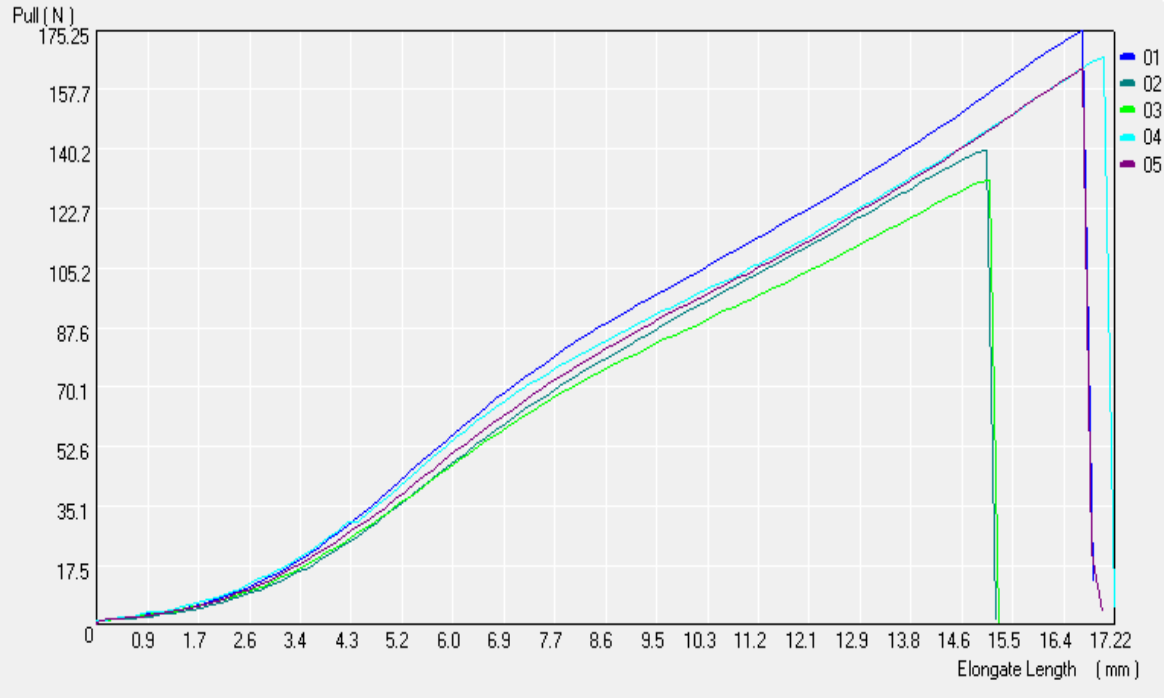


Figure G81: Load elongation curve for sample from run number 40 in warp direction

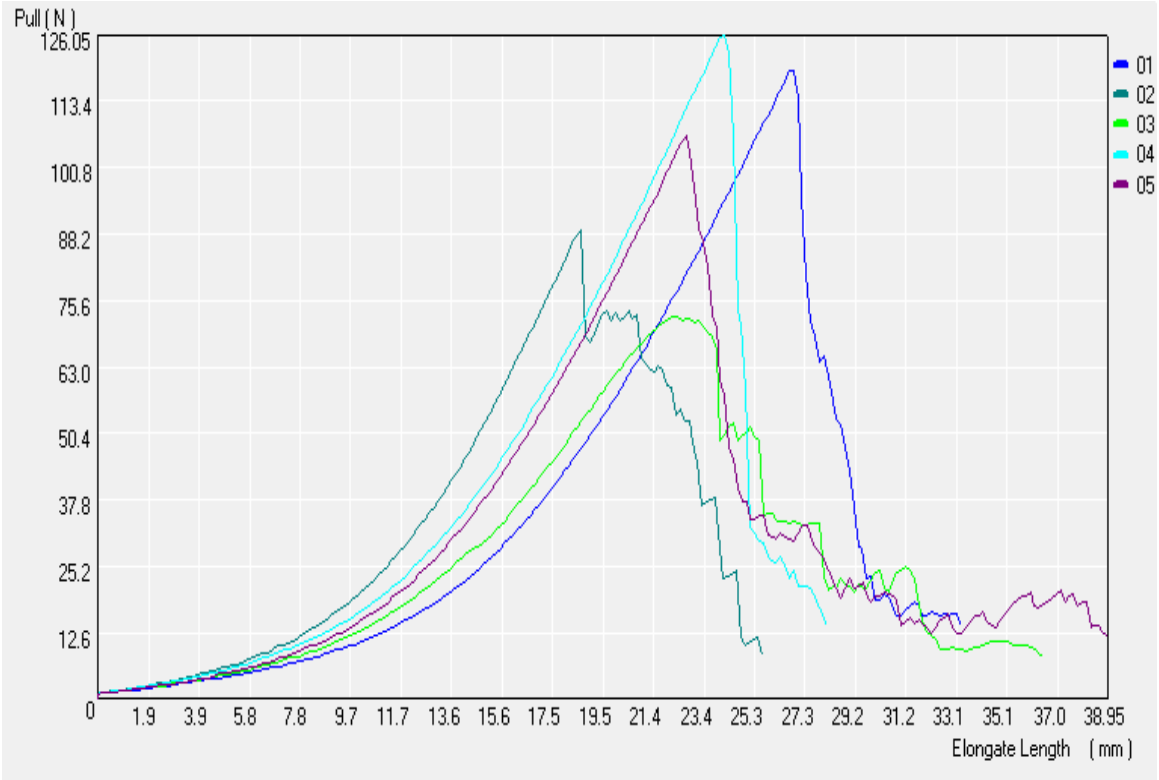


Figure G82: Load elongation curve for sample from run number 40 in weft direction