EXTRACTION AND APPLICATION OF NATURAL DYES FROM *ALLIUM BURDICKII* ON COTTON SUBSTRATE

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TEC/PGMT/04/14

A Thesis Submitted In Partial Fulfilment Of The Requirement For The Degree Of Masters Of Science In Textile Engineering Of The Department Of Manufacturing, Industrial and Textile Engineering,

Moi University.

JULY, 2016

DECLARATION

Declaration by Candidate

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the prior written permission of the author and/or Moi University.

Agulei Karen Desta …….DATE: ……..

TEC/PGMT/04/14

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DEDICATION

I dedicate this thesis to my parents, Mr. V.G. Egonu and Mrs. Egonu Deborah, my siblings; Alero Immaculate, Otim Deogratius, Iperu Demmy, Adong Daisy, Elumu Daniel and Akullu Jennifer whose sacrifice towards my education has exposed me to the world of Engineering.

LIST OF ACRONYMS

APG	: Angiosperm Phylogeny Group
BBD	: Box-Behnken Design
CC	: Colour change
CS	: Colour staining
DCC	: Colour change to dry rubbing
DCS	: Colour staining to dry rubbing
FT-IR	: Fourier Transform Infrared
gms	: grams
H_20	: Water
HCL	: Hydrochloric acid
MIT	: Manufacturing Industrial and Textile
NMR	: Nuclear magnetic resonance
o.w.f	: on weight of fabric
P value	: Significance value
R_f	: Refractance value
Rsq	: Coefficient of determination
RT	: Room temperature
UV-Vis	: Ultraviolet visible
VOC'S	: Volatile organic compounds
WCC	: colour change to wet rubbing
WCS	: colour staining to wet rubbing

ABSTRACT

The quest for sustainable and cleaner production in the contemporary textile processing industry has attracted interest in natural dyeing of textiles because of their biodegradable nature and compatibility with the environment. Synthetic dyes have been in use for a long time due to their abundance, uniformity, reproducibility and applicability, but have limitations such as toxicity, non-biodegradability and environmental pollution. Lately, due to environmental considerations, commercial interest in natural dyes has gained prominence. Although natural dyes have been exploited from various plants such as *Allium cepa* skin, saffron and pomegranate rind, there is still a wide scope of unexploited resource such as *Allium burdickii* that grows in the tropical and temperate regions. These natural dyes are however non-substantive hence their application requires the assistance of mordants. This research therefore concerns with the extraction of a natural dye and investigation of the factors that influence the extraction and dyeing processes. The research was carried out from MIT Laboratory, Kyambogo University and Uganda National Research Institute. The objectives were to extract, characterize, assess the dyeing of 100% cotton fabric using natural dye extracted from *Allium burdickii* plant and analyze fastness properties of the dyed fabrics. Using both the leaves and bulbs of the *Allium burdickii* plant, dye samples were prepared using aqueous and solvent (methanol and ethanol) extraction methods and further investigated for the different physico-chemicals present. Using Box-Behnken experimental design four factors namely dyeing temperature, time, concentration of mordant and pH where chosen and dyeing conditions evaluated while applying the plant extract and mango bark (natural mordant) on cotton fabrics using pre, simultaneous and post mordanting methods and the fastness properties of the dyed fabrics evaluated using Mintab statistical approach. The study established presence of chromophores in the bulb but not in the leaves, aqueous extraction method as the best method and further optimized its extraction temperature, time and mass to liquor ratio as 60^0C, 60 minutes and 1:20 respectively. Some of the physico-chemicals that were present in the bulb extract were flavonoids, carbohydrates and proteins whereas saponins were absent in the leaves of the plant. Amongst the three mordanting techniques, post mordanting emerged as the best. The research further established that samples with low percentage of mordant (10% on weight of fabric) exhibited better wash and perspiration fastness with a rating of 3-4 whereas light and rubbing fastness (wet and dry) for all the mordanting techniques showed acceptable fastness of 4/5-5. From the research, the dye can be classified as a plant polygenetic, basic and mordant dye producing red dye. Under optimized extraction conditions, low concentrations of mordant and mass to liquor ratio, the dye extracted from bulbs of the plant showed acceptable fastness properties hence can therefore be utilized on cotton substrate. Besides that, this research has provided insights for the utilization of locally sourced *Allium burdickii* plant for dye applications in textiles. Nevertheless, to maximise the full potential presented by the *Allium burdickii* plant, there is need for further research in the quantitative and qualitative analysis of physico-chemical in the dye and use of different mordants and substrates during dyeing process.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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May the Good Lord bless and reward you abundantly.

CHAPTER 1 : INTRODUCTION

1.1. BACKGROUND OF THE STUDY

Nature in its occurrence is full of fascinating colours without which life would have been dull and monotonous. Colour is a property by which an object has the ability of producing different sensations to the eye due to the way the object reflects or emits light. Dyeing is an ancient art which predates written records. Its practice can be traced back to the Bronze Age era in Europe where primitive techniques of dyeing included sticking plants to fabric and rubbing crushed pigments onto clothes (Ado et al., 2014). During this period, dyeing performed using natural dyes was also a secretive art form where the most beautiful and exotic pigments were reserved for those who had the status to wear them (Brit., 2008; Saxena et al., 2012).The dyes were used for colouring food substrates, leather as well as natural protein fibres such as wool, silk and cellulosic fibres like cotton (Allen., 2000; Cordon., 2010).This form of colouring changed in 1856 when William Henry Perkin discovered the first synthetic dyes called Mauvein. The latter being cheap and easier to apply than the natural dyes quickly replaced natural dyes, and found favor in textile industries causing a cultural revolution which resulted into the commercialization of synthetic dyes (Perkin., 1856). This was so because synthetic dyes;

- Had a higher reproducibility and improved quality of dyeing that could be achieved at lower specific costs, provided a wide range of colours with excellent fastness properties.
- Had the ability to colour different types of fibres and fabrics and were highly available (Bechtold et al., 2006).

Most textile dyers and manufacturers therefore shifted towards the use of synthetic colourants because they were cost advantageous, easy to obtain in different grades, types and classes. As a result, this considerably lowered the cost of natural dyes because the quality of dyeing needed improvement (Taylor., 1989). For many decades, the practice and application of synthetic dyes and colourants expanded as that of natural dyes tremendously declined since the existing natural dyes could not satisfy the demands of the market. Despite their being threatened by the application of synthetic dyes for over a century, the use of natural dyes never eroded away completely.

They did survive in diverse parts of the world especially in some niches and special segments of the market like in the dyeing of different leather textiles, in the decentralized sectors of specialty products, and alongside the application of synthetic dyes in the large scale sector for general textiles/apparels (Vankar., 2007; Samanta et al., 2009; Konar et al., 2011). To maintain unique features of work, the practice was confined to craft spinners, weavers, knitters and small scale level dyers who attracted small scale exporters and producers dealing with highly eco-friendly textile production (Kamel et al., 2005; Saha et al., 2012). However, the increasing application of synthetic dyes amidst worldwide conscience of environmental pollution brought to the fore the threats and glitches associated with its production and usage. Their attendant side effects on human health, has led to a regenerated overwhelming international interest in natural dyes and natural fiber products dyed with eco-friendly natural dyes containing organic value. Therefore, a significant revival of interest in natural colourants has emerged.

Today, the use of natural dyes in textile dyeing has once again gained interest as an important alternative to synthetic dyes because some of these (synthetic dyes) have been reported to have carcinogenic effects besides causing environmental pollution (Paitoon., 2002; Kar et al., 2008). Most of the commercial dyers and textile export firms have therefore started re-examining possibilities of maximizing the use of natural dyes in dyeing and printing different textiles while aiming at niche markets (Cordon., 2010). Apart from dyeing and printing, the demand of natural dyes for use in food manufacturing industries, pharmaceuticals and cosmetic has greatly increased over the last decade. This is so because natural dyes produce very extraordinary soothing, and soft shades that complement each other as compared to synthetic dyes.

They have also gained economic advantage over synthetic dyes because some are anti-microbial, non-toxic, non-carcinogenic and biodegradable (Sengupta et al., 2015; Bhuyan et al., 2008; Kamel et al., 2005). On the other hand, synthetic dyes which are widely available at an economic price and produce a wide variety of colours, occasionally cause skin allergy and other harmful effects to the human body as well as embodying undesirable toxicity/chemical hazards accruing from their synthesis, application and life cycle. Aniline for example which is used extensively in the production of certain types of dye releases toxic vapour which is potentially carcinogenic (Lakshmi., 2015; Sengupta et al., 2015). If you look at a yarn dyed with madder under the microscope, you will see a subtle variation of colour. A yarn dyed with the synthetic equivalent of madder (alizarin and purpurin) does not have this wealth of uniform colour variation (Onal.,1996). Furthermore the textile processing industry is one of the major environmental polluters. In order to process a ton of synthetic dyes, one might have to use as much as 230 to 270 tons of water. The effluent generated by

this much water pollutes the environment as it contains heavy loads of chemicals including dyes used during textile processing. Therefore, the two main ways to limit the environmental impact of textile processing is to either construct sufficiently large and highly effective effluent treatment plants or make use of dyes and chemicals that are environment friendly like natural dyes.

Considerable research is being done around the world to discover and popularize new sources of natural colouring agents. In the developing world, research has shown that there is a high potential of natural dye utilization capable of enhancing income of the local people through ‘sustainable' harvest and sale of the dyes (ITDG., 2003). In Uganda, some research on extraction of natural dyes has been carried out and the natural colourants obtained utilized as sources of dyes in the dyeing of mats, ropes and other home-based craft materials (Wanyama et al., 2011). The use of natural dyes can therefore be a substitute for many hazardous synthetic dyes. Serious efforts are now being made to identify more raw materials so as to boost, standardize the recipes and usage of natural dyes. In this research *Allium burdickii* has been identified for study.

1.2.ALLIUM BURDICKII PLANT

1.2.1. Uses of the plant

The term wild onion also referred to as bulb onion is exclusively applied to a number of Allium species which are one of the largest among the fifty-seven genera comprising of over 500 species. Onions are one of the world’s cultivated vegetables with their culinary and medical uses spanning history and the globe (Hedges et al., 2007).

1.2.2. Taxonomy and geographical distribution

The evolution of Allium species stretches along the bio-geographical regions, mediterranean basin and west Northern America. From these centers, Allium plants spread widely all over the northern and southern hemisphere. Allium comprises of monocotyledonous flowering plants which include the onion, garlic, chives, scallion, shallot, leek as well as hundreds of other wild species. The heterogeneous genus such as *Allium burdickii* (Figure 1.1) encompasses a great number of perennial plants with underground storage organs consisting of either bulbs or rhizomes.

Figure 1.1: *Allium burdickii* plant

According to APG III classification system, *Allium burdickii* has been classified as shown in Table 1.1.

Table 1.1: The classification of *Allium burdickii*

Kingdom	Plantae
Clade	Angiosperms (Monocats)
Orders	Asparagales
Family/ Subfamily	Liliaceae/ Allioideae
Genus	Allium
Sub-genera	Anguinum
Species	Allium burdickii

Table 1.2 further gives a wider description of *Allium burdickii plant which* has linearly or elliptic oblong narrow leaves.

Table 1.2: Description of *Allium burdickii*

Plant part	Description
Leaves	Narrow leaves less than 1½" across and fewer-flowered umbels (less than 21 flowers)
	Produces 2-3 basal leaves of length 6-9" and (¾-1½)" across
	Either linear-oblong or elliptic-oblong in shape, have smooth margins and parallel venation.
	Leaf surfaces range from pale green to medium green, glabrous with an erect, ascending, arched or sprawling leaf orientation.
Petioles	Pale green and glabrous (unlike the reddish ones in wild leek)
	Very short and often hidden in the ground litter
Bulbs	Smaller in size with less exerted stamens in its flowers.
	Enclosed by a fibrous sheath with one or more other bulbs.
Root system	Comprising of an ovoid bulb with fibrous roots below.
Habitat	Tropical and temperate regions (Hanelt., 2015)
Cultivation	Dappled sunlight, fertile and relatively loose soil with decaying.

Plants from this genus like *allium cepa* have been exploited for the extraction of dyes and the dye further applied on textile substrates such as cotton, silk and wool (Önal., 1996; Keusgen

et al., 2008; Osabohein., 2014). Therefore to successfully commercialize the application of natural dyes on any particular textile fiber, suitable or appropriate and standardized techniques of dyeing for that particular fiber need to be adopted. Furthermore, to obtain newer shades with acceptable colour fastness behaviour and reproducible colour yield, appropriate scientific dyeing techniques and procedures also need to be derived. According to Pan (2003), the concept of production of natural dyes with lowered specific cost involves the use of cheap by-products from other agricultural activities, like tree bark from the timber industry, or leaves from the abundantly available plants like *Deodar, Jackfruit and Eucalyptus* (Pan et al., 2003; Kar., 2008). More research is therefore needed to explore these natural resources. In this research, an attempt has been made to give a scientific overview on dyeing of textiles with *Allium burdickii* dye.

1.3. PROBLEM STATEMENT

Today, most processes executed in the textile and clothing industry discharge atmospheric emissions that are disturbing the eco-balance. Dyeing of fabrics which accounts for most of the waste is a long process where at each stage some harmful chemicals used generate waste. This waste poses a threat to the workers' health and also to the general population through environmental pollution. The production of some synthetic dyes further generates hazardous waste containing toxic and heavy chemicals such as hydrocarbons and ammonia from printing; VOC's, aniline vapours from dyeing as well as dioxin, formaldehyde and toxic heavy metals like copper, zinc and chrome. These in turn have produced hazardous effluent whose disposal has become a major environmental and economic challenge. When such heavy chemicals are disposed in water bodies, aquatic life is affected by the removal of

oxygen supply, causing death and possible extinction. Through the food chain, they also affect the health of mankind.

Such environmental issues associated with the production and application of synthetic dyes, coupled with the modern dynamics of development, have once again revived consumer interest in natural dyes. Similarly, the worldwide growing appreciation of the organic value of eco-friendly products, has focused consumer interest towards use of textiles dyed with natural dyes. The current dyestuff requirement for the textile industry is about 3 million tonnes (natural dyes taking only 10-25%) and considering this fact, the use of natural dyes in mainstream textile processing is a big challenge. Besides that, available scientific studies and systematic reports on dyeing of textiles with natural dyes are still insufficient, yet there are plenty of natural products still untouched, hence the relevance of this research project.

1.4. JUSTIFICATION OF THE STUDY

Nature has gifted us with more than 500 dye-yielding plant species, and a rich biodiversity harbouring a wealth of useful resources. Natural dyes are considered eco-friendly because they are renewable, biodegradable, skin friendly safe and easy to handle (Gupta., 1998). Though natural colouration is known from ancient time as artisanal practice for handicrafts, painting and handloom textiles, the chemistry of interaction of such colourants with textile materials is of relatively high interest in production of eco-friendly textiles. Therefore, there is need to build a knowledge base and database with the production of appropriate shade cards for different textiles using improved, biodegradable, environment friendly mordant

extraction methods. This will help popularize the use of natural dyes and solve some of its problems relative to application methods, reproducibility and colour fastness.

Furthermore, there still exists an enormous presence of unexploited plant resource base in the wild that is readily available and eco-friendly, and guaranteeing safety of operation. Despite that, no synthetic dye has the luster, under-glow of rich colour, soft light and shadow that gives so much pleasure to the eye as the natural dye. Moreover, presently it is more urgent to revitalize the sacrament of natural dye and dyeing techniques as an alternative to the use of unsafe synthetic dyes.

1.5. SIGNIFICANCE OF THE STUDY

Exploitation of the plant will offer not only a great potential of rich diverse source of dyes, but also provide an alternative and sustainable income to farmers and local populations through harvest and sale of plant dyes, thus enhancing and increasing national resource development of domestic products. Furthermore, the natural dyes and colourants will not only be used for textile dyeing but as alternative colouration of foods, medicines, hair dye, cosmetics, handicraft items and toys, leather processing and other economic purposes. The exploitation of *Allium burdickii* in this study will reinforce and enhance knowledge and database as research efforts in this area have been negligible. Natural dyes are therefore an essential part of the world's ecological and cultural heritage as their selection and use to create colours is beneficial to all civilizations.

1.6. OBJECTIVES OF THE STUDY

The general objective of this research work was to analyze the dyeing of cotton substrates using natural dye extracted from *Allium burdickii* plant.

The specific objectives were

i). To extract and characterize natural colouring matter from the leaves and bulb of *Allium burdickii* plant.

ii). To assess and optimize the factors affecting dyeing of the cotton substrate

iii). To analyze the colour fastness of the dyed substrates.

1.7. SCOPE OF THE STUDY

In this research, the coverage was; extraction of natural colourants from leaves and bulb of *Allium burdickii*, characterization of the colourants, application of colourants on cotton fabric using mango bark as a mordant, identification of the shades obtained, analyzing fastness to washing, light, perspiration, wet/dry rubbing and comparison of results using statistical techniques.

CHAPTER 2 : LITERATURE REVIEW

Synthetic dyes have been globally used in textile industries due to their availability. However the advantages and disadvantages associated with their production and usage have obliged dyers to search for alternative sources, particularly natural dyes. For the last one decade or more, research has been carried out to explore the concealed components found in plants, animals, insects and other natural sources. This chapter therefore contains accounts of literature reviewed on the extraction, application and analysis of natural dyes on textile materials. The literature survey indicates that there is no work reported in the field of extraction and dyeing of cotton fabrics with *Allium burdickii*.

2.1. NATURAL DYES

The word ‘natural dye’ covers all the dyes or colourants derived from natural sources like different parts of various tree species and plants, invertebrates and minerals (Konar et al., 2011). Scientifically, dyes are defined as chemical compounds that are attracted to substrates in a more or less permanent state, and evoke the visual sensation of colour. They can further be defined as molecules which have the ability to absorb and reflect the visible part of light at specific electromagnetic spectrum to give the human eye a sense of colour (Institue of Chemical Technology). Such dyes that are majorly from plant parts are extracted by either aqueous method, acids or basic solvent method. For some plant parts like fruits, the dyes are extracted by pressing out the juice or drying the fruit followed by crushing it (Antima et al., 2012; Ponmozhi et al., 2011). The dye extracted from these sources usually has low to medium fastness; therefore improvement in their shade can be archived through use of

mordants, or by varying the media and dyeing conditions (Konar et al., 2011; Saxena et al., 2014).

There are diverse types of mordants which have been applied on textile substrates which on application give different results with the same dye or different classification of dyes. Natural dyes have been classified in several ways depending on their unique chemical structure and particular way of bonding that is, chemically where the substrate bonds strongly with the dye compounds or held by physical forces. Unlike synthetic dyes with a single entity, the structure of natural dyes comprises of complex chemical constitutions with mixtures of closely related chemical compounds.

2.1.1. Classification of natural dyes

The earliest nomenclature of natural dyes ever known was according to alphabetical order and botanical names. This nomenclature was difficult to understand and remember because the common names were area specific (in the local languages). As research advanced, a colour index which served as a reference for both the chemical and technical properties of the dye was developed. Within this class, dyes were arranged according to the hue i.e. the dyes whose chemical structures was known were given a constitution number that denoted their chemical constitution. For example, the CI of natural indigo was 75780 (CI Natural Blue 1) where; CI denotes Colour index, Natural indicates type of dye, Blue indicates the hue and 1 identifies the number (Saxena, et al., 2014). The classification as further discussed in Table 2.1, advanced from colour indices to numerous methods such as colour, chemical composition/ structure, biological function in plant/organism such as chlorophyll, hemoglobin and physical properties among others.

Table 2.1: Classification of natural dyes

Classification	Description of classification
By Bancroft	These include substantivedyes (dyes which dye fibers directly such as indigo and turmeric) and adjective dyes which require mordanting with a metallic salt such as logwood and madder.
By Humme (Dedhia, 1998)	Monogenetic : produce one shade irrespective of the concentration of mordant. Polygenetic dyes: produce different shades with various kinds of mordants e.g. Alizarin. Natural dyes extracted from allium species have been found to be polygenetic (Sanjeeda et al., 2014)
Origin or Source (Taylor., 1989; Chengaiah et al., 2010)	These include plants, minerals and animals. Plants are extracted from plant parts such as the roots, leaves, barks, flowers, fruits, seeds and tree trunks. Examples are indigo (oldest natural dye), saffron, Tyrian, madder red and Henna. More popular plant dyes are shown in **Table 2.2**.
	Minerals are derived from earth core, clay and purified inorganic compounds e.g. iron-buff, narkin-yellow, manganese brown and Prussian-blue while animals/Insects includes cochineal and kermes dyes.
Colour (Gupta, 1998)	According to predominating colour either red, yellow, blue and black dyes
	Red is based on anthraquinone and its derivatives. They hide in roots, barks or bodies of dull grey insects. Yellow the liveliest and most abundant hue is based on Flavonoid. Flavones 44 and 3-hydroxyflavones are the main chromophores. These hide in leaves and vegetable fruits.
	Black is found in Tannin rich plants. These dyes are substantive towards cellulosic and protein fibres. They are also obtained from yellow and red dyes through mordanting
Other classifications such as by application and chemical composition are further explained in 2.1.1.1.	

As earlier on discussed, dyes have been extracted from various plant parts such as henna and madder. Additional plant dyes are discussed in Table 2.2.

Table 2.2: Common vegetable dyes

Plant part	Dyestuff
Flowers/Petals	Tesu, Marigold, Kusum, Dahlia,
Fruits/Seeds	Pomegranate rind, Latkan, Myrobolan (Harda), Beetle nut.
Leaf	Cardamon, Tea, Coral Jasmine, Eucalyptus, Lemon Grass, Henna
Bark/Branches	Purple bark, Sandal wood, Shillicorai, Khair, Sappan wood, Red.
Root	A. cepa, Turmeric, Beet-root
Tyrian purple from Murex brandaris and madder red from Rubia tinctorum	

2.1.1.1. Classification according to the method of application

This method of classification entails the use of either vat, direct, acid or mordant dyes.

Vat dyes especially indigo and wood dyes are water insoluble dyes where under reduction conditions, the carbonyl group becomes an anionic phenolate group so that the leucoform (state when they are soluble in alkaline/aqueous solution) penetrates into the fiber being dyed. However, on exposure to air, the dye oxidize back into its insoluble form hence getting trapped into the fiber structure i.e. the pigment aggregate become trapped into the fiber structure.

Mordant dyes (the vast majority of natural dyes) don't have affinity for textile substrates hence for proper fixation into the substrate, treatment with a mordant (generally a metal salt) is required. In order to obtain complete fixation, the mordant dye/solution to be used should have sufficient electron donating groups capable of forming appropriate functional groups in the structure of the fibre (a complex with the transition metal salt). This is so because during dyeing, the dye interacts with the mordant–fibre complex forming insolubly bright coloured species as well as improving the fastness properties of the textile fabric. Some of the examples of mordant dyes are cochineal from insects, madder, Persian, Kermes, Fustic, oak, mango bark and myrobolan. Pomegranate rind, turmeric (*Curcuma longa*) and harda have affinity for cellulosic fibres thus are directly applied onto the fibre. These are advantageous because they have less wash and light fastness than vat and mordant dyes (Taylor., 1989; Gulrajani et al., 1992; Cordon., 2007; Samanta et al., 2003, 2011). `

Acid dyes when applied in an acidic medium constitute either sulphonic or carboxylic group(s) that form an electrovalent bond with amino groups of silk and wool. The fabrics dyed with these dyes require an after treatment with tannic acid (back tanning) so as to improve their fastness properties. An example of such a dye is saffron (Crocus sativus). Lawsone, anthraquinone dyes and other flavonoid dyes have comparatively low solubility, molecular mass and no strong solubilizing groups.

Disperse dye another famous classification is usually applied on synthetic fibres from neutral to mildly acidic pH by post mordanting with either chromium, copper or tin salts. Other dyes applied in such pH conditions are basic or cationic dyes where on ionization, they give coloured cations that form an electrovalent bond with –COOH group of silk and wool. The disadvantage of these dyes such as berberine dyes, is that they have poor light fastness (Cordon., 2007; Konar et al., 2011).

2.1.1.2. Classification according to chemical composition

This system categorizes dyes according to the nature of their chromophores. Zhang (2010) grouped natural dyes into seven kinds namely carotenoids, anthroquinones, napthoquinones, flavonoids, curcuminoids, indigoids and chlorophyll as illustrated from Figure 2.2 to 2.7 (Zhang et al., 2010; Konar et al., 2011). Carotenoids are highly conserved in all plant species. They are lipid soluble pigments integrated into light- harvesting complexes that function as light harvesting pigments and photo-protectants by channelling photons to the photosynthetic reaction centre and quenching damaged free radicals (Kopsell et al., 2004; Armel et al.,2009).

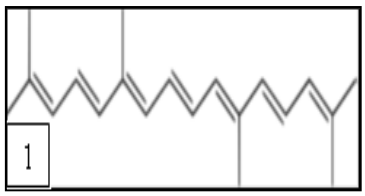


Figure 2.1: Carotenoids

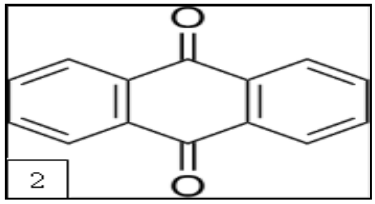


Figure 2.2: Anthraquinones

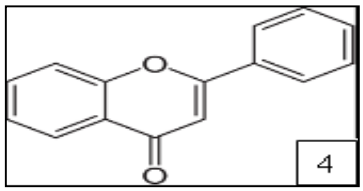


Figure 2.3: Flavonoids

Flavonols and anthocyanins are the main subclasses of flavonoids present in plants, the latter being found only in red onions (Basak et al., 2012; Kopsell et al., 2004; 2010). They have a variety of colours such as orange, red maroon and blue. The intensity and stability of these subclasses is independent on factors such as the structure and concentration of dyes, temperature, pH, light intensity, quality and presence of other pigments together with metal

ions, enzymes, oxygen, ascorbic acid, sugar, sugar metabolites and sulphur oxides (Markakis.,1982; Francis., 1989; Mazza et al.,1993). In red onions, the major existing subclasses of flavonoids present are the flavonols and anthocyanins (Lanzotti., 2006; Rosa et al., 2010). The other chemical groups of natural dyes is listed from Figure 2.4 to 2.7.

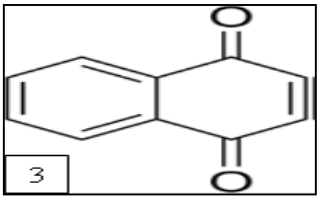


Figure 2.4: Napthoquinones

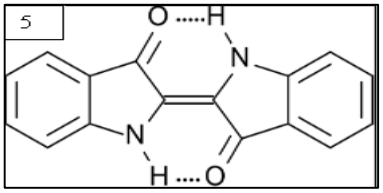


Figure 2.5: Curcumoids

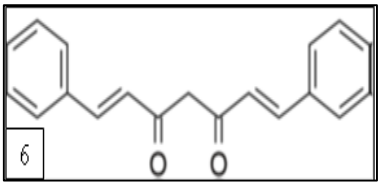


Figure 2.6: Indigoids

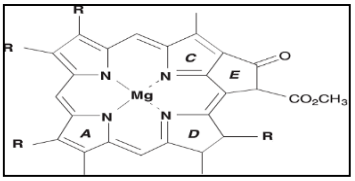


Figure 2.7: Chlorophyll

According to this classification, Keusgen (2008) reported that the characterizing chemical compounds in Allium plants are polysaccharides (mainly fructans), polyphenols, saponins and several compounds of the sulfur-containing amino acid cysteine. Erick (2010) also agreed that Allium genus produces majorly chemical compounds derived from cysteine sulfoxides which give them a characteristic (alliaceous) onion or garlic taste and odor content (Keusgen et al., 2008; Block., 2010).

2.1.2. State of Natural Dyes in the Current Industry

Natural dyes are generally obtained from natural sources such as plants parts, animals and insects. In order to obtain a natural dye from any natural source, the source should have sufficient dye yielding component such as carotenoids, anthraquinones, napthoquinones, flavonoids, curcuminoids, indigoids and chlorophyll. Studies have been conducted to investigate the availability of natural dye from various plants around the world, their ease of use and possible application on various natural fibres. Scholars such as Sharma (2012) carried out case studies to examine the availability of natural dye yielding plant species in Garhwal Himalya, India. The study reported on the dye yielding plants belonging to thirty three families along with their vernacular names, habits, distribution, parts used and nature of dye obtained. This study showed that the people of Garhwal Himalya, India have traditionally

been engaged in extraction, processing and preparation of dyes using plants parts such as roots, rhizomes, stems, barks, leaves, flowers, fruits, seeds and the whole plant (Sharma et al., 2012). Among the 46 species and 33 families, Fabaceae was the most dominant with six species, followed by Acanthaceae with three species, Asteraceae, Euphorbiaceae, Lythraceae, Mimosaceae, Polygonaceae and Zingeberaceae with two species each whereas the remaining 24 families had one species each. The survey concluded that there is a need to document the treasure of indigenous knowledge systems so as not to lose vital information on the utilization of natural resources. The findings also advocated for the commercialization of some of the natural dyes through systematic and scientific approach with identification of resources, extraction, purifications and analysis of chemical structure in order to enhance their usage.

Muyoski undertook another case study in Garrissa County, Kenya to document trees and other plant species used as sources of natural dyes and tannins. The research established that Twenty three (23) different trees and Shrubs identified by their botanical names had the potential for natural dye production. The trees recognized were Commiphora holtiziana, Acacia bussei, L. inermis L (Elan) and Commiphora campestris Engl among others. Further findings established that the main sources of livelihood in Garrissa community was livestock production, sale of natural dye and tannin products. Both men and women in this community used Lawsonia inermis L for hair dyeing and skin decoration (Musyoki et al., 2012).

Besides that, Wanyama (2011) also carried out a research to establish the potential sources of natural dyes from indigenous plants in Uganda. Several elements such as roots, leaves, seeds, fruits and barks were collected for experimentation. Generally, the plant parts used

were harvested, washed, spread on polythene bags, cut into pieces and left to dry. The dried parts were then ground into powder and used for extraction. The study established that forty plant species belonging to Twenty two (22) families had the potential to produce natural dyes compounds for textile applications. However, the most common plant species were Bixa orellana Linn, Justicia betonica, Curcuma longa Linn, Indigofera arrecta, Albizia coriaria, Syzygium cordatum and Harungana madagascariensis. Amongst all, Mimosaceae was the most dominant with seven species while Myrtaceae and Caesalpiniaceae each had four species (Wanyama et al., 2011). Natural dyes have also been extracted from the leaves, bulb and skin of Allium plants (Onal., 1996, 1999; Keusgen et al., 2008; Sharif et al., 2010; Eltaweel., 2013; Osabohein., 2014). From the literature above, it can be concluded that floras are a valuable source of natural dyes and using parts such as roots, leaves, stems and bulbs of plants such as Allium, weld, saffron flower and other natural sources like insects and animals, natural dyes can be extracted.

Although the plant species is available, there is still need for more researchers to explore local flora for their potential use as alternative colourants for textiles application. (Pan et al., 2003).

2.2.1.1. Advantages and disadvantages of natural dyes

The advantage of natural is that unlike synthetic dyes which are synthesized from petrochemical processes, natural dyes are friendly to the environment. Some dyes like madder are considered as host in tea gardens while indigo is renewable and biodegradable i.e. the waste residue after extraction is used as fertilizer for crops thus eliminating disposal

problems. Natural dyes can be extracted from by- products of some industries, hence fit the zero emission approach (Samanta et al., 2009; Asif et al., 2010; Konar et al., 2011).

Secondly, natural dyes are obtained from renewable sources that contain value-added benefits to our health. Many natural dyes are UV protective (Chen et al., 2002, 2007; Zhang et al., 2010), antimicrobial (Gupta., 2004; Mohamed., 2013; Wangatia et al., 2015) and deoxidizing (Lee et al., 2002; Fenget al., 2007; Hwang et al., 2008; Lee et al., 2010) agents.

Thirdly, natural dyes can produce special colouring effects that cannot be produced by synthetic dyes. The shades produced are usually soft, lustrous, soothing to the human eye and are polygenetic (Konar et al., 2011; Sanjeeda et al., 2014).

The drawbacks associated with usage of natural dyes is the low to medium fastness properties especially poor light fastness. Almost all natural dyes except substantive dyes need fixation with mordants such as metal salts which are toxic and environmentally unfriendly. Natural dyes also have poor reproducibility, particularly the plant sources since they are affected by environment conditions like varying planting time, place and species. Other disadvantages include: non-availability due to difficulty in collection, bulk isolation of dye-stuff, standardization of dyeing procedure, colour yield and complexity of the dyeing process.

2.2.2.2. Future use of dyes

Natural dye itself is considered good to the environment. However, the extraction method, mordanting and dyeing methods used may not be environmentally-friendly, hence the need

for developing dyes and techniques that are as green as possible. This includes extraction of natural dyes from wastes of other industries; new methods of improving extraction/dyeing efficiency, use of biodegradable mordants extracted from natural sources, environmentally green treatment of fabrics to improve dye uptake, minimizing environmental pollution and energy consumption and dyeing of synthetic fibres with natural dyes. In order to minimize pollution during mordanting, natural mordants such as myrobolan, mango bark, tea leaves, pomegranate, cow dung as well as lemon juice can be used. For this research, mango bark has been chosen for use.

2.2. EXTRACTION METHODS OF NATURAL DYES

The control loop for modelling a dye bath first requires the monitoring of the bath, followed by modelling the parameters of the bath, and lastly controlling the process to achieve the target result (shade). In order to maximize the colour yield for suitable application onto the textile material, extraction of colourant from its source as a vital step, requires standardizing and optimizing extraction process and variables. This is of commercial significance because it leads to a reduction of the cost of extraction and dyeing process by limiting on wastage of samples.

Natural dyes as demonstrated in Figure 2.8 have been extracted using different methods such as; aqueous method, enzyme assisted extraction, supercritical fluid extraction, alcoholic/organic solvent extraction, and soxhlet extraction method using either alcohol or benzene. Using these methods, the mixture is filtered, evaporated and dried using ultra

filtration equipment, centrifuge rotary vacuum pump or extraction under reduced pressure, so as to obtain a solidified sample.

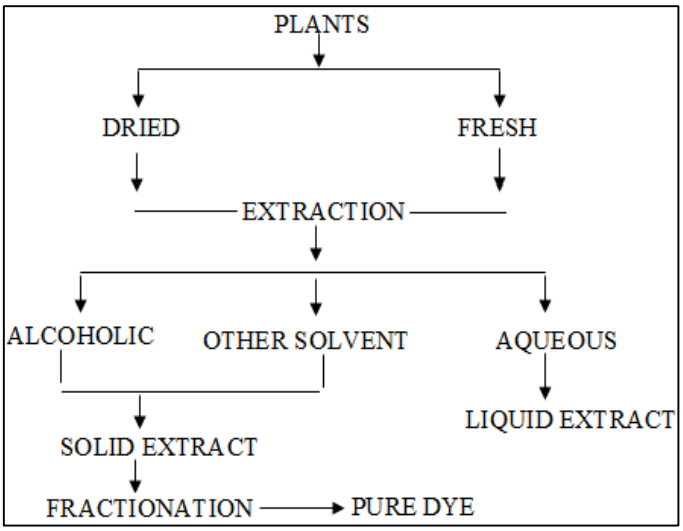


Figure 2.8: Simple illustration of natural dye extraction process

As a rule, vegetable dyes are extracted by pounding or cutting up the colouring material, immersion in water, heating to just below boiling point, and simmering until the colour has been fully extracted. Extraction can therefore be defined as the separation of desired colour components by physical or chemical means, with the aid of a solvent or aqueous media (Cordon., 2007; Konar et al., 2011). The common solvents used are water, hexane, ethyl acetate, ether, benzene, chloroform, methanol and ethanol. These are commonly used in combination with other technologies such as solidification/stabilization, precipitation and electro spinning (Bechtold et al., 2003). Extraction of bioactive compounds is influenced by various process parameters such as solvent composition, pH, temperature, extraction time and solid to liquid ratio. However, optimum conditions of extraction can be determined by

varying extraction parameters of the colourant and then measuring the optical density of the corresponding extracts using a spectrophotometer.

2.2.1. Extracting using aqueous solution

This type of extraction also known as the traditional/conventional method has been used to extract natural dyes from diverse sources. The main medium of extraction is water with or without addition of salt/acid/alcohol or alkaline. For optimal extraction conditions, the finely cut material or plant part is dissolved in measured quantity of water and extraction carried out under varying conditions such as extraction temperature, time, pH, material to liquid ratio, concentration of salt and mordant. In each case, the optical density or absorbance value of the aqueous extract can be evaluated using UV-Vis absorbance spectrophotometer, FTIR and other chromatography measures.

Various scientists have carried out experiments on extraction of natural dyes using this method. Grover (2011), extracted natural dye from the floral parts of *Woodfordia fruticosa* and applied it on cotton fabrics. The collected floral parts were divided into three parts and natural dye extracted in three different manners. The first method involved preparing an aqueous solution (10g of flowers in 100mL distilled water) and extraction carried out at temperature ranges of 80-85^{0}C. In the second method, 10g of uncrushed flowers were placed in distilled water and the pasty mass was for 10-15 days. After extraction, the extract was filtered and used for dyeing. In method three, 10g of crushed flowers were placed in a pot, left undistorted for 20-25 days and thereafter filtered through a piece of cloth and used for dyeing. The results established that the second method which gave a dark yellow-brown was the paramount extraction method (Grover et al., 2011).

In another experiment, colourant was extracted from the leaves of eucalyptus hybrid (*grewia optiva*) using aqueous method under varying conditions (Mongkholrattanasit et al., 2011). Gupta further reported on extraction of natural dyes from overnight soaked wattle bark using distilled water as a solvent. After extraction, 15-20% of residual powder was obtained. In another experiment, he extracted marigold and chrysanthemum dyes by boiling dry petals with acidified salt water (Gupta., 1998). Aqueous filtrates have also been used to assess various activities such as antioxidation, UV protection and antimicrobial activity. An example is Eltaweel (2013), who assessed antimicrobial activity using methanol and aqueous suspensions of onion extracts. For extraction, 50gm of onions were measured, washed with distilled water, cut into small pieces and finally squashed. Squashed preparation was done using 50ml of methanol, left to stand for 8hrs with a 10 minutes interval shaking. The extract was then filtered using muslin cloth followed by Whatman No.1 filter paper. The filtrate was evaporated to dryness at 45^0C and then stored in a sterile bottle under refrigerated conditions for use in the dyeing process (Eltaweel., 2013).

The common procedure associated with aqueous extraction under normal conditions is boiling either the dried or fresh samples from low temperatures to the boiling point of water, cooling the filtrate, filtering and storing it for further analysis. However, to optimize the extraction method of colour components in aqueous media, the sample/material is dried, finely cut, ground to powdered form, and finally extracted in water under a standard process. The extraction process of dye liquor is then carried out under varying condition such as extraction time, extraction temperature, pH of extraction liquor, concentration of colour/source material and material to liquor ratio (MLR). In each case, the optical density

or absorbance value at a particular (maximum) absorbance wavelength for the aqueous extract of the natural dye material can be estimated using UV-Vis absorbance spectrophotometer (Konar et al., 2011; Samantha et al., 2009). The continued usage of this technique has led to the optimization of extraction conditions of some natural dyes such as pomegranate rind, babool and marigold as illustrated in Table 2.3.

Table 2.3: Optimized aqueous extraction conditions

Name of dye	Procedure	Temperature(ºC)	Time (mins)	pH	M:LR
Pomegranate Rind	Pre-cut and dried rind is crushed to powder form. Residue is filtered to 40% (w/w)	90	45	11	1:20
Babool	Sun-dried pre-cut chips of babool bark are crushed to powder form and extracted in water.	100	120	11	1:20
Marigold (Genda)	Dried petals of marigold are crushed to powder and extracted. Residue is filtered	80	45	11	1:20
Catechu (Khayer)	Pre-dried powder of catechu is crushed to powder and extracted in aqueous medium.	90	Not specified	12	1:20
Jack fruit wood	Pre-cut and dried chips of jack fruit wood are crushed to powder form.	100	30	11	1:10
Red sandal wood	Dried pre-cut chips are crushed to powder form	80	90	4.5	1:20

After the extraction process shown in Table 2.3, the samples are filtered to obtain 40% (w/w) of a clear aqueous solution. This method (aqueous method of extraction) has been reported to be amongst the best extraction methods (Deo et al., 2000; Sarkar et al., 2005, 2006; Saxena et al., 2001). This is because with water, it's assumed that the inevitable solvent residue is not harmful. In contrast to this, in industrial solvents, maximum residues are defined for a certain purpose. Water also preferentially extracts polar compounds such as plant pigments and tannins since these need some special post treatment like ion exchange and caustic wash (Jones et al., 2006; Hans., 2011). Therefore, for the extraction of natural colourant from

Allium burdickii, pre-cut and dried chips of bulbs and leaves will be crushed into powder form, and the pigment extracted in aqueous solution under varying extraction conditions.

2.2.2. Solvent extraction

Flavonoids and anthocyanins are soluble in polar solvents with the glucosides and aglycones more soluble in water and alcohols respectively. These phenolics are commonly extracted from plant materials with water/alcohol or methanol/ethanol mixtures acidified with mineral acids (Harborne., 1989; Costa., 2000; Samantha., 2007) to prevent the degradation of the non-acylated anthocyanin pigments. This method has been applied successfully in the extraction of a variety of organic compounds ranging from herbs to other plant material, as well as natural colourant from natural source dye materials. Literature relating to the extraction of natural dyes using solvent extraction technique includes Manasa (2013) who used 50% ethanol and methanol for the extraction of natural dye from onion skin powder.

After preparation, the solutions were soaked for 1, 2 and 3 days respectively, thereafter filtered using Whatman No. 1 filter paper and used for the estimation of total physico-chemical parameters present in the dye. The study established that for the extraction of quercetin, rutin and total phenolic content, methanol gave the best results (Manasa et al., 2013). Sharif (2010) also dried onion skin samples (approximately 2.5g), mixed them with Diatomaceous Earth (ratio of 1g sample: 0.2g DE, to prevent aggregation of sample particles during extraction) and employed Pressurized Liquid Extraction method for the extraction of dye. After extraction, samples were re-dissolved in methanol for extraction using acidified methanol (Sharif et al., 2010).

The extraction of anthocyanins can be done using one solvent with various solvent techniques as demonstrated in the article above (Sharif et al., 2010), or a mixture of solvents with acid like Geetha (2011) who treated 0.5gm of onion peel with 10ml of two different solvents (methanol and acidified methanol). The solution was then centrifuged at 10,000 rpm for 10 minutes and the supernatant analyzed. Methanol emerged as the better solvent followed by acidified methanol, because it extracted more flavonoids (Geetha et al., 2011).

This method has been used to extract other natural dyes. Orska-Gawryś (2003) used High Power Liquid Chromatography /reversed-phase HPLC with diode-array and UV–Vis spectrophotometric detection for extraction and identification of natural dye extracts from archeological textiles on wool and silk fibers. Extraction of dye was carried out with HCL solution containing ethanol and warm pyridine. For pyridine extracts another mobile phase with an optimized gradient of organic modifier concentration was used. Shotipruk (2004) extracted anthraquinones form the roots of *morinda citrifolia* using pressurized hot water extraction (PHWE) method at different temperatures of 100, 170 and 220^0C. The study showed that the extraction yield increased with increase in temperature resulting into increased solubility, whereas pressure did not have an effect on the extraction yield. Kumaresan (2012) also employed ethanol in the extraction of eco-friendly natural dye from the stems of *Achras sapota* and flowers of *Spathodea campanulata* and compared their colour strength and fastness properties. The research found that a dye was present in both the stem and flowers (Kumaresan et al., 2012).

However due to the rigorous environmental regulations, Supercritical Fluid extraction (SCFE) technique has gained wide acceptance in recent years as an alternative to

conventional solvent extraction for separation of organic compound in many analytical and industrial processes. This method has also been applied successfully in the extraction of organic compounds from herbs and other plant material as well as natural colourant from natural products. Mohamed (2013) in a vitro study for example, used methanol extract from *Allium cepa* plant to assess the antimicrobial activity on Staphylococcus aureus (Mohamed., 2013). In another experiment, Osabohein (2014) carried out research to assess the dyeing and colouring potentials of ethanol extracts from the leaves of guinea corn and the skin of onion. The leaves of guinea corn (*Sorghum bicolor*) and skins of onion (*Allium cepa*) were collected, chopped, dried and ground to fine powder to allow most intimate contact with solvent (Stahl., 1965). Measured quantities of pulverized samples were then fed into the soxhlet extractor and mixed with absolute ethanol as the solvent in a ratio of 1:50 (powdered plant sample to ethanol solvent). The mixture of solvent-sample was thereafter refluxed for 3 hrs. The extract phases generated through several operations of the extraction process were distilled to recover parts of the solvent before evaporating to dryness to obtain dried solid dye samples. The crude extracts were recrystallized using carbon tetrachloride as solvent and finally air dried to obtain purified dye samples (Osabohein., 2014).

Apart from the mentioned techniques above, other methods of extraction of natural dyes include ultrasound-assisted extraction (Kamel et al., 2009); supercritical fluid extraction (Gulrajani, 1992); microwave-assisted extraction and enzymatic extraction. Although the methods of extraction of natural dyes are vast, in this research, aqueous method and solvent (using ethanol and methanol) extraction method was employed because of lack of equipment. These methods have also proven that they yield good fastness properties (Shankar et al., 2007; Manasa et al., 2010; Rosa et al., 2010).

2.3. PURIFICATION AND CHARACTERIZATION OF NATURAL DYES

Colourants are characterised by their ability to absorb specific visible parts of the electromagnetic spectrum in the range of 380 -780nm. For good colouring property, it has to have high absorption coefficient of about 10,000 to 40,000 mol/cm. Furthermore, its properties should enable it keep up with coloured material, stable in conditions such as phytochemical, chemical and oxidation, and be harmless to human health. Studies on the analysis/ identification of natural dyes started as early as nineteen hundred thirties where a French chemist performed micro chemical analysis and achieved the result by colour reactions with different chemicals. Abraham (1964) then reported on another method of using infrared structural analysis. The identification of natural dyes advanced with time and since then till today, many workers have used various methods and techniques such as thin layer chromatography, to identify natural dyes in textiles (Agarwal et al., 1985; 2009). Currently, there are numerous ways of analyzing the chemistry of natural colourants such as UV-Vis spectrometry, Chromatographic analysis, FT-IR, NMR and Mass spectrometry. However, for each method, the colourant is prepared differently. Ultraviolet/Visible absorption (UV/VIS) and Fourier Transformed–Infrared (FT-IR) spectroscopies are used as qualitative tools for identifying and characterizing molecular structures and the characteristic absorption spectra that constitute the characteristic fingerprint of the colourant (Espinosa et al., 2012).

2.3.1. UV-Vis Spectrophotometry

In this method, the hue and absorbance of the dye is determined using UV-Vis spectral scan of aqueous or non-aqueous extract/solution of the purified natural dye whose UV-zone and visible zone range from 190 to 700 nm or higher. The presence of dye along this range is

indicated by peaks and troughs in different wave length. Peaks and troughs in visible zone indicate the main colour and absorption, while the UV-Zone with or without peaks, shows the property of the dye under UV-light which may be correlated with its fastness behavior. Various UV-Visible spectroscopic studies have been conducted by different scientists such as Erica (1995), who performed a number of UV-Vis spectral scan on a number of natural dyes namely madder, cochineal, neem, beet sugar and indigo using different solvents for extraction. Neem bark colourant showed two absorption maxima at 275 and 374 nm while beet sugar showed three absorption bands at 220, 280 and 530 nm. In another experiment, *Gomphrena globosa* flower colourant extracted in 2005 showed one major peak at 533 nm. The dye did not show much difference in the visible spectrum at pH 4 and 7.

Extractions, spectroscopic and colouring potential of the dye from ginger rhizome were studied using UV- Vis Spectroscopy. Reports indicate that the dye is soluble in hydroxyl organic solvents, giving one homogenous component of Rf. value 0.86 on chromatographic separation with a wavelength of maximum absorption at 420 nm. Furthermore, colour measurements and chemical analysis have been performed on extracts from Possur plant using Video Spectral Comparator and UV-Vis spectrophotometer respectively. Maximum absorbance of the crude dye extracted at different temperatures was measured at a wavelength from 250-600nm. The results obtained were compared with the traditional method of dye extraction and it was observed that at a maximum wave length of 477nm, colourant extracted from PHWE was higher than the traditional method (Razak et al., 2011). Jasmani also studied the chemistry of natural colourant extracted from the skin of onion. The separation and determination of anthocyanin was carried out by high performance liquid chromatography

with diode array detector. The major anthocyanin compounds that were identified were cyaniding 3-glucoside, cyaniding 3-rutinoside and cyaniding chloride.

Furthermore, Video Spectral Comparator (VSC) was used to measure the colour quality of the extracts based on the CIE-Lab System (Sharif et al., 2010). Anthocyanins have been extracted from red-onion skins using acetic acid: ethanol: water (1:80:19v/v/v) mixture solution. First derivative spectrophotometric method was utilized to determine total dyestuff in the skin of the onion (Gümrükçü et al., 2003). Many studies have been done in this specific area (characterisation of dyes) using various methods. However for this research, characterization of extracts from *allium burdickii* plant will be performed using UV-Spectrophotometer. One percent aqueous dye solution will be prepared and an aliquot solution subjected to a wave length scan in a micro-processor or computer attached to a UV-Vis absorbance Spectrophotometer at a wavelength ranging from 200-1000 nm.

2.3.2. Photochemical analysis

Biologically active plant chemicals other than traditional nutrients that have a beneficial effect on human health have been termed phytochemicals (Hasler., 1998). They are the purely energetic compounds that occur in edible foods that when ingested have the prospect to avert or hold up the inception of an ailment. These are usually visible plant parts such as roots, stems, leaves, flowers, barks, tubers and seeds. The lofty quantity of organo-sulphur compounds is one of the major characteristics of the genus *Allium* (Lekshmi et al., 2015). *Allium sativum* (garlic) and *Allium cepa* (Onion) are the two food ingredients widely used in this gastronomy. There are four major groups of compounds found within onions that have health benefits when consumed by humans. These are: flavonoids (including those that

provide the yellow and red pigmentation in onions). This compound is the predominant pigment in onions with flavonols and anthocyanins especially derivatives of cyanidin existing in red onions (Lanzotti., 2006; HMPC., 2012). Flavonoids, majorly proportions of quercetin, isorhamnetin and their derivatives are present in both the bulbs and leaves of onions. They (flavonoids and tannins) are considered very useful substances during the dyeing process because of their ability to fix dyes with n fabrics (Mongkholrattanasit et al., 2011; HMPC, 2012).

Onions also contain a high concentration (35- 40% dry weight) of fructans (energy store for the plants) which constitute a major portion of the water carbohydrates. The third main group of phytochemicals, the sulphur compounds are formed when an onion is cut and thereafter the cell walls disrupt to produce allinase enzymes which rearrange forming various compounds like cepaenes, thiosulfates and onion lachrymatory factor. This derivative is used in plant defence. Saponins are a diverse group of biologically active glycosides widely distributed in the plant Kingdom. They are used for protection against pathogens (Darbyshire., 1978, 1981; Hedges et al., 2007). The occurrence of these compounds in *Allium* species including *A.cepa, A. sativum and A.porrum* has been reported by various authors such as Ponmozhi (2011), who employed aluminium calorimetric method for the confirmation of presence of flavonoids while using methanol and acidified methanol for the extraction anthocyanins from Pithecellobium- dulce fruit pericarp. His study confirmed the presence of flavonoids in the fruit pericarp and quantities extracted as 324 and 29mg/g for acidified methanol and methanol respectively (Ponmozhi et al., 2011).

Laleh (2006) studied the effect of light, temperature and pH on the stability of anthocyanin pigments in four berberis species after extraction of the pigments using acidified ethanol. The study established that hydroxylation of organic acids resulted into more stable molecules, however, co-pigmentation affected the stability of anthocyanins. The study further demonstrated that the presence of light accelerated the destruction of anthocyanins as compared to absence of light (Laleh et al., 2006). Other studies about the occurrence of this components in *Allium* species include (Archbold., 1940; Bacon., 1959; Darbyshire., 1978, 1981; Gümrükçü et al., 2003, 2008; Fan et al., 2008; Lanzotti et al., 2006; Rosa et al., 2010). However, for this research, flavonoids, carbohydrates, proteins, phenols, tannins and saponins were considered.

2.4. APPLICATION OF NATURAL DYE ON COTTON FABRICS

Colour obtained from multitudes of plants, animals and fungi has been used to colour skin, hair, food we eat, clothes and other different kinds of natural fibers that have been collected, examined and analyzed as sources of raw materials for textile industries (Samanta et al., 2007; Konar et al., 2011). The most common taxonomy of natural fibers used are those classified by botanical type. Using this system, there are six basic types of fibers namely; Bast/core fibers such as jute, flax, hemp, ramie, grass and kenaf; Leaf fibers such as banana, sisal, agave and pineapple; Seed fibers such as coir, cotton and kapok and finally reed fibers such as wheat, corn and all other types such as wood and roots (Broadbent., 2001).

Ancient artisans transformed these available fibers (mainly long fibers) into fabrics, at first by hand and later using simple mechanical devices. The short fibers on the other hand were

first carded or combed, then drawn and finally spun by pulling with gradual twisting to produce yarn which was interlaced to form fabric. Techniques of fabric production and their colouration has subsequently developed over many hundreds of years with the most suitable fibers being natural fibers. These have then become the basis of the textile industry in the world (Broadbent., 2001; Cordon.., 2007). Today, cotton, wool, jute, flax and silk are the most common important natural textile fibers used, while cotton remains the most common conventional fiber preferred. This fiber has been used in various textile applications such as dyeing.

Dyeing occurs at any stage of textile manufacture either on loose fibre or on the intermediate forms such as sliver or yarn, fabric or towards the end of the manufacturing cycle including garments and finished articles. The art of colouring with natural dyes which dates as far as the ancient civilization of Egypt, Samaria, Rome, Greece, Mexico, India and China (Cardon., 2007; Samanta., 2009; Gupta., 2004) is where colour is applied either on the fibers, yarns (known as yarn dyeing), fabric or on finished textile products, by either printing or dyeing (Saxena et al., 2014; Cordon., 2010). Printing is the localized application of different dyes to different specific areas on one face of a fabric according to a predetermined design, while the art of dyeing on the other hand is the method that involves contact between an aqueous solution/ dispersion of dyes and the textile material, under conditions that promote substantivity for the production of uniform colouration.

This can be attained through the following approaches;

a) Direct dyeing: where the dye in the aqueous solution in contact with the material is gradually absorbed into the fibres due to its inherent substantivity.

b) Dyeing with a soluble precursor of the dye which forms an insoluble pigment deep within the fibre on treatment after dyeing.
c) Direct dyeing: which follows a chemical reaction of the dye with appropriate groups in the fibre.
d) Adhesion of the dye/pigment to the surface of the fibres using an appropriate binder.

Dyeing can be carried out in any medium say alkaline, acidic or in a neutral medium, using any fibers such as natural/synthetic, fabrics like woven/knitted with either synthetic or natural dyes. For uniform colouration during the dyeing process, factors such as the selection of proper dye according to the textile material to be dyed, fiber characteristics like denier, staple length, luster, cloth construction and selection of the method of dyeing the fiber, yarn or fabric should be critically observed. The process of dyeing substrates may also necessitate additional treatment while in the dyeing machine and upon finishing the dyeing process, the material is scoured to remove adhering solution, unused and unfixed dyes.

Different researchers have reported on the available methods of dyeing fibers such as cellulosic, protein and synthetic with different synthetic and natural dyes. For example, Prabhavathi (2014) improved the colour fastness of selected natural by optimizing the dyeing conditions of cotton fabrics. His study established that the depth of shape increased with increase in mordant concentration (Prabhavathi et al., 2014). Kamel (2009) used ultrasonic and traditional method of dyeing to study the dyeing properties of cotton fabrics with crocus sativus natural dyes. Optimization process was done by considering different pH conditions, type of mordant and concentration of dye. (Kamel et al., 2009). Mirjalili (Year) also dyed Polyamide fibers using dye extract from Green Walnut Shells. The polyamide fabric was

dyed in Ahiba dyeing system with walnut dye. The dye bath comprised of 1% dye and 3% acetic acid and mordant respectively. The liquor ratio used was 1:40 while raising the temperature to 100^0C by a thermal gradient at 2^0C/min for 60minutes.

Grover (2011), prepared natural dye from floral parts of woodfordia fruticosa and used it to dye three different cotton yarns and fabrics. In the experiment, the effect of dyeing with various mordants and the colour fastness of dyed fabrics. A dark yellow-brown dye which had no effect on the human skin was obtained. The investigation also revealed that the use of combination of mordants in various ratios gave different shades and colour fastness results. The study concluded that instead of using synthetic dye fixates, some vegetable fixing agents can be used (Grover et al., 2011). Vegetable fixing agents' also known as natural mordants are extracts obtained from certain plants or organic materials. Usually, these plants or organic compounds have high contents of tannins such as myrobolan obtained from *Terminalia chebula* fruits, mango bark from *mangifera indica*, Lemon juice and vinegar (Raja et al., 2008; Prabhu et al., 2011). Very little attention has been paid on improving colour fastness with natural fixing agents as sources of dyes and colourants. However some studies have been made such as Prabhavathi (2014) who used five fixing agents namely vinegar, lime juice, alum, ammonia, calcium chloride and myrobolan to mordant fabrics using eucalyptus bark dye. The study concluded that all agents gave good fastness results, vinegar giving the most excellent results (Prabhavathi et al., 2014).

In another study, Wangatia (2015) compared mango bark mordanted cotton samples with those mordanted using alum. The investigation established that fabrics unmordanted and those pre-mordanted with mango bark had the highest K/S values. The investigation further

showed that post mordanting with mango bark gave better wash fastness performance. Further studies on dyeing with natural dyes include: Önal (1995) who dyed 1.5g of cotton fabrics at a varying pH of 2-8 for one hour at 90^0C with 0.1M mordant in 100ml dye bath. The solution was filtered and cooled. After analysis of results, pH 2, 4 and 7 were found as the most efficient pH whereas pH 8 didn't give desired results (Önal., 1995). Kamel (2005) also used both the traditional and ultrasonic method of dyeing to dye cotton fabrics (Kamel et al., 2005). In 2008, woollen fabrics were dyed with anthocyanin pigments from red onion.

Kumaresan (2012) also wetted out silk samples and dipped them in a dye bath containing required amount of dye and water and carried out dyeing for one hour at 60^0C (Kumaresan et al., 2012). The discussions that have been laid out so far show that scientists have performed dyeing of natural fibres under different conditions. The influential factors amongst many include: dyeing temperature, duration of dyeing, concentration of salt, concentration of mordant, pH, type of mordant, dyeing procedures, type of fabric and fabric processing techniques. Optimized conditions are however required in order to yield very good fastness properties for cotton, silk and wool fabrics. Through literature review, monitoring of dyeing temperature, duration of dyeing, pH and concentration of mordant have been proven as the most essential factors (Kamel et al., 2005; Cordon., 2007; Gordon., 2016).

However in comparison with natural fixing agents, the artificial colouring agents (synthetic mordants) show greater resilience and stability when exposed to oxidation, changes in temperature, pH and other factors. Often, these factors led to a shift in the resonance structures in the dye molecules while pH is known to change the spectra of dyes significantly. This is because at higher pH values, protons can be abstracted, which change the electronic

configuration of the dye molecule. Since absorbance of light is a factor of the electron configuration, any change in the configuration yields a change in the spectrum. In general, anthocyanins show colour variation caused by pH or metal chelation changes therefore, for proper measurement of dye bath absorbance, calibration of dyes should be done at specified pH levels. Apart from dyeing variables, it's also important to note that the colour coordinates of anthocyanin dyed fabrics is influenced by the pH values of dyeing bath, metal mordant and mordanting processes, which in turn reflects the basic colour effects of fabrics dyed using anthocyanin extracts as natural dyes.

2.4.1. Influence of the major dyeing conditions on substrates

Research in this area has been carried out on substrates such as silk, cotton, jute, blends mainly cotton/polyester, knitted fabrics and synthetic fabrics. Cotton has found long use as a textile fiber due to its outstanding characteristic and excellent physical and chemical properties. Conventionally, it has been dyed and using this approaches, researchers have studied effects such as dyeing temperature, time, pH, conductivity, sampling rate, concentration of mordant and salt on different natural and synthetic fabrics. The technique of dyeing is chosen based on the nature of the dye. For example; Angela and Little, 1977 combined the colour pigments from strawberry jam and packaged strawberries at the temperature of 37.7^0C. The recorded data for pH 2, 3 and < 1 showed that destruction of anthocyanin pigments increased with increase in pH. Nisar (2007) studied the dyeing properties of Natural dyes extracted from eucalyptus camaldulensis. The dye was applied on cotton fabric at different dyeing conditions (temperature, time and concentration of salt) using direct dyeing method. The study showed that the dye obtained displayed fairly good saturation on cotton with medium to good fastness properties. The strength/S of the dye

extracts obtained at room temperature was minimum, slightly better at 60^0C and maximum when extraction was carried out at 90^0C. As pertaining time and salt concentration, K/S value increased to maximum when stirring was done between 80 -100 minutes.

In another experiment, Ali (2010) established that the colour strength of wool fabrics dyed with red prickly pear dye increased with increase in temperature (Ali et al., 2010). Razak (2011) used Pressurized Hot Water Extraction Method (PHWE) to study the effect of temperature on the colour of Natural Dyes from Possur plant. The effect of PHWE was examined at temperatures 50, 75, 100 and 125^0C. Using a mass to liquor ratio of 1: 20, 2g of grounded powder were boiled using a hot plate for 30 minutes at atmospheric pressure. The observation were that;

a) At different temperatures, different colour shades were attained.
b) Temperature was the main factor that affected extraction efficiency and solubility (Razak et al., 2011).

There is ongoing research concerning the analysis of the effect of temperature on anthocyanins extracted from onion plants viz optimizing temperature conditions as reviewed. Önal (1995) performed the dyeing of wool, feather leather and cotton at 80, 35-40 and 80^0C respectively. The temperatures yielded consistently good to very good colour strength except for feather leather where low temperatures were used. (Önal., 1995). Gulsah (2008) studied the effect of amount of mordant, kind of mordant and different salts on dyeing of wool fibers. The study established an optimum temperature of 100^0C, pH 4 in the dyeing of woolen fabrics with red onion anthocyanin pigments (Gümrükçü et al., 2008).

Furthermore, in the analysis of the dyeing properties of cotton fabrics with cedrela toona bark dye, it was observed that with both the conventional and ultrasonic method, better colour strength was realized at 100 and 80^0C respectively. The reviews show that different natural dyes have different optimal temperatures but better colour strength, good dyeing conditions and acceptable fastness can be obtained with increase in temperature. However, increase in temperature results into increased percentage yield of dye and increased destruction of anthocyanin. Therefore to obtain substantial results while using the conventional method, the dyeing temperature of natural dyes with anthocyanins should range from 60- 90^0C. This is so because high temperatures accelerate degradation of the anthocyanins (Sharif et al., 2010; Lioe et al., 2012; Kopsell et al., 2010).

2.4.2. Optimization of process variables

Since antiquity, many guidelines for optimization of dyeing processes, though reluctantly observed by many textile industries, have been developed and used for analysis. These among many include investing in equipment and technical skills in dye house laboratory, skepticism of management and controlling dye bath conditions. These methods have evolved with time and today, the competitive market has forced textile manufacturers to look for ways of increasing productivity and resource efficiency without sacrificing quality. Thus the need to evaluate and improve process technology. Approaches such as dye bath analysis, response surface methodology and exhaust dyeing method have been employed.

Response Surface methodology (RSM) is a design statistical tool aimed at process optimisation and analysis of experiments (Hamanthraj et al., 2014). It is also an efficient experimental strategy for determining optimal conditions of a multivariable system rather

than optimisation by conventional method which involves changing one independent variable while keeping the other factors constant (Silva et al., 2007; Fan et al., 2008). Besides that, conventional methods are disadvantageously time consuming and incapable of detecting the true optimum condition of a dye because of the absence of interactions among factors and defining the effect of the independent variables alone, or in combination with the processes (Kaur et al., 2014; Karthikeyan et al., 2010). RSM design include Central composite (CCD) and Box- Behnken design (BBD) of experiments that have been applied for optimisation of extraction and dyeing parameters.

The RSM design depends on the number of design variables or factors, but adopts a DOE that gives a total number of ten factors ranging from two to ten except for BBD which excludes 2 and 8. CCD codes the factors into five levels as -1.414, -1, 0, +1 and +1.414 resulting into many experimental runs while BBD codes the factors into three levels as -1, 0 and +1 creating designs with desirable statistical properties (Yim et al., 2013). For this study, a BBD comprising of four factors (dyeing temperature, dyeing time, solid to liquid ratio and concentration of mordant) was adopted. This method was preferred as design model because it investigates independent process variables by defining the effect of the independent variable, whether it's alone or in combination in the process. Furthermore, the model resulted into relatively few combinations of the variables which were adequate for the estimation of potentially complex response functions (Bas et al., 2007; Hamanthraj et al., 2014).

The art of dyeing with natural dyes is being perfected in Africa. In West Africa, some communities in Mali such as the Bogolan community is dyeing fabric using Bogolan techniques. Their products which are on high demand globally are exported to Senegal,

Ghana, South Africa, France, Germany, Switzerland, Belgium, Japan, U.S.A and Canada. The Bamako, who rely heavily on species like *Anogeisuss leicarpa* export 520 tons of dyed clothes and products corresponding to 430 tonnes of dried leaves of *Anogeisuss leicarpa*. The use of these products has promoted African cultural values, supported cottage industries and in return improved livelihoods which indirectly have promoted related ventures like cotton and leather sectors (Jansen et al., 2005). In East and Central Africa dyeing of cotton substrates using natural dyes is picking up. Uganda also produces some really good raffia and banana stem basketry, particularly the Toro in western Uganda, who have the most intricate designs and still use natural dyes. Traditional products are easy to find, but the old methods have been adopted to make new items such as table mats and handbags for sale to tourists.

During the course of dyeing, whether on natural or synthetic fibres, it's very important to constantly monitor process parameters to ensure proper feedback on the effectiveness of the control algorithm, and the response of the system to the changes in bath parameters. In the case of pH, successful completion of many pharmacopeia tests, assays and application in various process dyeing stages requires adjustment to, or maintenance of a specified pH by the addition of buffer solutions. A buffer solution is a system (substance or combination of substances) that resists changes in the activity of an ion upon addition of substances that are expected to change the activity of that ion (the ion is in equilibrium with the substance capable of removing or releasing the ion). The amount of material that may be added to a solution without causing a significant change in ion activity is termed as buffer capacity whether it's added at low or high pH. The capacity of the buffered solution is adjusted to the conditions of use usually by adjusting the concentration of buffer substances.

Water itself is a buffering medium even in the absence of added buffering reagent (Lenoroc et al., 2016). There are various types of buffers but the most common types used are the mixtures of weak acids and salts of their conjugate bases for example the one used in this research: acetic acid/sodium acetate. The dissociation of acetic acid in this system can be written as:

$CH_3COOH \dashrightarrow CH_3OO^- + [H^+]$ and the dissociation constant $Ka = [H^+]$.

Where the acid dissociation constant is defined as Ka = [H+].

After buffer preparation, it should be stored in chemically resistant, glass-stoppered bottles of alkakli-free glass and used within 3 months of preparation. Solutions which become cloudy or show any other evidence of deterioration should be discarded.

2.5. MORDANTING OF NATURAL DYES

2.5.1. Types of Mordants

Natural dyes are non-substantive to textiles thus should be applied with the help of metallic salts or natural mordants that produce affinity for both the colouring matter and the fiber (Ferreira et al., 2004). Transition metal ions such as stannous chloride, ferrous sulphate, alum, chrome and copper sulphate have been used as mordants as they have strong coordinating power capable of producing weak to medium attraction or interaction forces that act as bridging materials thereby creating substantivity for the subsequent fiber. These salts combine with the fiber forming insoluble precipitates (fixing both the dye and mordant into

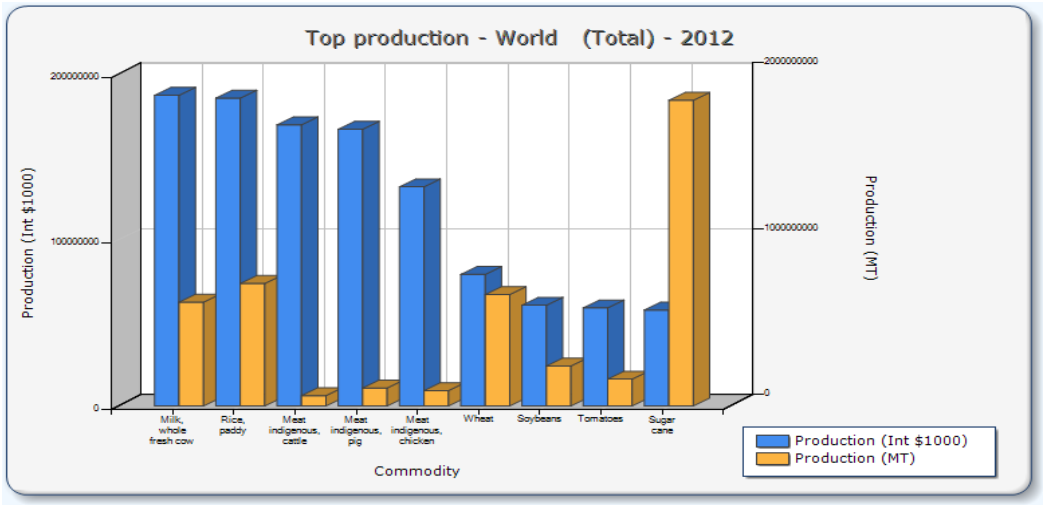
the fiber) and as a result form reasonable fastness levels (Konar et al., 2011; Samanta et al., 2009).

Many reviews have already been dedicated to developing mordanting agents which are non-toxic and ecofriendly. Some of the approaches exploited include the use of metals which are considered ecologically safe such as alum and iron sulphates; use of natural oil products, tannins and other natural plant extracts (Raisanen et al., 2001; Raja et al., 2008; Prabhu et al., 2011; Saxena et al., 2014). A mordant can be defined as a chemical agent used to set/fix dyes on fabrics through the formation of insoluble compounds with dyes i.e. facilitate the bonding of the dyestuff to the fiber. Mordanting on the other hand is the treatment of textile fabrics with metallic salts or other complex forming agents with the ability to bind the natural dyes onto textile substrates. This can be achieved by either pre, simultaneous, or post mordanting, using different selective mordants that result into the development of various shades, and increment in the dye uptake and improvement of colour fastness behavior of any natural dye.

There are different types of mordants but the major classifications are according to metal salts, tannins/tannic acid and natural oils (Singh et al., 2000). Amongst all, mordanting with metal salts such as aluminum, chromium, copper, Iron and tin has been the most exhausted method while less had been done concerning the use of natural mordants like tannins. Tannins/tannic acid are bitter and stringent substances occurring as excretions in plant parts such as barks, leaves, cutch, fustic, black oak, galls, pomegranate and fruits. Tannic acid occurs in many types of vegetable substances but nut galls are the richest source containing about 60-70% tannic acid (Konar et al., 2011; Saxena et al., 2014) The main tannins used in place of tannic acid on account of their low prices are natural tannins like myrobolan, mango

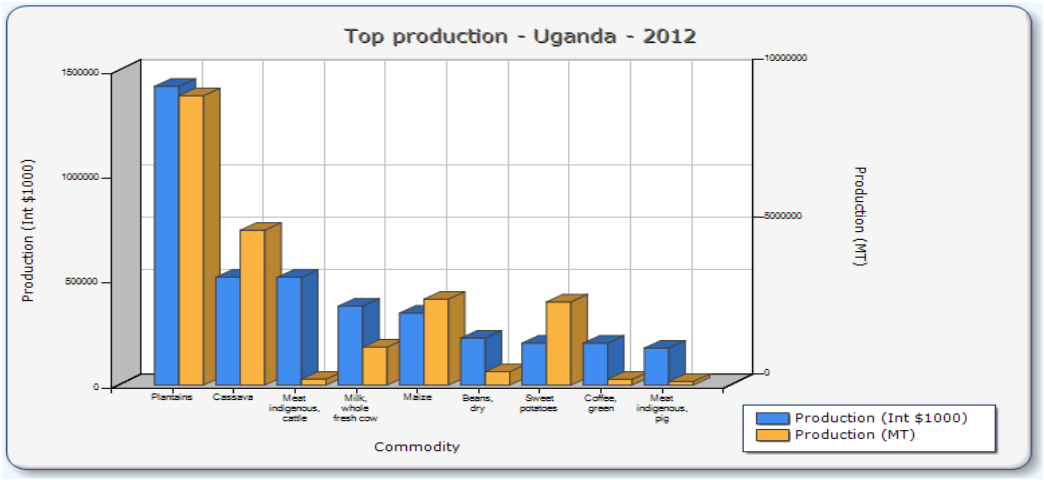
bark and leaves and tea. These mordants can be a clear solution (aqueous) or added into the dye bath with the fiber (powder). Dried myrobolan (*Terminalia chebula)* fruits for example is a natural dye with a have high tannin content used for producing bright yellow shades. The mordant has been used to fix different natural dyes onto textile substrates majorly cotton and cellulosic fibers. Besides application in textile industry, it has been established to have medical properties such as antimicrobial and antifungal.

The mango bark another mordant obtained from mangifera indica L., is an arborescent evergreen tree with simple, alternate, oblong ovate to oblong lanceolate leaves that are spirally arranged and produced in flushes. The mango is one of the most important fruits in the world. They are grown throughout the tropics, from the Caribbean to Africa, South-East Asia, Australia, as well as India, where the history of the fruit goes back over 6,000 years and closely connected to the Hindu religion. As long ago as the 16th century, mangoes had been distributed via cultivation throughout the Indian subcontinent, and eventually to all tropical regions of the world. Currently mango fruit production ranks 20th in total production among major fruit crops, worldwide, after Musa, (bananas and plantains, citrus (all types), grapes and apples (FAOSTAT DATABASE RESULTS, 2012). In the Africa, the production is approximately 1,672,828 metric tonnes (MT) with the major producing countries as Egypt, Madagascar, Nigeria, Sudan, Tanzania and Democratic Republic of Congo.



Source: FAOSTAT DATABASE RESULTS, 2012

In Uganda, the production is estimated at 500,000MT.



Source: FAOSTAT DATABASE RESULTS, 2012

The parts of the mango tree commonly used are the fruits and leaves. The mango bark has been used as a source of firewood in local communities, however it's one part that has not been fully utilized yet research shows that the bark possesses 16% to 20% tannin thus can be

employed for tanning hides. It also yields a yellow dye and with turmeric and lime, a bright rose-pink colour is obtained. Little research has been done on its use as a source of tannins. For example Wangatia (2005) who used extracts from the bark of mango tree (*mangifera indica*) as mordants. The extracts formed a yellow colour. (Wangatia et al., 2015). The tannins play an important role in cotton dyeing and are largely used for preparing cotton so as to enable it retain coloring matter permanently.

The main function of an oil mordant is to form a complex with alum when it is used as the main mordant. This is because oil is insoluble in water and doesn't have affinity for cotton hence won't easily be washed out from the treated fabric. Oil mordants contains fatty acids such as palmitic, stearic, oleic, ricinoleic and glycerides. During mordanting, the -COOH group of the fatty acids reacts with metal salt leading to the formation a COO-M, where M denotes the metal. Among all the kinds of oil available, sulphonated oils are well known owing to their better metal binding capacity than the natural oils. They are usually used in dyeing of madder to obtain Turkey red colour. All these mordants find application in the mordanting of numerous textiles such as silk, cotton, sisal, blends of fabrics, synthetic fabric and dyeing madder to obtain Turkey red colour (Samanta et al., 2009; Kumaresan et al., 2011; Grover et al., 2011; Saxena et al., 2014).

However, mordanting with salts such as chrome, copper and tin although they fix the dye well while providing an alternate palette, have been proven to cause health hazards in the sense that they produce toxic waste which requires special disposal hence not recommended for use. On the other hand, mordants such are alum, iron and tannins are safer and can produce myriad colours when used in conjunction with the appropriate natural dye. This is so because

they are naturally present in the environment in large amounts (Saxena et al., 2014; Cordon., 2010). Metals salts of iron, Aluminum, iron, chromium were used as mordants by traditional dyers, alum however did not combine as readily with cellulosic fibers as it does with protein fibres.

Mordanting can be attained by either pre mordanting (before dyeing), simultaneous mordanting (dyeing the fabric and mordanting at the same time) or post mordanting (after dyeing) using different types of mordants. The selection of mordant and mordanting techniques depends on conditions such as the nature of the substrate, its affinity for the substrate and type of dye to be used. Extensive work has been reported for the dyeing of textiles with natural dyes while adopting specific mordanting systems for a particular textile material such as (Jahan et al., 2000; Prabu et al., 2001; Gupta., 2004); Ferreira et al., 2004; Sarkar et al., 2005, 2006; Saxena et al., 2001; Sankar et al., 2005; Jansen et al., 2005; Cordon., 2010; Chengaiah et al., 2010; Zhang et al., 2010; Sharif et al., 2010; Saha et al., 2012; Basak et al., 2012; Lokesh., 2013; Yim et al., 2013; Saxena et al., 2014; Prabhavathi et al., 2014; Kaur et al., 2014; Wangatia et al., 2015; Lakshmi., 2015; Lenoroc et al., 2016).

2.5.2. Methods of mordanting Used in Dyeing with Natural Dyes

2.5.2.1. Pre-mordanting

Pre-mordanting is a technique which involves primarily mordanting the fabric before dyeing i.e. the mordant is applied to the fabric prior to dyeing. It’s the most common method of mordanting practised on cotton, cellulosic and some animal fibers such as cochineal because these often in unmordanted form don’t have affinity for many natural dyes. The advantage

of this method is that the standing baths can be reused many times after replenishing with the mordants. This makes the process economical as well as reducing the pollution load hence sufficient for large- scale application (Saxena et al., 2014; Cordon., 2010). The procedures for mordanting are;

i). Dissolve the mordant and added to a dye bath containing ample amount of water.

ii). Add the substrate and bring the whole mixture to boil for a period of about ¾ of an hour

iii). Cool the solution

iv). Gently remove the substrate to ensure even take-up of the mordant.

v). Rinse the substrate to remove unfixed dyes, dry under room temperature and analyze. The fabric can afterwards be dyed.

The disadvantage associated with this method is that there is a lot of fabric handling.

2.5.2.2. Simultaneous mordanting

As the name states, both the dyeing and mordanting process is carried out in the same dye bath and at the same time. For cotton and other cellulosics, the mordant is usually added to the dye bath at the start of dyeing so that both mordanting and dyeing processes take place concurrently (Saxena et al., 2014). The procedures for this method are;

i). First dissolve mordant in a separate bath.

ii). Transfer mordant solution to the dye bath and add the wetted fabric.

iii). Bring whole mixture to boil while stirring at intervals using a stirring rod.

iv). Simmering until maximum dye uptake.

v). Cool solution, remove fabric, rinse with mild detergent, dry and analyze.

Although this method is associated with less fabric handling, it gives colours that are not as permanent as pre-mordanted fabrics because mordanting is dissolved at a separate stage and later on introduced into the dye solution.

2.5.2.3. Post mordanting

In this method, the fabric after dyeing is treated with the mordant in a separate bath. The final colour is developed during the last phase. Iron salts are very often applied in this manner for producing grey and black colours (Saxena et al., 2014). The procedures are as follows;

i). Dissolve mordant in ample amount of water.

ii). During simmering (after dyeing), add solution to dye bath in the final five to ten minutes.

iii). Cool solution, remove substrate.

iv). Rinse with cold water to remove unfixed dyes, dry and analysis.

Tin and iron are often used in this way after pre-mordanting or simultaneous mordanting with another substance. This is because tin has the effect of blooming i.e. it enhances and brightens whereas iron saddens or dulls colours. This type of mordanting is quite satisfactory in the dyeing of several skeins with different salts in the same dye bath, because once combined with the fibers, the metallic ions do not react with one another. Many scientists have used these mordanting techniques in the dyeing of various natural fibers like cotton, silk, wool and synthetics such as polyamide and polyester (Vankar et al., 2007; Kumaresan et al., 2012; Mongkholrattanasit et al., 2011; Gümrükçü et al., 2003, 2008). Some of the studies that have

been conducted include; Teli (2009) who used $CuSO_4$ and $FeSO_4$ to study the influence of concentrations of mordants on cotton fabrics dyed with turmeric dyes. It was established that when fabrics were treated with tannic acid and then dyed with metal salts, the depth and performance properties of the fabric such as fastness to light, washing, rubbing (dry as well as wet) improved. Gulsah (2008) also studied the effect of amount of mordant, and kind of mordant on the dyeing of woolen fabrics with *Allium cepa. L* dye using all the three mordanting techniques. Suitable mordant quantity of 1g and mordants such as metals of Aluminum, Iron, Copper, Lead and Cobalt were used. The use of Iron, Cobalt and Aluminium gave maximum total colour differences with pre and post mordanting while for copper and lead, maximum total colour differences were observed in post mordanting. Nonetheless all the mordants except Aluminium hydroxide had their highest values of DE with together mordanting (Gulsah et al., 2008).

The action of a mordant on a substrate depends on various factors such as its concentration, kind of mordant used, type of substrate and the method of mordanting and dyeing. Usually, the type of mordant affects the fastness property of the dye and also changes the shade after dyeing. If the action of the mordant on the cotton substrate is hard (acidic mordant with an acidic dye), the best technique to employ is either pre or post mordanting because they limit the potential damage to the substrate (Wikipedia., 2016). Simultaneous mordanting is suitable when the dyer want to achieve little or no loss of the dye properties. The mordant chosen further has a marked effect on the final colour. However, each dye has different interactions with each mordant thus different shades can be obtained with the same mordant using different methods of mordanting (Elena., 2010; Asif et al., 2010).

Further collected works relating to the mordanting and dyeing of substrates with natural dyes include Sundarajan (2011) who used tannin acid, cow dung, lemon juice and pomegranate rind as natural mordants to standardize the dyeing effect of marigold and turmeric dyes on silk and knitted cotton fabric (Sundarajan et al., 2011). The study established that all the mordanted fabric showed good dye uptake. Kumaresan (2012) dyed silk fabrics using extracts from the stems of *Achras sapota* and flowers of *Spathodea campanulata*. Dyeing was performed under varying conditions using pre-mordanting, simultaneous and post mordanting methods. The findings were that the flowers of *Spathodea campanulata* with simultaneous method at three percent mordant concentration gave the best results (Kumaresan et al., 2012). Under different dyeing conditions, different mordanting methods yield various results as most of the mordants used generally affect the hue (shade) and purity of colour. Ali (2011) who studied the effect of pre-mordanting and post-mordanting of wool fibers with Aluminium sulfate, ferrous sulfate under different conditions reported that during pre-mordanting and post-mordanting with ferrous sulfate, there were huge changes in hue and a great deal of decrease in the chroma (purity of colour). The study further established that, alum and iron did not have any effect on fastness as appreciable increase in fastness properties occurred (Ali et al., 2011).

In another study, Deo and Desai (1999) dyed cotton and jute fabrics with aqueous extracts of tea containing tannins as the main colourant component. The dyeing was carried out with and without metal salts, using three different dyeing methods: pre-mordanting, meta-mordanting and post-mordanting. The colour of the fabrics was investigated using computer colour matching system in terms of K/S and CIELAB colour-difference values. Deep shades (K/S = 3.9) were obtained for jute in acidic media while cotton fabrics dyed in medium depths

gave a K/S value of 2.0 under identical conditions of dyeing. The resulting wash and light fastness of the dyed fabrics ranged from good to excellent. Many investigations have revealed that the use of combination of mordants in varying ratios, and use of gamma irradiations improves dyeing characteristics, gives different shades and improve colour fastness properties from fair to good. (Kumaresan et al., 2011, 2012; Bhatti et al., 2010).

CHAPTER 3 : METHODOLOGY

In this work a natural dye was extracted from wild onion plant. The effect of different concentration of mordants, pH, dyeing temperature and dyeing time using two extraction methods was studied by evaluating the fastness properties. The wild onion was collected from western region in Uganda and different plant parts such as leaves and bulbs were collected and used for experimentation. A summary of the methodology used is given in Figure 3.1. The substrate was procured from a factory in Kenya.

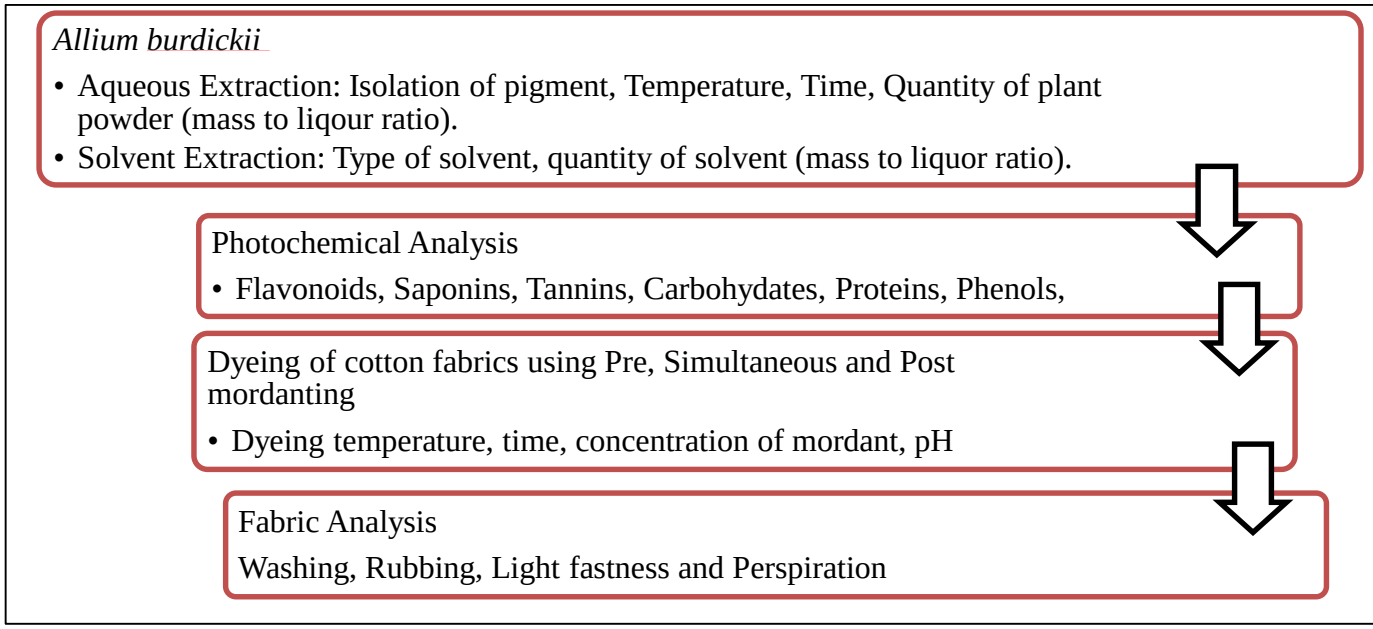


Figure 3.1: Flow map of methodology

3.1. EXTRACTION OF NATURAL COLOURANT

For standardization and optimization of a particular plant dye to maximize colour yield, cost of extraction as well as rate of dyeing, proper extraction conditions should be chosen.

Conventional method of optimization was employed and it involved selection of five factors namely type of dye, extraction method (aqueous and solvent), extraction temperature, duration of dye bath and mass to liquor ratio (Saikia et al., 2005).

The colouring substance that was used in this research work was extracted from *Allium burdickii* plant (Figure 5.1 and 5.2). The leaves and onion bulb of the plant were thoroughly washed with freshly prepared sterile distilled water and left to shade dry. For the onion bulb, after washing, the outer covering of the bulb was manually peeled off, rewashed again and finally left to shade dry (Eltaweel., 2013). After drying, the samples were cut into small pieces, grounded into powder using an electric blender, packed in clean sample containers and finally stored for analysis. Apart from the dye and the substrate other materials that were used included Solvents (distilled water, methanol and ethanol), formic acid, Lead chloride, buffer solutions, sodium sulphate, sodium acetate, acetic acid. The equipment that were used during the experimentations were water bath, Soxhlet apparatus, ST 10 Oahu's pH meter and UV-Visible Spectrophotometer.

3.1.1. Isolation of dyes

To optimize the pigment, a total of eight experiments were carried out using a water bath. 2, 4, 6 and 8gms of both leaves and bulbs were mixed in 100mL distilled water and extraction carried out at room temperature (for 2gm only) and 60^0C respectively for 60 minutes. The extracts were left to cool then filtered using Whatman No.1 filter paper. 1 ml of crude extract was diluted in 100mL distilled water and thereafter passed through the UV-Visible spectrophotometer for analysis.

3.1.2. Extraction method

3.1.2.1. Procedure for optimization of aqueous extraction of colourants

Different amounts (2, 4, 6, 8gms) of crushed *allium burdickii* bulbs were separately mixed in 100 ml pure distilled water and each extracted for 60 minutes over a water bath maintaining a temperature of 60^0C. After each process of extraction, the mixtures were removed from the water bath, left to cool, filtered using Whatman No. 1 Filter paper and the filtrates were analyzed using UV-Vis Spectrophotometer. For 4, 6 and 8gms, 1 ml of the total aqueous dye extract was diluted in 100 ml of pure distilled water. An aliquot was then introduced in a quartz cell (1 cm pathway) and analyzed in a UV/Vis spectrophotometer. A scan from 400 to 1000 nm was performed in order to generate the characteristic absorption spectra of the samples (Saxena et al., 2012; Espinosa et al., 2012).

3.1.2.2. Estimation of plant powder

5 samples of powdered *allium burdickii* bulb weighing 2, 4, 6 and 8gms were each placed in 250 Pyrex beakers and 100ml distilled water added. The mixtures were brought to boil over a water bath at 100^0C and subjected to stirring for 60 minutes respectively.

3.1.2.3. Determination of optimum solvent extraction conditions

Two solvents namely ethanol and methanol were used. The colourant was extracted by preparing ethanolic extract of powdered bulbs (2g in 80ml ethanol) placed in a 500ml capacity flask and extraction carried out at 25^0C, 40^0C (water bath boil) and 75-80^0C using a soxhlet apparatus placed over a water bath. The mixture of solvent- sample was thereafter refluxed for over 5 hrs. For the case of methanol, extraction with small additions of formic

acid was carried out at room temperature (Costa et al., 2010). The acid lowers the pH of solution and prevents the degradation of the non-acylated anthocyanin pigments. After extraction, the extract was evaporated using a condenser so as to concentrate the dye. The extract was then left to cool under room temperature, filtered using Whatman No. 1 filter paper and analyzed using UV- Spectroscopy.

3.1.2.4. Optimization of solvent ratio

The optimized solvent was thereafter used for optimization of ratio of water: solvent. Seven experiments were performed. 2gms of plant powder was dissolved in distilled water and optimized solvent in the ratios of 10:70; 20:60, 30:50, 40:40, 50:30, 60:20 and 70: 10 where 10:70 represents amount of distilled water: solvent. The solution was heated over a water bath at 65^0C for 60 minutes. After extraction, an aliquot was passed through the UV-Vis Spectrophotometer for analysis.

3.1.3. Extraction temperature

To understand the effect of extraction temperature on the dye, four sets of experiments constituting 2gs of *Allium burdickii* powder were dissolved in 100ml distilled water in a beaker and subjected to stirring at room temperature, 40, 60 and 80^0C for 60 minutes respectively. After extraction, the extracts were left to cool, filtered using Whatman No.1 filter paper and analyzed using UV- Vis spectrophotometer.

3.1.4. Extraction time

A set of 5 experiments each comprising of 2 grams of crushed *allium burdickii* were dissolved in 100ml distilled water in a beaker and subjected to stirring at 60^0C for 15, 30, 45, 60 and 90 minutes respectively.

3.1.5. Mass to liquor ratio

Seven experiments that is ratios from 1:10, 1:20, 1:30, 1: 40, 1:50, 1:100 and 1:200 were carried out where 1: 10 represents the amount of plant powder to distilled water respectively by heating 2gs of sample over a water bath a temperature of 60^0C for 60 minutes.

3.1.6. Photochemical analysis of extracts

The major components that were considered were flavonoids, saponins, carbohydrates, proteins and tannins. All the colourants extracts from the two extraction methods were scanned using the UV- Vis spectrophotometer. Analysis with some modification was performed according to Ponmozhi et al., 2011

3.1.6.1. UV- Vis absorption spectrophotometer

One percent of the prepared aqueous dye solution was placed in spectrophotometer glass tubes and the solution subjected to a wave length scan in a Shimadzu UV- 1700 CE Pharmaspec Visible absorbance Spectrophotometer (Pallab et al., 2013) at a wavelength range from 200 to 1000nm. The wavelength corresponding to the uppermost absorbance value was recorded and a graph of absorbance against wavelength plotted.

3.1.6.2. Procedures for photochemical analysis

The tests for presence of several photochemicals (flavonoids, saponins, tannins, carbohydrates, proteins and phenols) was carried out and the results recorded accordingly. Similarly, the stability of anthocyanin stability under pH 1.0, 4.5, 7 and 12 was tested by treating 1 ml of sample with 1 ml of pH solutions and the colour changes observed (Ponmozhi et al., 2011).

3.2. DYEING AND MORDANTING PROCEDURES

The optimized extraction conditions were used to prepare the dye bath solution. The warp count, weft count, ends/inch, picks/inch, area density and absorbency of the mercerized woven pure cotton fabric were studied.

3.2.1. Experimental design and optimization of dyeing parameters

Response Surface Methodology while adopting BBD (Bas, 2007; Hamanthraj, 2014) for the experimental data was employed for optimization of process variable and screening the most significant parameters affecting percentage exhaustion of dye. The number of experiments (N) required for the development of BBD is defined as;

$N= 2k (k-1) + C_o$ where; k is the number of factors and C_o is the number of central points.

In the study, four factors based on literature review and preliminary studied namely dyeing temperature, dye bath time, pH and concentration of mordant were chosen. The design yielded a total 27 different combinations that were applied to evaluate factors by testing each independent variable at three levels denoted by (+1), (0) and (-1) respectively. Table 3.1

shows the respective actual (uncoded) form where A, B, C and D signify dyeing temperature (^{0}C), dye bath time (minutes), pH and concentration of mordant on weight of fabric (o.w.f.) respectively and Table 3.2 shows the experimental runs for design.

Table 3.1: Actual levels of factors

Factor Levels	Factors			
	A	B	C	D
1	100	90	7	50
0	80	75	5.5	30
-1	60	60	4	10

Table 3.2: Experimental runs

Run	A	B	C	D
1	0	1	0	-1
2	-1	0	-1	0
3	-1	1	0	0
4	-1	0	0	-1
5	1	0	1	0
6	1	1	0	0
7	0	0	1	-1
8	0	0	0	0
9	1	0	0	-1
10	0	0	-1	1
11	0	-1	0	-1
12	0	0	0	0
13	1	0	-1	0
14	0	-1	1	0
15	1	0	0	1
16	0	-1	-1	0
17	0	0	0	0
18	-1	0	0	1
19	0	1	1	0
20	-1	-1	0	0
21	0	0	1	1
22	0	0	-1	-1
23	0	1	-1	0
24	-1	0	1	0
25	0	1	0	1
26	1	-1	0	0
27	0	-1	0	1

The dye extracted under optimized extraction conditions was subjected to various dyeing conditions according to the experimental design given in Table 3.2 while using three different mordanting techniques and mango bark as a natural mordant. The optimization of dyeing process was aimed at identify the levels of four factors that would present the maximum percentage exhaustion of dye with maximum retention of shade and acceptable fastness values.

3.2.2. Preparation of mango mordant

The mango barks were collected, washed and dried and then crushed into powder. According to Table 3.1, 10 to 50 % (o.w.f) of the powder was extracted using 200ml of pure distilled water at 90^0C for 1 hour and directly used for dyeing without dilution (Wangatia et al., 2015).

3.2.3. Dyeing procedures for cotton fabrics

The control measure that was used in all the dyeing conditions was dyeing without mordanting. In relation to the experimental design, the dyeing process with some modifications was carried out by immersing cotton fabrics in to the dye bath solution and the mixture brought to boil over a water bath according to pre, simultaneous and post mordanting methods using buffer solutions of pH (4-7) interval, time (60-90) minutes, mordant concentration (10-50 % o.w.f.) at a temperature range from 60- 100^0C (Gümrükçü et al., 2008). After dyeing, the dyed fabrics were removed, left to cool, washed gently in Sodium Lauryl Sulphate (SLS) to remove loose dye particles adhering to the fabric surface, air dried, stretched and stored for analysis. To achieve maximum dye exhaustion, sodium sulphate was added in to the dye bath and the exhaustion percentage estimated according to Prabhavathi et al., 2014.

Buffer tablets were used for pH 4 and 7 whereas for pH 5.5, an acetic buffer solution was prepared using carbon free water, sodium acetate and glacial acetic acid.272g of sodium acetate were dissolved in 500ml of water, heated over a water bath to 35^0C and cooled. 50ml of glacial acetic was thereafter added, followed by sufficient water to produce 1000ml. The pH was adjusted where necessary (Choudhary, 2008). The standard pH values given in the tables and elsewhere in the Appendix are considered to be reproducible within ± 0.02 unit at 25°C.

3.2.4. Mordanting procedures

The mordanting was done using pre-mordanting, simultaneous mordanting and post-mordanting procedures. In pre-mordanting the mordant was first added into a beaker containing ample amount of dye solution, followed by addition of fabric samples. The whole mixture was thereafter slowly brought to boil. After dyeing, the solution was allowed to cool, the fabric gently removed, washed (to remove excess dye stuffs), air dried and stored for analysis. Simultaneous mordanting involved dyeing and mordanting at the same time while post mordanting involved addition of the mordant after dyeing. The mordant was added to the dye bath in the final five to ten minutes of simmering, the fabric lifted out of the solution, left to cool, rinsed to remove unfixed dye, air dried and stored for analysis.

3.3. COLOUR FASTNESS ANALYSIS TESTS

Prior to testing, samples were conditioned as per ISO Standards. The test specimens were kept in laboratory conditions of 65% +_ 5 relative humidity and a temperature of 22^0C for 24 hours. The colour yields and colour strength of all the dyed fabric samples using the three

mordanting techniques were evaluated using ISO Standards, standard techniques and statistical measures. For fastness properties, analysis was carried out according to ISO standards methods namely ISO 105-C-06:2010(E) Colour fastness to domestic and commercial laundering; ISO 105-B02:2000(E) Colour fastness to artificial light: Xenon arc fading lamp test; ISO 105 Part D02 Colour fastness to rubbing and ISO 105 Part E04 for perspiration.

CHAPTER 4 : RESULTS AND DISCUSSIONS

In view of the objectives of this study, a series of experiments were carried out in the extraction of *Allium burdickii* dye from the bulbs and leaves of the plant under diverse conditions. The dye was then characterized by examining the presence of different phytochemicals, dyeing of cotton substrate and analysis of the dyed substrate.

4.1. EVALUATION ON EXTRACTION OF NATURAL COLOURANT

The effect of solvent on the yeild, quality of colourant, extraction temperature, mass to liquor ratio and time were studied using three solvents namely distilled water, methanol and ethanol. At various temperature conditions, the yield of colourants obtained using methanol was higher than using ethanol. The extraction of *Allium burdickii* dye under those varying conditions yielded a red dye (Figure 5.1) with presence of some vital phytochemicals.

4.1.1. Separation of dyes

Natural dye was extracted from the leaves and bulbs of *Allium burdickii* plant under conditions of 60^0C, 60 minutes and 100ml of distilled H_20 using different amounts of plant powder. The black, red, blue and green spectrums in Figure 4.1 represent extraction of dye using 2, 4, 6 and 8 grams per 100ml of distilled water. While varying the amount of plant sample, an Aliquot of the extracted dye from the leaves of *allium burdickii* when scanned under a spectrophotometer presented no peaks in the spectrums. “As the saying that dye is a colour but not all colour is a dye”. This was evident in the leaves which when extracted gave a green solution (Figure 5.1) however the active colour/dye generating components, the chromophores and auxochromes usually present in plants were absent in the extract.

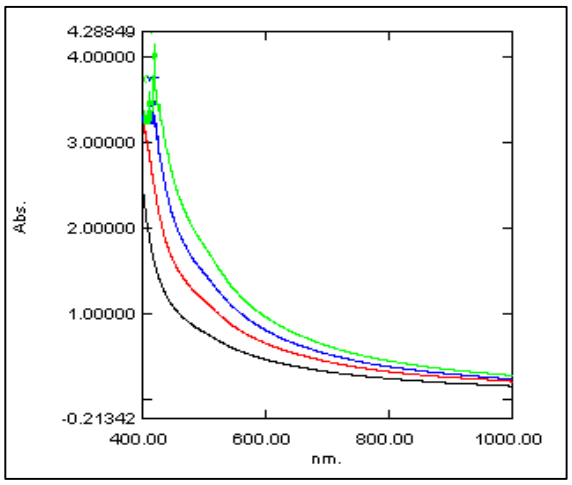


Figure 4.1: Absorption spectra for leaves

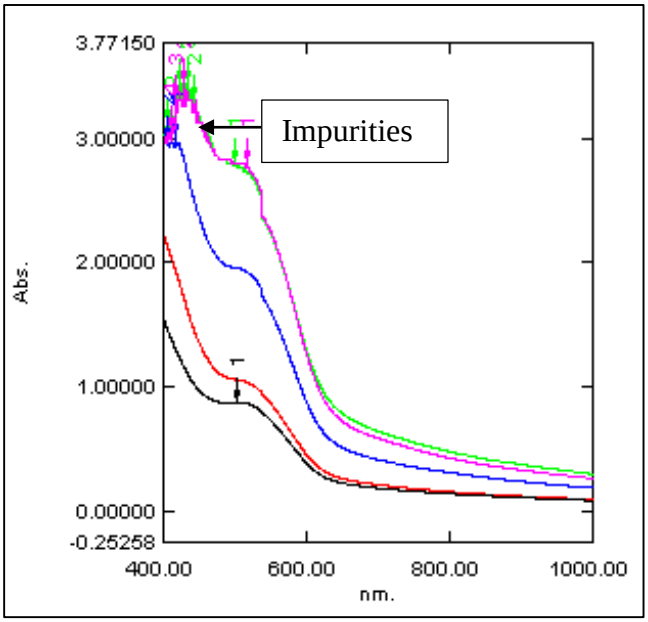
Therefore for further analysis on optimization of extraction conditions, the bulbs were used. This is because the dye extracted from the bulbs as illustrated in Table 4.1 showed the presence of various spectrums with peaks at specific absorbances.

4.1.2. Process optimization of extraction method

Two techniques of extraction namely aqueous and solvent methods were used. Optimization of each method was done by varying one extraction conditions such as amount of plant powder while keeping temperature, time and mass to liquor ratio constant.

4.1.2.1. Optimization of aqueous extraction of colourants

The optimum quantity of powdered bulbs for the extraction of dye as shown in Figure 4.2 was established as 2gms for all the extraction method under conditions of 60^0C, 60 minutes and 100mL distilled water.



Curve representation

Black curve: 2gms at room temperature

Red curve: 2gms at 60

Blue curve: 4gms

Pink curve: 6gms

Green curve: 8gms

Figure 4.2: Absorption spectra for bulb extracts

It was observed that as mass increased, the concentration of the dye increased hence increase in absorbance. Although the absorbances at 4, 6 and 8gms were higher than at 2gms as indicated in Table 4.1, various peaks were observed at wavelengths between 400 and 600nm. This implies that with these amounts, the longer stirring times extracted one to four impurities as shown in the spectrums. Therefore, the optimized amount considered was two grams since no impurities were extracted. The considered characteristic wavelength of the dye as denoted by numeric 1 at the 2gm spectrum was 505nm. This is in accordance to studies that have established that *Allium* species have a wavelength range between 240- 280 and 465 to 560 such as *allium cepa*, white and red onions with a characteristic wavelength of 434 &534, 360 and 520nm respectively (Sharif et al., 2010; Rosa et al., 2010; Manasa et al., 2010).

Table 4.1: Estimation of quantity of powder

S/N0.	Weight of Bulbs/ gm	Absorbance	Optical density
1	2 (RT)	0.244	1.708
2	2	0.2456	1.7192
3	4	0.3702	1.8634
4	6	0.2662	2.5914
5	8	0.4855	3.3985

(Condition of analysis: 2, 4, 6 and 8gm of plant extract scanned at 505nm).

Using a dilution factor of seven, the absorbance of respective samples was recorded. It's observed that absorbance increased with increase in mass. This is because the concentration of the dye increased. However for further optimization of extraction conditions, 2gm was chosen because at higher temperatures and longer stirring times, there was no denaturing of compounds.

4.1.2.2. Analysis on optimization of solvent extraction method

Methanol and ethanol were chosen for this analysis because since the dye is polar, it has been proven that this two solvents can be used (Costa et al., 2007; Samanta et al., 2007). The black, blue and red curves in Figure 4.3 represent extraction of dye at room temperature, 40^0C and 75-80^0C. For the extraction of *allium burdickii* dye, methanol as shown in gave better results. This is in accordance with Rosa (2010) who established that a combination of methanol: formic acid: water (50:5/vv) with 2g/L allowed complete extraction and stability of flavonoid

(Rosa et al., 2010). Furthermore Manasa (2013) confirmed methanol as the best solvent for extraction of pysico-chemicals present in *allium cepa* (Manasa et al., 2013).

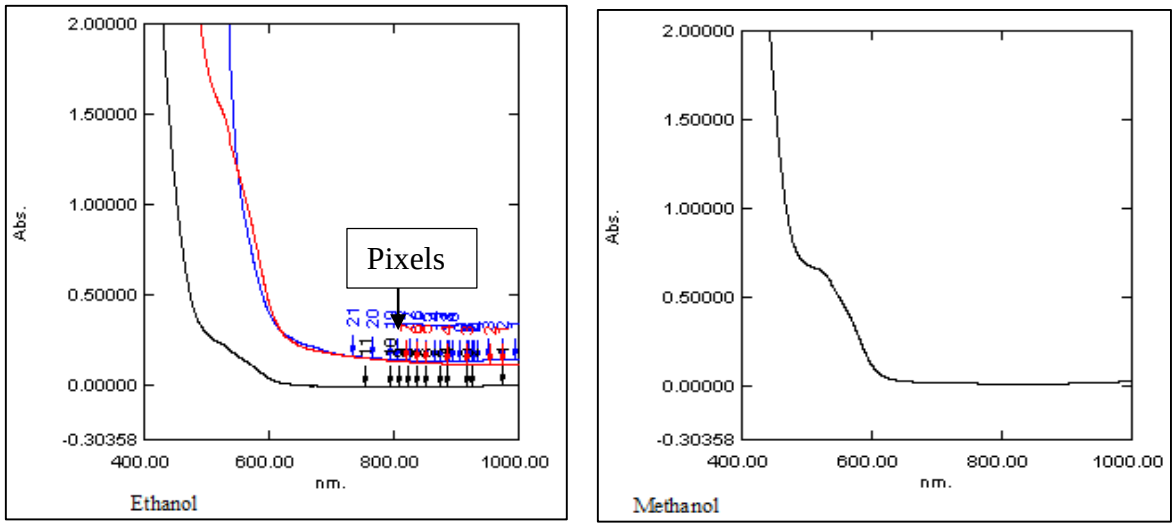


Figure 4.3: Absorption spectra for ethanol and methanol bulb extracts

At higher temperature Ethanol didn't sufficiently extract dye molecules. Along with the dye yielding compounds, it extracted very many impurities (pixels) ranging from one to 20 between the wavelength of 600-1000nm. However, at room temperature the absorbance was better than at 40 and 60^0C. Methanol on the other hand gave a good absorbance of about 0.6073 at room temperature hence was the solvent chosen for solvent extraction.

For the optimization of the quantity of solvent (methanol: H_20 mixture), the solvent was mixed with pure distilled water in the ratios ranging from 10:70 (methanol: H_20) to 70:10 (H_20: methanol). In the extraction process, 2 grams of plant powder were dispensed into the 80ml mixed solution (1:40) and the solution brought to boil at 64.7^0C for 60 minutes. After

extraction the solution was cooled, filtered using Whatman No.1 filter paper and an aliquot of 1ml passed through a spectroscopy scan from 400 to 1000nm. The highest absorbance represented by the green curve indicated in Figure 4.4 was attained in the ratio of 40:40.

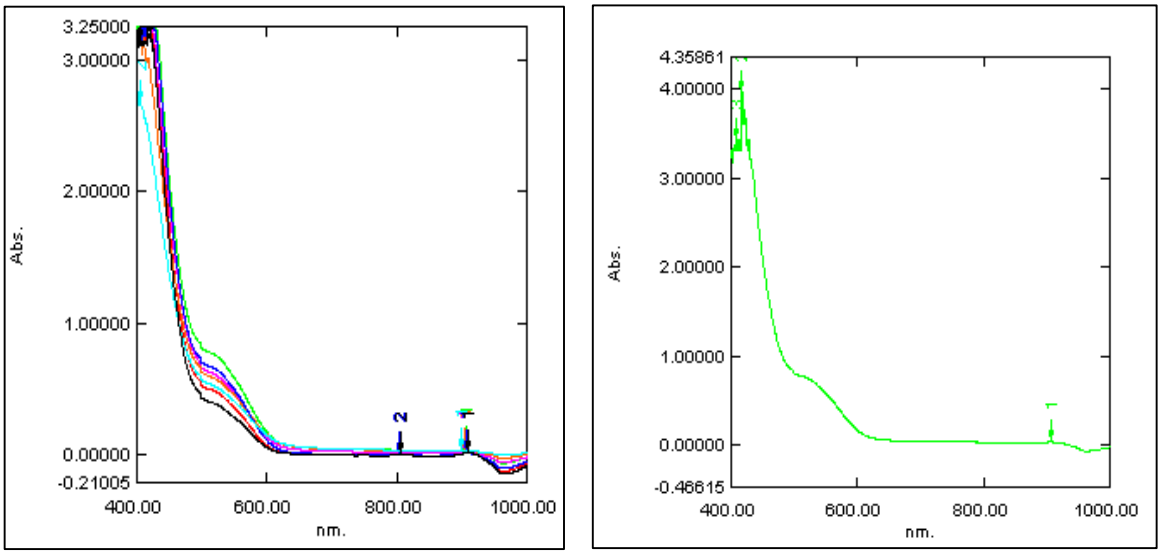


Figure 4.4 : Absorption spectra at different concentrations of solvent

The study further established that absorbance increased with increase in quantity of water up to an equivalent ratio of 40:40 beyond which absorbance decreased as shown in Table 4.2.

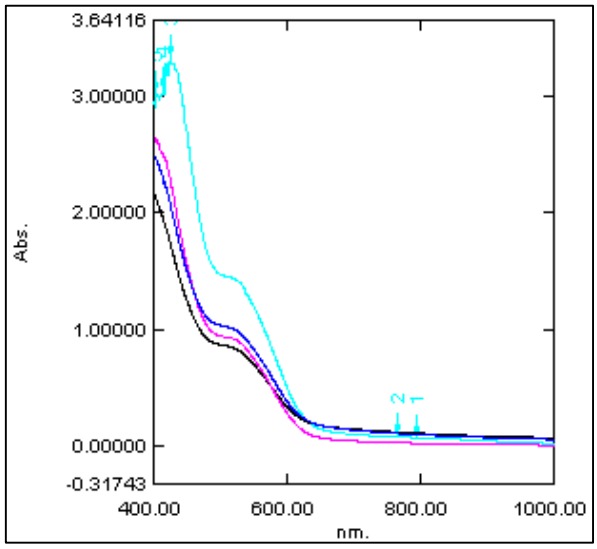
Table 4.2: Absorbance at different ratios

S/No.	Ratio of water: methanol		Colour (curve)	Absorbance
	Amount of (H_2O)	Amount of methanol		
1	10	70	Black	0.5551
2	20	60	Red	0.6083
3	30	50	Blue	0.7826
4	40	40	Green	0.9128
5	50	30	Pink	0.7385
6	60	20	Red	0.745
7	70	10	Light blue	0.7938

4.1.3. Effect of extraction temperature

The effect of temperature on extraction efficiency was investigated since it impacts the equilibrium (solubility) and mass transfer rate (diffusion coefficient) (Spigno et al., 2007). In all sample extracts (methanol, ethanol and water), the results indicate that yield of extracted colourant and absorbance marginally increased with increase in extraction temperature (Figure 4.5) The highest amount of colourant was extracted at 80^0C.

However the higher temperatures of 80^0C gave various peaks which meant that there was degradation of dye. The results were in accordance with Ju and Howard (2003) and Laleh (2006) who found out that higher temperature more than 70^0C cause rapid degradation of anthocyanin (Ju et al., 2003; Laleh et al., 2006).



Curve representation

Black curve: extracted at room temperature

Blue curve : extracted at 40^0C

Pink curve : extracted at 60^0C

Light blue : extracted at 80^0C

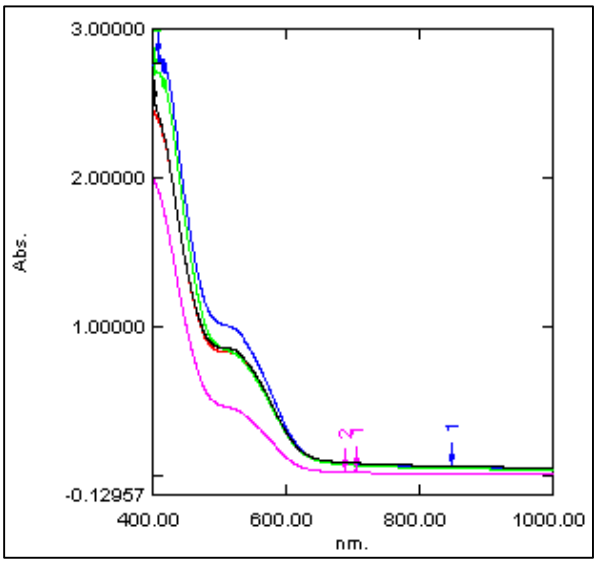
Figure 4.5 : Absorption spectrums of different extraction temperatures

Thermal degradation of anthocyanins could occur via two mechanism first the hydrolysis of the 3-glycoside linkage to form the more labile aglycon and secondly due to the hydrolyzation of the pyrilium ring resulting in the production of chalcone which are responsible for brown colour developed food containing anthocyanins (Ju and Howard., 2003; Sharif et al., 2010; Lekshmi et al., 2015).

4.1.4. Role of time in extraction of *allium burdickii* dye

The samples were incubated under proper conditions at different time intervals via 15, 30, 45, 60 and 90 minutes to investigate the influence of time on total yield of colourant. It was observed from Figure 4.6 that stirring of pigments at moderate times between 15 minutes to 45 minutes showed no degradation of dye and similar stability were observed whereas the degradation of dye gradually increased with increase in stirring time beyond 60 minutes. The

highest denaturing of dyes was observed at 90 minutes where absorbance decreased while no degradation of dye was observed when extracts were stirred for 15 and 30 minutes.



Curve representation

Black curve: 15 minutes

Red curve : 30 minutes

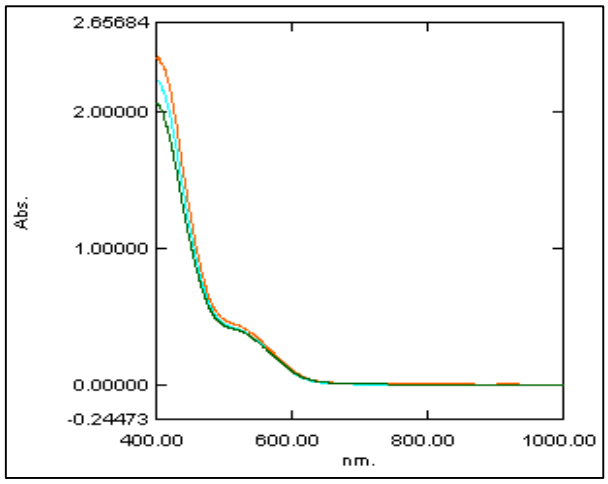
Blue curve : 45 minutes

Green curve: 60 minutes

Pink curve : 90 minutes

Figure 4.6: Absorption spectrums of dye extracted at different times

Generally, increase in time had a slight effect on the dye yield causing a scarce increase in absorbance. For the askew outcomes obtained at 60 and 90 minutes, the experiment was repeated at 30, 45 and 60 minutes respectively to ascertain the results as illustrated in Figure 4.7. The results indicated that extraction of the dye at 60 minutes gave the highest absorbance without denaturing the compositions and was thus chosen for further analysis.



Curve representation

Blue line : 30 minutes

Green line : 45 minutes

Red line : 60 minutes

Figure 4.7: Extraction time at 30, 45 and 60 minutes

The absorbance at these different duration of extraction that were recorded in Table 4.3 showed that 60 minutes yielded the highest and best amount of colourant. The increase in absorbance with increase in time implies that when we increase contact time of the dye, more dye was able to dissolve in water due to hydrolysis (Nagia et al., 2006). Denaturing of the dye at 90 minutes is in accordance to Farooq (2013) who found out that extraction time from 90 minutes didn't further increase colour strength.

Table 4.3: Optimization of extraction time

S/No.	Extraction time (minutes)	Optical density
1	30	0.426
2	45	0.445
3	60	0.474

(Conditions of analysis: 2gms of plant powder, 60^0C, 100mL distilled water)

4.1.5. Mass to liquor (M: L) ratio

Different ratios were used and their scan results recorded. Table 4.4 and Figure 4.8 show that increasing M: L ratio from 1:10 to 1:20 increases absorbance values but further increase in M: L ratio led to a decrease in absorbance values.

Table 4.4: Absorbance values of dye at different mass ratios

S/No.	Mass ratio	Absorbance
1	1:10	0.069
2	1:20	0.091
3	1:30	0.068
4	1:50	0.029
5	1 to100	0.018
6	1 to 200	0.014

The highest absorbance was detected when 40ml of distilled water were used (1: 20).

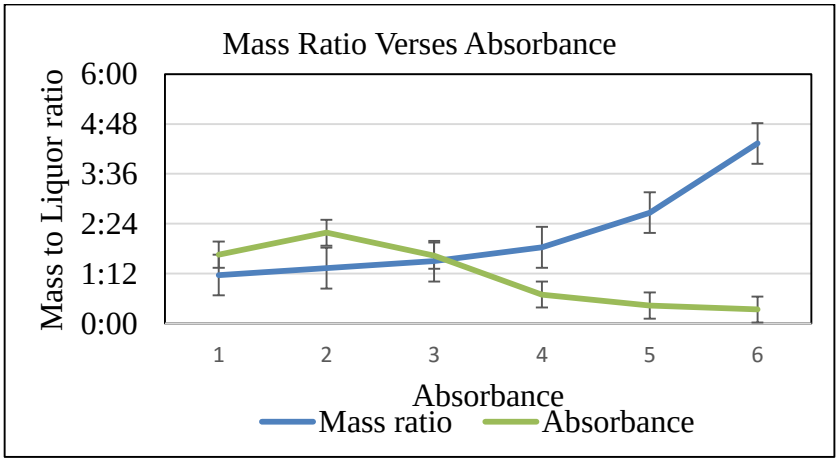


Figure 4.8 : Effect of M:L ratio at optimized temperature conditions.

When the M:L ratio is less, the dye molecules are congested hence they collide with each other which increases the affinity of dye molecules for each other but decrease their affinity for the fabric, thus a decrease in absorbance values (Farooq et al., 2013).

4.16. *Allium burdickii* optimized extraction conditions

Different natural dyes have different optimal extraction conditions. Therefore to obtain substantial results while using the conventional method in the dyeing process, there is need to monitor extraction conditions such as extraction temperature, time and mass to liquor ratio as some of they affect the yield of dye. The resulting optimized extraction conditions obtained when using *allium burdickii* bulbs is given in Table 4.5.

Table 4.5 : Optimized extraction conditions

Particular	Method	Plant powder	Temperature	Time	M:LR
Condition	Aqueous	2gms of bulb	60ºC	60 minutes	1:20

4.1.7. Presence of photochemical

The extraction of chemicals in burdickii leaves and bulbs was performed using water, methanol and ethanol and it was observed in Table 4.6 that the extraction procedures affected the detection of chemicals. Methanol and water extracts showed the presence of all physico-chemicals in the plant bulbs (except for saponins) while organic solvents except for flavonoids and carbohydrates (water extract) showed no presence of bioactive chemicals in leaves. The research also established methanol as a better extracting solvent than ethanol as

established from the spectrophotometric results in section 4.1.2.2, Geetha (2011) and Manasa (2010) that methanol extracted better dye than ethanol.

The presence of flavonoids and tannins was established in the plant bulbs. These results are in accordance with Gümrükçü (2003, 2008); Geetha (2011) and Markakis (1982) who established the presence of flavonoids in onions. The aqueous and solvent bulb extracts demonstrated the presence of flavonoids, tannins, phenols, proteins and carbohydrates (fructans) but no saponins for all the extracts. Bulb onion are rich sources of flavonoids (Kopsell et al., 2010) and since flavonoids are the major groups of phenolics (Rosa., 2010) in onions, the presence of phenols confirmed presence of flavonoids. Carbohydrates, proteins and tannins are other components found in *Allium* species (Lekshmi et al., 2015; HMPC, 2012; Hedges et al., 2007).

The leaf extract except for flavonoids (all extracts) and carbohydrate (aqueous extract) tests showed absence off proteins, saponins, tannins and phenols. This is in accordance with the Spectrophotometry results in section 4.1.1. The phytochemicals results obtained were in accordance to a report by Hedges (2007) and Lekshmi (2015) who reported on the nutritionally valuable content found in onions (Hedges et al., 2007; Lekshmi et al., 2015).

The intensity of colour in anthocyanins is independent on factors such as structure of the dye, temperature and pH. The stability of *allium burdickii* bulb extract at various pH conditions as indicated in Figure 5.3, 5.4 and 5.5 was studied.

Table 4.6 : Photochemical analysis results

S/No.	Particular	Aqueous filtrate		Solvent filtrate			
		Bulbs	Leaves	Ethanol		Methanol	
				Bulbs	Leaves	Bulbs	Leaves
1	Flavonoids	+	slightly +	+	slightly +	+	slightly +
2	Tannins	+	-	-	-	+	-
3	Saponins	-	-	-	-	-	-
4	Phenols	+	-	+	-	+	-
5	Proteins	+	-	+	-	+	-
6	Carbohydrates	+	slightly +	+	-	+	-

(Conditions of analysis: 2g (RT) and 2 g at 60^0C, 60 min, 100mL)

The red colour of methanol and aqueous extracts decolorized on addition of pH 4.5 solutions while at pH 7 and 12 (alkaline solutions), there was no colour changes in all extracts. For the ethanol extract, no colour change was observed in all pH conditions. This is attributed to the poor extraction of *allium burdickii* dye exhibited by ethanol. From the results obtained in the stability test, it was identified that anthocyanin were found to be stable in alkaline conditions.

4.2. STATISTICAL SCREENING AND OPTIMIZATION OF DYEING CONDITIONS

The fabric characteristics were as follows: a bleached and mercerized pure cotton fabric with ends/cm: 23; picks/cm: 13, warp count: 34Nm, weft count: 27Nm and grams per square meter: 126.2gms.

Various statistical methods and a Box-Bohnken (BBD) model of four factors was adopted for the optimization of dyeing conditions. Percentage exhaustion of dye was taken as the response of the system while the four process parameters were taken as input independent variables. The design point were all falling within a safe operating limit that is within the nominal high and low levels since BBD does not contain any points at the vertices of the cubic region. The results from the experimental design were used to optimize the dyeing experiment. The results indicate that there were many shades obtained after dyeing as the unmordanted fabric gave a pink/hot pink shade and the natural mordant a golden orange colour. The exhaustion of dye during the dyeing process is affected by factors such as temperature, concentration of salt, rate of dyeing and concentration of mordant and amongst these, time and temperature affect migration of dye molecules. For optimization of the mordanting technique, these factors were monitored and their resultant effect numerical analyzed as coded in Table 4.7.

Table 4.7: Coded factors

Codes for X	Particular	Codes for Y	Specific
X1	Dyeing Temperature	Y1	Pre-mordanting
X2	Dyeing Time	Y2	Simultaneous mordanting
X3	pH	Y3	Post Mordanting
X4	Concentration of mordant		

The relationship between X and Y values for all the three techniques was regressionally analyzed. The result indicated that all the regression models were statistically significant with a P-value of<0.001 for all techniques and an R_{sq} of 0.6106, 0.7113 and 0.9022 for pre mordanting, simultaneous and post mordanting. R_{sq} shows how much the change in an

independent variable affects the dependent variable. It ranges between 0 and 1 whereby the closer to 1, the stronger the relationship while the significance value (P) is 0.000. This implies that all the factors contributed to the adsorption of the dye molecules into the fabric. However, post mordanting was the most significant technique of adsorption and absorption of dye molecules because it had the highest R_{sq} value. The increase in dye uptake in post mordanting can be explained by increased swelling and hence enhanced dye diffusion.

4.2.1. Dyeing using pre mordanting technique

Dyeing under various conditions using this method contributed over sixty percentage to dye exhaustion. From the second order polynomial equation Y_2 and Figure 4.9 pH was found to be insignificant in pre mordanting whereas temperature had the greatest contribution.

$$\boldsymbol{Y_1 = -537 + 10.88X_1 + 5.27X_2 + 2.86X_4 - 0.0383X_1^2 - 0.0506X_4^2 - 0.0741X_1^*X_2}$$ Eqn. 4.1

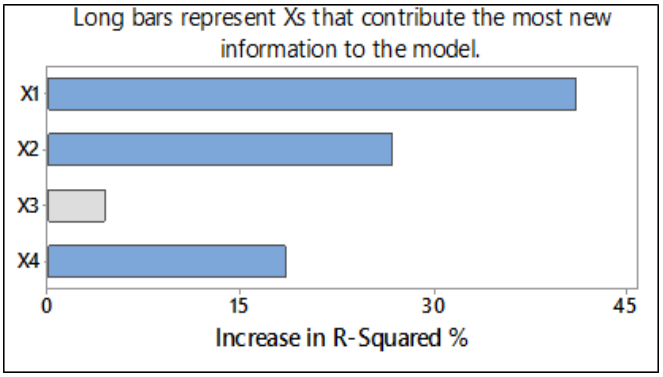


Figure 4.9 : Incremental impact of X variables to Y_1

All the variables directly affected exhaustion of dye molecules into the fabric as their increaments led to a gradual increase in diffusion of dye molecules into the cotton fabric.

However, the combination of time and temperature, increment in temperature and concentration of mordant inversly affected exhaustion.

4.2.1.1. Effect of different temperatures on dye exhaustion

Temperature is a factor that has a role in destabilizing anthocyanin molecular structure. The black curve and black dotted line in Figure 4.10 signify the predicted Y at different settings and optimal settings respectively. In this study it was noted that temperature inversely affected exhaution of the dye molecules into the cotton fabric in such a way that its increament beyond the optimal value of 60^0C led to a reduction in dye uptake.

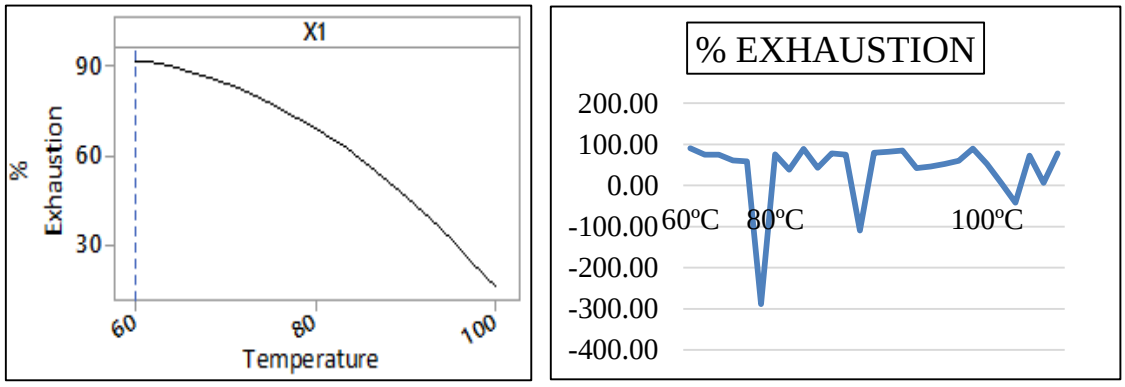


Figure 4.10 : Settings and sensitivity for optimal solution

The reduction in exhaustion was propably due to the degradation of dye as reported by Ju (2003) and Laleh (2006) that with an increase in temperature, there is greater destruction of anthocyanin attributed to hydrolyzation of the dye structure. The combined effect of temperature and time (Figure 4.11) shows a gradual decrease in mean exhaution as time increases.

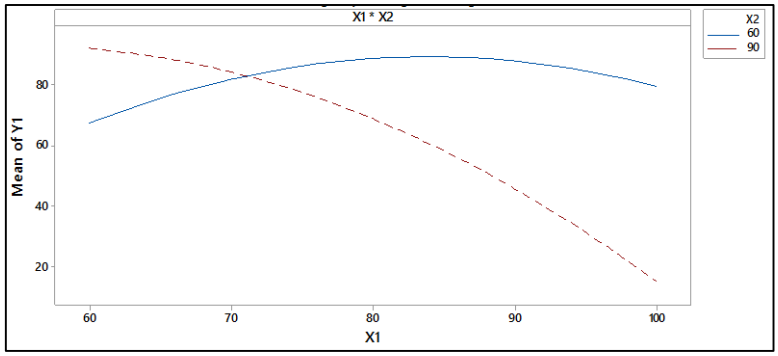


Figure 4.11: Combined effect of temperature and time

4.2.1.2. Influence of time on exhaustion of Allium burdickii dye

Figure 4.12, illustrates the action of dyeing time on dye uptake. The black dotted line represents the optimal settings while the black line is the predicted Y at different settings. The second graph represents the behaviour of percentage exhaustion against time for each of the twenty seven samples analysed. Its was observed that an increament in time from 60 to 90 miunutes gradually increased the transfer of dye molecules from the dye bath onto the cotton fabric.

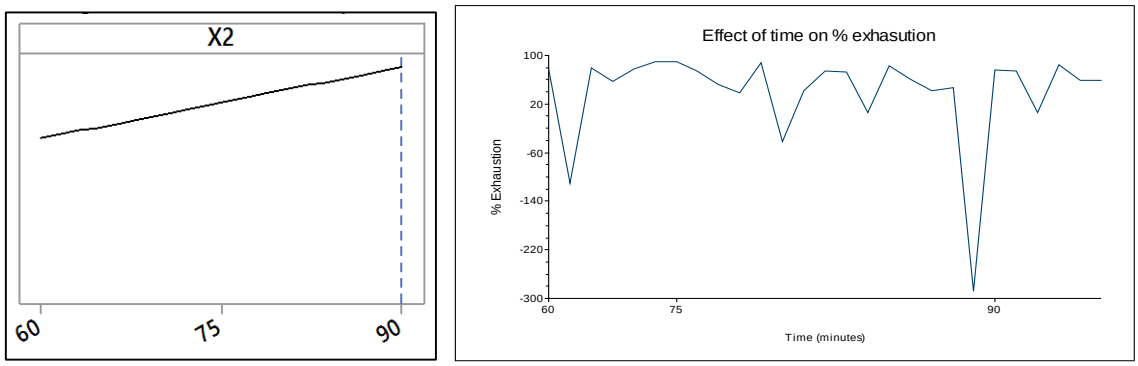
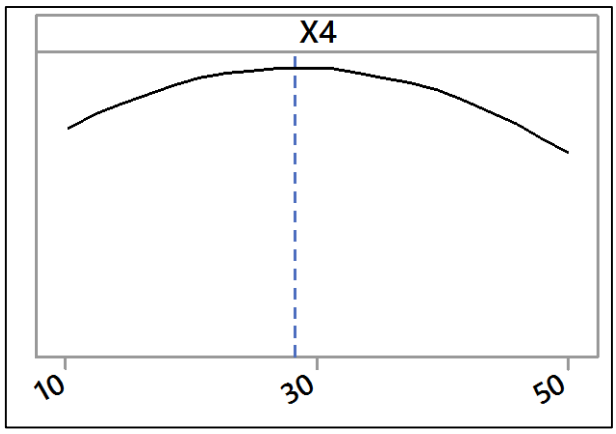


Figure 4.12: Effect of duration of dyeing cotton fabric with *allium burdickii*

The dyeing time which is related to the rate of dyeing is greatly influenced by many various factors such as the molecular size of the colouring species, degree of dye aggregation in aqueous solution, the rate of diffusion either in aqueoous soluion or within the fibre itself, substantivity of the colour species, dyeing temperature and pH of the dye bath. Exhaustion of dye is a function of time so as time increased, rate of exhaustion increased while the rate of dyeing decreased. This implies that the longer stirring time enabled absorption of dye molecules in to the fiber until equilibrium was attained at 90 minutes which was the optimized time of extraction. These results relate with Broadbent and other authors, who established that increase in time increases the percentage exhaustion of dye (Broadbent., 2001).

4.2.1.3. Effect of concentration of mordant

It is known that natural dyes need metal ion for adsoption of dye by forming an insoluble composition precipitate on the surface of fibre. The mordant depending on the type used serves to give the fabric a range of bright colours (Tastsaroni et al., 1994; Tera et al., 2012). Various shades were obtained when cotton fabrics were pre-mordanted with mango bark natural mordant. During mordanting, the dye as indicated in Figure 4.13, showed an intial increase in equilibrium exhaustion from 10% to an optimal concentration of 30% o.w.f, beyond which the pecentage dye uptake reduced. In pre mordanting, the fabric is first mordanted then dyed. Therefore the reduction of exhaustion with excess concentration of mordants was due to the aggregation of the extract molecules by addition of excess mordant which caused a reduction in extract solubility (Ali et al., 2010). This led to its precipitation thus difficulty of penetration of dye molecules into the fabric during dyeing.



Curve representation

Black line: Predicted Y at different settings

Dotted black line: Optimal setting

Figure 4.13: Effect of concentration of mordant on dyeability

4.2.1.4. Optimized Pre-mordanting dyeing conditions

The optimized dyeing conditions were successful using optimal functions of Minitab expert software and regression analysis. For dyeing of cotton fabrics using pre mordanting technique, mango bark natural mordant and *allium burdickii* dye, the optimized conditions are listed in Table 4.8.

Table 4.8 : Optimized pre-mordanting conditions

Particulars	Optimal conditions
Temperature (ºC)	60
Time (minutes)	90
Con. of mordant (% owf)	28.18

4.2.2. Simultaneous mordanting

In this method, the fabrics were dyed and mordanted concurrently using *allium burdickii* dye. The numerical terms obtained were after fitted into the statistical package to generate Eqn. 4.2 that modeled the relationship between Y_2 and X_1, X_2, X_3, X_4 and X_6) as percentage dye exhaustion, dyeing temperature, time, pH and concentration of mordant respectively.

$$\boldsymbol{Y_2 = 1271 - 12.44X_1 - 16.45X_2 - 18.68X_4 + 0.1698X_1^*X_2 + 0.1778X_2^*X_4}$$

Eqn. 4.2

From Eqn. 4.2, it can be noted that an increment in major contributing factors (Figure 4.14) that is dyeing temperature, time and concentration of mordant substantially decreased the exhaustion of dye into the cotton fabric while the combinations of temperature and time plus time and concentration increased exhaustion of dye in the fabric by 16 and 17%. The effect of pH was insignificant to this particular dyeing method.

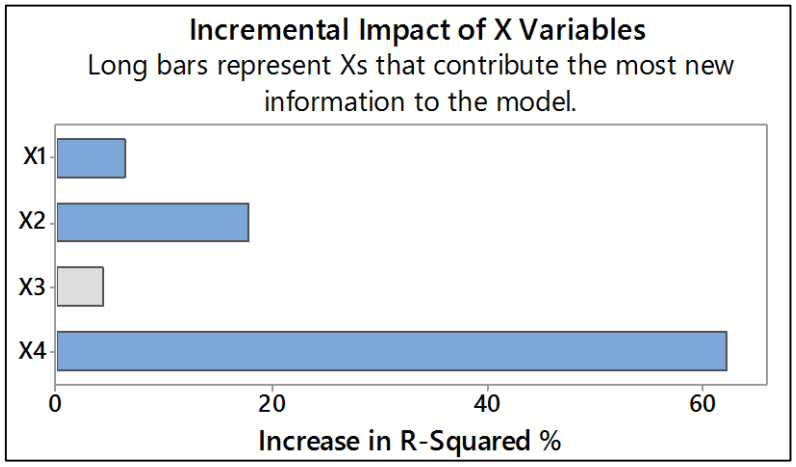


Figure 4.14: Contribution of each dyeing variable

4.2.2.1. Determination of effect of temperature on exhaustion of dye molecules

The dyeing procedure was carried out at three different temperatures namely 60, 80 and 100^0C using the conventional method. Figure 4.15 indicates how an increase in temperature beyond 60^0C caused a reduction in exhaustion. This was attributed to less diffusion of dye molecules into the fiber as high temperatures influence the physicochemical properties of water by decreasing the polarity of water and enhancing the solubility of less polar compounds in water. Increasing temperature also promotes dye de-aggregation on the dyeing solution liberating more individual dye molecules to enter the fiber hence reducing absorption of dye into the fabric.

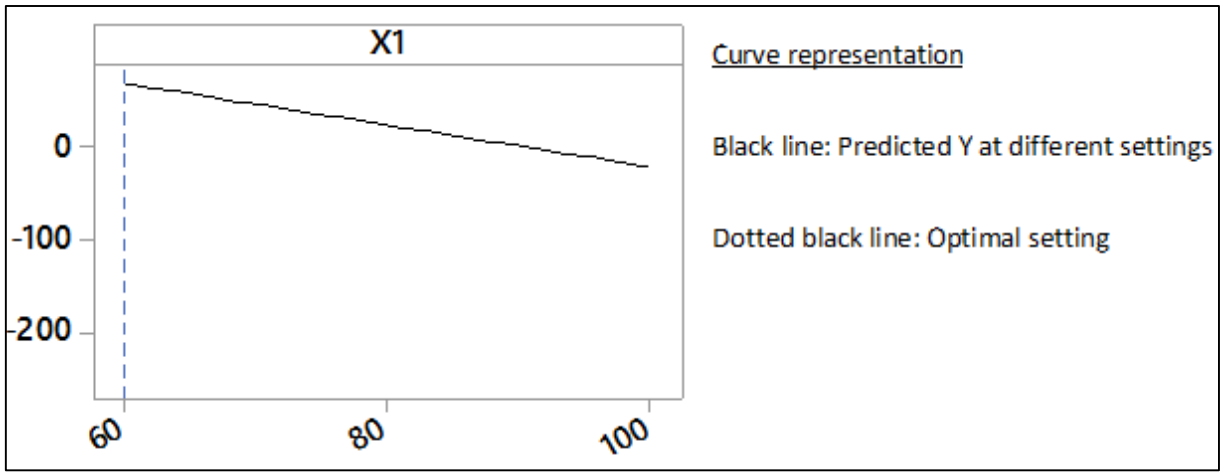


Figure 4.15 : Influence of temperature on simultaneous dyeing

4.2.2.2.Effect of dyeing time on exhaustion

The black, dotted and continous black lines in Figure 4.16 represent predicted Y at different settings, optimal setting and variation of Y along different time settings for all twenty seven experiments respectively.

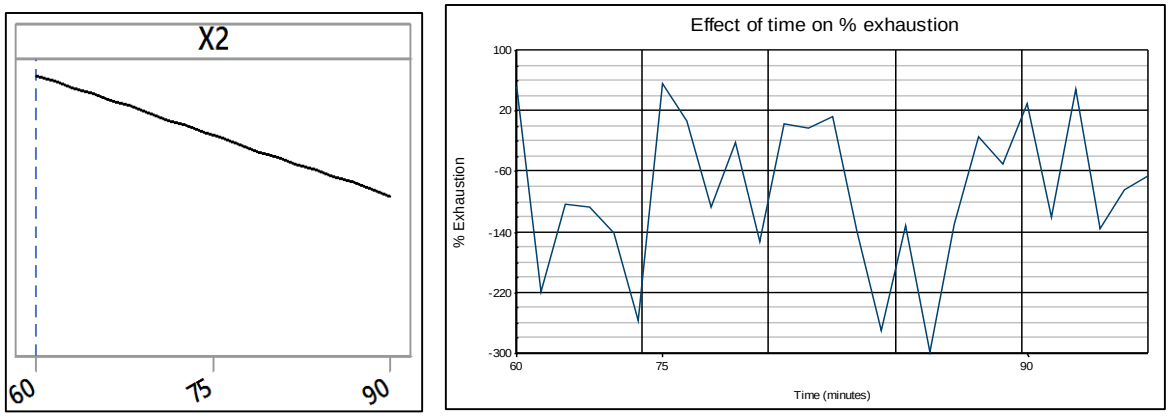


Figure 4.16: Effect of time on dye ehaution

As demonstrated in Figure 4.16, the optimised duration of dyeing was 60 minutes in which beyond this time, percentage exhaution of dye drastically decreased. The duration of dyeing lessened due to the reduction in the number of dyeing steps. Unlike pre mordanting, in simultaneous mordanting, both dyeing and mordanting take place concurrently. This implies the duration of time required to attain equilibrium exhaustion is shortened because adsorption and absorption of dye occur at once. This is further illustrated in Figure 4.16 B where there is a variation in individual time experimentations.

4.2.2.3. Influence of mordant of percentage dye uptake

The black and dotted balck line in Figure 4.17 signify the predicted Y at different settings and optimal setting respectively.This effect is simialr to duration of time where by an increment in concentration of mordant beyond 10% on weight of fabric caused a gradual decrease in diffusion of dye molecules into the fabric.

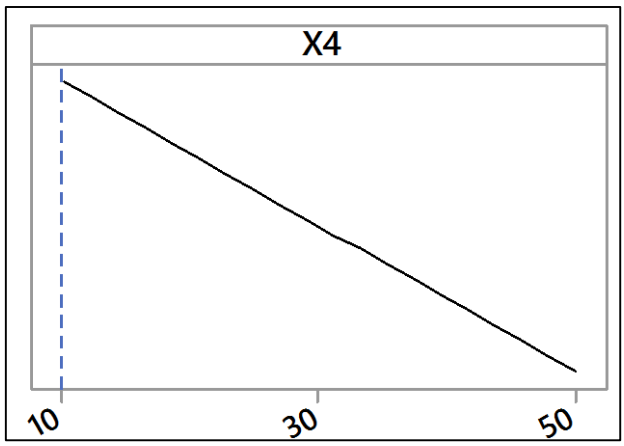


Figure 4.17: Influence of concentration of mordant on dye exhaustion

4.2.2.4. Opitmized simultaneous conditions

Optimum conditions favor attainment of uniform dyeing. Four factors namely dyeing temperature, time, pH and concentration of mordant were studied. The regression model establish pH as an insignificant factor and further optimized simultaneous dyeing conditions as indicated in Table 4.9.

Table 4.9: Optimized simultaneous conditions

Particulars	Optimal conditions
Temperature (ºC)	60
Time (minutes)	60
Con. of mordant (% owf)	10

4.2.3. Post mordanting

From the final Eqn. 4.3, it can be noted that post-mordanting technique had the highest effect on dye exhaustion. Its high R_{sq} value and P> 0.001, means that the model was significant. This implies that applying onion bulb dye on cotton substrate using post mordanting technique is the best method that allows maximum transfer of dye from the solution onto the fabric. Mordanting however did have an effect on the exhaustion of substrate because as concentration of mordant increased, dye exhaustion greatly also increased implying that *allium burdickii* dye has good substantivity for cotton fabric.

$$Y_3 = 104 - 12.70X_1 + 174X_3 + 14.73X_4 - 27.11X_3^2 + 2.04X_1^*X_3 - 3.918X_3^*X_4 \quad \text{Eqn. 4.3}$$

According to Eqn. 4.3, temperature (X_1), pH (X_3), concentration of mordant (X_3) and a combination of temperature and time increased dye directly affect percentage exhaustion of dye. Time as showed in Figure 4.18 was found to be insignificant while increment in pH and a combination of pH and concentration of mordant negatively affected exhaustion in such a way that their increments caused a decrease in percentage exhaustion.

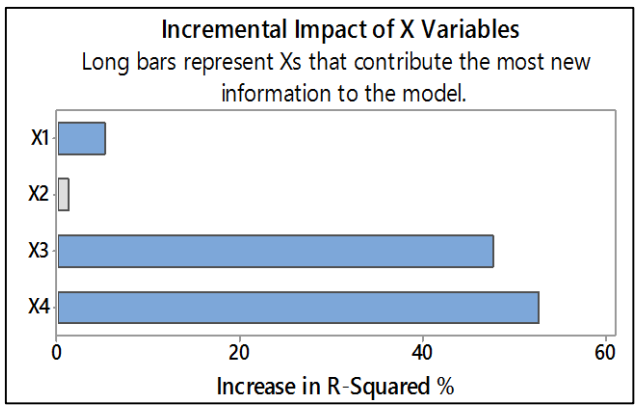


Figure 4.18: Significance of independent variable in the dyeing process

The rate of exhaustion varies with the dyeing conditions. In order to characterize the dyeing properties of the dye, while considering a constant concentration of salt, factors such as temperature, dyeing time, concentration of mordant, pH were coded in to Minitab software and exhaustion curves generated as illustrated in the succeeding units.

4.2.3.1. Impact of temperature on dye ability

Temperature is one of the major factors that affect extraction efficiency in aqueous extraction method. It affects the migration/transfer of dye molecules from the solution onto the fabric. From Figure 4.19, it is observed that as increase in temperature rapidly decreased the amount of dye adsorbed by the fiber. This is so because as temperature reached it optimal point (60^0C), equilibrium exhaustion was attained. Therefore beyond that temperature, the attraction of the dye for the fiber (affinity) decreases with further increase in temperature due to the denaturing of the dye molecule brought about by the strike and rush of the molecule (at high temperature, more energy is released leading to rapid movement of molecules hence their destruction).

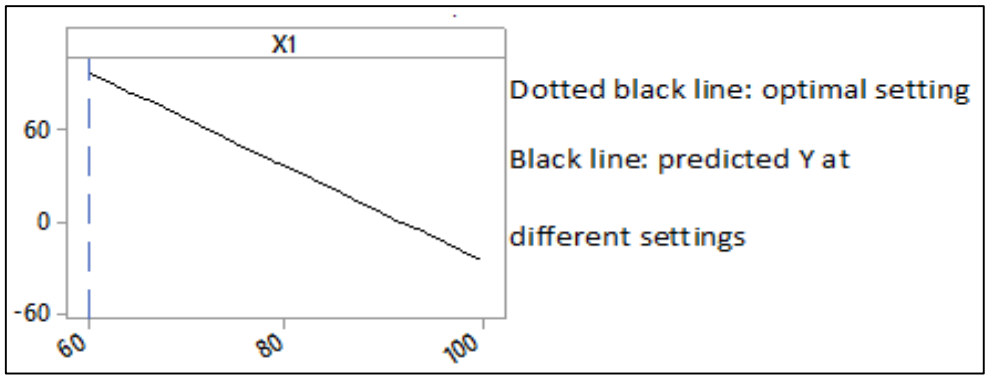


Figure 4.19: Effect of temperature on dye-ability of cotton fabrics.

Furthermore, dyeing is a heat releasing (exothermic) process whereby the interaction between the dye and fiber molecules is stronger than between the dye and water molecules in solution. Therefore, the dyeing equilibrium reacts to an increase in temperature by absorbing more heat energy. This in return shifts the endothermic direction by desorbing from the fibres hence a reduction in dye exhaustion at higher temperatures. The optimized temperature for dyeing using post mordanting was therefore 60^0C.

4.2.3.2. Effect of pH

The reaction of the dye with the cotton starts as soon as the pH of the dyebath is increased. As indicated in Figure 4.20 exhaustion first increased from pH 4.5 until pH 4.73 beyond which it started decreasing.

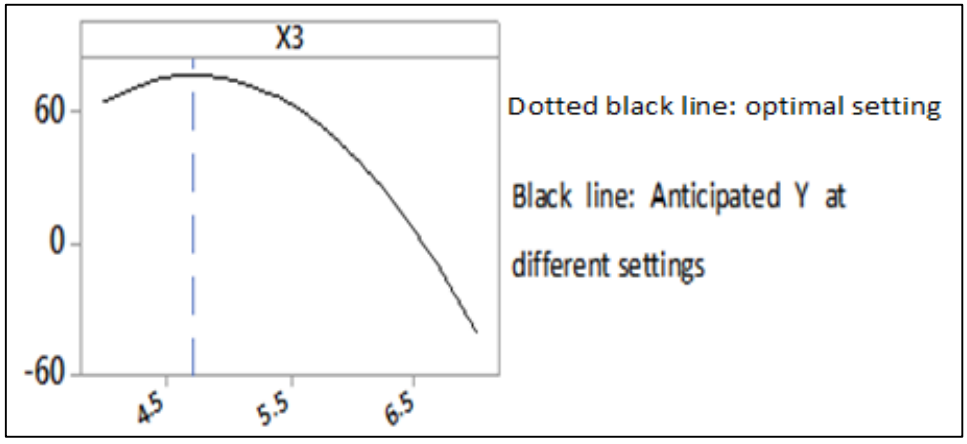


Figure 4.20: Effect of pH on dye-ability

When individual pH conditions were compared as demonstrated in Figure 4.21, pH 4 (blue line) gave better results, followed by pH 5.5 (red line) and lastly pH 7 represented by the

green line. This is so because cellulosic fibres have greater negative potential under alkaline than acidic conditions and due to the increasing dissociation of a number of cellulose hydroxyl groups, exhaustion lowers.

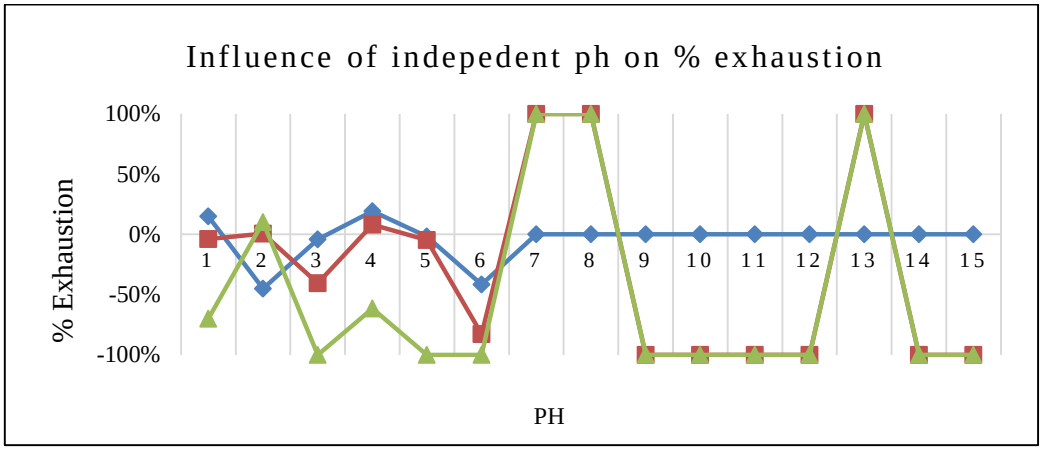


Figure 4.21: Influence of independent pH conditions

Exhaustion was further analysed at various temperature (60, 80 and 100^0C) and pH conditions as illustrated in Figure 4.22. The study established that increase in temperature across varying pH conditions generally caused a decrease in exhaustion of dye molecules in the cotton fabric. At a specific temperatureof 60^0C, exhaustion generally decreased with increase in pH and temperature 60^0C.

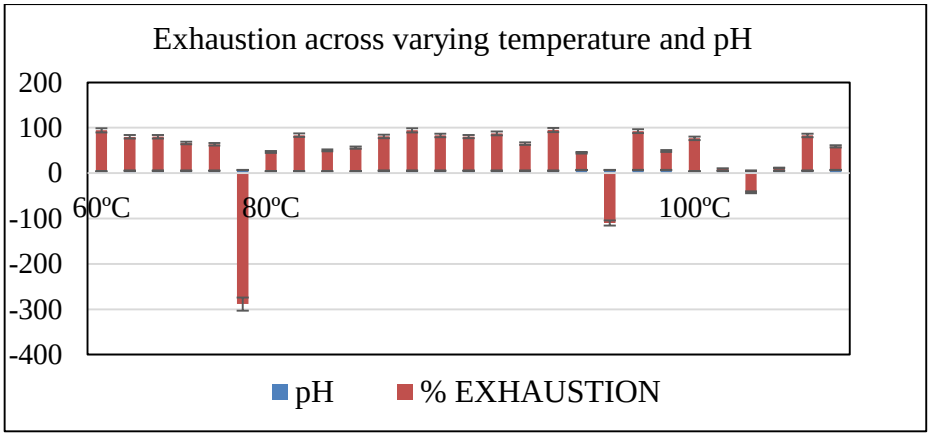


Figure 4.22: Combined effect of temperature and pH.

The trend is however different at 80^0C where we see an increase in exhaustion and then a decrease as pH increases from pH 4 to 7. At 100^0C, exhaustion decreases with increasing pH. pH is known to change the spectra of dyes significantly due to the shift in the resonance structure in the dye molecules. At higher pH values, protons can be abstracted which changes the electronic configuration of the dye molecule. Since absorbance of light is a factor of the electron configuration, any change in the configuration yields a change in the spectrum (Kamel et al., 2009; Laleh et al., 2006; Gordon., 2016). The combined effect of temperature and pH thus generally leads to a reduction in diffusion of dye molecules into the cotton fabric. Similarly, an increase in the combined effect of pH and concentration of mordant as demonstrated in Figure 4.23 led to a reduction in percentage exhaustion of dye.

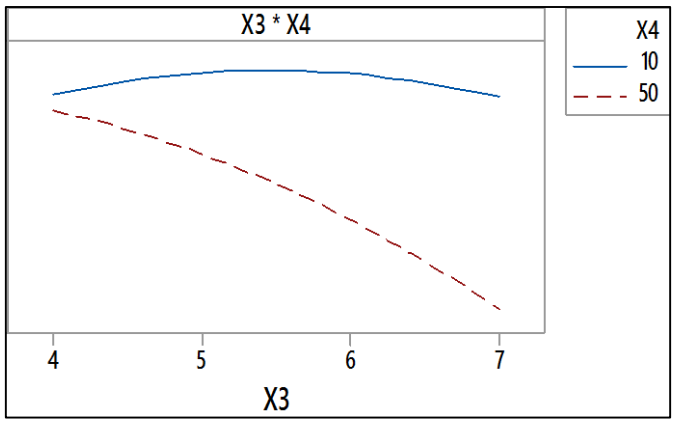


Figure 4.23: Combined effect of pH and concentration of mordant

4.2.3.3. Evaluation of concentration of mordant on adsorption of dye

Post mordanting is a technique of mordanting where by the mordant is added into the dye bath in the last five to ten minutes of simmering. When the mordant was added into the dye solution as demonstrated in Figure 4.24 percentage dye exhaution decreased. More to that, an upturn in concentration of mordant from 30 % to 50 % owf caused an additional reduction in the exhaustion.

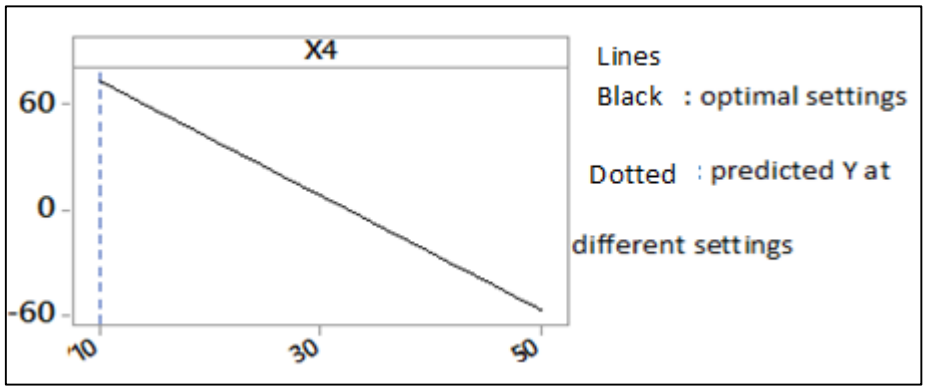


Figure 4.24: Evaluation of exhaution of cotton fabrics mordanted using post mordanting

4.2.3.4. Optimized post mordanting conditions

During the course of dyeing, whether dyeing natural or synthetic fibres, it's very important to constantly monitor process parameters so as to ensure that proper feedback on the effectiveness of the control algorithm and the response of the system to the changes in bath parameters. The optimization process involved varying four factor namely temperature, time, concentration of mordant and pH. The established optimal conditions for dyeing cotton fabric using *allium burdickii* dye are listed in Table 4.10.

Table 4.10: Optimized dyeing conditions using post mordanting technique

Particulars	Optimal conditions
Temperature (ºC)	60
pH	4.73
Con. of mordant (% owf)	10

4.3. ANALYSIS OF FASTNESS PROPERTIES

Colour fastness of any textile product is of considerable importance to the consumer as it directly affects the serviceability of the fabric. To investigate the effect of mordanting from *allium burdickii* extract, bleached and mercerized cotton fabrics were mordanted with mango bark mordant. The mordant was applied onto the fabrics using pre-mordanting, simultaneous and post mordanting separately and their fastness (fabrics) to rubbing, light, washing and perspiration conducted using AATC crock meter, X-rite Pantone Spectrophotometer, washing machine and AATC perspirometer respectively. Colour change (CC) and staining

(CS) of fabrics were determined for washing, dry and wet rubbing fastness while for perspiration, only staining of the fabric was determined.

The fastness rates for unmordanted and mordanted fabrics rated from very good to excellent for rubbing fastness (4/5- 5), considerable to noticeable (2/3-4) for perspiration, fair to very good (3/4- 4/5) for wash fastness and from very good to excellent (4/5-5) for unmordanted fabrics for all mordanting techniques.

4.3.1. Rubbing fastness of cotton fabrics

The control measure that was used was colour fastness of the dyed fabric without application of any mordant and as noticed in Table 4.11, unmordanted fabrics presented very good rubbing fastness properties ranging from very good (4/5) to excellent (5) for all three mordanting techniques while mordanted fabrics generally showed acceptable fastness with a rating of 4-5.

Table 4.11: Rubbing fastness of unmordanted dyed cotton fabrics.

Unmordanted			
Dry		Wet	
CC	CS	CC	CS
5	5	5	4.5

4.3.1.1. Combined dry rubbing fastness of cotton fabrics

From Figure 4.25 and 4.26, it can be seen that dry rubbing of all dyed fabrics (with exception of a few fabrics) using all the three mordanting techniques presented satisfactory results

ranging from very good (4) to excellent (5). Considering the highest (excellent) rates recorded, colour staining (CS) and colour change (CC) due to dry rubbing showed that post mordanting registered the best results followed by simultaneous and lastly pre-mordanting where DCS and DCC is the colour staining and colour change to dry rubbing.

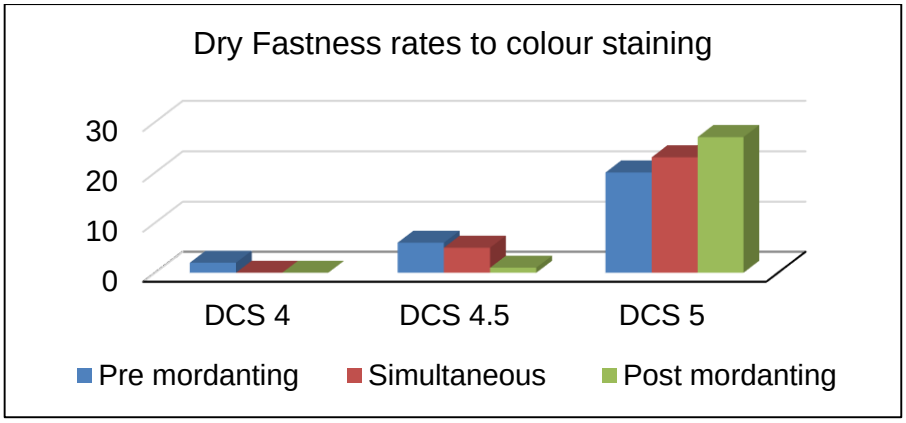


Figure 4.25: Dry rubbing rates to colour staining

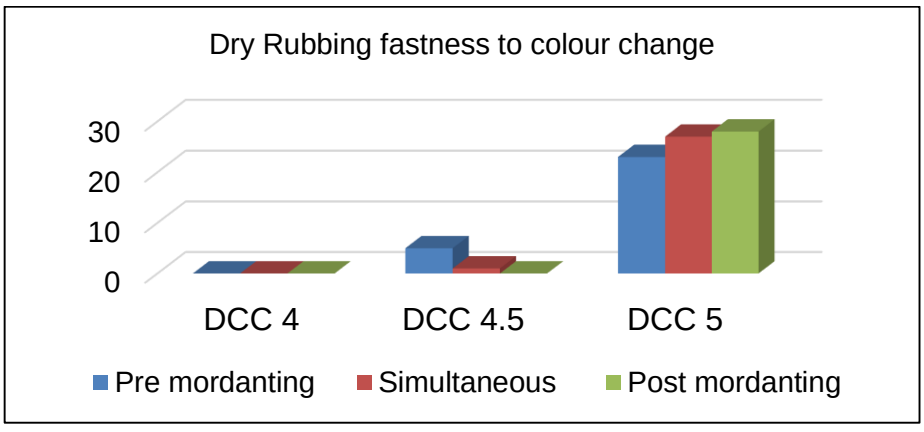


Figure 4.26: Dry rubbing fastness to colour change

However for pre and simultaneous mordanting, some of the fabrics disclosed rates of 4 (good) to 4.5 for CS and 4.5 for CC. This is pointed towards the fact that pre mordanting had a low coefficient of determination.

4.3.1.2. Evaluation of wet rubbing on cotton fabrics

Wet rubbing fastness to colour change (WCC) demonstrated in Figure 4.27 was equally good as most fabrics indicated acceptable rates of 3 to 5. In this particular, simultaneous mordanting presented the best results followed by post and pre mordanting.

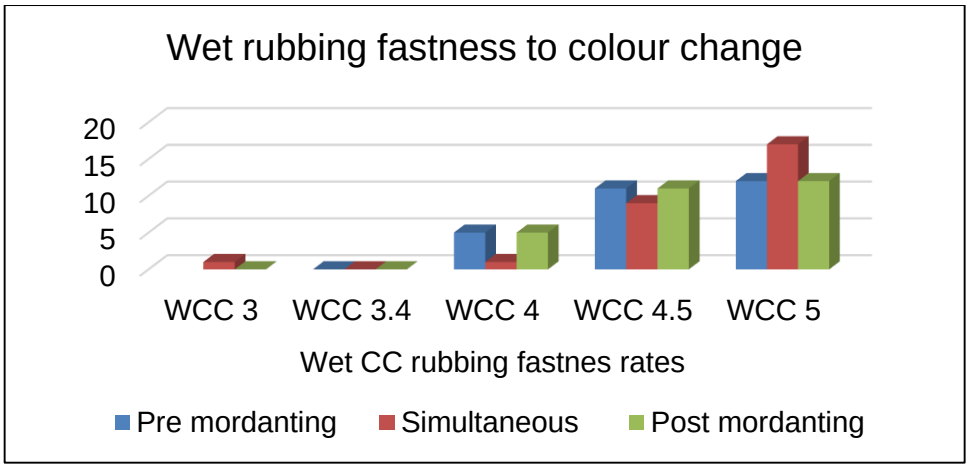


Figure 4.27: Wet rubbing fastness rates to colour change

The fastness properties of colour staining to wet rubbing (WCS) ranged from 1.2 to 5. Although a few dyed fabrics presented low retention of colour, majority of them presented colour rates of 4.5. Simultaneous mordanting gave the best results followed by post and pre mordanting technique.

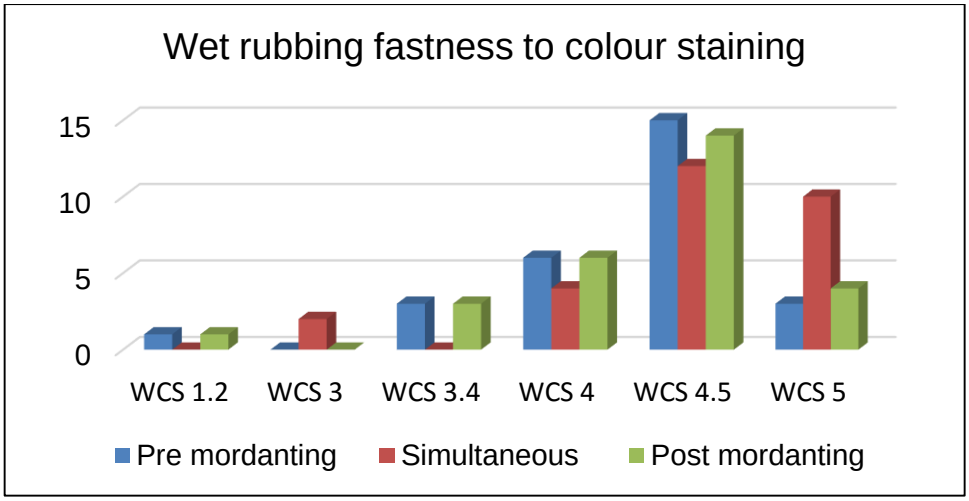


Figure 4.28: Wet rubbing to colour staining

As discussed early in the dyeing section, post mordanting emerged as the best dyeing technique and pre-mordanting as the least. Therefore the acceptable fastness properties obtained with post mordanted fabrics can be attributed to the maximum adsorption and diffusion of dye molecules into the fiber and affinity of the mordant with the colour and fabric. These results therefore affirm that mango mordant is a good mordant for dyeing and mordanting cotton fabrics using post mordanting technique with *allium burdickii* natural dye.

4.3.2. Effect of mordanting on perspiration properties on dyed cotton fabrics.

The perspiration fastness of for all unmordanted fabrics was noticeable good (3-4/5). With exemption of a few fabrics that gave a range of ½, it's evident from Table 4.12 and that the overall perspiration fastness grade for colour change under acidic and alkaline for all dyeing techniques was 3-4 which shows good perspiration fastness to colour change.

Table 4.12: Perspiration properties of the control fabric

% Mordant	Pre- mordanting		Simultaneous		Post-mordanting	
	Acidic	Alkaline	Acidic	Alkaline	Acidic	Alkaline
Umordanted	3	3	3	3.4	3	5

4.3.2.1. Effect of simultaneous mordanting on perspiration fastness

Both the tests moderately stained the cotton fabrics. The fastness rates as illustrated in Figure 4.29 and 4.30 ranged from fairly good to good (3- 4) for acidic medium and from 2-5 (fair to excellent) for alkaline.

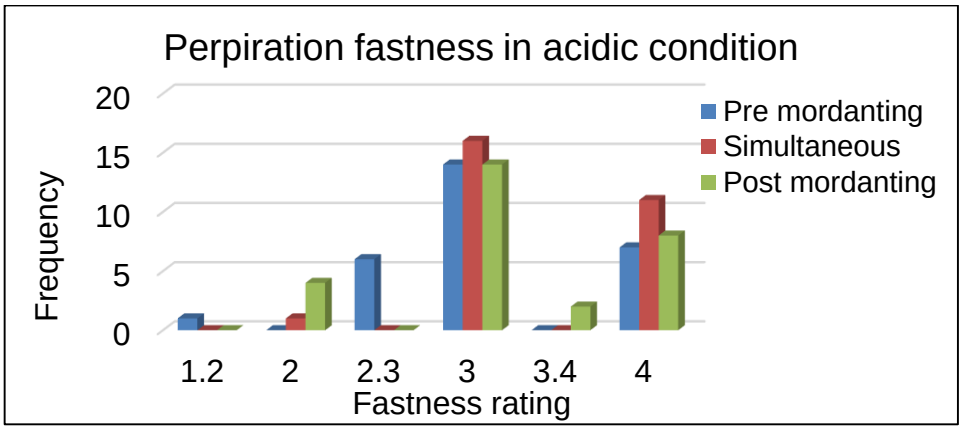


Figure 4.29: Perspiration properties of dyed cotton fabrics in acidic medium

Alkaline tests with exception of run 24 generally showed slight change to the fabrics while acidic properties showed noticeable staining to the fabrics. Some few fabrics (both acidic and alkaline) that were 30% o.w.f mordanted had a considerable staining of 2 on the fabrics.

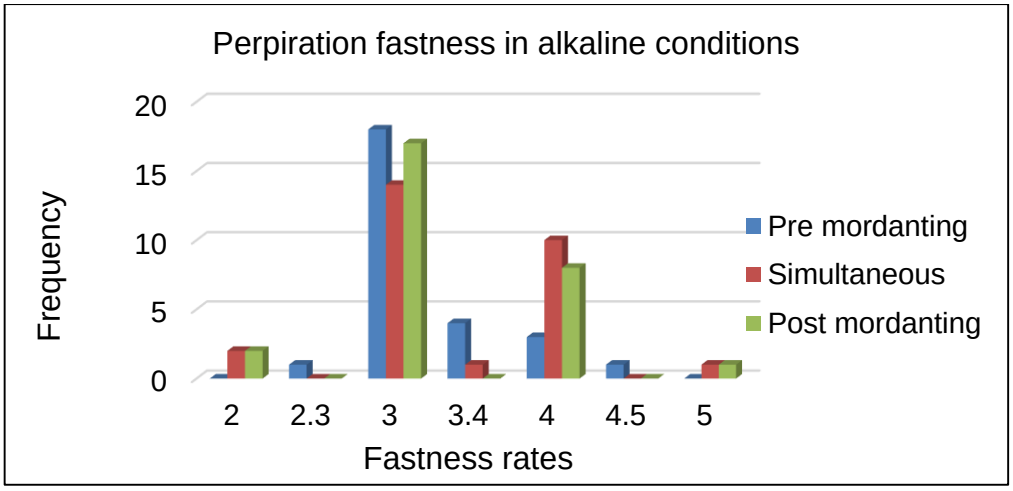


Figure 4.30: Perspiration fastness of dyed cotton fabrics in alkaline medium

Simultaneous mordanting exhibited better retention of colour for acidic perspiration and relatively good alkaline perspiration with rates of 3-4 as the most rates. This implies that this method using mango bark a natural mordant can be used to dye and mordant cotton fabrics.

4.3.2.2. Post and pre-mordanting effect on perspiration analysis

Post mordanted fabrics showed noticeable to a slight (3-4) change for both acidic and alkaline tests while for pre-mordanting, alkaline and acidic perspiration showed considerable (1/2) to a noticeable (4) colour change. When twenty seven runs were run using continuous predictor standardization, stepwise selection of terms and pre mordanting perspiration, alkaline and acidic perspiration models equated in Eqn. 4.4 presented R_{sq} values of 0.6544 and 0.5793. This implies that alkaline perspiration on light fabrics had a less impact on the fabrics thus for light fabrics pre-mordanting technique can be used (Mishuk et al.,2014).

$Y_{11} = 3.0897 - 0.004098X_1$

$$Y_{12} = 3.1775 - 0.002301X_1$$

Eqn. 4.4: Regression models for alkaline and acidic perspiration

Where Y_{11}, Y_{12} and X_1 are acidic perspiration, alkaline perspiration and percentage exhaustion respectively performed under pre mordanting conditions.

The relationship between exhaustion and perspiration analysis was statistically significant with P-values equating to 0.000. However a percentage increase in exhaustion for both models caused a decrease in perspiration rates. Post and simultaneous mordanting similarly presented statistically significant models and unlike pre mordanting, considering simultaneous acidic and post alkaline perspiration, an increase in percentage exhaustion showed an increase in fastness properties. The low to medium resistance to perspiration (low R_{sq} values) presented by all the three mordanting techniques can be attributed to the fabric construction. Unlike heavily constructed fabrics like twill and chambray fabrics, in this case, a plain weave which is a light fabric was used. Therefore this provided an opportunity for alkaline and acidic perspiration to react with the fabrics colour for a long time. However, amongst all the three techniques, fabrics post mordanted present the best perspiration fastness affirming the findings obtained during dyeing that post mordanting was the best technique.

4.3.3. Light fastness

The resistance of colours to fading, changing shade or darkening under the influence of light is known as light fastness. The numerical description of a colour always requires three parameters such as the three values X, Y and Z. These three coordinates serve to demonstrate whether two colours re identical. According to 1931 standard colorimetric, Y gives the direct

measure of darkness or lightness of sample. If $X_1 = X_2$, $Y_1 = Y_2$ and $Z_1 = Z_2$, then the samples have identical colours under those given viewing conditions otherwise colours appear different (Broadbent, 2001). For this analysis, delta E values were considered. Delta E is the measure of fading of a material that depends on initial reference and subsequent readings of L*, a* and b* values. The light fastness for twenty seven mordanted cotton fabrics was analyzed and the results tabulated in Table 4.13. Unmordanted fabrics showed a low rate of fading of 2.69 while cotton fabrics pre and simultaneously dyed at 100^0C, 75 minutes, pH 5.5 and 10% mordant (Run 9) gave the highest measure of fading of 7.44 and 11.7 respectively. However, post mordanted fabrics under the same condition presented a fading of 3.39 (lower fading). The general fastness rates were between 1. 19 (more desirable light fastness) to 5 (less desirable) implying that a relative amount of colour was retained into the fabrics when they were exposed to light.

Pre mordanting method (Table 4.13) presented the highest measure of fading as compared to simultaneous and post mordanting techniques. The fading rate for the all the fabrics was not so consistent due the low diffusion of dye molecules into the fiber as earlier on discussed in the dyeing process. Besides that, variability in the initial reference L*, a* and b* values as a results of calibration of the equipment and the actual variability of the colour coating may have led to the high rates of fading. Simultaneous and post mordanting on the other hand had the highest retention of colour (least rate of fading) when cotton fabrics were exposed to light. Their values ranged from 1.19 (more desirable fastness) to 4.90 (less desirable) signifying that much of the colour was retained in the fabrics when they were exposed to light for over 40 hours.

Table 4.13: Effect of mordanting on light characteristic of dyed cotton fabrics

DELTA E VALUES				
RUN N0.		Pre-mordanted	Simultaneous	Post
1	10	4.21	3.73	3.94
2	30	5.02	1.57	1.77
3	30	2.70	1.97	2.64
4	10	4.42	1.71	7.24
5	30	2.49	1.72	2.38
6	30	5.18	4.09	1.28
7	10	3.37	1.35	3.49
8	30	6.57	2.64	4.17
9	10	7.44	11.17	3.39
10	50	2.71	6.29	4.21
11	10	4.85	5.85	5.57
12	30	4.45	2.43	2.44
13	30	4.57	5.49	1.37
14	30	2.08	1.42	1.19
15	50	6.32	1.69	3.01
16	30	4.37	3.96	2.24
17	30	4.77	5.03	4.31
18	50	3.37	2.85	3.37
19	30	3.88	2.32	2.75
20	30	2.47	3.66	1.41
21	50	1.32	1.25	2.04
22	10	2.94	2.92	2.69
23	30	3.79	2.68	3.21
24	30	3.58	2.54	4.90
25	50	2.40	1.54	4.35
26	30	4.16	2.40	2.89
27	50	5.54	4.67	2.84

Post mordanting method and simultaneous produced darker shades for some dyes whereas for others, colour retention reduced due to the loss of some dye and mordant due to the dye-mordant complex formation in the dye bath. Pre mordanting produced light shades.

4.3.4. Wash Fastness

For analysis of wash fastness, post mordanted cotton fabrics were considered since the method showed better dyeing, rubbing, perspiration and light fastness results. Twenty seven fabrics (obtained from the experimental design) which were dyed were analyzed for their wash fastness. It can be noted from Table 4.14 that the fastness rates for both colour change (CC) and colour staining (CS) of the fabric with exception of a few fabrics were relatively good ranging from 3 to 4.5. Unmordanted fabrics present excellent fastness of 4/5 to 5 for both colour staining and colour change. This implies that the dye has substantivity and affinity for the fabric which enable the auxochromes to properly diffuse and desorb into the fabric.

Fabrics mordanted with 10% mordant presented better fastness compared to those at mordanted at 30 and 50%. Run 10, 12, 21 and 25 presented the lowest retention of dye with a rating of 2 although their respective fabric colour change rates of 4/5, ¾, 4/5, and 4 were good. The highest staining of cotton fabrics is because during washing, the unfixed dyes were remove thus causing a lot of staining. These results are in accordance with Wangatia, (2015) who established that the greatest retention of colour in the fabric after washing was obtained when mango extract was post mordanted on the dyed fabrics.

Table 4.14: Wash fastness results for post mordanted fabrics

RUN NO.	% Mordant	CS	CC
Unmordanted		5	4.5
1	10	4.5	4
4		4.5	3
7		4	4.5
9		3	4.5
11		4	4
22		4.5	1.2
2	30	3.4	4
3		3.4	4.5
5		4	4.5
6		4	3.4
8		3	4.5
12		2	4
13		3.4	4
14		3.4	4.5
16		4	5
17		3.4	4.5
19		3	4
20		4	4
23		3.4	4.5
24		2.3	3
26		4	4.5
18	50	4	4
10		2	4.5
15		3	4
21		2	3.4
25		2	4.5
27		3.4	4.5

CHAPTER 5 : CONCLUSION AND RECOMMENDATIONS

The present work was carried out to extract, characterize and analyze the dyeing of cotton substrates using natural dye extracted from *Allium burdickii* plant. The extraction with variation in conditions such as optimization of pigment, extraction temperature, time, type of solvent and mass to liquor ratio were optimized. Using cotton fabric and mango bark as the natural mordant, the resultant optimized extraction results were used to optimize the dyeing conditions and after fastness properties analyzed.

5.1. CONCLUSION

A red solution was extracted from *allium burdickii* plant using both solvents and aqueous method. The maximum absorbance recorded when the extracted was passed through a UV-Vis Spectrophotometer was 505nm and the optimized extraction conditions established as aqueous extraction method using dye obtained from *Allium burdickii* bulbs while boiling it at 60^0C for 60 minutes using 2gs per 100ml of water plant and a mass to liquor ratio of 1:20. The physico-chemicals found in the dye were flavonoids, tannins, carbohydrates, proteins and phenols for bulbs extracts but no saponins in the leaves.

After optimized extraction, the extract was filtered, diluted and immediately used for dyeing using pre-mordanting, simultaneous and post mordanting. Amongst the three mordanting techniques, post mordanting emerged as the best. The optimized dyeing conditions for Pre mordanting were temperature 60^0C, time 90 minutes, concentration of mordant as 28.28% on weight of fabric (owf) and concentration of salt as 3gs per 100 mls of distilled water; 60^0C, 60 minutes and concentration of mordant as10% (owf) for simultaneous and 60^0C, pH

4.73 and concentration of mordant as 10% owf for post mordanting. Variations in pH were insignificant during simultaneous and pre mordanting while changes in time were insignificant during post mordanting. The study further established that for all the mordanting techniques, increase in temperature and combined effects caused a gradual decrease in dye exhaustion. The dye was therefore classified as polygenetic basic mordant dyes.

The dyed fabrics exhibited acceptable fastness of 4/5 -5 for wet and dry rubbing while for perspiration and washing the rating with exception of a few fabrics was generally good (3-4.5). The unmordanted and mordanted samples with low percentage of mordant exhibited better washing fastness. For light fastness, simultaneous, post and pre mordanting in that order had the highest to the lowest retention of colour for all the cotton fabrics. The values with exception of a few fabrics generally ranged from 1.19 (more desirable fastness) to 5.27 (less desirable). This implies that most of the fabrics were able to retain their shade when they were exposed to light for over 40 hours.

5.2. RECOMMENDATION

The recommendations from this research are; where possible, the MIT department can purchase some more equipment such as the water bath for temperature control in experimentation, HPLC for qualitative analysis of compounds and phytochemical quantification, more glass tubes for the light fastness machine and its conjugate blue wool samples for use in the extraction and analysis of results.

Nevertheless, to maximise the full potential presented by the *Allium burdickii* plant, there is need for further research in the quantitative and qualitative analysis of physico-chemical in the dye and extraction of the natural dye using different techniques. Further research can also be carried out in the dyeing process such as double mordanting of substrates, use of different mordants and substrates during dyeing process, using advanced techniques of dyeing and analysis of the colour measurements of dyed substrates.

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APPENDICES

Figure 5.1: Leaf extract

Figure 5.2: Bulb extracted colourant

Figure 5.3: Stability test for aqueous extract

Figure 5.4: Stability test for methanol extract

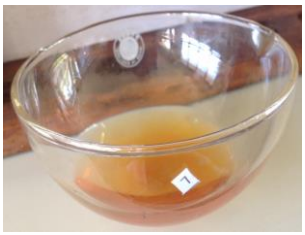

Figure 5.5: Stability test for ethanol extract