Extraction of Natural Dyes from Locally Grown Plants in Ethiopia and Dyeing of Cotton fabrics

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This is to certify that the thesis prepared by Girma Biratu, entitled: Extraction of Natural Dyes from Locally Grown plants in Ethiopia and Dyeing of Cotton Fabric and submitted in the partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering (Process Engineering) compiles with the regulation of the University and meets the accepted standards with respect to originality and quality

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Abstract

Natural dyes were the only colourants used for colouring of textiles beginning from ancient times to nineteenth century. Using of natural dyes are safe for human's health and environmentally friend even though they have drawbacks such as not easily available in the market, needs complex processing steps and relatively poor fastness properties when compared to synthetic dyes. The purpose of this paper was to extract dye from impatiens tinctoria, allo and wild strawberry (Fragaria Vesca L.) plants grown in Ethiopia by using aqueous extraction method. Next crude dye yield of the extact was calculated and un-mordanted and pre-mordanted cotton fabric was dyed. For impatiens tinctoria the maximum yield was 21.3% while the least was 7.8%, in case of allo the maximum yield was 17.4% while the least was 4.5% where as for wild strawberry, the maximum crude dye yield was 18.4% while the least was 7.7%. Dyed fabrics were analyzed in terms of colour strength (K/S) and colour appendices (CIE L a* b*) by using Data colour 6100. Dyed cotton fabric was also analyzed for its fastness properties like: rubbing fastness (dry and wet) by using crock meter, washing fastness (colour change and colour staining) by using atmospheric washer while light fastness was determined by solar box 1500. The results showed that cotton dyed by pre-mordanting with alum and ferrous sulphate showed increased depth of shade and improved fastness as compared to un-mordanted cotton fabric. The CIE L* a* b* result showed: For the wild strawberry, L* values were in the range of 42.56 to 84.26, a* lay in the range of 0.97 to 4.62 and b* values extended from 0.92 to 24.42; Allo lightness(L*) lay in the range of 34 to 85.63, a* values extended in between -2.01 and 4.9, b* lay in the range of 5.94 to 41.23 and Impatiens tinctoria lightness lay in the range of 65.23 to 81.31, a* values lay in the range of 3.52 to 4.70, the values of b* extended in the range of 2.84 to 13.92. The values of k/s also varied in between 0.381 to 14.12. The fastness results (≥3 in case of washing and rubbing fastness and ≥5 for light fastness) indicated that they were in the range of commercially acceptable standards.*

Acknowledgment

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Acronyms

ANOVA...................Analysis of Variance

CIE........................... Commission Internationale d'Eclairage

IS..............................International Standard

MLR.........................Mass to Liquid Ratio

o.w.f.......................on weight of fabric

IT ....*Impatiens tinctoria*

1. Introduction

1.1. Background of the study

Dyes have been used to colour textile fabrics, fibers and yarns. They are applied to textiles in the form of a solution or paste to make them attractive to buyers (Korankye, 2010). Colour is accepted as a common language that consumers are usually concerned with more than any other characteristics. The art of dyeing is as old as civilization of the world. Dyed textile remnants found at different places provide evidences to the practice of dyeing in ancient civilizations. Different regions of the world had their own natural dyeing traditions by utilizing natural resources available in that region (Saxena and Raja, 2014).

Natural dyes were the only used colourants for colouring of textiles beginning from ancient times to nineteenth century and using of them started to decline after the invention of synthetic dyes in the second half of the nineteenth century. In 1856, William Perkins accidently synthesized a basic dye, in place of the natural dyes. After the invention, using of natural dyes declined tremendously as the existing natural dyes failed to full fill the demand of the market, ease applicability, reproducibility and improved quality at lower cost of synthetic dyes (Kechi *et al.,* 2013). Due to the expansion in the field of synthetic dyes and rapid industrialization of textile products, there is almost complete replacement of natural dyes by synthetic dyes as synthetic dyes has the properties of easy availability, ready-to-apply form, simple application process, consistency of shades, and better fastness properties. For this reason, the tradition of using natural dyes could survive only in certain isolated pockets (Singh and Purohit, 2012).

Natural dyes are broadly classified as plant, animal, mineral, and microbial dyes based upon their sources, (Saxena and Raja, 2014). In history, plants have been used for the extraction of natural dyes. More than 500 dye yielding plants species have been found naturally for colouration of textiles (Tiwari, 2005). Colouring agents of these plants are derived from various parts of plants such as roots, leaves, barks, twigs, stems, heartwood, wood shavings, flowers, fruits, rinds, hulls, husks, and fruits. Only few natural dyes possess desirable colouring properties on natural fibers (Siva, 2007). Insects were also the main source of natural dyes of animal origin and most of these provided red colours except Tyrian purple, produced from the secretions of the sea mollusc Murex that produce fast deep violet colour on fabrics. Cochineal was an important animal origin dye obtained from the insects of the species called Dactylopius coccus to dye textiles. The dye is obtained from the bodies of female insects that live on cactus (Opuntia species). Some mineral pigments found in nature such as cinnabar, red ocher, yellow ocher, raw sienna, malachite, ultramarine blue, azurite, gypsum, talc and charcoal black have been used for colouration purposes (Tiwari, 2005). Some bacteria produce coloured substances as secondary metabolites. Bacillus, Brevibacterium, Flavobacterium, Achromobacter, Pseudomonas, Rhodococcus spp. are some of the pigment-producing bacteria.

Natural dyes cannot attach directly to the fabric to produce colours; consequently it needs a bridge that connects the dye to fabric which is known as mordant. Mordant promotes the binding of dyes to fabric by forming a chemical bridge from dye to fiber that insoluble in water hence improves the staining ability and fastness properties. The mordant is usually in the form of salt acts as an electron acceptor in coordination bonds between fabrics and dyes. The use of mordant in dyeing process gives different colours on the fabric (Dominique, 2007). Alum, ferrous sulphate, copper sulphate, sodium or potassium dichromate, stannous chlorides are commonly used mordant for natural dyeing.

Natural dyes produce an extraordinary diversity of colours that complement each other and have dozens of compounds so that they can be used for dyeing almost all types of natural fibers (Saxena and Raja, 2014). Recent researches also show that they can be used to dye some synthetic fibers. Apart from their application in textiles, natural dyes are also used in the colouration of food, medicines, handicraft items and toys, and in leather processing, and many of the dye-yielding plants are used as medicines in various traditional medicinal systems.

There are several challenges and limitations associated with the use of natural dyes. The current dyestuff requirement from the industry is about 3 million tones. Considering this fact, the use of natural dyes in mainstream textile processing is a big challenge. As agricultural land is primarily required to feed an ever-increasing world population and support livestock and biodiversity should not be compromised for the extraction of dyes, sustainability of natural dyes is a major issue (Saxena and Raja, 2014). The serious limitation associated within the natural dyes in the process of dyeing with natural dyes are: very lengthy and time consuming of dyeing process, reproducibility of shades, absence of proper documentation and years of their application on various substrates have been lost. Therefore, it becomes necessary to develop new techniques of colouration and also to standardize these processes with the help of modern scientific so that these dyes can offer themselves as an effective eco option.

Now day, global environment awareness trend encourages the replacement of synthetic dyes that release large amount of waste and unfixed colour that cause health hazards, pollution and disturb eco balance. During last two decades natural dyes have witnessed a process of revival with the increasing awareness of consumers far eco textiles and need to preserve environment has lead to the revival of old practice of colouration with natural dyestuff. Due to the carcinogens of synthetic dyes and their intermediates, some synthetic dyes and their intermediates are being looked at as an "eco solution" to the ill effects of synthetic dyes. Recent environmental awareness has again revived interest in natural dyes mainly among environmentally conscious people. Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer. One of the best alternatives way through which we can minimize the environmental impact caused by textile processing is using of dyes that are environmentally friendly. One of the possible solutions is using of natural plant dyes that come from plants parts that include flowers, leaves and roots while seeds, fruits and young shoots also serve as a source of natural dyes (Bechtold *et al.,* 2002; Samanta and Agarwal, 2009).

In Ethiopia, natural dyes have been utilized for colourations of textiles for a long time as evidenced from the colourful pictures drawn on canvas before 19th century and ancient dyed cultural clothes found in Orthodox Churches and museums. Ethiopia has an abundance plant species that have dye yielding properties (Kechi *et al,* .2013). Although there is no complete documentation available as scientific literature, some of the villagers of Ethiopian region are extracting dyes from leaves, roots, flowers or barks of some plant species mostly by fermenting, boiling, scrapping, powdering and mixing with other materials to get the desired colour.

In this study, the extraction of the principal colourants from three plant species locally known as *Ansosila* from its roots, *allo/mokko* from its leaves and Strawberry from its fruits, and evaluation of the dyeing and colour fastness properties (the resistance of a material to change any of its colour characteristics or extent of transfer of its colourants to adjacent white materials in touch (Samanta and Agarwal, 2009) on cotton fabrics was conducted.

1.2. Statement of the problem

Though various workers have reported different results on the extraction of colour components from different dye-bearing plant species, still now many species remain unexplored. Therefore, it is necessary to explore the natural colourants from abundantly occurring natural plants. According to the report of Centre for education (2012), Ethiopia has over 6500-7000 plant species of which about 15 % are endemic. Out of these, the dye-yielding plants in Ethiopia have not been identified scientifically though large biodiversity of plants are expected to have important colour constituents for textile colouration. On the other hand, in Ethiopia, traditional natural dyeing experience is very limited and remains only in the areas of colouring bodies and hands of few craftsmen. However, natural dyes have also the tendency to give a better result when they are applied to dye clothes.

When natural dyes are compared with synthetic dyes, they are safer and eco friend. Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer (Saxena and Raja, 2014). Now days with the public enhanced cognizance to eco-safety and health concerns, eco-friendly and non-toxic bio-resource products are regaining popularity in different spheres of our lives. Natural dyes, obtained from plants which are renewable and sustainable bio-resource products with minimum environmental impact not only have the tendency to be used in colouration of textiles but also as food ingredients and cosmetics (Kadolph, 2008**)**. The application of synthetic dyes has detrimental effects on environment as well as on the body. The negative impacts of synthetic dyes on the body are associated with allergic, toxic, carcinogenic and other harmful responses. Amidst growing environmental and health concerns eco-friendly nontoxic natural dyes re-emerged as a potential viable ‘’ Green chemistry’ option as an alternative/co-partner to some extent to synthetic dyes**.** Therefore the main purpose of present study was to identify few potential dye plants through yield analyzing, dyeing and testing the colour strength, CIE L*a* b* values and fastness properties of dyed sample using standard methods.

1.3. Objective of the study

1.3.1. General objective

The main objective of this study was to extract dye from locally available potential dye plants and evaluating performance for dyed cotton fabrics.

1.3.2. Specific objectives

The specific objectives were;

- To extract dye from plant species of *Allo/Mokko (Anogeissus leiocarpa), Impatiens tinctoria* and wild straw berry using aqueous extraction method.
- To optimize the operating conditions such as extraction temperature and time.
- To evaluate the fastness characteristics of the selected dyes on cotton fabrics.
- To evaluate effects of mordants on the fastness and colourimeter values by dyeing cotton fabrics.

1.4. Significance of the study

This study has the following significances:
Even though Ethiopia as well as Africa is known for its abundance in plant diversities, still now, only few researches have been done in identifying plants which can serve for the production of dyes. Africa is rich in different plant species with potential to produce novel natural products with dye yielding properties. Unfortunately many of these plants remain unknown physic chemically, undocumented and lie in the wild unexploited and yet represent an enormous reservoir of new dye molecules awaiting discovery. So, this study can serve to identify some dye yielding potential plants for dyeing of clothes.

Using of these natural dyes in textile industry has the advantages as it is environmental friendliness, an ecologically sound product which would also appeal to the "Green-minded" consumer and easy of availability. Therefore, it is possible to say that using of these natural colourants is a possible means of conserving the environment. Natural dyes are also believed to be safe because of their nontoxic, non allergic and biodegradable in their nature.

In our country, Ethiopia, now a day micro and small scale enterprises are established on different sectors of which textiles and garment can be raised as an exemplary. Therefore knowing the natural colourants in the art of dyeing creates job opportunity for local spinners and weavers by adding values to their products. On the other hand, this research could serve as a reference material for practical use for the extraction of natural dyes from local plants found in the environment as substitute for synthetic colourants used in the textile which do not harm human. In addition, this research can create versatility in obtaining and producing natural dyes from the environment, including the forest reserves. Finally, this study also has an advantage of encouraging other researchers who want to do the same topic in the future as an important step.

2. Literature Review

2.1. History of using dyes in textile

Dyed textile remnants found during archaeological excavations at different places all over the world provide evidence to the practice of dyeing in ancient civilizations. Natural dyes were the only used colourants for colouring of textiles from ancient times till the nineteenth century (Kechi *et al.,* 2013). As the name suggests, natural dyes are derived from natural resources. Colouring materials obtained from natural resources of plant, animal, mineral, and microbial origins were used for colouration of various textile materials. Different regions of the world had their own natural dyeing traditions utilizing the natural resources available in that region. Use of natural dyes started to decline after the invention of synthetic dyes in the second half of the nineteenth century. Concerted research efforts in the field of synthetic dyes and rapid industrialization of textile production resulted in almost complete replacement of natural dyes by synthetic dyes on account of their easy availability in ready-to-apply form, simple application process, consistency of shades, and better fastness properties. The tradition of using natural dyes could survive only in certain isolated pockets (Saxena and Raja, 2014).

2.2. Dyes in textiles

A dye is an organic compound composed of a chromophore (the coloured portion of the dye molecule) and an auxochrome (which slightly alters the colour). The auxochrome makes the dye soluble and is a site for bonding the fiber. Dyes are molecules that can be dissolved in water or some other carrier so that they will penetrate the fiber. Dyeing processes may be used either to colour fibers and yarns before they are made into cloth or to colour the fabric itself. Dyeing also provides a means to decorate fabrics. Dyes may be applied as a solution or paste to patterns created on fabric. To be usable in colouring fabrics, a dye must be highly coloured; must yield goods that are “colourfast” or resistant to colour change or loss during use and care; and, must be soluble or capable of being made soluble in water or other medium in which they are applied, or they must themselves be molecularly dispersible into the fibers of the fabric (Korankye, 2010).

Dyes are the most common way to add colour to fibers, yarns and fabrics. Dyes are applied to textiles in the form of a solution or paste. Colour for the textiles industry is mostly obtained from dyes and pigments. Colour is one of the most significant factors in the appeal and marketability of textiles products (Kadolph, 2005). Colour is also a very interesting part of textiles as customers expect two things: aesthetically pleasing colours and prints; and colour permanence. In addition, primarily colour is considered in the selection and purchase of clothing to a large extent.

2.2.1. Natural Dyes

Natural dyes comprise those colourants (dye and pigments) that are obtained from animal and vegetable matter without chemical processing (Agarwal A., 1992). Natural colours are beautiful to behold (Korankye, 2010). Colouring matter extracted from the roots, stems, leaves or barriers, and flowers of various plants have little or no colouring power by themselves except when they are used in conjunction with mordants. Lack of colour fastness resulted in the discovery of mordants – substances which aid in the absorption of dyes.

a) Advantages of natural dyes

Recent environmental awareness has again revived interest in natural dyes mainly among environmentally conscious people. Natural dyes are considered eco-friendly as these are renewable and biodegradable; are skin friendly and may also provide health benefits to the wearer. Natural dyes can be used for dyeing almost all types of natural fibers. Recent research shows that they can also be used to dye some synthetic fibers. Apart from their application in textiles, natural dyes are also used in the colouration of food, medicines, handicraft items and toys, and in leather processing, and many of the dye-yielding plants are used as medicines in various traditional medicinal systems (Saxena and Raja, 2014).

Some plant-derived dyes have other applications such as food ingredients and medicines in traditional medicine systems and hence a commercial supply chain of these dyes is in place. Some of the natural dyes were well known in the past for their dyeing properties and have remained in use even now, albeit on a small scale. A renewed interest in natural dyes has increased their commercial availability (Ali *et al*., 2006 ; Saxena and Raja, 2014).

b) Limitation of natural dyes

There are several challenges and limitations associated with the use of natural dyes. The use of natural dyes in mainstream textile processing is a big challenge. As agricultural land is primarily required to feed an ever-increasing world population and support livestock and biodiversity should not be compromised for the extraction of dyes, sustainability of natural dyes is a major issue (Saxena and Raja, 2014; Verma *et al.*, 1998).

c) Potential Sources of Natural Dyes

Natural dyes are derived from natural resources and based upon their source of origin; these are broadly classified as plant, animal, mineral, and microbial dyes although plants are the major sources of natural dyes. As interest in natural dyes grew, information from the old literature was collected and traditional dyeing practices in different regions were documented and compiled by various researchers (Saxena and Raja, 2014).

Plant Origin

Historically, plants have been used for the extraction of a majority of natural dyes. Various plant parts including roots, leaves, twigs, stems, heartwood, bark, wood shavings, flowers, fruits, rinds, hulls, husks, and the like serve as natural dye sources. The famous natural blue dye, indigo is obtained from the leaves of the plant Indigofera tinctoria (Korankye, 2010).

A. Blue Dyes

Indigo is the only important natural blue dye. Leaves of the plant *Indigofera tinctoria* are the best source of this dye. This very important dye popularly known as the ‘‘king of natural dyes’’ has been used from ancient times till now for producing blue colour and is today most popular for denim fabrics. The colouring matter is present in indigo plant leaves as a light yellow substance called indicant Natural Dyes. The leaf production from one acre of cultivated indigo plants is approximately 5,000 kg which can yield about 50 kg of pure natural indigo powder after processing. It is produced by fermenting the fresh plant leaves, and cakes thus prepared are used for dyeing purposes. Apart from indigofera species, there are several plants that can be used to produce indigo dye.

Woad is a natural indigo-producing plant in Europe. Apart from this, dyers knotweed (Polygonum tinctorium) and Pala Indigo (Wrightia tinctoria) are some of the plants used to produce indigo traditionally.

B. Red Dyes

There are several plant sources of red natural dyes. A few popular sources are listed below.

Madder

Madder is the red colour producing natural dyes from the plants of various Rubia species. The dye is obtained from the roots of the plant. It is also popularly known as the ‘‘queen of natural dyes.’’ The main colouring constituent of European madder Rubia tinctorum is alizarin. The yield of roots from the 3-year-old plant is between 3–5 tonnes per hectare and about 150–200 kg of dye.

Brazil Wood/Sappan Wood

A red dye is obtained from the wood of Caesalpina sappan, a small tree found in India, Malaysia, and the Philippines which is known as sappan wood or ‘‘Patang.’’ The same dye is also present in Brazil wood (Caesalpinia echinata), the name (Saxena and Raja) being derived from the word braza meaning glowing like fire due to the bright red colour of its wood. Aqueous extraction can be used to extract the dye.

Morinda

The root and bark of the tree Morinda citrifolia growing in India and Sri Lanka is used for getting red shades. Maximum colouring matter can be obtained from the 4-year-old tree. Mature trees have very little dye. Dye is extracted from the chipped material with water after a preliminary wash to remove free acids. Various shades including purple and chocolate can be produced with the use of mordants.

Safflower

Safflower is an annual herb known to have originated in Afghanistan. It is mainly cultivated for oil from its seeds which are rich in polyunsaturated fatty acids. The safflower florets were traditionally used for extracting dye which was valued florits bright cherry-red colour. It contains two colouring matters, a water-soluble yellow present in abundance (26–36 %) which was not used as a dye and the scarlet red water-insoluble carthamin present only to the extent of 0.3–0.6

C. Yellow Dyes

Yellow dyes are available from several plant resources. Some of the prominent sources are listed below.

Turmeric

Turmeric is a well-known natural dye. The dye is extracted from the fresh or dried rhizomes of turmeric. The dye present is chemically curcumin belonging to the Diaroylmethane class. It is a substantive dye capable of directly dyeing silk, wool, and cotton. The shade produced is fast to washing but its fastness to light is poor. The natural mordants such as tannin obtained from myrobolan can be used to improve the fastness properties. Turmeric dyeing can be over dyed with indigo for production of fast greens.

Saffron

Saffron is an ancient yellow dye belonging to the family Iridaceae and is obtained from the dried stigmas of the plant Crocus sativus. It is grown in the Mediterranean, Iran, and India, and used for cooking as well as medicinal purposes. The dye is extracted from the stigmas of flowers by boiling them in water. It imparts a bright yellow colour to the materials. It can directly dye wool, silk, and cotton. Alum mordant produces an orange yellow known as saffron yellow.

Annatto

Annatto Bixa orellana is a small tree belonging to the family Bixaceae. The tree is known for the yellow orange dye obtained from its seeds. It is extensively used for the dyeing of cotton, wool, and silk and also used for colouring butter, cheese, and the like. The pulp is rich in tannin. The alkali extraction method is used for extracting dye at boiling conditions. It produces reddish orange shades on cotton, wool, and silk.

Barberry

The barberry (Berberis aristata) plant roots, bark, and stems are used to extract the dye. The main constituent of the dye is berberine which is an alkaloid. It is a basic dye and can be used to dye silk and wool directly. The dye produces a bright yellow colour with good washing fastness and average light fastness. Cotton can be dyed after mordanting (Saxena and Raja, 2014).

Pomegranate

Rinds of pomegranate (Punica granatum) fruits are rich in tannins and are used for mordanting purposes. A yellow dye is also present which can be used to dye wool, silk, and cotton with good fastness properties. It is also used along with turmeric for improving the light fastness of the dyed materials.

Onion

The outer skin of onion (Allium cepa) which is generally thrown away as waste can be used to extract yellow colour natural dye. The dye is flavonoid in chemical constitution, and produces bright colours on wool and silk. Cotton can be dyed with suitable mordant. The washing and light fastness of the shade produced are moderate.

Animal Origin

Red animal dyes derived from certain species of tiny scale insects known as cochineal (*Dactylopus coccus costa*) that fed on red cactus berries. These insects were gathered by hand and ground into pigment, requiring 70,000 carcasses to make a pound of dye. By 1600, approximately 500,000 pounds of cochineal were shipped annually to Spain. The dyes were highly valued from ancient times and right through the Middle Ages. Aimson (1999) stated that the purple robes of royalty in Ancient Rome were dyed using a substance extracted from a rare crustacean called Trumpet Shell (Purple Fish) which was found near Tyre on the Mediterranean coast. An estimated 8,500 shellfish were crushed to produce one gram of the dye, which made it so expensive that only kings could afford to use it. Major sources of animal dyes are:

• Cochineal (red) – from bodies of cochineal insects.

• Tyrian purple or crimson – from the bodies of some types of marine snails.

• Sepia (brown) – from secretions of several types of cuttlefish.

Table 1: Categories of some natural dyes

Natural dye classification		
Colours	**Chemical classifications**	**Common names**
Yellow and Brown	Flavone dye	Weld, Quercitron, Fustic, Osage, Chamomile, Tesu, Dolu, Marigold, Cutch
Yellow	Iso-quinoline dyes	Barberry
Orange-Yellow	Chromene dye	Kamala
Brown and Purple-Grey	Naphthoquinone dyes	Henna, Walnut, Alkanet, Pitti
Red	Anthraquinone dye	Lac, Cochineal, Madder (Majithro)
Purple and Black	Benzophyrone	Logwood
Blue	Indigoid	Indigo
Neutral	Vegetable,Tannins, Gallotannins, ellagitannins, and catechol tannins	Wattle, Myrobalan, Pomegranate, Sumach, Chestnut, Eucalyptus

Insects were the main source of natural dyes of animal origin and most of these provided red colours. The oldest animal origin dye, Tyrian purple, produced from the secretions of the sea thraq Murex is an exception. This dye produced a very fast deep violet colour on fabrics. It was very expensive as thousands of thraqu were needed to get a gram of the dye. Hence it was considered a symbol of royalty and was used to colour the clothes of the royal family. Cochineal was an important animal origin dye obtained from the insects of the species called Dactylopius coccus which is still being used to dye textiles. The dye is obtained from the bodies of female insects that live on cactus (Opuntia species). The principal colouring matter is carminic acid. The cochineal dye produces crimson red colour on animal fibers and has good washing and light fastness properties. Its bright red aluminum calcium chelate known as carmine is used as food colour. Kermes is another animal origin crimson red dye derived from the insect Kermes licis. This dye has been known since ancient times to colour animal fibers but was inferior to cochineal in fastness properties. Lac was also well known in ancient times for colouration of animal fibers. It is obtained from the hardened secretions (stick lac) of the insect Kerria lacca found on the twigs (Chairat et al., 2008).

Mineral Origin

Some mineral pigments found in nature such as cinnabar, red ocher, yellow ocher, raw sienna, malachite, ultramarine blue, azurite, gypsum, talc, charcoal black, and so on, have been used for colouration purposes. Apart from the red ocher that was used by the monks for colouration of their robes, these were mainly used in paintings and murals along with gum as binder (Agarwal and Tiwari, 1989).

Microbial and Fungal Origin

Bacillus, Brevibacterium, Flavobacterium, Achromobacter, Pseudomonas, Rhodococcus species are bacteria that produce colored substances as secondary metabolites (Joshi, 2003). Some bacteria produce indigo upon exposure to petroleum products. Microbes as a dye source offer an advantage as these can be easily grown on cheap substrates under controlled conditions. They investigated the growing conditions for pigment production and its extraction. Extracted pigment from Serratia strain was characterized and dyeing characteristics for various textile substrates indicated that pink coloration obtained on wool was fast to washing but its very poor fastness to light did not encourage future work for use as textile dye. Pigments from the fungus Monascus purpureus are used for coloration of some traditional oriental food items. It has been used for fabric coloration also. Trichoderma species has been used for coloration of silk and wool with excellent washing fastness (Vigneswaran *et al.,* 2004).

Lichens and mushrooms have been used as sources of colorants in Europe and in some other parts of the world. Orchil dye from lichens was used to create violet and purple shades as a cheap alternative to costly purple dye from molluscs. They have also been used to dye wool to shades of yellow, brown, and reddish brown. Orchil and litmus colorants obtained from lichens are not found in higher plants. Dyes derived from mushrooms have become popular since the 1970s. Some Cortinarius species have intensely colored fruiting bodies and are the best mushroom dyes. Cortinarius sanguineus (blood-red webcap) contains Anthraquinone pigments emodin and dermocybin in glucoside form (Hynninen et al. 2000).

Classification of Dyes

Based on their application, chemical composition and colour, natural dyes can be classified in to different groups;

1) Based on the major chemical constituents

On the basis of major chemical constituents present, natural dyes are divided as follows **(**Saxena and Raja, 2014**):**

Indigoid dyes

Indigo is the primary source of the blue colour. Chemically it is indigotin and is found in largest concentration in the leaves of some Indigofera species such as I. tinctoria, I. errecta, and I. sumatrana. Since Indigo is not soluble in water it has to be reduced to its water-soluble leuco form through a reduction process for dyeing textiles. After dyeing, the leuco form is oxidized to its original blue indigotin structure by atmospheric air. It has excellent colour fastness properties. Tyrian purple obtained from Mediterranean anthraqu of the Purpura and Murex genus is another indigoid dye that also has excellent fastness properties. Chemically, it is the 6, 6' dibromo derivative of indigo

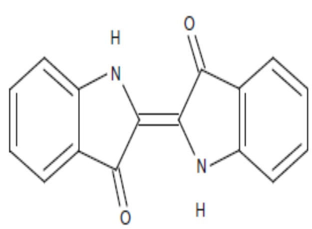

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Figure 1: Indigotin

Anthraquinone dyes

A large number of red colour-producing dyes of natural dyes are under this category. Alizarin obtained from European madder (Rubia tinctorum) is an exemplary red dye. Other dyes include lac, cochineal, morinda, and Indian madder (manjishth/manjeet). But arthamin from safflower (Carthamus tinctorius) florets is an old traditional red dye having a benzoquinone structure.

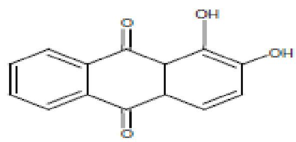

Figure 2: alizarin (1,2-dihydroxy anthraquinone)

Naphthoquinone, Benzoquinone dyes

Some of the natural dyes belonging to this category are henna, walnut shells, and so on. The colouring matter of henna is lawsone which is 2-hydroxy anthraquinone and walnut shells contain juglone which is 5-hydroxy anthraquinone. These dyes also produce orange, red, or reddish brown shades like Anthraquinone dyes. The basic structure of the Naphthoquinone is depicted in Figure below.

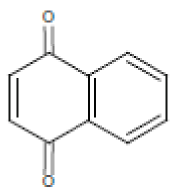

Figure 3: Naphthoquinone

Flavonoid dyes

Most of the yellow natural dyes have hydroxyl or methoxy substituted flavones structure. Dyes with this chemical constitution are found in Weld (Reseda luteola), flavone luteolin, marigold (Tagetus spp.), Logwood (heartwood of Haematoxylon campechianum), dye from the wood of Caesalpinia echinata (Brazil wood), Caesalpinia sappan (Sappan wood) belongs to this group.

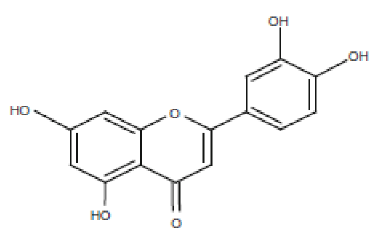

Figure 4: Luteolin

Carotenoid dyes

The major dyes in this class are bixin found in annatto seeds and crocin found in saffron stigma. Orange dye from the corolla tubes of Nyctanthes arbor-tristis flowers or nictanthin also has a similar carotenoid structure.

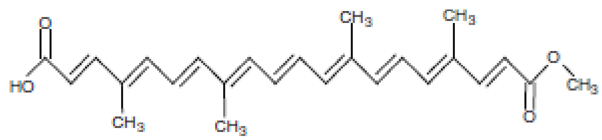

Figure 5: Bixin

Tannin-based dyes

Tannins are polyphenolic compounds that are present in many natural resources used for dyeing purposes. The dyes with tannin generally require mordants for fixing onto the fabric. This class of dyes also tends to change colour with the change in mordant depending upon the dye-mordant complex. Dye obtained from the bark of Acacia nilotica and wood of Acacia catechu (Cutch) have a polyphenolic structure.

2) Classification based on application

Natural dyes can be classified in to the following major types based on their application (Gulrajani & Gupta, 1992).

Substantive dyes

Substantive dyes are used by simply combining the dye stuff with the fiber and it has substantively to the fiber. An example is turmeric the spice which works on cotton as well as wool and silk; others included onion, walnut, husk and tea.

Vat dyes

The vat dyes work the same way on protein and cellulose by being introduced in to the surface of the fiber in their soluble form and then converted in to an insoluble form. They are complex to use. For example, the vat dye indigo and the ancient Tyrian purple dye extracted from shell fish.

Mordant dye

Most natural dyeing is done with the use of mordant, most commonly used are the heavy metal ions, but sometimes tannins. The mordant allows many natural dyes which would otherwise just wash out to attain acceptable wash fastness. Mordant remains in the fiber permanently holding the dye. Each different metal used as mordant produces a different range of colours for each dye.

Acid dyes

Acid dyes are applied from an acidic medium. The dye molecules have either sulphonic or carboxylic group (s) which can form an electrovalent bond with amino groups of wool and silk. An after treatment with tannic acid known as back tanning improves the fastness of these type of dyes, *e.g.,* saffron.

Disperse dye

Disperse dye has a relatively low molecular mass, low solubility and no strong solubilizing groups. Disperse dyes can be applied on to hydrophobic synthetic fiber from neutral to mildly acidic pH. They can also be applied to silk and wool.

d) Recent Trends of Natural Dyeing

Many manufacturers in the United States, India, China, and other countries are engaged in the production and selling of natural dyes and raw materials used for the production of it. Presently an approximately 1 % share of textiles is only being dyed with natural dyes. Mostly these are applied in the cottage sector such as traditional artisans, enthusiasts, and small entrepreneurs (Saxena and Raja, 2014).

To assure the sustainability of natural dyes it needs to be increased in a manner by utilizing the by-products and wastes from agriculture and agro processing industries and judicious collection of forest produce. This may be supplemented by growing important dye-bearing plants on wastelands and marginal lands thus providing an alternative cash crop to cultivators. Establishment of proper characterization and certification protocols for natural dyes would definitely improve consumer confidence in natural dyed textiles and would benefit both producers and users. If natural dye availability can be increased by the above-described measures and the cost of purified dyes can be brought down with a proper certification mechanism, there is a huge scope for adoption of these dyes by small-scale dyeing units as they lack the resources to install and operate expensive effluent treatment plants needed to bring the synthetic dye effluent within the limits set by regulatory authorities. If at any time in the future, the availability of natural dyes can be increased to very high levels by biotechnological interventions such as tissue culture or genetic engineering resulting in mass production of these dyes by microbes at low cost, then only can their usage become sustainable for mainstream textile processing. At the level where scientific developments stand today, natural dyes are a sustainable option only for small-scale applications and they can complement synthetic dyes as an eco-friendly option for the environment-conscious consumer and a means of providing livelihood to various stakeholders of the natural dye value chain (Saxena and Raja, 2014).

Between January and September 2010, exports of natural dyes grew to an impressive annual rate of 181.0%, mainly boosted by the higher price of carmine cochineal, and set off by the growing international demand. This report presents the latest information on the performance of the production of inputs used in the production of natural dyes such as paprika, marigold, annatto and turmeric. It provides information on the average yield of these crops, farm-gate prices and global market analysis of dyes and development of Peruvian exports and imports of natural colours. In these years the demand of natural dyes and the interest for these, followed much the fashion trend, with ups and downs recurrent, currently we are in one phase of increase. The fields of industry that today are more interested to introduce the natural dyes are intimate dress , to the children clothes until to the interior, fields where more the naturalness is more important and where the problems of allergies are greater (Singh and Purohit, 2012).

e) Natural Dyeing Principles

Natural dyes work best with natural fibers such as cotton, linen, wool, silk, jute, and sisal. Application of natural dyes requires some special measures to ensure evenness in dyeing. Many factors have to be accounted for when one works with natural dyes. They are: nature of material to be dyed, measurements of mordants and dyestuffs, temperature, agitation, natural dyes are unpredictable, wet fibers look darker and rinsing (Samanta and Konar, 2012).

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f) Mechanism of dyeing

Almost every plant can yield colour whether leaves, bark, wood, roots or fruits are used. Nearly all require some sort of mordant. Natural dyes can neither dye animal nor vegetable fibers directly, but require a mordant, which depends upon the nature of the dye. A colouring material that has the strength to bind itself to a fiber and remain there by staining the fiber is considered to be the best. If the dye is acidic, the mordant must be basic (the most common basic mordants are the salts of Cr, Al, Sn, Fe) on the other hand, if the dye is basic, the mordant must be acidic (the most common acidic mordant is tannin or tannic acid) (Samanta and Konar, 2012).
When the fabric to be dyed is first soaked into a solution of the metallic salt (i.e. mordant), it forms the insoluble metallic hydroxide. Mordants increase binding of dye to fabric by forming a chemical bridge from dye to fiber. The mordanted fiber is then dried and placed in a solution of the dye. Dyeing is held by the hydroxide of the metal on the fiber by means of chelating complexes which formed when the resulting dye has a five- or six- membered ring, which is possible only when OH group in the dyestuff present is ortho- to one of the following groups: -OH, -CO, -NO, -NO2, -COOH, -NH, -NH2 and -N=N-. The chemistry of bonding of dyes to fibers is complex; it involves direct bonding, H-bonds and hydrophobic interactions (Samanta and Konar, 2012).

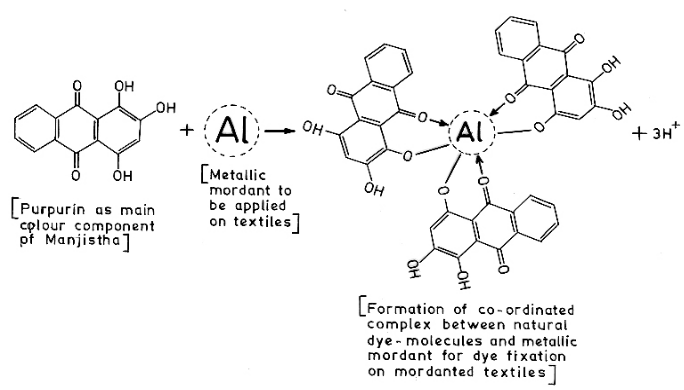


Figure 6: Reaction between alum and purpuri

g) Plants used within this study

a. **b.** **c.**

Figure 7: Plants used within this study (a. Allo (*Anogeissus leiocarpa*) **c**. Ansosila (*Impatiens tinctoria*) c. Wild Strawberry (*Fragaria vesca*))

Allo

Allo is also called *Moko* in Afan Oromo according to the local language has small and medium sized leaves and grown in low level altitude areas along the rivers. It has been used for colouring of cloth made from cotton and has the highest affinity to cotton fabrics even in the absence of mordants. According to the information obtained from the elders, leaves and tips of shoot (greenish parts) are grounded and boiled within water along with fabric for dyeing.

Anogeissus leiocarpa is found in a large range of ecosystems, from dry savannah to wet forest borders, in wooded grassland and bush land, and on riverbanks in Eritrea, Ethiopia, Sudan, Cameroon, Congo-Kinshasa, Benin, Côte d'Ivoire, Gambia, Ghana, Guinea, Mali, Niger, Nigeria and Senegal. Optimal growth conditions are 200-1200 mm annual rainfall, from sea level up to an altitude of 1900 m in fertile soils. It often grows gregariously on fertile soil in moist situations. The African birch (*Anogeissus leiocarpa* (DC.) Guill. & Perr.) is a slow growing evergreen shrub or small to medium-sized tree, reaching up to 15-30 m in height. The bark is grey to mottled pale and dark brown; leaves are alternate to nearly opposite, simple and entire, covered in dense silky hair when young. Flowers are pentamerous, pale yellow and fragrant. Fruits are rounded yellowish to reddish brown colour that contains one seed, enclosed horizontally in a dense cone-like fructification. The moisture content of *Allo* leaves ranges in 40% to 50% on dry base (Andary *et al*., 2005).

The leaves are famous for their use as a yellow dye in ancestral Bogolan textile techniques in Mali and Burkina Faso (Agaie et al., 2007). Derivatives of ellagic acids ("anogelline") extracted from the bark have been shown to delay the degradation of collagen (Jansen et al., 2005). The leaves of *Anogeissus leiocarpa* are rich in tannin: they contain ellagic, gallic and gentisic acids, derivatives of gallic and ellagic acid, and several flavonoids (derivatives of quercetin and kaempferol) that are very useful for dyeing (Andary et al., 2005).

Strawberries

The phenolic compounds in strawberries are anthocyanins, responsible for the red colour in Strawberry. The plant is acclimatized to different environments and, therefore, could be cultivated worldwide, intensively in Europe and North America in open fields, whereas in China it is cultivated mainly in greenhouses (Zeljka marjanovic-balaban, 2012).

The main anthocyanins contained in Strawberry are cyanidin-3-glucoside, 3.9-10.6%; pelargonidin-3-glucoside, 89-95%; and pelargonidin-3-arabinoside, 3.1-3.9% (DEFRA, 2016). Anthocyanins in strawberries are the major known polyphenolic compounds, responsible for fruit colour, and can be used as natural pigments (red and blue colours). The Anthocyanins content of strawberries is influenced by cultivar selection, environmental factors such as light, temperature, and agricultural methods.

The water content of strawberries ranges from 80.51 to 85.19%. Its protein content ranged from 0.50-0.92% to 1.42-1.65%. Energy value of berries is low (below 50 kcal/100 g). Different studies show that the berries species contains calcium (5-50 mg/100 g), iron (0.30-1.30 mg/100 g), zinc (0.10-0.60 mg/100 g), ascorbic acid (1.9- 60.51 mg/100 g) and riboflavin (0.02-0.05 mg/100 g) (Zeljka marjanovic-balaban, 2012).

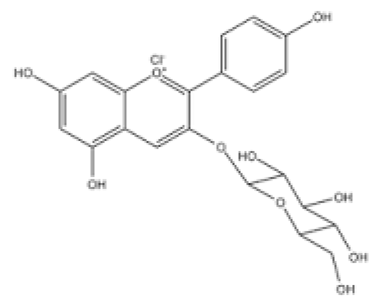


Figure 8: pelargonidin-3-glucoside

Impatience tinctoria

Impatiens tinctoria locally also known as *Ansosila*, is a herb up to 20cm tall growing from an underground tuber is widespread in damper areas of the plateau. Its flowers has pink, purple or white colour. The tuber of impatiens tinictroria has been used by Ethiopian women to dye their nails and palms by drying it over fire and adding water to make paste (Burger, 1967). From laboratory analysis also the moisture content of *Ansosila* was found to be in the range of 66.1% to 69.1%.

The impatience tinctoria has 2-methoxyl-1,4-naphtoquinone compounds which imparts for the colour produced by it (Fassil, 1981).

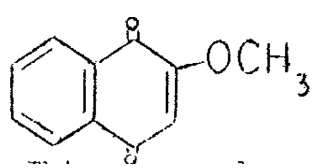


Figure 9: Methoxyl-1, 4-naphthoquinone

h) Comparison between Natural and Synthetic Dye

Natural dye

Natural dyes have both advantages and disadvantages (Samanta and Konar, 2012).

The advantages of natural dyes are;

Natural dyes offer no effluent problem and will provide a natural finish to textile treated with these materials; Plants from which most natural dyes generated definitely assist in preserving the eco-balances; the resources for natural dyes production are not only replaceable but also biodegradable; they have pharmacological effects and possible health benefits; they can give harmonizing colour and the extraction of aqueous dye with alkali is most economical and produces acceptable results.

Disadvantages

The disadvantages of natural dyes are: Low dyeing efficiency, only few have good fastness to light and washing; costly either in money or time (process complexity and the cost of the mordant is equal or greater than cost of synthetic dye) ;some of the mordants are harmful and mostly they are used for protein and cellulosic fibers.

When synthetic dyes are compared with natural dyes, they have the following advantage and disadvantage.

Advantages

Their synthesis requires quick and simple procedure, they are inexpensive, they are good in fastness to wash and light.

Disadvantages

Chemicals used in synthetic dyestuff may be carcinogenic and have skin allergic problem; they are based on toxic raw material; they causes environmental pollution; and knowledge of colour design is necessary.

Cotton

Cotton is the most important natural textile fiber, used to produce apparel, home furnishings, and industrial products. Raw cotton fiber, after ginning and mechanical cleaning is approximately 95% cellulose (Table. 2). The structure of cotton cellulose is a linear polymer of β-D-glucopyranose.

Table 2: Composition of typical cotton fibers

Constituent	Composition (% on dry weight)	
	Typical (%)	Range (%)
Cellulose	95	88-96
Protein	1.3	1.1-1.9
Pectin substance	0.9	0.7-1.2
Ash	1.2	0.7-1.6
Wax	0.6	0.4-1
Total sugars	0.3	0.1-1
Organic acid	0.8	0.5-1
Pigment	Trace	-
Others	1.4	-

Standard method of estimating percent protein from nitrogen content (% N)

2.2.2. Synthetic dyes

Since loss of colour in use is a major source of consumer dissatisfaction, the use of the appropriate dye for a particular fibre is crucial to colour fastness hence reputable manufacturers should choose dyes carefully. In the past, dyes were produced individually by harvesting natural fruits, vegetables and other items, boiling them, and submerging fabrics in the dye bath. This long and tedious process was the common practice until the mid-1800s (Joseph, 1977). In 1856, William Perkin, an English chemist working in London, made an accidental discovery of a purple dye while trying to synthesize quinine by reacting aniline sulphate with an oxidizing agent.

This purple dye, which Perkin called *mauve*, was found to dye silk and although it was not particularly fast, it became popular. Today, industry uses synthetic dyes almost entirely because they hold their colour better and cost less to produce than natural dyes. Pre-packaged dyes are also readily obtainable in almost every colour, and are available to anyone who can purchase the

end product. Perkin's discovery showed chemists that dyes and pigments could be produced synthetically in a laboratory and it was no longer necessary to search out natural products for use as colourants. Besides industrial use, professional and home dyeing of apparel and household decorations is practiced widely based on the different types of dyes and their ability to resist fading.
As Storey (1985) indicates, dyes were mainly derived from vegetable matter and a few mineral colours until the latter half of the 19th century, but rarely from animal or mineral sources. Specifically, the World Book Encyclopedia (2001) states that until the 1850s, all dyes were made from various parts of plants and certain animals, and that the earliest fabrics excavated by archeologists show evidence of ornamentation through the use of natural fibres of contrasting colours. Natural dyes are hardly used today except for educational and recreational purposes.

2.3. Mordants

According to Aimson (1999), mordants play an essential part of the dyeing process. Mordanting is very necessary, except for plants which contain a lot of tannin and do not necessarily require mordants. Mordants "bite" into the fibre, and make the dye stick to the fibres and also have the ability of changing the colours of dyes. The most commonly used mordants are Alum (Potassium Aluminum Sulphate), Chrome, cupper sulphate, Ferrous Sulphate. Stannous chloride and Tannic acid. Chrome and Tin are poisonous, so Alum is recommended for first attempts at mordanting. All yarns and fabrics must be well washed and rinsed before a mordant is applied.

3. Materials and Methods

3.1. Materials

3.1.1. Fabric

A commercially prepared ready- to-dye bleached plain weave of 100 % cotton fabric was obtained from Bahir Dar Textile Share Company, Amhara region, Ethiopia were used for tis study.

3.1.2. Dye plants

Traditionally used 3 varieties of dye yielding plants: (*Ansosila* (*Tinctoria Impatience*), *Allo* and wild strawberry were obtained from Addis Ababa district (Merkato), Oromia region (Abuna Gindeberet Woreda) and Oromia region (West Shoa Zone, Danno Woreda) respectively.

3.1.3. Chemicals

Laboratory grade alum ($KAl(SO_4)_2 .12 H_2O$) and ferrous sulphate ($FeSO_4. 7 H_2O$) were used as mordants while dilute solution (2g/l) of sodium carbonate (Na_2CO_3) was used to adjust the pH of the dye solution to 7. Reference detergent A soap (5g/L) was used for wash fastness test.

3.1.4. Equipments and apparatuses

Table 3: Equipments/ apparatuses and their function

Equipments	**Function**
Grinder	Used for size reduction
pH meter	Used to measure pH of the solution
Flasks	Used to hold a pulverized sample
Weighing balance	Used to measure mass
Data colour 6100 A º spectrophotometer	Used to measure CIE L a b, colour strength, colour indices
Oven dryer	Used to dry samples
pipette	Used to measure small volume of solution
Bottom round flask 100ml, 250ml and 500ml	Used to measure volume of solution
Crock meter	Used to determine rubbing property
Glove	Used to protect from chemicals
Dust mask,	Used to protect from dusts
Water bath	Used for heating
Fadometer	Used to determine light fastness property
Thermometer,	Used to measure temperature
Measuring cylinder	Used to measure volume of solution
Launder-o-meter	Used to determine wash fastness property
petridishes	Used to hold samples while drying
needle	Used to sew cotton fabrics

3.2. Methods

3.2.1. Dye Extraction

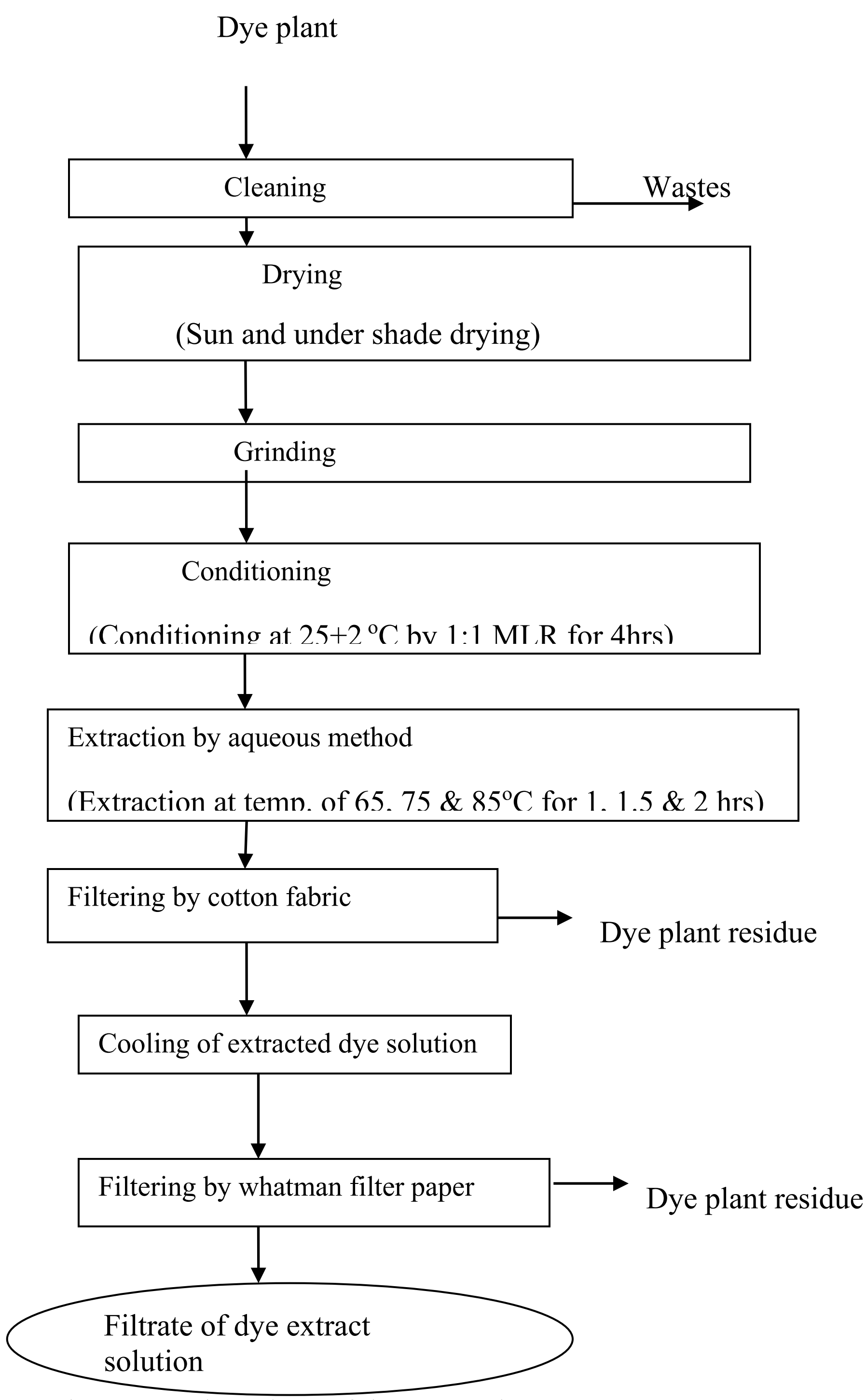


Figure 10: Flow sheet of dye extraction

The plants selected for natural dye extraction were initially washed to remove dusts and soil residues (fig. 10). Next, the cleaned natural dye sources (in the case of *allo*) leaves were dried under the shade, while ripen fruit of Strawberry and root of tinctoria impatience were dried partly under shade and sun which then converted to powder form by using laboratory size reduction machine. The powdered dye plant sources were conditioned for 4 hours at room temperature before the extraction by heating was begun from dye plant source equivalent to weight of fabric ready for dyeing. The extraction was carried out for 1, 1.5 and 2 hours at 65 ºC, 75 ºC and 85 ºC within aluminum foil covered flask (500ml) by heating with water at 1:20 material to liquor ratio (MLR) (i.e., sample powder to water ratio). After the dye was extracted, it was filtered through fine cotton fabric. Finally, after the filtrate was cooled, it was filtered through filter paper. The pH cooled dye extract was measured directly by using pH meter. To obtain the crude dye yield from each dye plants the following formula was used:

$$\text{Yield (\%)} = \frac{\text{mass of crude dye (powder)}}{\text{mass of sample(raw material)}} * 100$$

3.2.2. Mordanting

Pre mordanting of ready to dye plain weave of cotton fabric was carried out by ferrous sulfate ($FeSO_4$. 7 H_2O) and alum (KAl $(SO_4)_2$ .12 H_2O). The mordant 4% on weight of fabric (o.w.f) was dissolved in tap water to make a material to liquor ratio of 1:40. The samples was dipped into the mordant solution and incubated for 0.5 hour at temperature of 80 ºC in the machine used for dyeing. After mordanting, the fabric samples was removed and dried at room temperature.

3.2.3. Dyeing

The dyeing of mordanted cotton fabrics was conducted by using extracted dyes in dyeing machine (atmospheric washer). 5 g of cotton fabric samples was dyed directly with 100ml dye extract. The dyeing was carried out at 85 $\pm$ 2 ºC for 1 hour. After completion of dyeing time, the fabrics were rinsed several times with cold water. Finally dyed samples were air dried (see fig. 9 below).

The dyeing of unmordanted cotton fabrics were conducted by using extracted dyes in dyeing machine. 5 g of each cotton samples was dyed directly with 100ml dye extract. The dyeing was carried out at 85 $\pm$ 2 ºC for 1 hour. After completion of dyeing time, the fabrics were rinsed several times with cold water. Finally dyed samples were air dried.

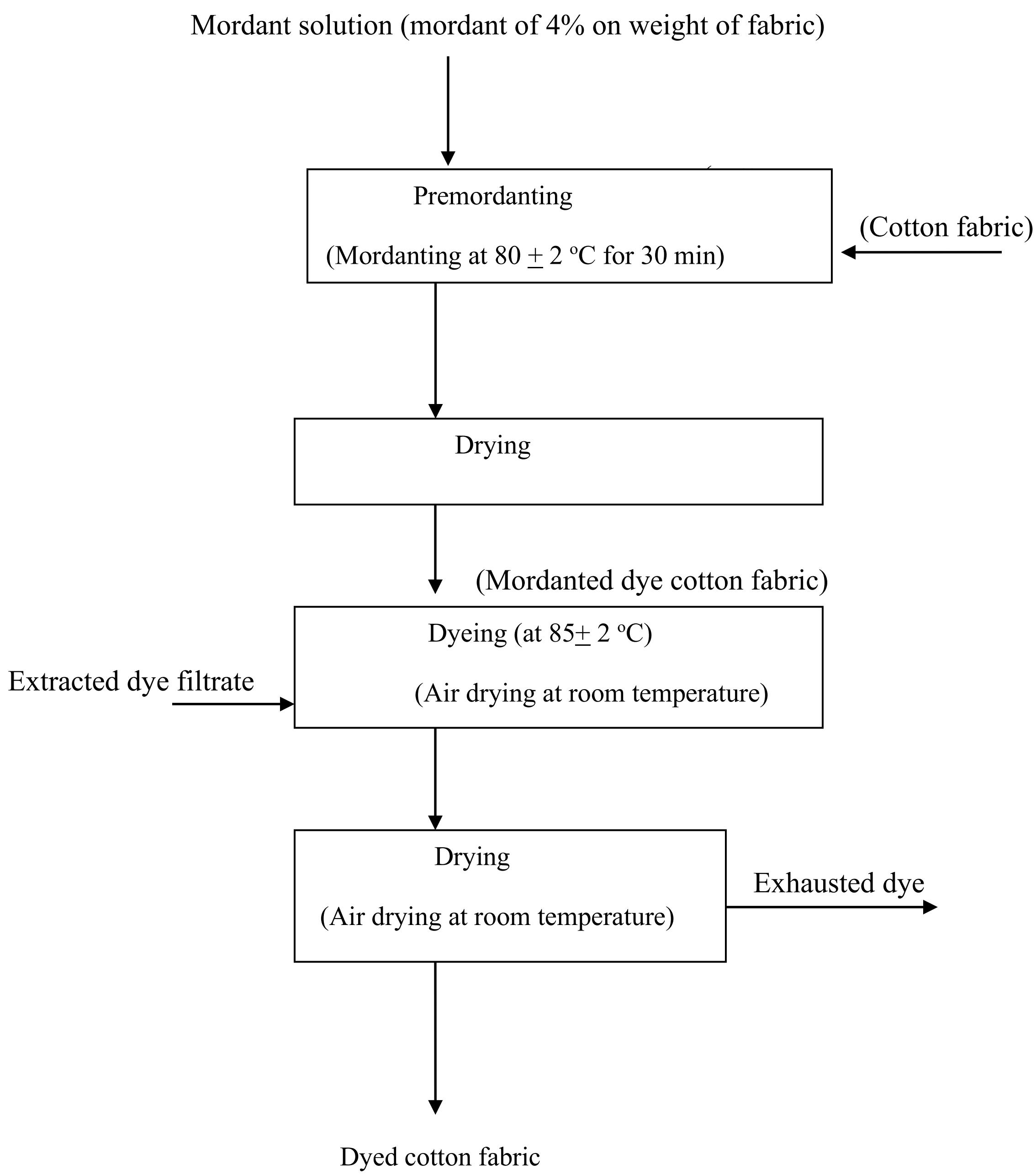


Figure 11: flow sheet of dyeing process for pre mordanted cotton fabric

3.2.4. Evaluation of Fastness properties

Dyed fabric samples were tested for wash, light and rubbing fastness properties.

3.2.4.1. Wash fastness

Wash fastness was performed at 40ºC for 30 min according to ISO 105 C06: 2006 (B) test specifications

Dyed cotton and bleached cotton fabric of 100 mm × 40 mm piece were prepared and sewed together along all four sides. The prepared solution of 5g/l of reference detergent A soap was added to the composite specimen in the 150ml container. Then the container was closed and mantled into the washing machine operated at the specified temperature; and timing begun as soon as the container was closed. After the operation was completed, the composite specimen was removed and gently agitated and rinsed under a cold running tap for 1 min.

3.2.4.2. Rubbing fastness

Rubbing and light fastness tests were performed using ISO 105 –X12:2002 test methods.

White rubbing cotton of 5cm x 2cm was used for dry and wet rubbing. Then sample was placed on the crocking machine and rubbing of the to and fro was allowed for 10 times. For the dry rubbing, the samples were tested for staining of white cotton while for the wet rubbing the process was repeated with the white cotton being wetted first in tap water. The result of the evaluation was done based on the staining of the white cotton due to rubbing on the fabric. The tested rubbing cloth was dried at room temperature and the results were evaluated.

3.2.4.3. Light fastness

The change in colour of the specimen with the changes that have occurred in the standard pattern under solar box 1500 was carried out to determine the fastness of light. The specimen was prepared with the size of 50mm by 10mm.

3.2.5. Determination of Colour strength (K/S)

Reflectance of the dyed samples was measured by Data colour 6100 reflectance spectrophotometer. Using the built-in software program of the instrument the colour strength expressed in terms of the highest K/S value.

3.2.6. Determination of CIE L*a*b*

The Data colour 6100 spectrophotometer was used for measuring CIE L*a* b* by considering sample dyed without mordant as standard and samples dyed with mordants is considered as matches.

3.2.7. Research Design

Experimental data analysis was done by using Design Expert software analysis. Experimental design selected for this study had four factors. Plant types (three levels): *Allo*, *Ansosila*, and wild Strawberry; Mordant types (three levels): without any mordant, Alum and ferrous sulphate and process parameters (time and temperature with three levels each: 1hr, 1.5hr and 2hr, 65^{o}C, 75^{o}C and 85^{o}C) with the three replications while the response variable were yields, colour strength, colour coordinates and fastness properties. `

4. Results and discussion

4.1. pH of dye extract solution

Before dying, the colour from each dye source was extracted by heating with water. The pH of the aqueous extracts was measured at 25^0C using pH meter (Table 4).

Table 4: pH of dye extracts in aqueous solution

Plant species	pH
Impatience tinctoria	5.1
Allo	4.4
Wild Strawberry	3.3

As it could be seen from the above table, the dye extracts were all showed pH below 7(they were all acidic) and the acidity varied from plant to plant i.e., wild Strawberry was more acidic, *allo* the next and *Impatience tinctoria* was the least as compared to the others. The acidity of dye plant extracts might be due to the presence of acid component like Ascorbic acid and Tannic acid along with other colouring components in each dye plant source (Yohannes Fassil, 1981, Zeljka marjanovic-balaban, 2012). In the case of acid dyeing, a low pH helps to form the hydrogen bonds that attach acid dyes to protein fibers such as silk and wool, as well as nylon. However, acid dyes do not work on cellulose fibers such as cotton. Cellulosic fibers can be dyed at relatively high pH. A high pH activates the cotton fiber, forming a cellulosate anion which can then attach the dye molecule, leading to a reaction that produces strong, permanent covalent bonds (Burch, 2008). Due to this reasons, the extracted dye was needed to be neutralized to pH 7 by using sodium carbonate.

4.2. Yields vs. extraction factors

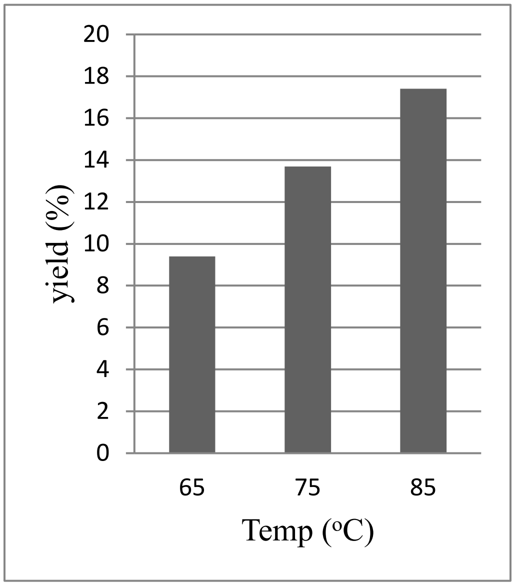
Crude dye yield is the quantity of dye powder obtained after evaporation of water from the extracted dye solution. The solid dye powder left after the evaporation of water from aqueous extracts is called crude dye yield. According to this study, dye yield values were corresponded to crude dye rather than purified dye. Therefore, it is expected that further purification of this crude dye is important to obtain purified dyes.

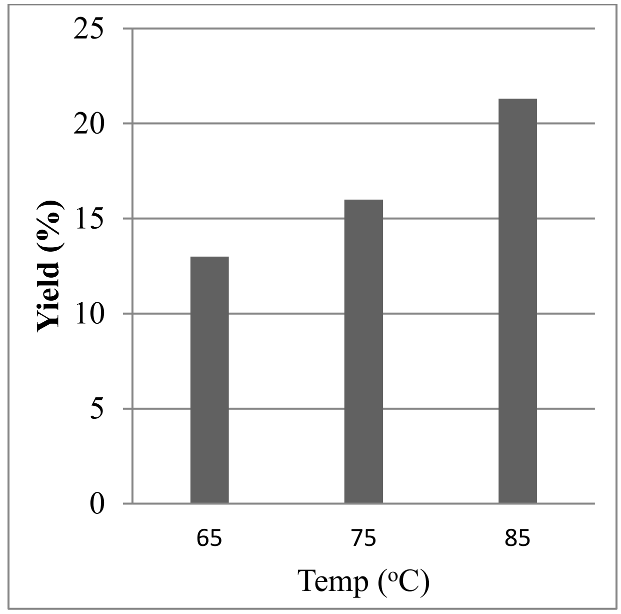
The following table represented yield of crude dye obtained with respect to extraction parameters.

Table 5: Yield vs. extraction parameters

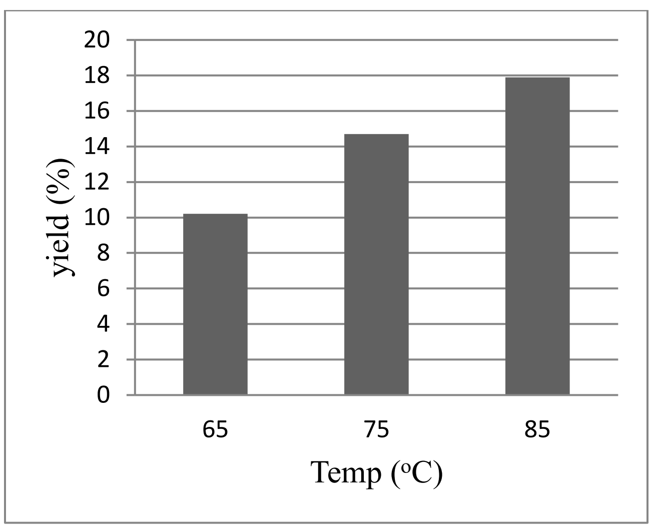
Type of plant	Temperature (°C)	Time (hour)	Yield of crude dye (%)
Allo	65	1	4.5
		1.5	7.0
		2	9.4
	75	1	9.9
		1.5	12.0
		2	13.7
	85	1	14.0
		1.5	16.9
		2	17.4
Impatiens tinctoria	65	1	7.8
		1.5	10.9
		2	13.0
	75	1	13.3
		1.5	14.5
		2	16.0
	85	1	16.5
		1.5	18.0
		2	21.3
Wild strawberry	65	1	7.7
		1.5	9.0
		2	10.2
	75	1	10.5
		1.5	13.0
		2	14.7
	85	1	17.0
		1.5	18.4
		2	17.9

4.2.1. Effects of extraction temperature on crude dye yield





a. b.

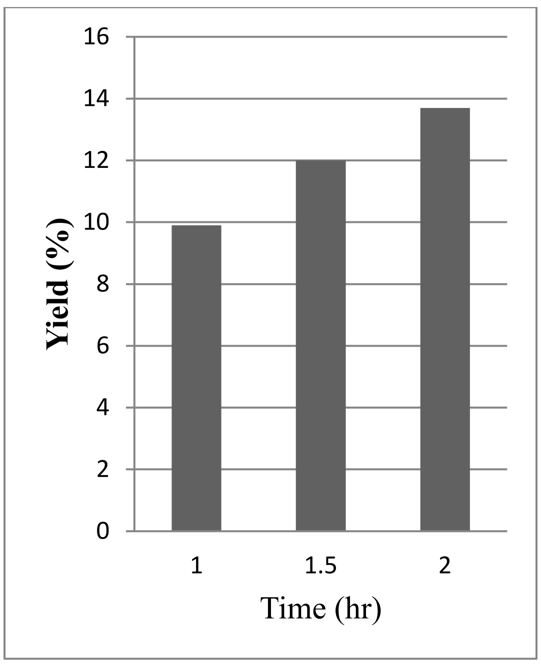


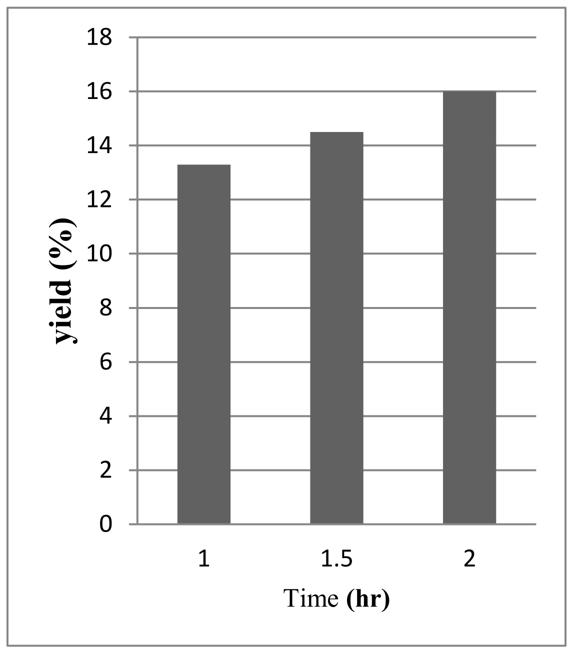
c.

Figure 12: Graph of yield vs. temperature (taken as examples from the whole data) a) Allo for 2 hr b) Ansosila for 2hr and c) wild strawberry for 2hrs.

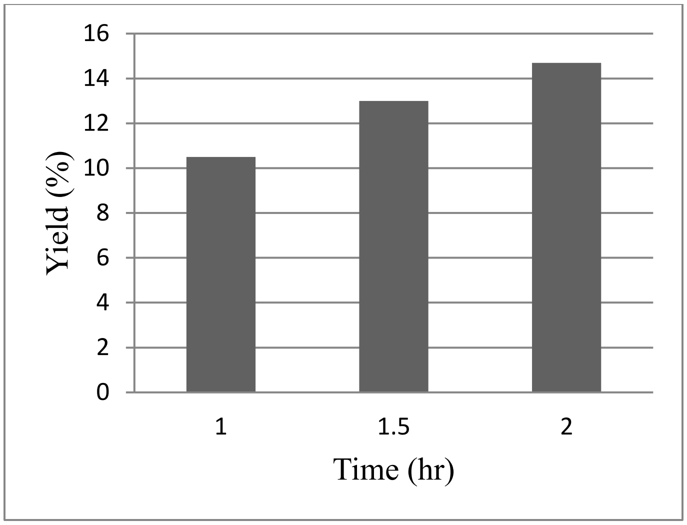
Yield of the crude dye was predominantly determined by extraction temperature (table 6). The yield of allo crude dye increased from 9.4% at 65 °C to 13.7% at 75 °C and further increased to 17.4% at 85°C by keeping of extraction time for 2hr (fig. 12a and table 5). The yield of impatiens tinctoria crude dye result also indicated that the yield increased from 13 % at 65 ºC to 16 % at 75ºC and further increased to 21.3% at 85ºC by keeping of extraction time for 2hr (fig. 12b and table 5). On the other hand, the crude dye yield of wild strawberry increased from 10.2 % at 65 ºC to 14.7 % at 75 ºC and further increased to 17.9% at 85ºC when extraction time was kept 2hr (fig. 12c and table 5). The increment of this crude dye yield is due to the increment of dye material solubility in water as temperature increases between the stated ranges. From this more concentrated dye solution extract, more crude dye powder can be obtained.

4.2.2. Effects of Extraction time on crude dye yield





a b



c.

Figure 13: Graph of yield vs. time (taken as examples from the whole data) a) *Allo* for 75 ºC b) *Ansosila* for 75 ºC and c) wild strawberry for 75 ºC.

Extraction time is also an important factor in dye extraction process and it had a direct relationship with the yield of crude dye (fig. 13 and table 5) depending upon the extraction temperature. Up to 85ºC, the increment of extraction time favored of yielding more crude dye. So, as time increased from 1hr to 2hr given that extraction temperature was constant (e.g. 75 ºC), higher crude dye yield was obtained. In case of allo, the yield of crude dye was 9.9% at extraction conditions of 1hr and increased to 12% at 1.5hr and further increased to 13.7% at 2hr when temperature was 75ºC. For the impatiens tinctoria, the yield of crude dye was 13.3% at extraction conditions of 1hr and increased to 14.5 % at 1.5 hr and further increased to 16 % at 2hr when temperature was 75ºC. On the other hand, the crude dye yield of wild strawberry was 10.5% at 1hr and increased to 13% at 1.5hr and further increased to 14.7 % at 2hr when the extraction temperature was 75ºC. The increment of crude dye yield when extraction time increased is due to the capacity of solvent to penetrate in to the interior of dye bearing materials. When extraction time becomes longer, more of the soluble materials become to be dissolved. The interactive effect of extractive temperature and time for a given plant variety on the crude dye yield is significant analytically since Prob > F less than 0.05(table 6).

4.2.3. Effect of Plant variety on the yield of crude dye

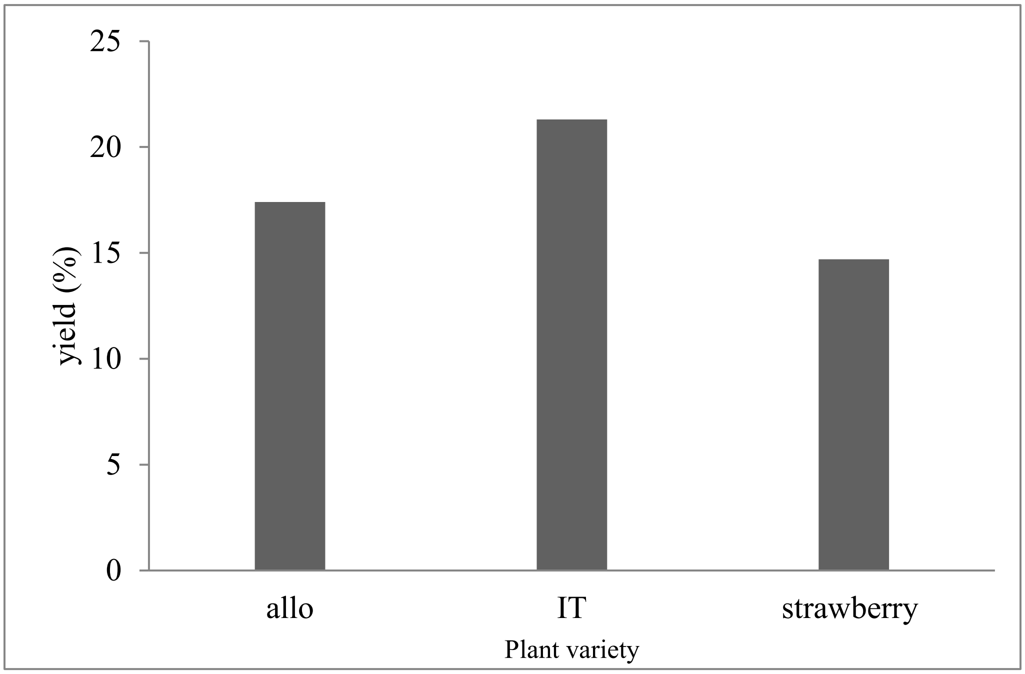


Figure 14: Graph of yield vs. plant species at temperature of 85 ºC and 2hr (taken as examples from the whole data of table 5).

Plant variety had a significant effect (p>F less than 0.05, from table 6 below) on crude dye yield. Impatiens tinctoria resulted 21.3% of crude dye at 85ºC and 2hr. Allo at the same temperature and time gave 17.4% (fig. 14) and strawberry on the other hand gave 17.9 crude dye yields.

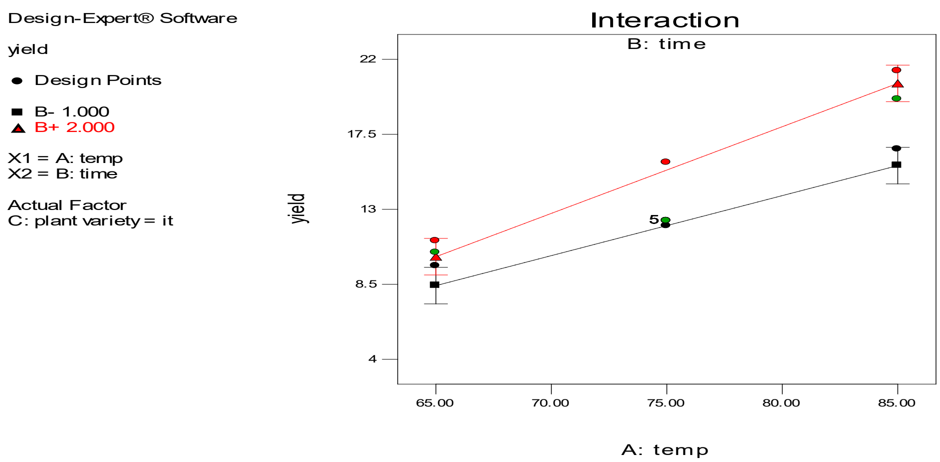
The dye yield obtained from three different type of dye plant sources varied from 4.5-21.3% (table 5 above). The lowest value (4.5%) was obtained from *allo* plant extracted at 65 ºC for 1 hr where as the highest dye yield (21.3%) was obtained from impatiens tinctoria at 85ºC for 2 hours. According to Kechi *et al.*, (2013), the dye yield values of some dye plant sources seem the following: *Wonbela* (14.14%), *Dokima* (23.87), *Gesho* (24.48%), *Gimea* (15.43%), *Fesson* (20.76%) etc. It must be pointed out that in the present study no attempt was made to further purify the solid dye obtained from each dye plant source.

Table 6: ANOVA analysis for yield- extraction parameters

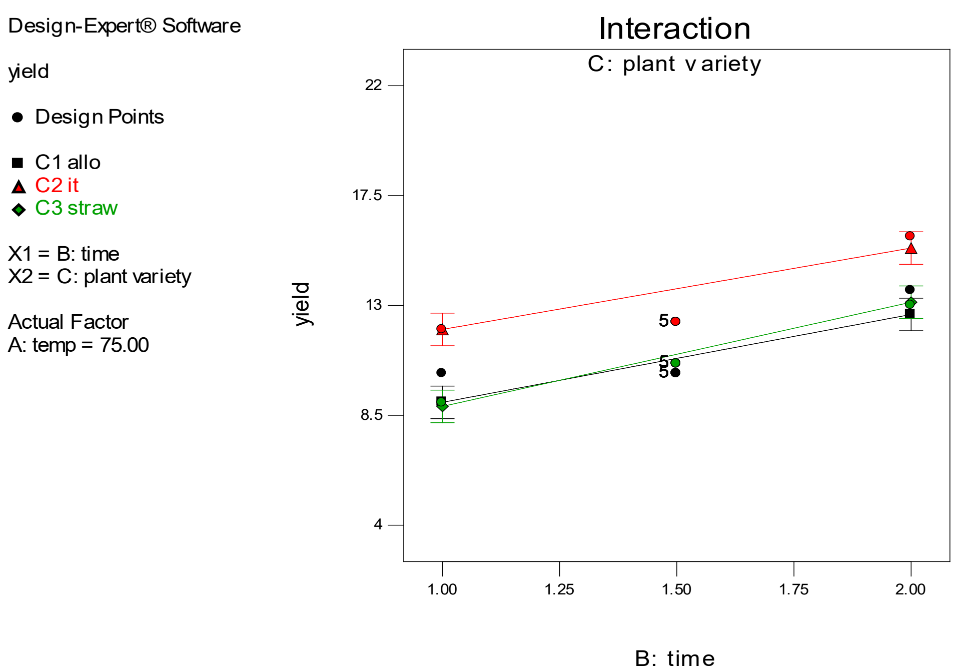
Response yield
ANOVA for Response Surface Reduced Cubic Model
Analysis of variance table [Classical sum of squares - Type II]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	479.66	11	43.61	50.37	< 0.0001	significant
A-temp	*344.97*	*1*	*344.97*	*398.47*	*< 0.0001*	
B-time	*62.72*	*1*	*62.72*	*72.45*	*< 0.0001*	
C-plant variety	*66.65*	*2*	*33.32*	*38.49*	*< 0.0001*	
AB	*3.63*	*1*	*3.63*	*4.19*	*0.049*	
AC	*0.018*	*2*	*8.889E-003*	*0.010*	*0.9898*	
BC	*0.69*	*2*	*0.35*	*0.40*	*0.6739*	
ABC	*0.98*	*2*	*0.49*	*0.57*	*0.5744*	
Residual	23.37	27	0.87			
Lack of Fit	*23.37*	*15*	*1.56*			
Pure Error	*0.000*	*12*	*0.000*			
Cor Total	503.03	38				

The Model F-value of 48.02 implies the model is significant. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case temperature, time and plant variety were all significant model terms while time-temperature, time-plant variety and temperature-plant variety combination variation were insignificant model terms. Values greater than 0.1000 indicate the model terms are not significant. This means increasing or decreasing each parameters value did not have an impact on the response.



a.



b.

Figure 15: Interaction effects of extraction parametres on crude dye yield
a. temp. vs. time and b. time vs. plant variety)

As it could be seen from the above figure 15a, the effects of time on the crude dye yield depends on the level of temperature, represented by the two lines on the graph. On the upper line, there was relatively less overlap in the left vs. right. This indicated that at higher time (2hr) there was much effect. The story also similar for the bottom line on the graph where time is 1hr. Here, also there was no overlapping indicating that the effect of time was significant. Getting back to bottom line it's obvious that when more crude dye yield is needed, it is best to make time at the highest value (2hr). Therefore, for optimization of crude dye yield, the best parametres were high temperature at longer time(time approximated to 2hr). From fig.15b, two lines appeared on the plot bracketed by least significant difference (LSD) bars at either ends. The lines were parallel indicating that smaller different effects of changing extraction time do have lower effects on the yield of the plant variety. This indicated the effects that brought by changing levels of time did not have any combined significant effect with plant variety.

4.3. Fastness properties, colour strength and colour indices

The dyed fabric resistant to washing, light and rubbing for commercial acceptability is very important. Therefore, testing fastness properties of shades produced by selected dye plants was analyzed in this study.

Figure 16: cotton fabric dyed with natural dyes (cotton dyed by a. *Ansosila* dye at 85ºC for 2hr(alum mordanted) b. Wild strawberry at 75 ºC for 1.5hr(ferrous mordanted), c. *Allo dye at 75* ºC for 2hr(alum mordanted) d. *Allo* dye at 65 ºC for 1hr(unmordanted) e. Wild strawberry at 85 ºC for 1hr (ferrous mordanted) f. *Allo* dye at 85 ºC for 1hr (ferrous mordanted) g. *Ansosila* dye at 85ºC for 1.5hr (unmordanted) h. *Allo* dye at 85 ºC for 1.5hr (alum mordanted) i. *Ansosila* dye at 85ºC for 1.5hr (ferrous mordanted)

Table 7: Fastness properties, colour strength and colour indices of *Impatiens tinctoria*

Plant variety	Temp. (^0C)	Time (Hour)	Mordant type	k/s	Colour indices			Wash fastness		Rubbing fastness		Light
					L	a*	b*	cc	cs	wet	Dry	
Impatiens Tinctoria	65	1	None	0.4	81.31	4.22	3.2	4/5	4/5	4/5	4/5	5
			Ferrous	1.25	72.19	4.77	13.92	4/5	4/5	4/5	4/5	5
			Alum	0.4	75.5	3.7	3.75	4/5	4	4/5	4/5	6
		1.5	None	0.37	79.1	4.11	3.1	4/5	4/5	4/5	4/5	5
			Ferrous	1.24	71.2	4.54	13.15	4/5	4/5	4/5	4/5	5
			Alum	0.4	77.21	3.72	3.6	4/5	4/5	4/5	4/5	5
		2	None	0.396	79.1	4.01	3.04	4/5	4/5	4/5	4/5	5
			Ferrous	1.68	70.52	4.39	12.61	3/4	4	4/5	4/5	6
			Alum	0.405	76.94	3.75	3.47	4/5	4/5	4/5	4/5	7
	75	1	None	0.405	75.5	3.7	3.75	4	4	4/5	4/5	6
			Ferrous	1.396	67.8	3.79	10.87	4/5	4/5	4/5	4/5	5
			Alum	0.412	77.96	3.52	4.02	4	4/5	4/5	4	6
		1.5	None	0.388	78.01	3.95	4.02	4	4	4	4	7
			Ferrous	1.625	67.1	3.98	12.23	4/5	4	4	4	7
			Alum	0.46	78.21	3.65	4.09	4	4	4	4	7
		2	None	0.5	76.21	4.15	5.92	4/5	4/5	4/5	4/5	5
			Ferrous	1.828	66.21	4.22	13.6	4	4	4	4	6
			Alum	0.5	77.9	3.79	4.22	4	4/5	4	4	7
	85	1	None	0.501	80.03	3.75	2.84	3/4	4	4	4	7
			Ferrous	1.413	65.23	3.82	10.6	4	4/5	4	4/5	6
			Alum	0.654	73.57	4.01	9.8	4	4	4	4	5
		1.5	None	0.703	70.64	4.87	4.01	4/5	4	4/5	4/5	7
			Ferrous	0.837	71.89	4.29	10.01	4	4/5	4	4	6
			Alum	0.784	73.78	4.27	9.12	4	4	4	4/5	6
		2	None	0.746	70.52	4.79	8.8	3	4/5	3	4/5	5
			Ferrous	1.985	68.01	4.8	11.02	3/4	4	3/4	4	5
			Alum	0.748	66.8	4.7	9.36	3/4	4	3/4	3/4	6

cc: colour change cs: colour staining

Table 8: Fastness properties, colour strength and colour indices of *Allo*

Plant variety	Temp. (^{0}C)	Time (Hour)	Mordant type	k/s	Colour indices			Wash fastness		Rubbing fastness		Light
					L	a*	b*	cc	cs	wet	Dry	
Allo	65	1	None	0.381	85.63	1.52	5.94	4/5	4/5	4/5	4/5	7
			Ferrous	5.722	45.36	2.49	9.49	4/5	4/5	4/5	4/5	7
			Alum	3.021	71.3	-2.01	41.23	4/5	4/5	4/5	4/5	6
		1.5	None	0.421	82.42	0.9	12.5	4/5	4/5	4/5	4/5	5
			Ferrous	5.92	45.65	3.07	10.17	4/5	4/5	4/5	4/5	7
			Alum	4	69.21	-1.82	39.5	4/5	4/5	4/5	4/5	7
		2	None	1.43	79.12	0.32	20.1	4	4	4	4	6
			Ferrous	6.09	49.13	3.54	11.59	4/5	4/5	4/5	4/5	6
			Alum	8.282	68.07	-1.01	38.04	4/5	4/5	4/5	4/5	7
	75	1	None	1.797	76.45	0.4	19.41	4/5	4/5	4/5	4/5	5
			Ferrous	6.62	48.13	2.3	11.35	4	4/5	4/5	4/5	6
			Alum	5.92	74.54	-1.2	36.76	4/5	4/5	4/5	4/5	7
		1.5	None	1.431	77.15	0.21	19.02	4/5	4/5	4	4	7
			Ferrous	6.34	45.65	3.21	10.95	4/5	4	4/5	4/5	6
			Alum	5.73	74.06	-1.3	36.5	4/5	4/5	4/5	4/5	7
		2	None	1.98	74.45	1.2	19.75	4	4/5	4	4/5	5
			Ferrous	7.019	44.02	3.45	11.3	4/5	4/5	5	4/5	5
			Alum	6.21	66.70	-1.33	31.92	4/5	4/5	4/5	4/5	7
	85	1	None	6.387	70.88	1.88	20.38	4/5	4/5	4/5	4/5	7
			Ferrous	6.498	46.17	2.36	11.84	4/5	4/5	4/5	4/5	6
			Alum	6.387	59.43	3.15	31.84	4/5	4/5	4/5	4/5	7
		1.5	None	3.182	68.12	2.21	21	4	4	4	4/5	7
			Ferrous	11.127	39.05	3.65	12.2	4	4/5	4/5	4	5
			Alum	6.784	65.16	0.34	32.9	4	4/5	4	4/5	6
		2	None	1.828	67.26	2.28	21.93	4	4	4	3/4	5
			Ferrous	14.12	34	4.9	12.07	4/5	4/5	4	4	6
			Alum	8.24	59.43	3.13	31.84	4/5	4/5	4/5	4/5	5

cc: colour change cs: colour staining

Table 9: Fastness properties, colour strength and colour indices of Wild strawberry

Plant variety	Temp. (^0C)	Time (Hour)	Mordant type	k/s	Colour indices			Wash fastness		Rubbing fastness		Light
					L	a*	b*	cc	cs	wet	Dry	
Wild strawberry	65	1	None	0.524	84.26	0.97	0.92	4/5	4/5	4/5	4/5	5
			Ferrous	0.942	79.26	1.27	0.92	4	4/5	4	4/5	5
			Alum	0.713	78.72	0.99	10.8	4/5	4/5	4/5	4/5	5
		1.5	None	0.56	84.13	1.17	16	4//5	4	4/5	4/5	7
			Ferrous	1.7	69.23	2.4	7.7	4/5	4/5	3/4	3/4	6
			Alum	1.01	77.71	1	13.5	4/5	4/5	4/5	4/5	5
		2	None	0.57	82.9	1.28	14.4	4/5	4/5	4/5	4/5	7
			Ferrous	1.219	67.46	2.21	7.04	3/4	4	4	4	5
			Alum	1.17	75.37	1.05	16.8	4/5	4/5	4	4	6
	75	1	None	0.59	83.86	1.15	9.59	4	4	4	4	6
			Ferrous	2.19	69.14	3.01	9.59	4	4/5	4	4	6
			Alum	1.96	74.84	1.44	22.88	4	4/5	4	4	6
		1.5	None	0.77	81.1	2.55	17.2	4/5	4/5	4/5	4/5	5
			Ferrous	2.18	66.23	3.2	9.2	4/5	4	4	4	7
			Alum	2.03	72.09	2.05	19.2	4/5	4/5	4/5	4/5	6
		2	None	0.906	79.32	2.37	15.12	4/5	4/5	4/5	4/5	7
			Ferrous	4.675	42.64	4.37	9.24	4/5	4/5	4/5	4/5	6
			Alum	2.13	71.95	1.41	17.41	4	4/5	4	4	7
	85	1	None	0.62	79	2.17	13.75	3/4	4	3/4	3/4	6
			Ferrous	2.62	56.08	3.56	9.55	4/5	4/5	4/5	4/5	5
			Alum	1.487	74.26	2.19	18.64	4	4/5	4	4/5	5
		1.5	None	0.84	78.45	1.83	12.7	4	4/5	4	4	7
			Ferrous	3.532	51.5	3.87	9.29	3/4	4	3/4	4	6
			Alum	1.457	74.79	2.17	19.73	4/5	4/5	4/5	4/5	7
		2	None	0.933	77.22	1.68	14.38	3/4	4	3/4	3/4	6
			Ferrous	4.923	49.61	4.62	9.79	4/5	4/5	4/5	4/5	5
			Alum	2.96	69.61	2.95	24.82	4	4/5	4/5	4	6

cc: colour change cs: colour staining

4.3.1. Wash fastness of dyed samples

The wash fastness result indicated that dye extracted from the selected local plants ranges from 3 / 4 to 5. These might be due to better rate of diffusion of dye and state of dye inside the fiber, tendency of the extracted dyes to aggregate inside the fiber (thereby increasing the molecular size) and formation of mordant dye fiber complex that has the effect of insolubilizing the dye.

After soap wash, little change in colour was noticed in some dyed samples. This might be due to several factors, such as: dye decomposition, thus converting to colourless or a differentially coloured compound, dye detaches from the substrate due to the wear dye-fiber bond between the natural dye and the fiber and ionization of the natural dye during alkaline washing. Since most of the natural dyes have hydroxyl groups, which ionize under alkaline conditions, some of the samples dyed in acidic conditions faded when washed with alkaline soaps. The use of mild nonionic soaps is recommended for use with these dyes.

Natural dyes mostly require a mordant to be fixed onto the fiber that have an affinity for the dye and the fiber then forms an insoluble precipitate with the dye in the fiber. Wash fastness with both mordants were acceptable. Little changes to colour staining and colour change to washing with soap was observed. The wash fastness of fabric dyed with and without mordant was analyzed. These results were assessed in the usual way in terms of visual values for the staining of adjacent cotton material and alternation in shade. It is indicated that sample with natural dye extract and iron mordant gave rating good to very good wash fastness in comparison with very good to excellent rating for shade developed with only natural dyes. The very good to excellent wash fastness of sample dyed with natural dyes was due to the strong covalent bonds between the reactive dye molecules and the fabric.

The dyed samples were subjected to wash fastness at 40^0C. The wash fatness results shown in table 7 to 9 are expressed in terms of change in shade and degree of staining of white fabric. In case of direct dyed (without mordant) samples, all dye plants have shown commercially acceptable wash fastness grade i.e. ≥ 3 at 40ºC. The Wash fastness for most dye plants was improved with alum and iron mordants particularly at 40^0C wash test. The improvement in wash fastness with iron mordanting was more significant than alum mordanting at 40ºC wash tests. An improvement in fastness grade for mordanted cotton was expected due to metal complex formation between the colouring component and the metal salt. All the dyed samples showed fastness grade of 4 to 5 for degree of staining indicating the absence of staining of adjacent white fabric during washing both at 40ºC for mordant and unmordant dyed cotton.

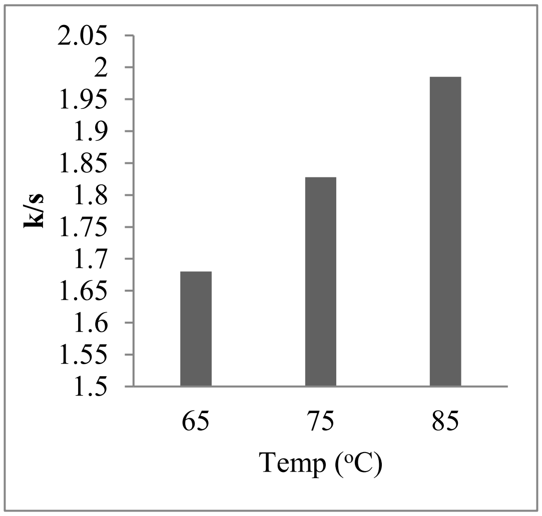
4.3.2. Rubbing fastness

The colour change to dry and wet rubbing for all the treated samples were summarized in tables 7-9 using grey scales. Commercially acceptable rub fastness was exhibited by the cotton fabrics dyed by using of the dye extracted from *all*o, strawberry and impatience tinctoria as all of their value ranges 3 / 4 to 5. Dry rubbing had shown better result as compared to wet although both of them were in the range of acceptable grey scale standards. Complexing the fiber with mordant had the effect of insolubilizing the dye, making it colour fast. The fabrics dyed with them showed good fastness properties

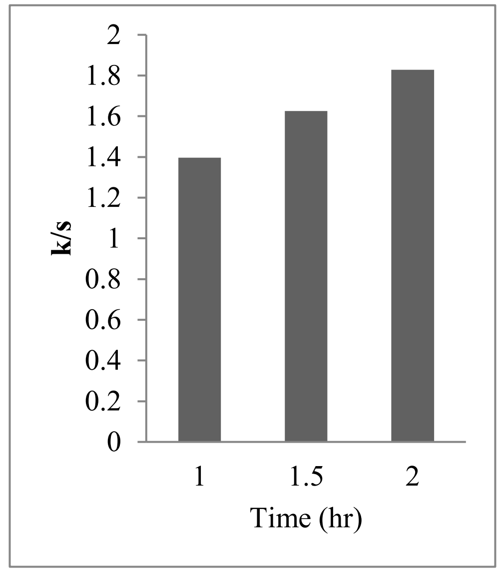
4.3.3. Light fastness of dyed samples

As it could be seen from tables 7 to 9 above, light fastness results had shown an acceptable colour fading (5 to 7 from blue scale reading). The resistance of a dye or pigment to chemical or photochemical attack is an inherent property of the dye chromophore, but at the same time the auxochrome may also substantially alter the fastness either way. The substitution pattern of dyes seems to play an important role in determining their light fastness. A particular substituent may increase the electron density around the reaction site of the molecule facilitating oxidation, or it may reduce the electron density with a resultant increase in case of reduction. Samples dyed with all type plants used to give dye by using iron and potassium aluminum sulphate as a mordant have a good light fastness. This is due to the formation of a complex with transition metal which protects the chromophore from photolytic degradation, and the photons sorbed by the chromophoric group dissipate their energy by resonating within the six member ring thus formed, and hence protecting the dye.

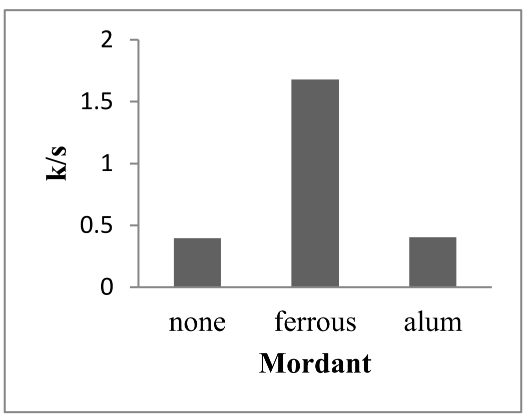
4.3.4. The colour strength (K/S)



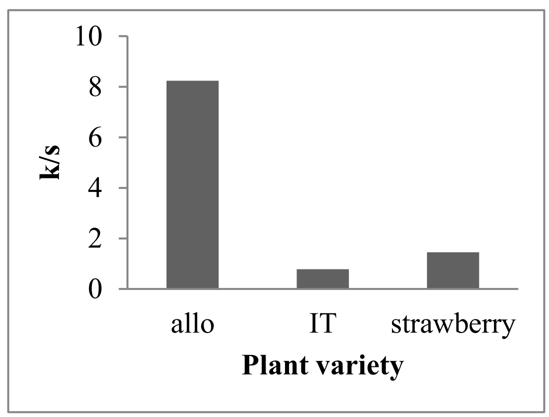
a.



b.



c.



d.

Figure 17: a. k/s vs. temperature (mordant (ferrous sulphate), time (2hr) and Ansosila were taken as an example) b. k/s vs. time (ferrous sulphate, temperature (75°C) and Ansosila) c. k/s vs. mordant type (where time (2hr), temperature (65°C) and IT were taken as an example) d. . k/s vs. plant variety (where time (1.5hr), temperature (85°C) and alum were taken as an example).

The colour strength of both mordanted and unmordanted dyed cotton fabric samples were measured using data colour eye 6100.

Table 10: ANOVA result for k/s vs extraction parameters.

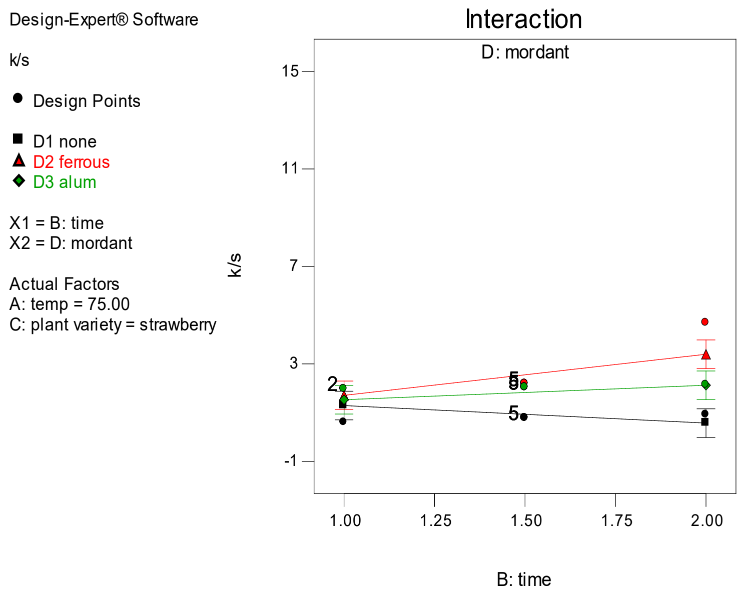
Response k/s

ANOVA for Response Surface Reduced Cubic Model

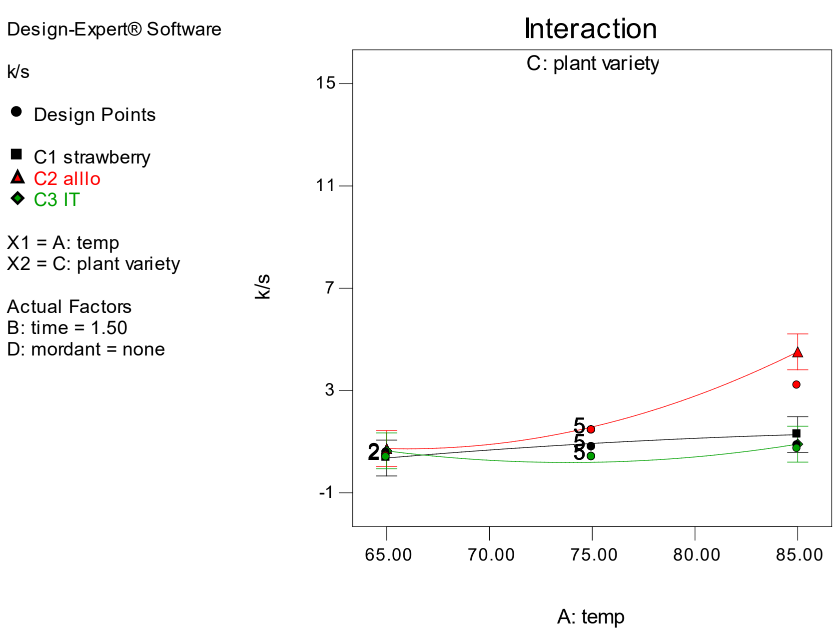
Analysis of variance table [Classical sum of squares - Type II]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	707.42	31	22.82	21.67	< 0.0001	significant
A-temp	*42.39*	*1*	*42.39*	*40.26*	*< 0.0001*	
B-time	*13.59*	*1*	*13.59*	*12.91*	*0.0005*	
C-plant variety	*363.08*	*2*	*181.54*	*172.43*	*< 0.0001*	
D-mordant	*151.81*	*2*	*75.90*	*72.09*	*< 0.0001*	
AB	*0.13*	*1*	*0.13*	*0.13*	*0.7214*	
AC	*22.62*	*2*	*11.31*	*10.74*	*< 0.0001*	
AD	*0.11*	*2*	*0.056*	*0.054*	*0.9479*	
BC	*2.63*	*2*	*1.32*	*1.25*	*0.2914*	
BD	*13.07*	*2*	*6.53*	*6.21*	*0.0030*	
CD	*70.95*	*4*	*17.74*	*16.85*	*< 0.0001*	
ABC	*1.31*	*2*	*0.66*	*0.62*	*0.5384*	
ABD	*4.40*	*2*	*2.20*	*2.09*	*0.1301*	
ACD	*18.11*	*4*	*4.53*	*4.30*	*0.0032*	
BCD	*3.21*	*4*	*0.80*	*0.76*	*0.5527*	
Residual	89.49	85	1.05			
Lack of Fit	*89.49*	*49*	*1.83*			
Pure Error	*0.000*	*36*	*0.000*			
Cor Total		796.92	116			

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case time, temperature, plant variety, mordant, combination of tempearture-plant variety, time-mordant and plant variety-mordant have a significant impact on the colour strength while combination of temperature-time, temperature mordant type, time-plant variety and time-temperature-plant variety were not a significant model terms(table 10).



a.



b.

Figure 18: Interaction effects of extraction parametres on colour strength a. mordant vs. time and b. temperature vs. plant variety)

As it could be seen from the above figure 18a, the effects of time on the colour strength depends on the mordant type, represented by the three lines on the graph. For the overall of mordanting type, except alum, there was relatively less overlap in the left vs. right. This indicated that for ferrous mordanted there is much effect. This was also similar for the unmordant on the graph where there was no mordant used. Therefore, for optimization of colour strength, the best parametres are higher time for the sake of ferrous mordanted and relatively medium time for unmordanted while this was not the issue for alum mordanted. From fig.18b, *allo* lines appear on the plot bracketed by higher significant difference bars at either ends. the *Impatiens tinictoria* and wild strawberry lines are parallel indicating that smaller different effects of changing extraction temperature do have lower effects on out put that comes with the interactioon of plant variety. This indicates that the effects that brought by changing levels of tempereature do not have any significant interaction effect with plant variety.

4.3.4.1. Effects of extraction temperature on colour strength

Extraction temperature had a significant effect (Prob > F less than 0.05, from table 10) on colour strength. The colour strength of impatiens tinctoria increased from 1.68 at 65 ºC to 1.828 at 75 ºC and further increased to 1.982 at 85ºC by keeping of extraction time for 2hr (fig. 17a). Colour strength of dyed cotton fabric increased along with extraction temperatures for all three plant varieties given that all other plant varieties for 2hr (table 7). The increment of this colour strength was due to concentration increment of dye as temperature increases between the stated ranges

4.3.4.2. Effects of extraction time on colour strength

The colour strength of dyed cotton fabric by impatiens tinctoria dye extract resulted that it increased from 1.396 at 1hr to 1.625 at 1.5hr and further increased to 1.828 at 2hr by keeping of extraction temperature 75 ºC (fig. 17b). On the other hand, the colour strength of wild strawberry decreased from 2.19 at 1hr to 2.18 at 1.5hr and increased to 4.675 at 2hr when extraction temperature was kept 75 ºC (table 9). The colour strength of allo decreased from 6.62 at 1hr to 6.34 at 1.5hr and increased to 7.019 at 2hr when extraction temperature was kept 75 ºC (table 8). This increment is due to the concentration increment of dye extract solution.

4.3.4.3. Effects of plant variety on colour strength

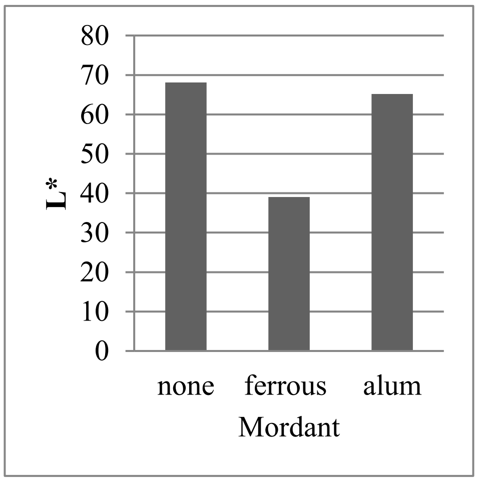
Plant variety had a significant effect on colour strength. The colour strength (k/s) obtained from three different type of dye plant sources varied at the specified temperature and time (fig. 17d and tables 7-9). The lowest value was obtained from impatiens tinctoria where as the highest dye yield was obtained from allo.

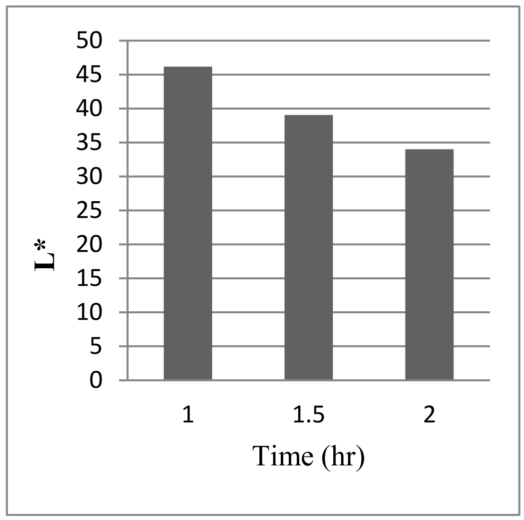
4.3.4.4. Effects of mordanting on colour strength

The colour strength of both mordanted and unmordanted dyed cotton fabric samples were measured using colour eye 6100. Two different mordants (ferrous sulphate and alum) used in 4% o.w.f, keeping in mind the toxicity factor of some mordants. The dye sources like impatience tinctoria and wild Strawberry showed low K/S values in case of unmordanted cotton fabric indicated that these dye sources did not have direct affinity to cotton while *allo* dye showed relatively higher K/S values at the same wavelength (400 nm) indicating direct affinity to cotton. All the pre-mordanted samples showed higher K/S values compared to unmordanted dyed cotton. The increase in K/S values was higher in case of iron mordanted cotton (fig. 17c). This kind of observations was expected because one of the purposes of mordanting is to bind the dye on cotton sample in the form of metal complex formation which results in increase dye uptake. This is attributed to the fact that the metal ions of mordants act as electron acceptors from electron donating groups of dye to form co-ordination bonds with the dye molecule, making them insoluble in water (Mongkholrattanasit *et al.*, 2011). Functional groups such as hydroxy, amino or carboxy on the fiber can occupy the unoccupied sites on metal ion interaction with the fiber. Thus, a ternary complex is formed by the metal ion of which one site is linked with the fiber and the other site is with the dye.

Better colour strength results are dependent on the metal salt used (Kamel *et al.*, 2009). Strong coordination tendency of Fe enhances the interaction between the fiber and the dye, resulting in high dye uptake (Jothi, 2008). Thus the increase in K/S values after mordanting was due to increase in dye uptake as well as deepening of the shade due to metal complex formation. The shade obtained after mordanting also depends on the nature of metal salt used for complex formation. The alum produced reddish brown shades whereas iron mordant produced grey shades. $FeSO_4.7H_2O$ and $KAl_2SO_4.12H_2O$ not only cause differences in hue colour and significant changes in K/S values but also L* values and brightness index values. Most of the metal salts exhibited the highest K/S values due to their ability to form coordination complexes with the dye molecules. This strong coordination tendency of Fe enhances the interaction between the fiber and the dye, resulting in high dye uptake, while all other metals show similar coordination.

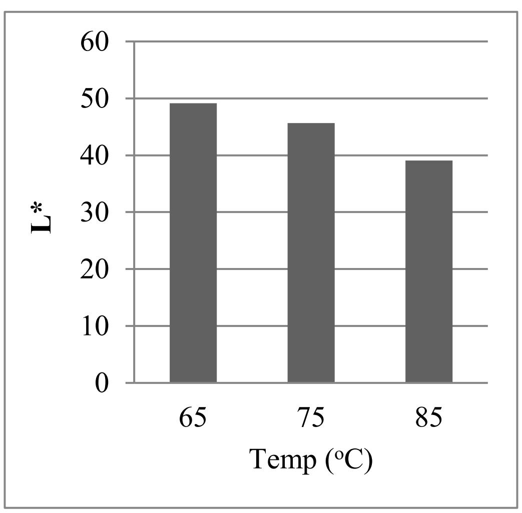
4.3.5. The CIE L a* b* values of dyed samples

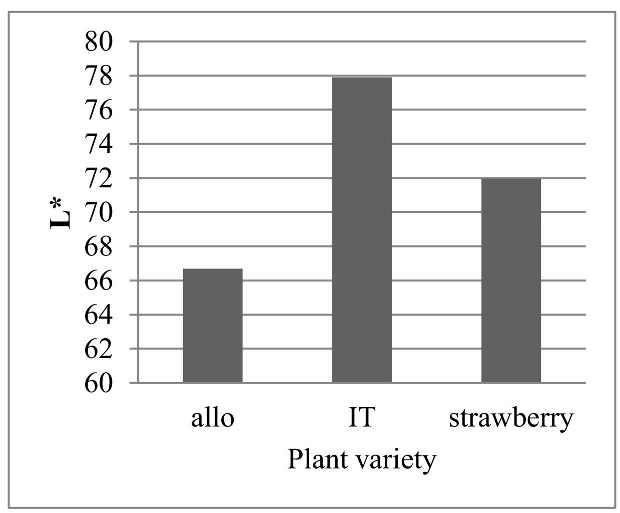




a.

b.



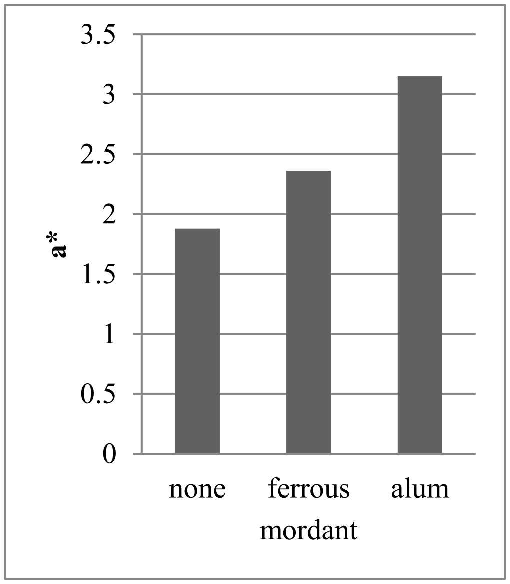


c

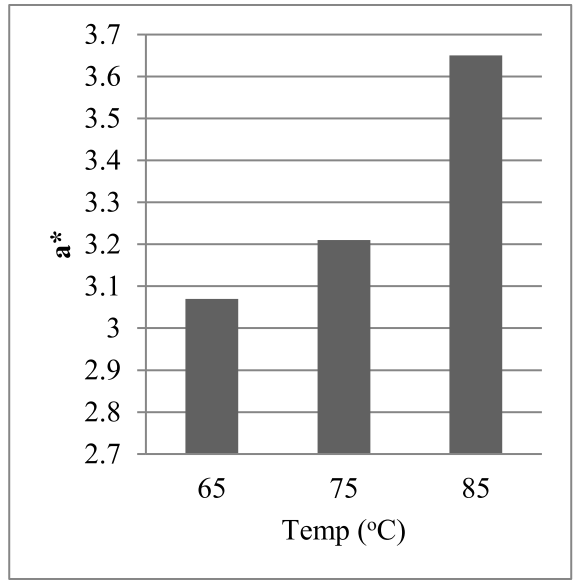
d.

Fig. 19: L* vs. extraction parameter (a. Allo/85°C/1.5hr b. Allo/85°C/ferrous c. Allo/1.5hr/Ferrous

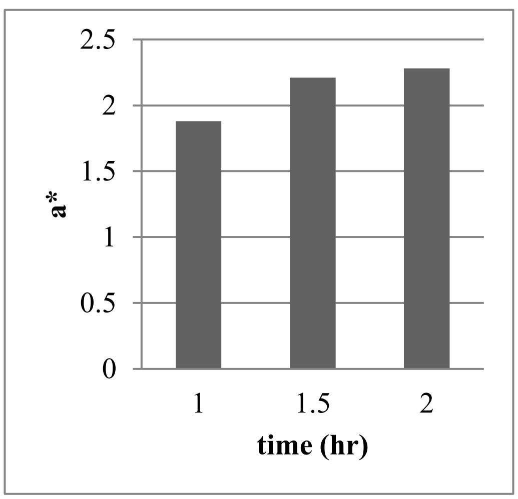
and d. 75ºC/2hr/Alum)

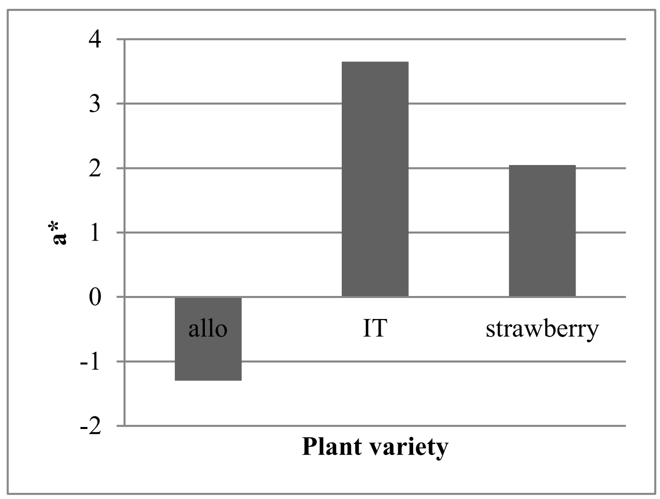


a.



b

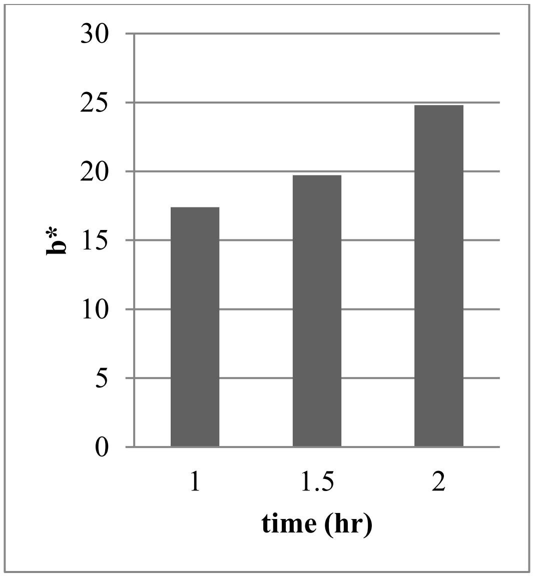


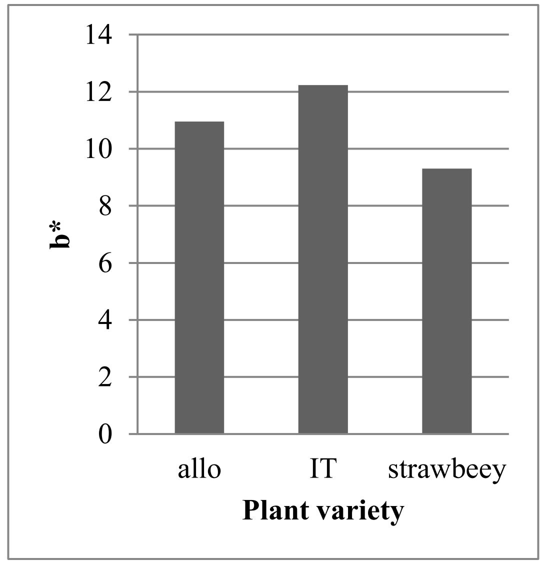


c

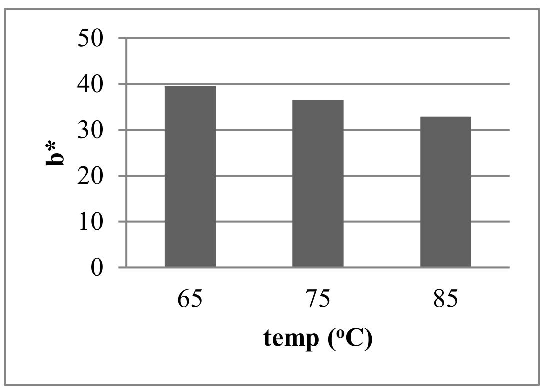
d

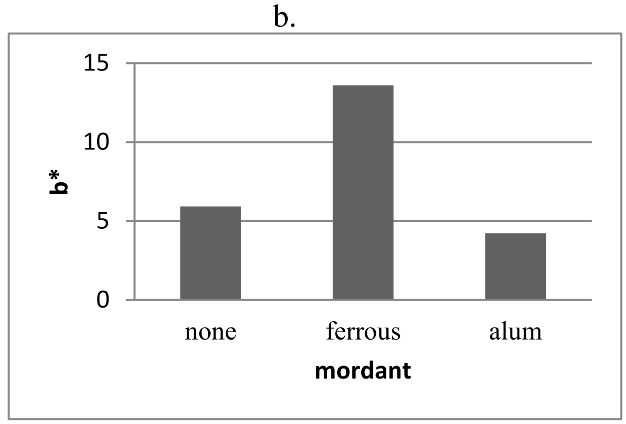
Fig. 20: a* vs. extraction parameter (a. Allo/85ºC/1hr b. Allo/1.5hr/Ferrous c. Allo/85ºC/None and d. 75ºC/1.5hr/Alum)





a. b.





c. d.

Fig. 21: b* vs. extraction parameter (a. Strawberry/85°C/Alum b. 75 °C /1.5hr/ferrous c. 1.5hr/Allo/Alum and d. IT/2hr/ 75°).

The CIE system is based on the appearance of colour to the theoretical standard observer. The dyed samples were analyzed in terms of CIE Lab coordinates (L (lightness), a* (red-green) and b* (blue-yellow)). L* value refers to the lightness of colours ranging from zero for black, 50 for grey and 100 for white. The positive and negative values of a* refer to red and green colour components while the positive and negative values of b* refer to yellow and blue colour components respectively.

In order to quantify the colour of dyed samples, the CIE L* a* b* values were measured for samples dyed in the presence and absence of mordants (fig. 19). The Lightness (L*) indicates the increase or decrease of the depth of shade. Lower values of L* means deepening of shade and higher values of L* indicate lower shade depth. Comparison of L* values indicated that in case of pre-mordant dyed samples, there was deepening of shade (table 7-9). The decrease in L* value was more significant for iron (II) mordant dyed than alum mordant dyed samples (fig. 19a), indicating greater colour deepening with iron (II) mordant. The colour deepening with mordant is attributed to the metal complex formation between dye and metal and it's binding with the fiber. Cotton dyed fabric by allo dye extract resulted the following L* values: unmordant dyed fabric 68.12 at 1.5hr, ferrous mordanted 39.05 and alum mordanted 65.16 for extraction temperature and time were 85 ^{o}C and 1.5hr (fig. 19a) respectively. Cotton dyed with ferrous gave lower L* value. This implied the witness of ferrous mordanted cotton fabric gave a darker shade as compared to alum mordanted and unmordanted cotton fabric.

Wild strawberry lightness lay in the range of 77.22 to 84.26 for unmordant, 79.26 to 42.56 for ferrous mordanted and 79.71 to 68.62 for alum mordanted (table 9). Impatiens tinctoria lightness lies in the range of 70.52 to 81.31 for no mordant, 65.23 to 72.19 for ferrous mordanted and 66.8 to 77.21 for alum mordanted(table 7). Allo lightness lies in the range of 67.26 to 85.63 for no mordant, 34 to 49.13 for ferrous mordanted and 59.43 to 74.54 for alum mordanted. The L* of dyed cotton fabric by allo dye extract result indicated that there was an inverse relationship between extraction time and lightness properties given that other parameters were constant (fig. 19b). The L* of dyed cotton fabric by allo dye extract result also indicated that there was an inverse relationship between extraction temperature and lightness when other parameters were kept constant (fig. 19c). On the other hand, for plant varieties, keeping other parameters constant, L* values for impatiens tinctoria > wild strawberry>allo (fig. 19d).

The a* values indicate the redness of shade. Higher value of a* reveals more redness in colour. The alum mordanted samples showed higher redness compared to iron mordanted samples due to change in shade towards red-brown as compared to shade change towards grey in case of iron mordanted samples (fig.20a, tables 7 to 9). a* lay in the range of 0.97 to 2.55 for no mordant, 1.27 to 4.62 for ferrous mordanted and 0.99 to 2.95 for alum mordanted(tables 7,8 and9). For allo a* values lay in the range of 0.21 to 2.28 for no mordant, 0.21 to 4.9 for ferrous mordanted and -2.01 to 3.15 for alum mordanted; Impatiens tinctoria a* values lay in the range of 3.75 to 4.57 for no mordant, 3.70 to 4.22 for ferrous mordanted and 3.52 to 4.70 for alum mordanted.

In the case of yellowness (b*) values: b* lies in the range of 0.92 to 15.12 for no mordant, 0.9 to 9.79 for ferrous mordanted and 10.8 to 24.42 for alum mordanted. Allo b* value lay in the range of 5.94 to 21.93 for no mordant 9.49 to 12.2 for ferrous mordanted and 31.84 to 41.23 for alum mordanted (table 8); for impatiens tinctoria b* situated in the range of 2.84 to 8.8 for no mordant, 10.1 to 13.92 for ferrous mordanted and 3.42 to 9.80 for alum mordanted. The vales of b* is increasing and decreasing along with time and temperature of extraction respectively (table 21a, c) keeping other parameters constant. The highest value of b* was obtained with IT plant variety and when Iron (II) sulphate was used (fig. 21b, d).

5. Conclusion and Recommendation

5.1. Conclusion

From this study it was possible to conclude the followings. The leaves of *all*o, the roots of impatiens tinctoria and ripen fruits of wild strawberry (Fragaria Vesca L.) dye can be successfully used for dyeing of cotton fabrics to obtain a wide shade ranges.

Mordanting cotton fabrics with the use of 4% o.w.f of ferrous sulphate and alum by premordanting methods for subsequent dyeing with dye solution of *allo* and wild strawberry (100 % o.w.f) gave maximum K/S values as compared to impatiens tinctoria. The increase in K/S value after pre-mordanting is due to the changes in confirmation because of the interaction bonds between fibers and metallic salts, and fibers and dyes along with the inherent colour of the corresponding mordants (in case of ferrous sulphate). The use of ferrous sulphate in dyeing of cotton fabrics gave a deep brownish /grey colour owing to the inherent colour of the metal salt that anchored to the corresponding fiber, besides the improvement in K/S value due to the natural dye component. In general, dyeing by pre-mordanting method produced deeper shades when compared to direct dyeing. From the dyeing results, the cotton fabrics dyed using 4% $FeSO_4.7H_2O$ as a mordant, dye extracted from allo at 85ºC for 2 hours yields the highest colour strength while dyeing that involves 4% $KAl(SO_4)_2.12H_2O$ at the same parameters by allo dye extract solution were also found to render a higher surface colour strength. The improvement in colour strength with iron mordant was more significant than alum.

The wash fastness at 40ºC and rub fastness for pre-mordanted dyed samples were both acceptable as the experimental result indicated for both fastnesses was ≥3 while Light fastnesses resulted ≥ 5 (blue scale) for three dye plants were also good. The CIE L*a*b* values showed deepening of shade after mordant dyeing. Alum mordant showed redness and more pure shades compared to iron mordant. On contrary, samples dyed directly without any treatment with mordant produces light shades. The degree variation of shades is largely affected by temperature, time, plant variety and presence or absence mordants. The overall performance of mordant dyed samples in terms of wash and rubbing fastness was good to a level of commercial acceptance, whereas, there was scope for further improvement of light fastness.

To sum up the above findings strongly shows some clues that Ethiopian natural resources could have the tendency for textile colouration and possibility to be engaged in the export market.

5.2. Recommendations

Using of natural resources for protecting the environment from pollution and ecological imbalances is favored during now days. For instance, utilization of renewable and environmentally friend resources for colour in textiles helps to safeguard human health and life on earth.

Detailed scientific studies with natural dyes have to be established in order to upgrade their usage comparable to those of synthetic dyes. To commercialize natural dyes, they need to conform to stringent standards that are applied to synthetic dyes. To do this, much research works should be conducted to transform traditional practices to scientific practices in order to overcome raised limitation on plant dyes.

Even though many works must be done in order to prove whether this plant dyes is applicable to dye cotton fabrics or not, due to some limitation in availability of resources within a laboratory in our country, to quantify and analyze every parameter, it was so difficult. So, the researchers who want to do on the same title and dye plant should conduct analysis of structural formula and some other information specific to these dyes (especially *allo* dye).

The dyes which were extracted and calculated to obtain yields in this study were only on their crude forms. But purification of these crude dyes to obtain appropriate dyes is very interesting especially in saving packaging costs and decrease the volume of unwanted materials (non colouring components).

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Appendices

Appendix A

Table 11: parameters vs. K/s, colour indices and fastness results

Run	Temp	Time	Plant Variety	Mordant	k/s	Colour indices			Fastness				
									Washing		Rubbing		Light
						L	a*	b*	cc	cs	wet	dry	
1	75.00	1.00	Allo	Alum	5.92	74.54	-1.2	36.76	4/5	4	4/5	4/5	7
2	75.00	1.50	Strawberry	Ferrous	2.18	66.23	3.20	9.20	4	4/5	4	4	7
3	85.00	2.00	IT	Alum	0.748	66.8	4.7	9.36	3/4	4	3/4	3/4	6
4	75.00	1.00	Strawberry	Ferrous	1.96	69.14	3.01	9.14	4	4/5	4	4	7
5	75.00	1.50	IT	None	0.388	78.01	3.95	4.02	4	4	4	4	7
6	75.00	2.00	Strawberry	Alum	2.13	71.95	1.41	17.61	4	4/5	4	4	7
7	65.00	2.00	Allo	None	1.43	79.12	0.32	20.1	4	4	4	4	6
8	75.00	1.50	IT	Alum	0.46	78.21	3.65	4.09	4	4/5	4	4	7

19	18	17	16	15	14	13	12	11	10	9
65.00	75.00	75.00	75.00	65.00	75.00	75.00	75.00	85.00	75.00	85.00
2.00	2.00	2.00	1.50	2.00	1.50	2.00	1.00	1.00	1.50	1.50
Allo	Strawberry	IT	Strawberry	Allo	IT	Allo	IT	IT	Allo	IT
Alum	None	Alum	Alum	Ferrous	Ferrous	Alum	None	None	Alum	None
8.282	0.906	0.5	2.03	6.09	1.625	6.21	0.405	0.501	5.73	0.703
68.07	79.32	77.9	72.9	45.92	67.1	66.70	80.03	75.04	74.06	70.64
-1.01	2.37	3.79	2.05	3.54	3.98	-1.33	3.71	4.87	-1.3	4.87
38.04	15.12	4.22	19.2	11.59	12.23	31.92	2.84	8.01	36.5	8.01
4/5	4/5	4	4/5	4/5	4	4/5	4	3/4	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4	4/5	4	4	4/5	4
4/5	4/5	4	4/5	4/5	4	4/5	4	3/4	4/5	4/5
4/5	4/5	4	4/5	4/5	4	4/5	4	3/4	4/5	4/5
7	7	7	6	6	6	7	7	7	6	7

30	29	28	27	26	25	24	23	22	21	20
75.00	85.00	75.00	65.00	75.00	75.00	65.00	85.00	75.00	75.00	65.00
1.50	2.00	1.50	1.50	1.50	1.50	1.00	1.00	1.50	1.50	1.50
Strawberry	Strawberry	Strawberry	Strawberry	IT	Allo	IT	Strawberry	IT	IT	Strawberry
Alum	None	Alum	Ferrous	Alum	None	Alum	None	Ferrous	Ferrous	None
2.03	0.933	2.03	1.7	0.46	1.431	0.4	0.62	1.625	1.625	0.56
72.90	77.22	72.90	69.23	78.21	77.15	75.5	79	67.1	67.1	84.13
2.05	1.68	2.05	2.40	3.65	0.21	3.7	2.17	3.98	3.98	1.17
19.2	14.38	19.2	7.77	4.09	19.02	3.75	13.75	12.23	12.23	16
4/5	3/4	4	3/4	4	4	4/5	3/4	4/5	4/5	4/5
4/5	4	4/5	4/5	4	4/5	4	4	4/5	4	4
4/5	3/4	4	3/4	4	4	4/5	3/4	4/5	4/5	4/5
4/5	3/4	4	3/4	4	4	4/5	3/4	4/5	4/5	4/5
7	6	6	6	7	7	6	6	6	7	7

41	40	39	38	37	36	35	34	33	32	31
85.00	85.00	85.00	75.00	65.00	75.00	65.00	75.00	75.00	75.00	75.00
1.50	1.00	1.50	1.50	1.50	1.00	2.00	1.00	1.50	1.50	1.50
Strawberry	Allo	Strawberry	Allo	Allo	Strawberry	Strawberry	Strawberry	Allo	Allo	IT
Alum	Alum	None	Alum	Alum	Alum	Alum	None	Ferrous	Alum	None
1.457	6.387	0.84	5.73	4	1.96	1.17	0.59	6.34	5.73	0.388
74.79	70.67	78.45	74.06	69.21	74.84	75.37	83.86	49.13	74.06	78.01
2.17	-0.81	1.83	-1.3	-1.82	1.44	1.05	1.15	0.21	-1.3	3.95
19.73	34.66	12.7	36.5	39.5	22.88	16.81	9.59	10.95	36.5	4.02
4/5	4/5	4	4/5	4/5	4	4	4	4/5	4/5	4
4/5	4/5	4/5	4/5	4/5	4/5	4	4/5	4	4/5	4
4/5	4/5	4	4/5	4/5	4	4	4	4/5	4/5	4
4/5	4/5	4	4/5	4/5	4	4	4	4/5	4/5	4
7	7	7	7	7	6	6	6	7	7	7

52	51	50	49	48	47	46	45	44	43	42
65.00	75.00	85.00	75.00	75.00	85.00	85.00	85.00	75.00	75.00	65.00
2.00	1.50	1.50	1.50	2.00	2.00	2.00	1.50	1.50	1.00	2.00
IT	Strawberry	Allo	IT	IT	Allo	Strawberry	IT	Allo	IT	Strawberry
None	Alum	Ferrous	None	Ferrous	None	Alum	Ferrous	Ferrous	Alum	None
0.396	2.03	11.127	0.388	1.828	4.013	2.96	0.837	6.34	0.412	0.57
79.1	72.90	39.05	78.01	66.21	67.26	69.61	71.89	49.13	77.96	77.22
4.01	2.05	3.65	3.95	4.22	2.28	2.95	4.29	0.21	3.52	1.68
3.04	19.2	12.20	4.02	13.69	21.93	24.82	10.01	10.95	4.02	14.38
4/5	4/5	4	4	4	3/4	4	4	4/5	4	4/5
4/5	4/5	4/5	4	4	4	4/5	4	4/5	4/5	4/5
4/5	4/5	4/5	4	4	4	4/5	4	4/5	4/5	4/5
4/5	4/5	4	4	4	¾	4	4	4/5	4	4/5
5	5	5	7	6	6	6	6	5	6	7

63	62	61	60	59	58	57	56	55	54	53
75.00	85.00	65.00	85.00	85.00	85.00	75.00	85.00	75.00	65.00	75.00
1.50	1.00	1.00	2.00	1.00	1.50	1.50	2.00	1.50	1.50	2.00
Strawberry	Allo	Strawberry	Allo	Allo	Strawberry	Strawberry	IT	Allo	Strawberry	Strawberry
None	Ferrous	None	Ferrous	None	Ferrous	Ferrous	Ferrous	Alum	Alum	Ferrous
0.77	6.498	0.524	14.12	6.387	3.532	2.18	1.985	5.73	1.01	4.675
81.10	46.17	84.26	34.0	70.88	51.50	66.23	68.01	74.06	77.71	42.64
2.55	2.36	0.97	4.9	1.88	3.87	3.20	4.8	-1.3	1.00	4.37
17.20	11.84	0.92	12.07	20.38	9.29	9.20	11.02	36.5	13.50	9.24
4/5	4/5	4/5	4/5	4/5	3/4	4/5	3/4	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4	4/5	4	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	3/4	4/5	3/4	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4	4/5	4	4/5	4/5	4/5
4	5	5	5	5	6	4/5	5	7	5	6

74	73	72	71	70	69	68	67	66	65	64
75.00	65.00	75.00	75.00	85.00	65.00	75.00	75.00	75.00	75.00	75.00
1.50	1.50	1.50	1.50	2.00	1.00	1.50	1.50	2.00	1.50	1.00
Strawberry	Allo	Allo	IT	IT	IT	Allo	Allo	Allo	Allo	IT
Alum	None	None	Ferrous	None	None	Ferrous	None	Ferrous	None	Ferrous
2.03	0.421	1.431	1.625	0.748	0.4	6.34	1.431	7.019	1.431	1.396
72.90	82.42	77.15	67.1	70.52	81.31	49.13	77.15	44.02	77.15	67.8
2.05	0.9	0.21	3.98	4.79	4.22	0.21	0.21	3.45	0.21	3.79
19.2	12.5	19.02	12.23	8.80	3.20	10.95	19.02	11.30	19.02	10.87
4/5	4/5	4/5	4/5	3	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	3	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
5	5	5	7	5	5	5	6	5	5	5

85	84	83	82	81	80	79	78	77	76	75
65.00	65.00	75.00	75.00	65.00	75.00	75.00	65.00	75.00	85.00	65.00
2.00	2.00	2.00	1.50	1.50	1.50	1.50	1.00	1.50	1.50	1.00
IT	Strawberry	Allo	Strawberry	IT	Strawberry	IT	IT	Strawberry	Allo	Allo
Ferrous	Ferrous	None	None	None	None	Alum	Ferrous	None	Alum	None
6.098	1.219	1.98	0.77	0.37	0.77	0.46	1.253	0.77	6.784	0.381
70.52	67.46	74.45	81.10	79.1	81.10	78.21	72.19	81.10	65.16	85.63
4.39	2.21	1.2	2.55	4.11	2.55	3.65	4.77	2.55	0.34	1.52
12.61	7.04	19.75	17.2	3.1	17.2	4.09	13.92	17.2	32.90	5.94
4/5	4	4	4/5	4/5	4/5	4/5	4/5	4/5	4	4/5
4/5	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4	4	4/5	4/5	4/5	4/5	4/5	4/5	4	4/5
4/5	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
5	5	5	5	6	5	5	5	5	6	5

96	95	94	93	92	91	90	89	88	87	86
65.00	85.00	65.00	65.00	75.00	75.00	75.00	85.00	75.00	85.00	65.00
1.00	1.00	1.50	1.50	1.50	2.00	1.50	1.00	1.50	1.50	1.50
Strawberry	IT	IT	IT	IT	IT	Strawberry	Strawberry	Strawberry	IT	Allo
Alum	Ferrous	Ferrous	Alum	None	None	Ferrous	Alum	Ferrous	Alum	Ferrous
0.713	1.415	1.24	0.404	0.388	0.5	2.18	1.487	2.18	6.784	5.92
78.72	65.23	71.2	77.21	78.01	76.21	66.23	74.26	66.23	73.78	45.65
0.99	3.82	4.54	3.72	3.95	4.15	3.2	2.19	3.20	4.27	3.07
10.8	10.60	13.15	3.60	4.02	5.92	9.20	18.64	9.20	9.12	10.17
4/5	4	4/5	4/5	4/5	4/5	4/5	4	4/5	4	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4	4/5	4/5	4/5	4/5	4/5	4	4/5	4	4/5
4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5
5	6	5	5	5	5	5	5	5	6	7

107	106	105	104	103	102	101	100	99	98	97
75.00	75.00	65.00	75.00	85.00	65.00	75.00	75.00	75.00	85.00	85.00
1.00	1.50	1.00	1.50	1.00	1.00	1.50	1.50	1.00	1.00	2.00
Allo	IT	Allo	IT	IT	Allo	Allo	Strawberry	Allo	Strawberry	Allo
Ferrous	Alum	Alum	Alum	Alum	Ferrous	Ferrous	None	None	Ferrous	Alum
6.62	0.46	3.021	0.46	0.654	5.722	6.34	0.77	1.797	2.62	8.24
48.13	78.21	71.3	78.21	73.57	45.36	49.13	81.1	76.45	56.08	59.43
2.30	3.65	-2.01	3.65	4.01	2.49	0.21	2.55	0.40	3.56	3.15
11.35	4.09	41.23	4.09	9.8	9.49	10.95	17.2	19.41	9.55	31.84
4/5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5
4/5	4/5	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5
6	5	6	5	5	7	5	4	5	5	5

108	75.00	1.50	IT	Ferrous	1.625	67.1	3.98	12.23	4	4/5	4	4/5	5
109	65.00	2.00	IT	Alum	0.405	76.94	3.75	3.47	4/5	4/5	4/5	4/5	6
110	75.00	1.50	Allo	Alum	5.73	74.06	-1.3	36.5	4/5	4	4/5	4	5
111	75.00	1.50	Allo	None	1.431	77.15	0.21	19.02	4/5	4/5	4/5	4/5	5
112	65.00	1.00	Strawberry	Ferrous	0.942	84.26	0.97	0.92	4	4/5	4	4/5	5
113	75.00	1.50	Strawberry	Ferrous	2.18	66.23	3.2	9.2	4/5	4/5	4/5	4/5	6
114	75.00	1.50	IT	None	0.388	78.01	3.95	4.02	4/5	4/5	4/5	4	6
115	75.00	1.50	Allo	Ferrous	6.34	49.13	0.21	10.95	4/5	4	4/5	4	7
116	85.00	1.50	Allo	None	3.182	68.12	2.21	21	4	4	4	4	6
117	85.00	2.00	Strawberry	Ferrous	4.923	49.61	4.62	9.79	4/5	4/5	4/5	4/5	5

*L**=lightness, *a**=redness, -*a**=greenness, *b**=yellowness, -*b**=blueness, cc: colour change Cs: colour staining

Appendix B

Table 12: Time, temperature and plant variety vs. Yield

Run	A:temp	B:time	C:plant variety	yield
1	75.00	2.00	allo	13.6
2	75.00	1.50	allo	10.2
3	65.00	1.00	allo	4.8
4	65.00	1.00	Strawberry	5.5
5	85.00	2.00	Strawberry	18.4
6	75.00	1.50	Strawberry	10.6
7	85.00	1.00	allo	13.4
8	75.00	1.00	Strawberry	9.0
9	85.00	2.00	IT	21.3
10	75.00	1.50	allo	10.2
11	65.00	1.50	IT	10.4
12	75.00	1.50	allo	10.2
13	65.00	1.50	Strawberry	7.0
14	75.00	2.00	Strawberry	13.0
15	85.00	2.00	allo	17.4
16	65.00	2.00	Strawberry	8.5
17	85.00	1.00	IT	16.6
18	65.00	2.00	allo	8.2
19	85.00	1.50	Strawberry	16.0
20	85.00	1.00	Strawberry	12.6
21	75.00	1.50	IT	12.3
22	75.00	1.00	IT	12.0
23	65.00	2.00	IT	11.1
24	65.00	1.50	allo	6.8
25	75.00	1.50	IT	14.5
26	75.00	1.00	allo	9.4
27	75.00	1.50	allo	10.2
28	75.00	1.50	IT	12.3
29	75.00	1.50	IT	12.3
30	75.00	1.50	allo	10.2
31	65.00	1.00	IT	9.6
32	75.00	1.50	Strawberry	10.6
33	75.00	1.50	IT	12.3
34	75.00	1.50	Strawberry	10.6
35	85.00	1.50	IT	19.6
36	75.00	1.50	Strawberry	10.6
37	75.00	1.50	Strawberry	10.6
38	85.00	1.50	allo	15.4
39	75.00	2.00	IT	15.8