**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTE OF TECHNOLOGY**

**SCHOOL OF CHEMICAL AND BIO ENGINEERING**

# Valorization of orange peel for dye synthesis and its application for dyeing cotton fabric

By

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A thesis submitted to the School of Chemical and Bio Engineering presented in partial fulfillment of the requirement for the degree of Master of Science (Process engineering), Addis Ababa Institute of Technology, Addis Ababa University, Addis Ababa, Ethiopia

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I declare that this thesis entitled "Valorization of orange peel for dye synthesis and its application for dyeing cotton fabric" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Dr.Eng.S.Anuradha Jabasingh instructor in Addis Ababa University, School of Chemical and Bio Engineering.

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# List of Acronyms

| | |
|---|---|
| AATCC | American Association of Textile Chemists and colorists |
| Adj.$R^2$ | Adjusted R-square |
| ANOVA | Analysis of Variance |
| BBD | Box-Behnken Design |
| °C | Degree Centigrade |
| CI | Confidence Interval |
| $CO_2$ | Carbon dioxide |
| Conc. | Concentration |
| DF | Degree of Freedom |
| DOE | Design of Experiment |
| FN-R | standard for Novocal orange dye |
| FTIR | Fourier Transformation Infrared Spectroscopy |
| g | Gram |
| GS | grain scale |
| h | Hour |
| ISO | International Standard Organization |
| L | Liter |
| mL | Milliliter |
| mm | Millimeter |
| MY | May |
| $NaCO_3$ | Sodium Carbonate |
| PLC | Private Limited Company |
| Pred.$R^2$ | Predicted R-squared |
| $R^2$ | Regression coefficient |
| rpm | Rotation Per Minute |
| RSM | Response Surface Methodology |

# Abstract

A further usage of peels from orange as natura dyes is presented in this paper. Natural dye is generally applied in an aqueous solution, and requires a mordant to improve the fastness of the dye on the fiber. Because of its good affinity, brilliant colours, nontoxic, non-allergic nature on textile materials, easy accessibility and less damaging effect on human health, it can be used in food, pharmaceutical, and textile industries. The aim of this study is to valorize orange peels for dye synthesis and to evaluate its yield. Orange peel is used as a raw material for the extraction of natural dye using soxhlet extraction method. Design of experiment for RSM was used to analyze and optimize the effect of extraction temperature (65°C, 72.5°C, and 80°C), extraction time (1.5h, 3.25h and 5h) and orange peel to ethanol ratio (0.05g/mL, 0.075g/mL and 0.1g/mL) on extraction of natural dye from orange peels. A maximum yield of natural dye of 40.109% was achieved under selected optimal conditions with high value of combined desirability a three-variable, three-level Box-Behnken design was used to develop a statistical model. From experiment, the yield of natural dye was obtained as 40.106%. FTIR and UV-Vis spectrophotometric studies were performed on the dye extract. The dyes produced were applied on cotton fabric and $Na_2CO_3$ was used for fixing the color on the fabric. Colour dyeing and testing were carried out using data color tool analysis (L*, a*, b*) and fastness properties of dyed cotton fabric were investigated according to AATCC-61 and crocking ISO 105×12.


**Keywords:** Cotton fabric, FTIR, Natural dye, Orange peel, Soxhlet extraction method.

# 1. Introduction

## 1.1. Background

Textile processing industry is one of the major environmental polluters in the world as the effluent from these industries contains a heavy load of chemicals including dyes used during textile processing. There are two main ways to limit the environmental impact of textile processing. One is to construct sufficiently large and highly effective effluent treatment plants, and the other way is to make use of dyes and chemicals that are environmental friendly such as natural dyes. The rich biodiversity of our country has provided us plenty of raw materials, yet sustainable linkage must be developed between cultivation, collection and their use (Gyanendra et al., 2015). A color additive is a substance capable of imparting its color to a given substrate such as paint, paper and cotton. Dyes and pigments are the most important colorants used to add a color to the fabrics. A dye must be soluble in the application medium usually water at some points during the coloration process. It should exhibit some substantivity for the material being dyed and should be absorbed from the aqueous solution (Gürses, 2016). Dyes are organic compounds widely used for imparting color to the textiles and they are produced either chemically or naturally (Ammayappan et al., 2016).

Dyeing is a process of adding colourants in the form of dyes and chemicals to textile fibres, yarns or fabrics. A dye is any chemical substance that has affinity for its substrate (i.e. fibre, yarn or fabric). There are basically two types of dyes that are used for dyeing. These are synthetic and natural dyes. Mostly, synthetic dyes are made from petroleum by-products and coal-tar which are corrosive to machine parts, have repulsive smell and are poisonous to human beings. Natural dyes on the other hand are easily accessible and have less damaging effect on the human health because of the way, they are extracted. Although they are not as pure and fast as the synthetic dyes, most of them possess qualities such as good affinity, brilliant colours and fastness properties which make them compete favourably with synthetic dyes. Natural dyes can be classified into animal, plant and mineral dyes depending on their source of procurement (Gbadegbe et al., 2014). Natural dyes are known for their use in coloring of food substrate, leather, wood as well as natural fibers like wool, silk, cotton and flax as major areas of application. Natural dyes may have a wide range of shades. The use of natural dyes that are nontoxic and non-allergic on textile materials has gained significant importance due to ever increasing awareness and concerns regarding environmental pollution as in the case of synthetic dyes. Calls for the use of natural dyes on textiles have been just one of the consequences of increased environmental awareness (Samanta and Konar, 2011). Natural dyes are less toxic, non-pollutant, less health hazard, very brilliant, rare color idea, and no allergic reactions (Edeen, 2015).

Agro-industrial wastes are generated during the industrial processing of agricultural or animal products including orange peels. These orange peels are generated in large amounts throughout the year and are the most abundant renewable resources on earth. Due to the large availability and composition rich in compounds that could be used in other processes, there is a great interest on the reuse of these peels, both from economic and environmental viewpoints. The economical aspect is based on the fact that such peels may be used as low-cost raw materials for the production of other value-added compounds with the expectancy of reducing the production costs. The environmental concern is because most of the peels contain phenolic compounds and other compounds of toxic potential; which may cause deterioration of the environment when the peel is discharged to the nature (Solange et al., 2012). Oranges are one of the most popular fruits and have an annual yield over than 100 million tons globally. The orange peel represents approximately 20-30 % of the total orange mass and therefore is an abundant, cheap and readily available biomass (Noureddine et al., 2017).

The production or the extraction of natural dye from orange peel can be commercialized in solution form or in powder form. The orange peels used for the extraction of natural dyes are easily accessible or available from our surroundings at cheaper or low cost (Teresa et al., 2015). Plants are the major sources of natural colorants and almost all their parts such as stem, leaves, fruits, and seeds are used for extracting natural color. They have antimicrobial, antifungal, insect repellent, deodorant, disinfectant and other medicinal values. The choice of dyes and dyeing methods for textiles depends upon the type of fabrics, their utilization, fastness to in-service requirements and type of preparatory and finishing processes. Many types of dyes can be used to dye fabrics but in this research dyeing of cotton is carried out using natural dyes that are extracted from local plants found in our country, namely orange peel (Jihad, 2014).

Therefore, simple soxhlet extraction was investigated to extract the natural dyes from orange fruits. This method contains two phases during the extraction which are liquid (ethanol) and solid (orange peel) phases. The quantity of analytes extracted from different matrices depends on the type of matrix, conditions, and techniques of extraction. There are many factors such as types of solvent, extraction time, pH, temperature and orange peel to ethanol ratio that might significantly influence the extraction efficiency. The positive or negative role of each factor in the mass transfer of the process is not always obvious (Nurul et al., 2016).

**Figure 1-1:** Prepared local orange peel in Ethiopia

## 1.2. Statement of the problem

In Ethiopia, agriculture is the foundation of the economy leading to the generation of thousands tons of agricultural wastes. Ethiopia's fruit productions and exports play a significant role in the local economy as a means of earning livelihoods for nearly five millions farmers, creating jobs and generating foreign exchange revenues. The annual fruit production for MY 2017/18 was estimated at 780,000 metric tons and the fruit crops occupied a total area of 104,000 hectares. From these, Orange in Ethiopia covers about 20,787 tons of the total fruits produced and from these around 5196.75 tons of orange peels are disposed (Ababa, 2018).

Collecting and daily consumption of orange in high amount leads to orange peels. Daily disposal of these peels usually represents a problem to the environment. The management of these peels represents a major problem for the food industry and the nearby community. Generally, the generation of orange peel is dramatically increasing each year. Most of the orange peel is generated from household, agricultural areas and industrial areas, etc. which are normally used for incineration or landfill sites. However, incineration is an expensive disposal method and causes air pollution, while in landfills the orange peel is broken down by microorganisms and contaminates the groundwater. The import of synthetic dyes for textile industries are corrosive to machines, have repulsive smell, toxic and allergic on textile materials, poisonous to human beings and generally damages the environment. This leads to the suitable application of finding orange peel products from different processes. This research conducts the economic utilization of orange peel for the production of value added products (natural dyes) and their application to cotton fabrics.

Although natural dye production from citrus fruits is not started in Ethiopia, following the growth of chemical industries its demand has increased from time to time. The natural dye from orange peel has a potential to replace the synthetic dye due to the lower environmental impact and simple processing methods. Hence, the orange peels could lead to the development of cheap, efficient and environmentally sound production of natural dye. This may have considerable economic benefits to the food processors, environmental agencies, pollution control organization, and reduces utilization of synthetic dyes. Therefore, the benefits of orange peels for the synthesis of natural dye explores in this research and the method could be extended to the industrial zones of Ethiopia in order to establish natural dye manufacturing industries.

## 1.3. Objectives

### 1.3.1. General Objective

The main objective of this study is to valorize orange peels for synthesizing natural dyes and to test the dye on the cotton fibers.

### 1.3.2. Specific Objectives

The specific objectives of this research are:

- ✓ To characterize the orange peels (proximate analysis and functional group determination)
- ✓ To extract the dye from orange peels and to optimize the factors affecting extraction yield (extraction temperature, extraction time and orange peel to ethanol ratio)
- ✓ To determine the yield of dye and to characterize the extracted dye using FTIR and UV-Vis spectrophotometer
- ✓ To check model validation of the predicted and experimental values
- ✓ To investigate suitability of the dye extract for cotton fabric application
- ✓ To assess the colour analysis, shades and color fastness properties of the dyed cotton fabric

## 1.4. Significance of the study

This research has benefits to many stakeholders in the economy and the final goal of this research can be considered from different perspectives. Ethiopia is an importer of synthetic dyes and the Ethiopian government spends a substantial amount of its foreign currency reserves on these synthetic dye based products. Hence, by producing natural dye from locally available raw materials (orange peel) the currency for our country is overwhelmed. In general, the significance of this research can be seen from different perspectives:

- Enhance knowledge and understanding on the potential utilization of orange peels to bring economic benefit
- To ensure safety on the human health by preventing the deterioration of the environment when the orange peel is discharged
- Reduces the ecological burden of the society namely the disposal of orange peels by extendding industrial zones
- Provide as alternative raw material  for dye production
- Enhances eco-friendly dyeing of fibers using natural dyes and
- Minimize the impact of synthetic dye since high concentration of natural dyes has the potential to replace it.

## 1.5. Scope of the study

This research generally covers valorization of orange peels for dye synthesis and the application of the extracted dye for dyeing of cotton fabric. It includes collection of orange peels from juice house, preparation and characterization of the orange peels by using oven drier and muffle furnace for proximate analysis (moisture content, ash content and volatile matter), FTIR determination for functional group of the peels, extraction of dye using soxhlet extraction method, investigation of the main and interaction effect of extraction factors (extraction temperature, extraction time, and orange peel to ethanol ratio), determining the model equation and hence the optimum conditions for dye extraction. It also covers the characterization of the dye using FTIR and UV-Vis spectrophotometer and its application for the dyeing of cotton fabric using dyeing machine, dispense machine, and gyro-wash. The colour strength and the fastness properties of the dyed cotton fabric were determined in addition to the colour analysis.

# 2. Literature review

## 2.1. History of dyes

Various industries including textiles, rubber, paper, plastics, leather, cosmetics, food, and mineral processing industries use dyes in order to color their products. Dyes in textile industries have improved the quality of human lifestyle to a certain extent. There are over 100,000 available dyes and about $7\times10^5$ tons of dyestuff manufactured yearly (Koti, 2012). Dyes can be described as colored substances which have a similarity to the substrate to which they are applied. It can be divided into two groups, which are synthetic dyes and natural dyes. Traditionally, all dyes used in textiles were from natural origin until the revelation of first synthetic dye mauviene (basic dye) in 1856. Since then, the synthetic dye industry has developed at an elevated rate and almost wiped out the use of natural dyes across the world. Due to its low production cost, brighter colors, better resistance towards environmental effects, and easy-to-apply factor, the discovery of synthetic dyes has overcome the role of natural dyes in the society. However, synthetic dyes are mostly toxic and carcinogenic. Moreover, this dye has become one of the key sources of ground water pollution as a consequence of the rapid development of the textile industries. The release of colorant effluent of the synthetic dyes has initiated a fear on the human health and species living in water resources. Inefficiency in delivering these dyes onto textile fibers can cause the colorants that contain harmful substances being released together with the effluents (Wan et al., 2011).

The disposal of the synthetic dyes from the industries into the environment may also affect the photosynthetic activity of the hydrophytes, by reducing the light penetration. They are toxic to some aquatic organisms due to their unmanageable nature. Nowadays, interest in natural dyes has noticeably increased as a result of the environmental safety concerns surrounding the manufacturing usage of synthetic dyes. Natural dyes can be obtained from natural sources like plants, animals, and minerals. Across the world, varieties of plant sources are used for natural dyes. It is reported that about 300 plant species have been identified as traditional dye sources. Any plants ranging from unwanted weeds to cultivated plants can have the possibility to act as a natural dye. Different parts of plant such as seeds, flowers, leaves, barks, and roots can be used to extract dyes (Nurul et al., 2016).

## 2.2. Valorization of Orange peels

Today, citrus fruits are cultivated in almost all regions of the world. The citrus processing industry yearly generates tons of residues, including peel and segment membranes from the extraction of citrus juice in industrial plants. The management of these peels, which produce odor and soil pollution, represents a major problem for the food industry. During the processing of oranges, large quantities of solid and liquid peels are generated. The peels obtained from fruits and processing industry is extremely diverse due to the use of wide variety of fruits, the broad range of processes and the multiplicity of the product (María et al., 2011).

As an example, tropical and subtropical orange processing has considerably higher ratios of by-products than the temperate oranges. Due to increasing production and processing of oranges, disposal represents a growing problem since the orange peels is usually prone to microbial spoilage, thus limiting further exploitation. On the other hand, costs of drying, storage and shipment of by-products are economically limiting factors. Therefore, agro-industrial peels are often utilized as feed or as fertilizer (Mariusz et al., 2017).

Orange is the main citrus fruit investigated and commercialized. Orange has higher amount of peels that could be used as a good source of bioactive compounds. The outer part or the skin of an orange is called orange peel. The orange peel is a waste material (Rabiul et al., 2012). The orange peels are generally wasted when orange fruits are mainly used by juice processing industries. Since the juice yield of citrus is less half of the fruit weight, a very large amount of orange peels is formed every year (Mamta and Arora, 2013). One alternative to improve the management of these peels is the implementation of new processes for their recovery, for instance, through the production of organic fertilizers, pectin, bio-oil, essential oils, and antioxidant compounds, or as a substrate for the production of several compounds with high added value such as microbial proteins, organic acids, ethanol, natural dyes, enzymes and biologically active secondary metabolites and adsorbent materials. These are excellent alternatives to add value to these substances (Rezzadoria et al., 2012).

Orange peel contains soluble sugars and pectin as the main components. Orange peel is in fact constituted by soluble sugars, 16.9 % wt; starch, 3.75 % wt; fiber (cellulose, 9.21 % wt;

hemicellulose, 10.5 % wt; lignin 0.84 % wt; and pectin, 42.5 % wt), ash, 3.50 % wt; fat, 1.95 % wt; and protein, 6.50 % wt. The total sugar content of orange peel varies between 29 and 44 % (Harvey, 1936), soluble and insoluble carbohydrates being the most abundant and economically interesting constituents of this residue . The orange peel also known as pericarp is composed of two layers (the external layer of the peel and albedo). The external layer of the peel is a pigmented, relatively thin layer and contains oil glands. The color of the orange is connected with the presence of β-carotene (orange pigment) in the peel. For the special smell of the orange fruits the aroma oil which is collected from the oil glands are responsible. The external layer of the orange is protected against loss of water and also against microorganisms by a natural wax. Albedo is the inside part of the peel (Mariusz et al., 2017).

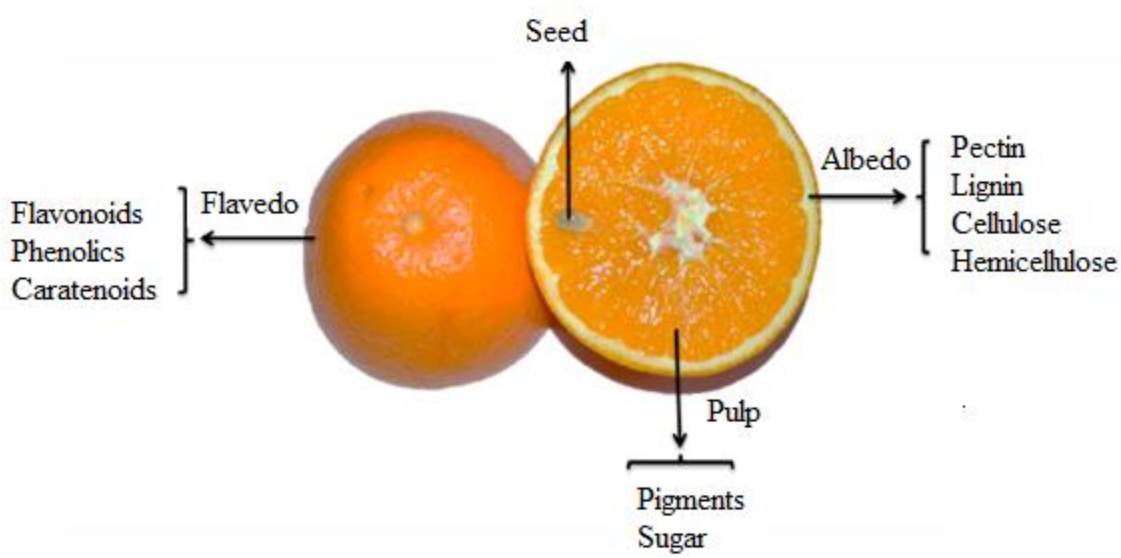


**Figure 2-1:** Anatomy of orange fruit

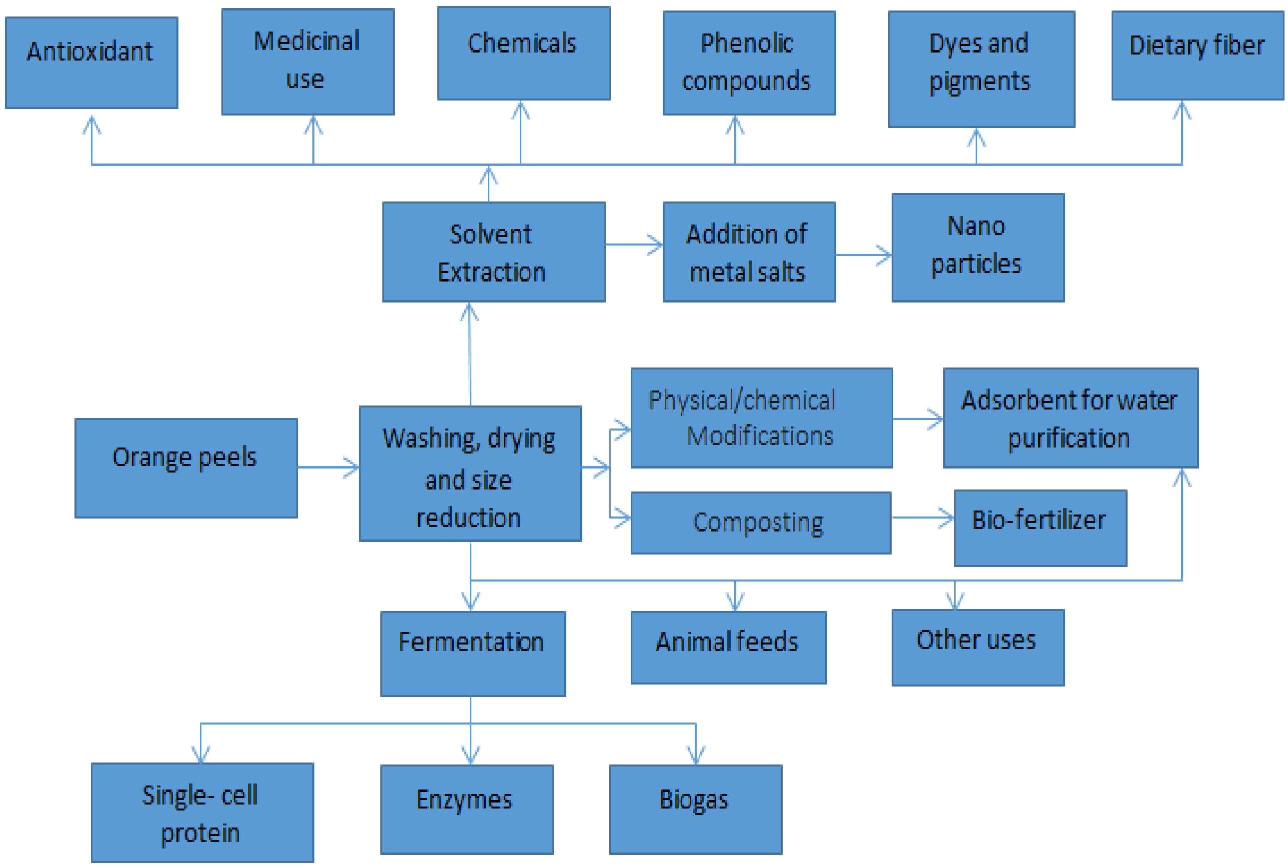


**Figure 2-2:** Valorization of orange peels (Pathak et al., 2016)

### 2.2.1. Extraction and Characterization of Carotenoids

Removal and purification of the carotenoids from orange peel gave a natural dye suitable for food and textile industries. The recovery of carotenoids from the outer layer of orange peel was carried out with acetone, ethanol and hexane as the extraction solvent. Other solvents used for carotenoid extraction from citrus peel were petroleum ether, carbon disulphide, and methylene chloride. Maceration of the peel by an enzymic preparation and subsequent extraction with hexane increased the dye yield by 65% (Aravantinos et al., 1992).

Carotenoids are susceptible to degradation due to a number of reasons, such as chemicals, heat, light and enzymes (Lin et al., 2016). The steps in determining microbial carotenoids are culture, cell disintegration, extraction, separation and quantitation. Cell disintegration is usually achieved by mechanical breakage and acid or alkaline hydrolysis, liquid or supercritical $CO_2$ extraction

(Weber et al., 2007). Enzymatic digestion of cells also appears as an attractive option, presumably resulting in higher recovery rates of carotenoids from the microbial matrix. Most of the extraction processes employed acetone, ethyl acetate, cyclohexane, petroleum ether, alcohol and chloroform for recovery of carotenoids of orange peel. Carotenoids have been isolated and for identification and structure clarification, visible spectrophotometry, and mass spectrometry are being used (Hodisan et al., 1997). Quantification of dyes is usually done based on calibration curves of available commercial standards or purified dyes; other peaks may be quantified using conversion formulae (Chandi and Gill, 2011).

Orange peel derived natural dyes are easily extracted, completely biodegradable, and readily available. Carotenoids are a class of natural pigments that are primarily found in orange peel, and they typically possess 40 carbon molecules and multiple conjugated double bonds. Because of their various functions and interesting properties, carotenoids have become a fascinating field for interdisciplinary research in chemistry, biochemistry, medicine, biology, and other branches of science (Anna et al., 2015). β-carotene is a natural yellow-red pigment. Its chemical formula is $C_{40}H_{56}$. Its sources are mainly plants, with a yellow-red Colour as carrots and oranges. Soxhlet extraction is a type of atmospheric liquid extraction, utilizing solvents at boiling temperature and low pressures (ambient pressure), for the selective extraction of targeted compounds. Soxhlet extraction is a conventional technique providing the highest recovery of carotenoids. Thus, it is commonly used for evaluating the performance of other methods (Macías-Sánchez et al., 2010).

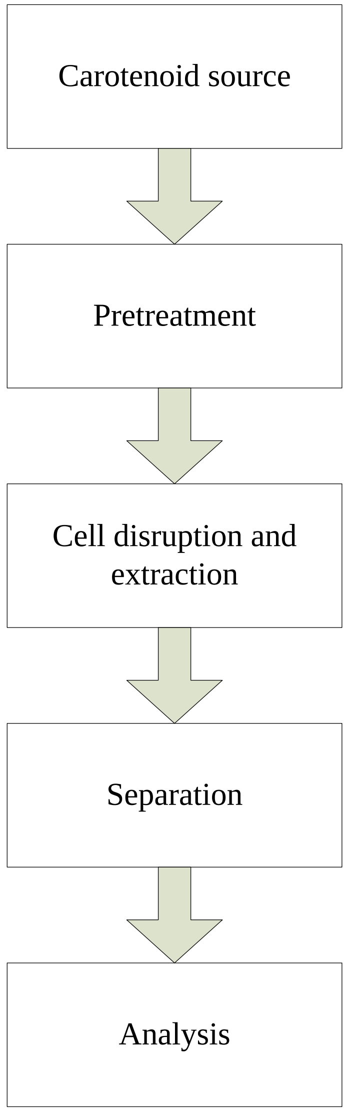


**Figure 2-3:** Steps involved in the extraction and analysis of carotenoids from natural sources(Ramesh et al., 2018)

## 2.3. Varieties of orange peels

Different citrus species and varieties are cultivated in the Ethiopia. The common varieties were sweet orange, mandarin, lime, lemon, grapefruit, citrus hybrids, sour orange and citron which produced in orchards. The most dominant sweet orange variety produced in the country was Valencia (in 61.1% of the locations considered) followed by unknown variety (58.3%), Washington Naval (47.2%) (Dagnew et al., 2014)

**Navel oranges:** Navel oranges are well suited Mediterranean and subtropical climates were they attain good external and internal colour. Extreme tropical climates are not well suitedfor navel production which limits adaptability worldwide. They have a distinctive flavor , are easily peeled and sanctioned and tend to be lower in acid content than most orange varieties. The most popular variety is 'Washington nevel' but a section of other varities are available. Large to extra large, round to oval, deep yellow to orange color. Rough, medium thick peel. Usually seedless. Peels and section very easily. Seasonal Availability: January, October, November, December. This the orange peel variety used in the study .

**Valencia Oranges:** Medium to large size, round to oval shape, yellow to orange color (sometimes tinged with green) with a smooth, thin peel. Usually seedless or with only a few seeds. Valencias have orange colored flesh, which is loaded with golden juice of fine rich flavor and aroma. Seasonal Availability: February, March, April, May, June

## 2.4. Classification of natural dyes

Natural dyes are simply dye substances extracted from natural sources and are usually more reliable, cheaper and can be supplied more readily. Natural dyes have a complex chemical composition. Unlike synthetic dyes, they are usually not a single entity but a mixture of closely related chemical compounds. Natural dyes have been used since prehistoric times for dyeing and printing fabrics. The coloring matters from plants, insect and animals are referred to as natural dyes of which plant and insect dyes find their application in dyeing textiles, wood and leather. Non-toxic dyes of plant and insect origin are also used in food and cosmetic industries. The chemical classification and the source and application of colorants are discussed below(Sujata and Raja, 2014).

**Carotenoids:** In these the colour is due to the presence of long conjugated double bond. The class name carotene is derived from the orange pigment found in carrots. Carrots are considered to be the richest sources of Beta-carotene and the color is due to the presence of long conjugated double bond.

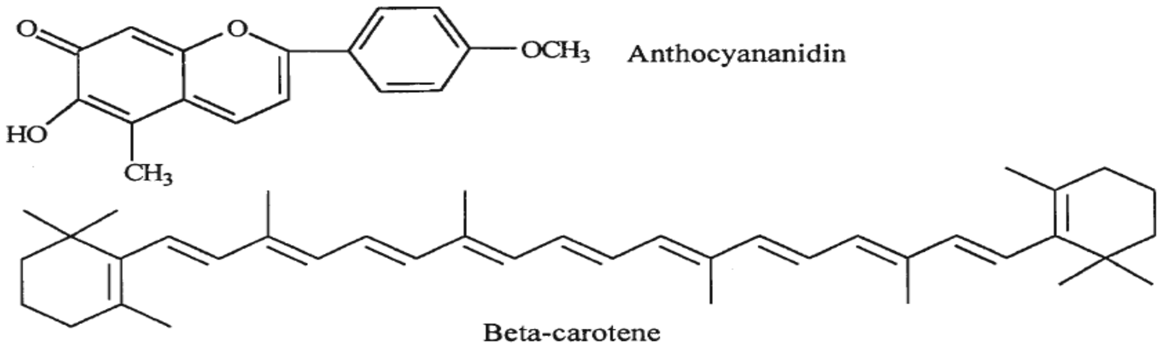


**Figure 2-4:** Anthocyananidin and beta-carotene structure

**Flavone:** Most of the yellow natural dyes have a hydroxyl or methoxy substituted flavone structure. Dyes with this chemical composition are found in a wide variety of natural resources. It is obtained from flowers and seeds of various primulas.

**Tannins:** Tannins are constitutive polymeric polyphenols .They have relatively high molecular mass with a typical aromatic ring structure with hydroxyl substituents. Tannins 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 color with the change in mordant depending upon the dye-mordant complex.

**Indigoid Dyes:** Indigo is the major and most important dyeing in this class as among natural dyes, it is almost always the source of the primary color blue. Chemically it is indigotin and is found in largest concentration in the leaves of some Indigofera species such as *Indigotinctoria*, Indigo errecta and Indigosumatrana.

**AnthraquinoneDyes**: Some of the most important red dyes are based on the anthraquinon structure. They are obtained both from plants and insects. The most famous natural dye in this category is alizarin obtained from European madder (*Rubiatinctorum*).

## 2.5. Properties of Natural Plant Fiber

### 2.5.1. Cotton Fiber

Cotton is a cellulosic fiber obtained from natural sources. As cotton occupies 50% of the consumption of fibres by weight in the world it is called as the king of all fibres. Cotton is the fabric for every home and is the most widely produced of textile fabrics today. Cotton fiber grows in a ball around the seeds of the cotton plant of the genus *Gossypium* and is soft and comforting basic fibers. However, cotton fiber quality is strongly influenced by the grade, color, length, and characteristics of the fiber. External appearance, brightness, and color are the important criteria for the gradation of cotton fiber. The color of raw cotton is normally white or gray but other colored varieties are also available such as reddish, chamois, and yellowish-brown, among others. The cotton fiber quality is most strongly influenced by the length that divides cotton fiber into two major categories: long staple fiber having a length more than 28 mm and short staple fiber having a length shorter than 28 mm. Cotton fibers having good strength characteristics are considered as good quality cotton for practical applications (Sohel et al., 2014).

**Table 2-1:** Physical and chemical properties of cotton fibers

| Physical properties | |
|---|---|
| Colour | White, creamy white, bluish white, yellowish white, or grey. |
| Tensile strength | Moderately strong fiber |
| Elongation at break | Doesn’t stress easily |
| Elastic recovery | Rigid and inelastic fiber |
| Effect of heat | Excellent resistance to thermal degradation |
| Fiber density | 1.54g/cm$^3$ |
| Moisture regain | 8.5% |
| Chemical properties | |
| Effect of alkalis | Cotton fiber has excellent resistance against alkalis. The fiber swells in caustic soda (NaOH), but doesn’t get damaged. |
| Effect of acids | Cotton fiber is damaged and disintegrated by cold concentrated acids or even hot diluted acids. It is not affected by weak acids in cold conditions. |
| Effect of organic solvents | Cotton has good resistance against organic solvents used for cleaning. |
| Effect of microorganisms | Bacteria, fungi, and mildews can attack cotton fiber and hot and humid conditions are favorable for their growth. |

## 2.6. Extraction of Natural dyes

### 2.6.1. Extraction methods

As natural dye materials contain coloring matter or dye along with a number of other plant and animal constituents such as water-insoluble fibers, carbohydrates, protein, chlorophyll, and tannins, extraction is an essential step not only for preparing purified natural dyes. As natural coloring materials are not a single chemical entity and the plant matrix also contains a variety of non-dye plant constituents, extraction of natural dyes is a complex process. The nature and solubility characteristics of the coloring materials need to be finding out definitely before employing an extraction process. The different methods for extraction of coloring materials are (Mansour, 2018):

#### 2.6.1.1. Aqueous Extraction

Aqueous extraction was traditionally used to extract dyes from plants and other materials. In this method, the dye-containing material (orange peel) is first broken into small pieces or powdered and sieved to improve extraction efficiency. It is then soaked with water in earthen, wooden, or metal vessels for a long time usually overnight to loosen the cell structure and then boiled to get the dye solution which is filtered to remove non-dye peel remnants. The process of boiling and filtering is repeated to remove as much dye as possible. Generally, centrifuges are used to separate residual matter. Use of trickling filters can ensure removal of fine plant material particles and ensure better solubility of the purified natural dye. As most of the dyeing operations are carried out in aqueous media, the extract obtained by this method can be easily applied to the textile materials. Disadvantages of this extraction method are long extraction time, large water requirement, use of high temperature, and low dye yield as only water-soluble dye components get extracted whereas many dyes have low water solubility (Ashis and Agarwal, 2009).

#### 2.6.1.2. Organic Solvent Extraction

Unit processes such as solvent extraction followed by suitable separation method can be utilized to produce high value-added chemicals such as medicinal compounds, bioactive compounds, natural dyes, dietary fibers. The organic solvent extraction phase uses either a single solvent (water, ethanol, ethyl acetate and hexane) as solid-liquid extraction or an aqueous form of these solvents as a two phase extraction method. In general, ethanol is preferred because at the point of consumption of the molecules obtained, ethanol is considered as generally considered as safe according to American Food and Drug Administration (Azmir et al., 2013).

Furthermore, acid addition to organic solvent is recommended for anthocyanin extraction from peels. Another important point for extraction is extraction time and temperature. Natural dyes depending upon their nature can also be extracted by using organic solvents such as acetone, petroleum ether, chloroform, ethanol, methanol, or a mixture of solvents such as mixture of ethanol and methanol, mixture of water with alcohol, and so on. The water/alcohol extraction method is able to extract both water-soluble and water-insoluble substances from the plant resources. The extraction yield is thus higher as compared to the aqueous method as larger number of chemicals and natural dyes can be extracted. Purification of extracted dye is easier as solvents can be easily removed. Extraction is performed at a lower temperature thus chances of degradation are fewer. The disadvantages of the method are the presence of toxic residual solvents and their greenhouse effect (Mansour, 2018).

#### 2.6.1.3. Enzymatic Extraction

As plant tissues contain cellulose, starches, and pectins as binding materials, commercially available enzymes including cellulase, amylase, and pectinase have been used by some researchers to loosen the surrounding material leading to the extraction of dye molecules under milder conditions. This process may be beneficial in the extraction of dye from hard plant materials such as bark, roots, and the like.

#### 2.6.1.4. Supercritical Fluid extraction

Extraction is an emerging area in natural product extraction and purification. A gas functions as a supercritical fluid above its critical values of temperature and pressure. Such a fluid has physical properties somewhere between those of a liquid and a gas. Supercritical fluid is able to dissolve many substances like a liquid, as solubility of a substance in any solvent is higher at higher pressure and temperature and such conditions are needed to maintain a gas in the supercritical state. Supercritical fluid extraction using $CO_2$ is a good alternative to solvent extraction as it is nontoxic, cheap, easily available, and does not leave residues (Mansour, 2018). Super critical fluid extraction is the usage of the fluid at their super critical stage. Accepted as GRAS, $CO_2$ was the generally used fluid in this method. Although it requires a special equipment, it is fast process and requires less amount of sample, and solvent than conventional solvent extraction (Castro-López C, 2017).

#### 2.6.1.5. Subcritical water extraction

It is performed by keeping water in its liquid form at higher degrees of temperature such as 100 – 300 °C by controlling pressure. Therefore, this process reduces water polarity and provides the solubilization of both hydrophobic and hydrophilic molecules. This method also needs specialized equipment (Domínguez-Rodríguez G, 2017).

## 2.7. Dyes

Dye is an organic and inorganic molecule, used to impart color to the textile fibers. Dyes are classified based on their mode of application and the different types of dyes with their sustainability. When a textile fabric is placed in the dye bath (dye solution), the item absorbs the molecules of the dye and assumes the colour of the dye. Because dyed textiles vary in their ability to hold colour, chemical additives or mordants such as salt and acid are sometimes used to regulate absorption of the dye into the fibre. This suggests using the proper dye for particular fibres, which also demands knowledge of the affinity of the fibre or substrate for particular dyes. The implication is that all textiles could be made colour fast to an extent so that the fabric can hold its colour under normal use, laundering or exposure to sunlight (Korankye, 2010).

### 2.7.1. Natural dyes

Natural colorants are dyes and pigmentary molecules that are obtained from plant, animal or mineral sources with or without chemical treatments. Many investigations have been carried out for extraction of colorants from different parts of plants and for their chemical identification. Most natural dyes are commonly extracted from different parts of the plants that are indispensable for the survival of plants. In Ethiopia huge amount of orange peels are wasted daily. So these wasted peels can be used for extraction of dyes for application in textile industries in place of synthetic dye. Besides application in textile industry, the dyes can be used in the food industry, and making different colorful candles. The advantages of natural dyes are cost effective, renewable, non-carcinogenic in nature, no disposal problems and have no allergic reaction on skin (Sinha et al., 2012).

### 2.7.2. Synthetic dyes

Dyes derived from organic or inorganic compound are known as synthetic dyes. Examples of this class of dyes are Direct, Acid, Basic, Reactive, Mordant, Metal complex, Vat, Sulfur, Disperse dye etc. 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. The following properties are often considered to be advantages of natural& synthetic dyes (Jihad, 2014).

**Table 2-2:** Advantages and disadvantages of natural dye (Jihad, 2014)

| Advantages of natural dyes | Disadvantages of natural dyes |
|---|---|
| The use of natural colorants will offer no effluent problem and will provide a natural finish to textile treated with these materials | Low dyeing efficiency |
| Cultivation of plants from which most natural dyes are generated will definitely assist in preserving the eco-balances | Costly either in money or time |
| The resources which most natural dyes are generated are not only replaceable but also biodegradable | Only few have good fastness to light and washing |
| Have pharmacological effects and possible health benefits | Some of the mordants are harmful |
| Can give harmonizing color | Mostly used for protein and cellulosic fibers |
| Technology for production could vary from simple aqueous to complicated solvent system and super crucial fluid extraction techniques | |

**Table 2-3:** Advantages and disadvantages of synthetic dyes (Jihad, 2014)

| Advantages of synthetic dyes | Disadvantages of synthetic dyes |
|---|---|
| Quick and simple procedure (easy to process) | Certain chemical compounds used in synthetic dyestuff have been found to be carcinogenic and have skin allergic problem |
| Inexpensive | Most of the synthetic dye chemicals not only based on toxic raw material but also their use in textile wet processing produce effluents harmful to environment |
| Good fastness to wash and light | Knowledge of colour design is necessary |

## 2.8. Mordants

Most natural dyes need chemical species called mordants for binding the dye to cotton fabrics to improve color fastness. Mordants help in binding of dyes to cotton fabric by forming a chemical bridge from dye to fiber thus improving the staining ability of a dye with increasing its fastness properties. Some of these mordants are chemical agents which are not eco-friendly therefore it is important to use natural dyes with eco-friendly mordants for their health and environment benefits. The color fastness and characteristics of natural dyes on cotton fabrics are influenced by the mordanting method applied whose effects vary with the source of the dye (Loum and Janani, 2013).

Most of the natural dyes have no substantively cellulose or other textile fibres without the use of a mordant. The majority of natural dyes need a mordanting chemical (preferably metal salt or suitably coordinating complex forming agents) to create an affinity between the fibre and the dye molecules of natural colourant. These metallic salts as mordant form metal complexes with the fibres and the dyes. Aluminium sulphate or other metallic mordants anchored to any fibre, chemically combine with certain mordantable functional groups present in the natural dyes and bound by coordinated/covalent bonds or hydrogen bonds and other interactional forces (Sumathy, 2013). Thus, for proper fixation of natural dyes on any textile fibre, mordanting is essential in most of the cases. Mordanting can be accomplished either before dyeing (pre-mordanting), or during dyeing (simultaneous mordanting) or after dyeing (post-mordanting) (Mohammad et al., 2016).

Therefore, 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 (Bichromate of Potash), sodium carbonate, and Ferrous Sulphate. Others include, Tin crystals and stannous chloride, Tannic acid, Aluminum chromium, and Copper. Chrome and Tin are poisonous, so Alum and sodium carbonate are recommended for first attempts at mordanting. All cotton fabrics must be well washed and rinsed before a mordant is applied (Korankye, 2010).

## 2.9. Characterization of natural dyes

The aqueous extraction of the corresponding dye solution is concentrated using rotary evaporator at lower temperature (50°C) to a semi-dried solid mass using water bath at 200-300 rotation per minute. For characterization, purified aqueous dye solution separately and is subjected to wavelength scan in a microprocessor or computer attached UV-Vis absorbance spectrophotometer . UV-Vis spectral scan of aqueous/non-aqueous extract/solution of purified natural dyes having both UV-zone and visible zone (190-700 nm or higher) indicating peaks and troughs in different wave length shows its main hue, absorption etc. Peaks and troughs in visible zone thus indicate main colour and absorption. UV-Zone with/without peaks shows the property of the dye under UV-light, this may be correlated with fastness behavior. UV-Visible spectroscopic studies are carried out by different scientists to identify the UV-Vis spectral scan of a number of natural dyes viz, madder, cochineal, indigo, etc., using different solvents for extraction (Samanta and Konar, 2011).

## 2.10. Factors affecting extraction of dyes

Many factors affect the process of dye production, including temperature, extraction time, mass to volume ratio and extraction of bioactive compounds is influenced by various process parameters such as solvent composition, pH, temperature, extraction time and solid to liquid ratio. Solvent extraction is a common form of chemical extraction using organic solvents e.g. hexane, ether, chloroform, benzene, ethanol, methanol etc. (Hemanthraj et al., 2014).

### 2.10.1. Effect of temperature

Both the solubility and mass transfer rate (diffusion coefficient) can influence the extraction temperature. In theory, the penetrability and solubility of the solvents increased with the increase of the temperature, thus resulting in an increased of extraction efficiency and speed. On the other hand, the target compounds (natural dyes) may decompose if the temperature is higher. A study on the influence of temperature on the overall yield is therefore important (Mardawani et al., 2013).

Experiments were carried out to study the effect of temperature over the extraction yield of dyes and colors. During extraction of dye the effect of temperature is the most important factor on the efficiency of the product. The extraction temperature of natural dyes varies from room temperature (25ºC) to boiling temperature (100 ºC). At high temperature, solubility of dye is increased so it comes more in filtrate and less in residue (Farooq, 2013).

Temperature plays a very important role in the extraction of natural dyes and the effect of the temperature on dye extraction was studied by carrying out the soxhlet extraction at different temperature ranging from temperature 65°C − 80°C for different extraction time and orange peel to ethanol ratio. The three levels of temperature were selected because of the fact that most literatures give a clue to select the optimal temperature between 50°C and 95°C.

**2.10.2. Effect of solid to liquid ratio**

The solvent quantity is also an important factor to influence the extraction yield. The removal of solute requires a lot of energy using water as solvent. Therefore, if more water usage in extraction may lead to higher energy consumption. The material to liquor ratio affects the dye molecules are congested, and they collide with each other to increase the affinity of dye molecules for each other and decrease their affinity for the fabric (Farooq, 2013). Soxhlet extraction process is also affected by solid to liquid ratio. In this study, the orange peel was used as solid and ethanol as liquid (organic solvent). To observe the influence of extraction the solid to liquid ratio was carried out at different ranges 0.05-0.1g/mL. The three levels of the extraction were selected because of the fact that mass to liquid ratio is carried out between 0.05-0.2g/mL.

**2.10.3. Effect of extraction time**

Extraction time is one of the important factors for extraction of dyes and colors from plant materials. It is associated with the final concentration of dyes and colors and the efficiency of extraction. The effect of extraction time was studied by conducting extraction using water as the solvent, carried out at 80°C. The extraction time was varied and it is important to determine the duration of the extraction process required to extract most of the desired natural dyes. Typically, this would be the time at which equilibrium of solvent concentration between inner and outer cells is established. Using this information, suitable duration can be selected for the process (Mardawani et al., 2013).

Extraction time is one of the important factors for extraction of pigments and colors from plant materials. The extraction yield was increased rapidly at the initial stages of extraction, but ends with a slower extraction rate (Farooq, 2013). The optimum time of extraction for maximum natural dye extraction varies with the extraction conditions. The other factor studied in dye extraction was the extraction time at different temperatures and mass to liquid ratios. To observe the influence of extraction the extraction time was studied at different ranges from 1.5 – 5hours. The three levels of the extraction time were selected because of the fact that soxhlet extraction process is carried out between 1 and 10h (Nurul et al., 2016).

## 2.11. Dye applications

Natural dyes are mostly employed for dyeing of natural fiber textiles (cotton fabrics) to enhance their eco-friendly characteristics. They are usually applied to cotton fabrics by dyeing. Natural dyes like synthetic dyes can also be used to dye cotton fabrics at all stages. Orange peels containing flavonoids are used to produce yellow color shades. The process for the dyeing of textiles with natural dyes differs from the synthetic dye application process because only some natural dyes can be applied directly to textiles. In most of the cases the dye is not substantive to the fiber on which it is being dyed therefore an additional step of mordanting is involved, making it a two-step process (Sujata and Raja, 2014).

Natural dyes are known for their use in colouring of food substrate, leather, pharmaceutics as well as natural protein fibres like wool, silk and cotton as major areas of application (Ashis and Agarwal, 2009). From this orange peel dyes were used for the application of cotton fabric in textile and garment industries using mordants for fixation of the dye on the fabrics.

# 3. Materials and Methods

The experimental work was conducted in the laboratory of the department of chemical engineering of the faculty of engineering, Ethiopian institute of technology (EIT-M), Mekelle and Quiha MAA-garment and textile factory.

## 3.1. Raw material preparation and characterization

The samples of orange peels were collected from fruit vendors (juice house). The sample was packed in plastic bags and transported to Ethiopian institute of technology-Mekelle (EIT-M), Department of chemical engineering laboratory. The orange peel wastes were washed using tap water in order to remove unwanted matter. After washing the albedo of orange peels was removed through knife, flavedo was air dried for 24h and oven dried at 50°C for 2 days. The dried material was then ground into powder form using mortar grinder and the powder was passed through a sieve to obtain uniform particle size of 1.6 mm. The sieved powder was then used for dye extraction at different experimental conditions.

### 3.1.1. Determination of proximate composition

Moisture content was determined after oven drying to a constant weight at 105°C (AOAC, 1995, 2000). The weighing of the orange peel samples for moisture content determination was made with a balance with a precision of 0.0001g. Ash was determined by incineration of the sample in a muffle furnace at 550°C for 5h.

#### 3.1.1.1. Determination of Moisture Content

The method is based on drying a sample in an oven and determining moisture content by the weight difference between dry and wet material. 30g of the cleaned air dried orange peels was taken in a crucible and dried in an oven at a temperature of 105°C for 6 hours and the weight was taken after every 2 hours. The procedure was repeated until a constant weight was obtained. After each 2 hours, the sample was removed from the oven and cooled in desiccators for 30minutes. It was then removed and re-weighed. Therefore, the weight differences of raw material before and after drying were calculated as:

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

Where $W_1$= is original weight of the sample taken

$W_2$= is weight of the sample after drying

#### 3.1.1.2. Determination of Ash Content

A dry crucible containing 20g of oven dried sample of orange peel was placed in a muffle furnace set at 550°C for 3 hours and the sample was cooled in a desiccator for 30mins and weighed on analytical balance. The ash contents were analyzed according to AOAC methods (Feumba et al., 2016). The % of ash content was calculated using the following formula:

$$\text{Ash content (\%)} = \frac{W_1}{W_2} \times 100 \quad (2)$$

Where $W_1$=weight of sample residue after ignition (g)

$W_2$= weight of dry sample taken (g)

#### 3.1.1.3. Determination of volatile organic compound

The dried sample after moisture removal was taken in a crucible and placed in electrically heated oven at a temperature of 920°C for 10 minutes and then cooled in desiccators for 30 minutes. It was then removed and re-weighed. The percentage of weight loss gave the volatile matter content (Ozioko, 2012). The weight of volatile matter on dry basis of orange peels was determined as the difference between the dry weight of samples and the weight of the sample residue after ignition.

$$\text{Volatile matter (\%)} = \frac{W_2 - W_1}{W_2} * 100 \quad (3)$$

Where $W_1$= weight of sample residue after ignition (g)

$W_2$= weight of dry sample taken (g)

#### 3.1.2. Pre-treatment of orange peels

The orange peels collected from the fruit vendor were thoroughly washed with tap water to remove some trash or dirt, filtered, then air dried for 24 hours and finally, oven dried at 50°C for 2 days. The dried substrates were pulverized in a dry mortar grinder, passed through standard sieves with a pore size of 1.6mm and stored in polythene container for natural dye production. This pretreatment of orange peel was done to make their chemical constituents more accessible and to protect contamination of the raw material by microorganisms before using for dye extraction and a commercially prepared ready- to-dye, plain weave 100% cotton fabric of 30g was purchased from Quiha MAA-garment and textile Company, Ethiopia.

## 3.2. Chemicals used

The chemicals and analytic reagent grades used were sodium hydroxide, sodium carbonate, distilled water, tap water, ethanol absolute (99.5%), ethyl acetate (99.5%), salt (NaCl), acetic acid and detergents.

## 3.3. Equipment

The equipment used during this study includes mortar grinder, knifes, sieve analysis, magnetic stirrer, volumetric flask, filter paper, test tubes, cuvette, burette, electronic weighing balance(precision, ±0.0001), oven (MB45, OHAUS, Switzerland),different size of conical flasks and beakers, measuring cylinders, separating funnel, dryer, water bath (HWS-26),aluminum foil, crucible furnace, desiccator, gloves, Kjeldahl flask, Petridis, thermometer, soxhlet extraction apparatus, Extraction thimbles, rotary evaporator, dispenser machine(i.e. Auto lab dispenser and auto lab control),dyeing machine, fastness property tester, gyro-wash, uv-vis spectrophotometer, and FTIR.

## 3.4. Methods

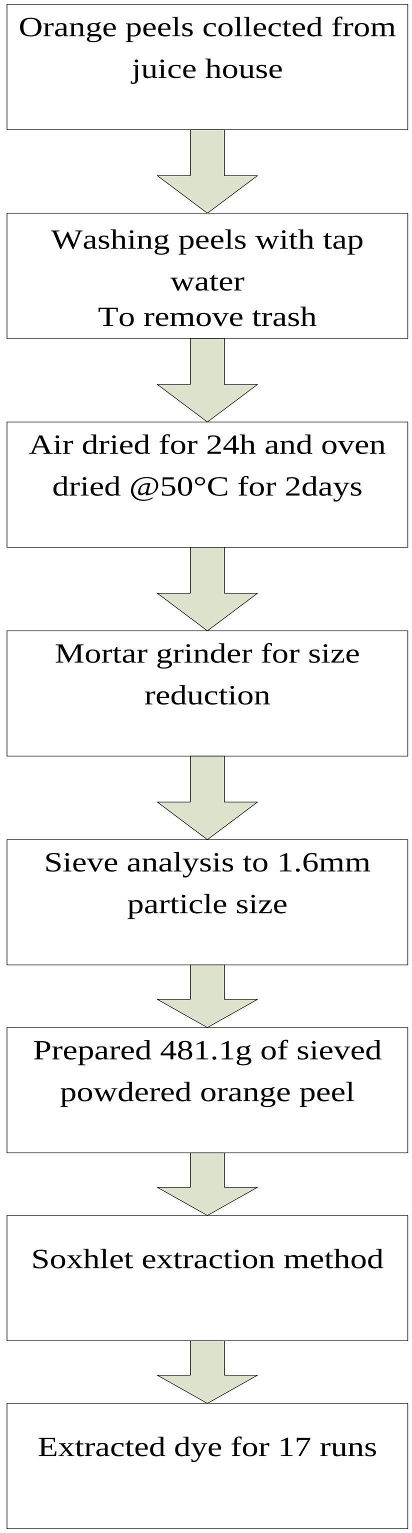


**Figure 3-1:** Framework of the experimental extraction of dye

### 3.4.1. Dye Extraction

Soxhlet extraction method was employed for obtaining coloring components from the orange peels. Orange peels were collected from juice house and washed thoroughly with tap water to remove soil and dust particles. The washed orange peels were shade-dried, grounded, and sieved resulting in a fine powder. Extractions were done using soxhlet extraction method adjusted with electro-thermal heater using ethanol as an organic solvent. The dried ground samples were prepared together with orange peel to volume of ethanol ratio of 0.05g/mL, 0.075g/mL and 0.1g/mL. Subsequently the mixtures were subjected to different temperatures (65°C, 72.5°C and 80°C) and time (1.5h, 3.25h, and 5h) combinations individually. 283mL, 378mL and 565mL of ethanol was poured into round bottom flask.

28.3g of the crushed sample was placed in the thimble and was inserted in the centre of the extractor. The soxhlet equipped with a condenser was placed onto a flask containing the ethanol. The soxhlet was heated from 60°C-80°C. When the solvent was boiling, the solvent vapour travels up a distillation arm and floods into the chamber housing the thimble of solid. The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing of the solid material. The extract soaks through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This was allowed to continue for extraction time of 1.5h, 3.25h and 5h. It was then removed from the tube, cooled in the desiccators, and determines the amount of dye extracted using rotary evaporator at 50°C and 250rpm. Then a separating funnel were used to separate the natural dye from unwanted(i.e. oil and non-polar) compounds by adding ethylacetate.

## 3.5. Experimental design

Data analysis was carried out by DESIGN EXPERT 11.1.0.1 software box Behnken design (BBD) to evaluate the effects of the process variables. Optimal conditions for dye extraction were studied based on the RSM. In this investigation, natural dye was produced using soxhlet extraction method and a three-variable box Behnken design for RSM was used to develop a statistical model to describe the production of natural dye from orange peels. Three different levels were considered for temperature (65°C, 72.5°C, and 80°C), orange peel to ethanol ratio (0.05g/mL, 0.075g/mL, and 0.1g/mL) and extraction time (1.5h, 3.25h and 5h) for extraction.

Significance within and between extractions was set from analysis of variance (ANOVA) at P value ≤ 0.05.

**Table 3-1:** Independent variables and their levels

| Variables | Factors X | Levels | | |
|---|---|---|---|---|
| | | -1 | 0 | 1 |
| Temperature, °C | $X_1$ | 65 | 72.5 | 80 |
| Extraction time, h | $X_2$ | 1.5 | 3.25 | 5 |
| Orange peel/ethanol ratio, g/mL | $X_3$ | 0.05 | 0.075 | 0.1 |

RSM was used to optimize the extraction of natural dyes from orange peels. A box Behnken design was used in the optimization of process variables with three factors at three levels. The responses function ($Y$) was partitioned into linear, quadratic, and interactive components. Experimental data were fitted to the second-order regression equation:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \cdots \quad (4)$$

Where $\beta_0$ is the intercept; $\beta_1$, $\beta_2$, and $\beta_3$ are linear coefficients; $\beta_{11}$, $\beta_{22}$, and $\beta_{33}$ are squared coefficients; $\beta_{12}$, $\beta_{13}$, and $\beta_{23}$ are interaction coefficients

The experimental design and statistical analysis were performed using Design-Expert software (version 11.1.0.1). The model adequacies were checked in terms of the values of $R^2$ and adjusted $R^2$. ANOVA was employed to determine the significance of the models. The optimum values of the variables tested was obtained by numerical optimization based on the criterion of desirability.

## 3.6. Dye determination

The natural dye extract was concentrated by using a rotary evaporator at 45°C and 250rpm. The aqueous concentrates were then placed in a separating funnel and an equal volume of ethyl acetate was added to remove lipids, chlorophylls, and other non-polar compounds from the mixture. The dye content in the fractions was collected into beaker and fractions containing the highest content of dye(11.35g) were chosen for identification analyses (Anuar et al., 2013). From the extracted dye the per cent yield of the natural colourant was calculated after the liquid extract was evaporated at 50°C in a rotary vacuum evaporator. The dried extract was collected, stored in a desiccator and used for estimation of the percent dye yield by applying the following formula:

$$\%\ \text{Yield} = \frac{\text{weight of dye extracted}}{\text{weight of sample used}} * 100 \qquad (5)$$

## 3.7. Characterization of dyes

### 3.7.1. Double beam uv-vis spectrophotometer

The spectrophotometer is universal among modern laboratories. Ultraviolet (UV) and Visible (VIS) spectrophotometry has become the method of choice in most laboratories concerned with the identification and quantification of organic and inorganic compounds across a wide range of products and processes. Modern spectrophotometers are quick, accurate, and reliable. UV-vis spectroscopy is a technique for measuring absorbance as a function of wavelength. A sample is irradiated with an intensity of UV-vis light and the intensity after the sample is measured. A scan from 300 to 600 nm was performed in order to generate the characteristic absorption spectra of the sample (Espinosa et al., 2012). Uv-vis spectrophotometer measures the intensity of light passing through a liquid sample (i.e. dye solution) at different wavelengths and estimates the maximum wavelength that gives highest absorbance. Three samples of liquid dye were prepared in a cuvette with distilled water as a standard or reference point (blank).

### 3.7.2. FTIR spectroscopy analysis of orange peels and dye

Infrared spectroscopy is an essential and crucial characterization technique to elucidate the structure of matter at the molecular scale. The chemical composition and the bonding arrangement of constituents in a homo-polymer, copolymer, and polymeric materials in general can be obtained using Infrared (IR) spectroscopy. The FTIR spectrometers obtain the IR spectrum by Fourier transformation of the signal from an interferometer with a moving mirror to produce an optical transform of the infrared signal. Numerical Fourier analysis gives the relation of intensity and frequency, that is, the IR spectrum. The FTIR technique can be used to analyze gases, liquids, and solids with minimal preparation (Vladimir et al., 2012).

The sample was measured on Spectrum 65FT IR (PerkinElmer) in the range 4000-400 $cm^{-1}$ using KBr pellets. First, the sample (i.e. orange peels) for the analysis was milled in a ceramic pestle and mortar to powdery conditions. The orange peel powder was then mixed with potassium bromide (KBr) particles to make it stable to infrared analysis or until homogenized in an agate mortar. The mixture was then pressed to a small thickness, slightly below 1mm, and was placed into the sample compartment of FTIR attachment of the spectrometer which was continuously purged with dry air required for FTIR analysis. Then the power of the instrument was turned on and the initialization started. From the window that appeared, the instrument setup button was selected, scans and instrument set up dialog popped up. The sample name, scan range, and scan number was inputted. The sample was placed on the sample holder, apply and start button were pressed to collect the spectrum (Gergely et al., 2017).

Fourier transform infrared spectroscopy was used to examine the framework of vibration. The functional group of the produced dye extract was tested by FTIR sample measured on spectrum 65(PerkinElmer in the range 4000-400$cm^{-1}$) with resolution of 4$cm^{-1}$ and 2 number of scans using NaCl(Salt plates are used to take IR spectra of a liquid sample) windows. The functional group was determined based on the interpretation of the infrared spectrum obtained by comparing it with the standard spectrum group frequencies.

### 3.7.3. Dyeing of cotton fabric

The optimum extracted dye (11.35g) was prepared to dye 30g bleached cotton fabric at the following dyeing condition: 60°C temperature, 20 minutes dyeing time, 1:10 material to liquor ratio and 30g/L, 40g/L and 50g/L salt concentration.  A sample of 10grams of cotton fabric was dyed with extracted dye stuff concentration of 60mL and natural mordant concentration of 10, 20, and 30% of sodium carbonate was used for all three trials.

### 3.7.4. Mordanting

Natural dyes typically have low affinity to cotton fabric as compared to synthetic dyes. Consequently, they often require mordants to improve substantivity or for fixation. Sodium hydroxide was used for neutralization and sodium carbonate was used for fixation as a mordant in this research in three different ratios, namely 10%, 20% and 30%.

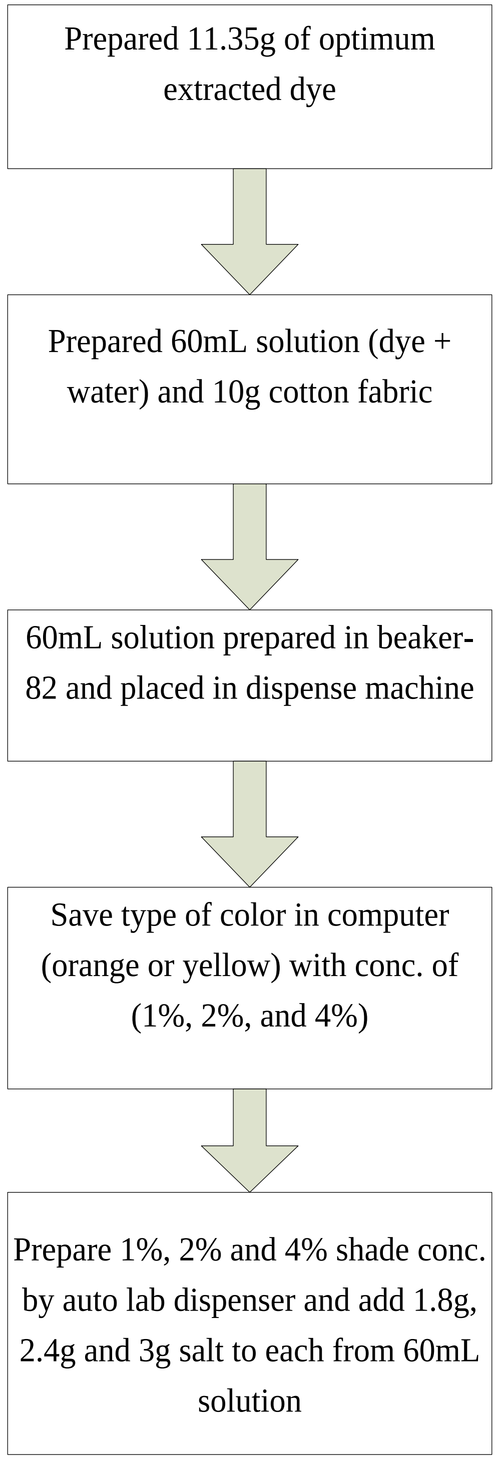


**Figure 3-2:** Flow diagram for cotton fabric treatment before dyeing

### 3.7.5. Color fastness tests

After dyeing 10g of cotton for 20min at 60°C, the dyed cotton fabric was assessed for color fastness with respect to washing and rubbing (dry and wet) fastness. The color fastness tests were used grey scale for assessing color changes and staining in the cotton fabric.

#### 3.7.5.1. Wash fastness

Wash fastness of the dyed cotton fabric was analyzed as per the AATcc_61 (ISO C01 to C06). Fastness to washing was tested for experimental dye against Commercial Novocol Yellow FN-2R Lab. Dyed specimens were cut in size in 5 x 10 cm and were washed in Launder-o-meter using detergents. The prepared cotton were then placed in the canisters along with the 8-10 steel balls and then fixed in the launder-o-meter and the change in color of the specimen was compared with the Commercial Novocol Yellow dyed cotton and the staining of the cotton fabric was assessed with standard grey scale.

#### 3.7.5.2. Rub fastness

Dyed cotton fabrics were tested for fastness to wet and dry rub according to standard test procedure crocking ISO 105×12 using Rub Fastness Tester.

**i. Dry rub test**

The 10g dyed cotton was placed on the horizontal platform and a felt pad was secured on the spindle brought in contact with the test specimen. The weight was already and the machine was operated for 10 revolutions. After the required revolutions were completed, the dyed cotton and the felt pad were removed from the machine. To assess the color change and transfer of color (degree of staining) standard grey scales were used.

**ii. Wet rub test**

Clean white felt pad was immersed in cold water and boiled until all the felts are completely wetted and after complete wetting the felts were allowed to be cooled. The felts were removed and excess water was slightly squeezed out prior to attaching it to spindle. The loads were adjusted and the spindle was brought into contact with cotton specimen for 60 seconds and the machine was allowed to operate for 128 cycles and the color change and color transfer form test piece to felt pad was assessed based on the grey scale.

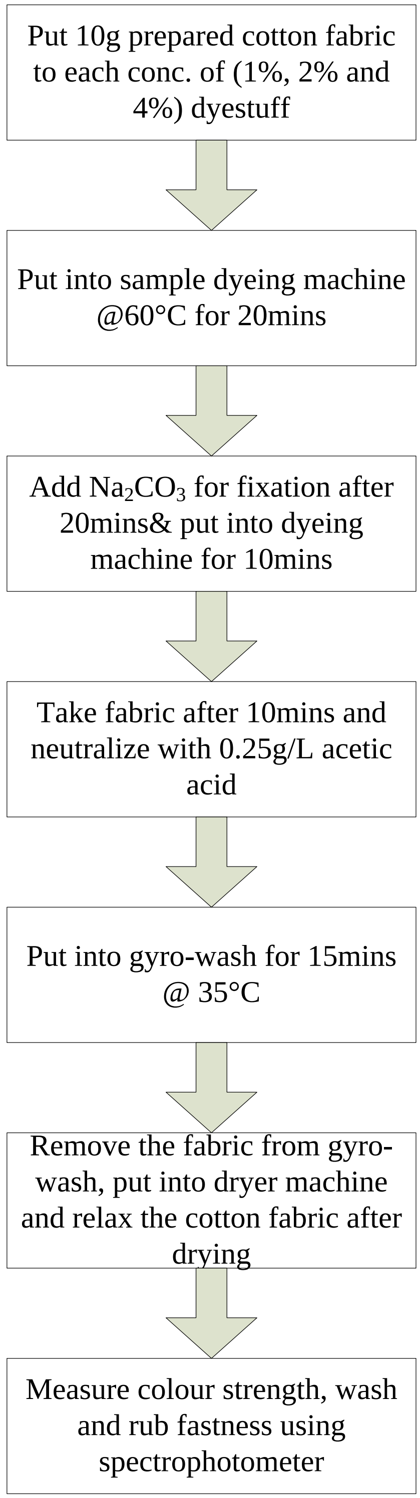


**Figure 3-3:** Flow diagram for cotton fabric dyeing

### 3.7.6. Color Analysis

At the completion of dyeing, the dyed cotton samples were removed from the lab dyeing machine and washed with tap water until there is no more colour bleeding followed by air drying under the shade. Dyed samples were evaluated for their colour strength using spectrophotometer with color tools software. Dyed fabrics were simultaneously evaluated in terms of CIELAB colour space (DL∗, Da∗, Db∗, and Dc*) values. The DL* axis is associated with the lightness of the colour and moves from top (value: 100, white) to bottom (value: 0, black), whereas Da* and Db* axes are associated with changes in redness-greenness. The coordinate a* is for red (+) and green (−), and b* is for yellow (+) and blue (−). The limits for a∗ and b∗ are approximate + or −80 and Dc* is for chroma.

# 4. Results and discussion

## 4.1. Proximate analysis of orange peels

### 4.1.1. Moisture content of orange peels

The moisture content of the orange peel differs based on the drying conditions. Therefore the moisture content was found to be 77.8% (obtained from fresh peels) and 10.32% (obtained from air dried peels) which varied due to the time the orange peels were put on the oven. Air-dried orange peels for $2-4$ days has less than 50% moisture content which is calculated according to eq(1) and (Appendix.A-1) but the effect of sunlight is considered as insignificance. The 10.32% found in this study was relatively low, and this may be due to the time at which it was harvested and sliced. The low value also designate that the peel can be accumulated for a long time without growing moldy. The ash content was found to be 3.67% from eq(2) and (Appendix.A-3) using muffle furnace at 550ºC. This value is analogous to other staples measured as good sources of minerals. The volatile organic matter content was found to be 81.78% from eq(3).

**Table 4-1:** Proximate Composition of orange peels

| Parameters | Concentration | (Pranav et al., 2017) |
|---|---|---|
| Moisture (%) | 10.32 | 7.91 |
| Ash (%) | 3.67 | 5.25 |
| Volatile organic matter (%) | 81.78 | 86.7 |

## 4.2. Fourier transformation infrared (FTIR) analysis of orange peels

FTIR spectrum of the prepared orange peels after grinding is demonstrated in Figure 4-1. In the spectra, it shows band shifting and possible involvement of hydroxyl groups(OH) around the broad intense absorption peaks of 3391 $cm^{-1}$ which represents hydrogen bonded-OH stretch. The peak at 2926$cm^{-1}$ is due to CH stretching asymmetric vibrations of CH groups and the peak at 1401$cm^{-1}$ is due to $CH_2$ and $CH_3$. The peak at 1736$cm^{-1}$ is due to C=O stretching and the stretching vibrations of –COOH and –$COOCH_3$ are attributed to this peak. The peak at 1631$cm^{-1}$ is due to the double bond of carbon (C=C). 1062$cm^{-1}$ is due to C-O-H or C-O-R bands. Generally, in orange peel, the intense bands seen at 3391, 2926, 1736, 1631, 1401, 1062, 771, and 602 $cm^{-1}$ correspond to the O–H/C–O stretching/C=O/N–H/O–H stretching/C–O/C=C/C–H stretching/bending vibrations respectively, and indicate the presence of alcohol, phenol, carboxylic group, amines, amides, ketones, ester, ether and amino acid group in OP. Therefore, the presence of organic compounds in OP is responsible for extraction of natural dye (Pranav et al., 2017).

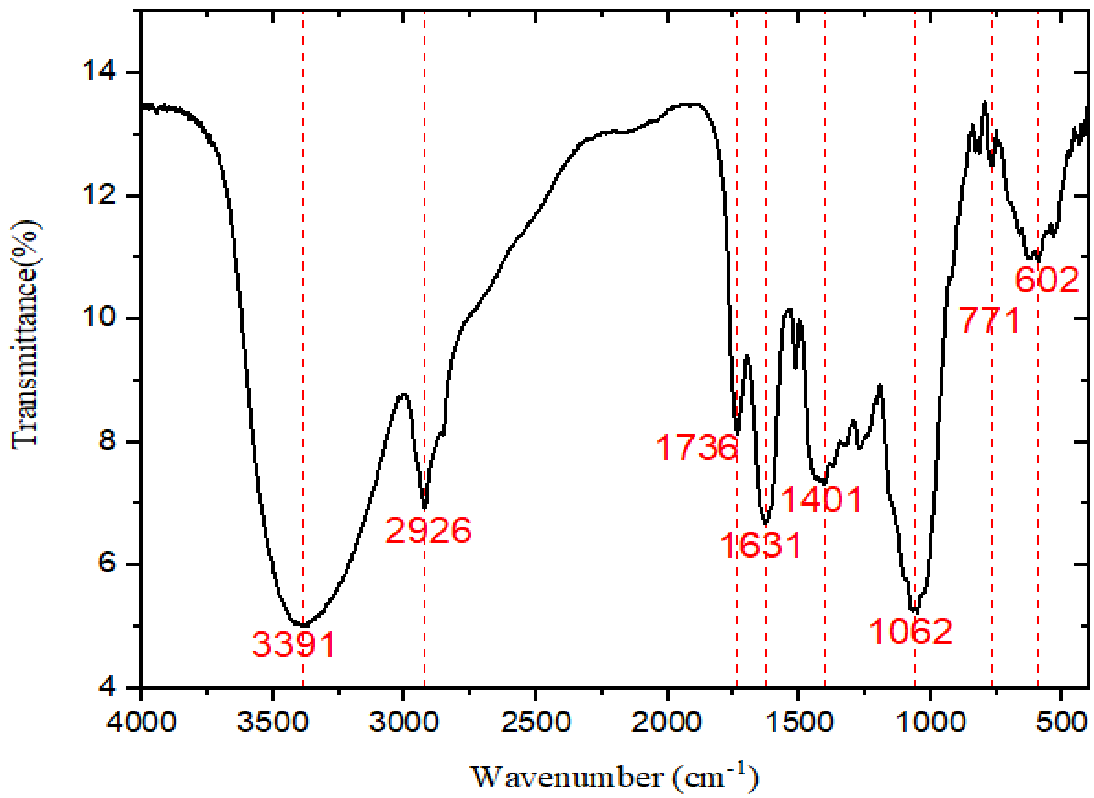


Figure 4-1: FTIR analysis of dried orange peels

## 4.3. Determination of yield of dye extracted from orange peels

The natural dye extracted from orange peel (i.e. 28.3g of orange peel was prepared for each of 17 experimental runs) was measured by adding equal amount of ethyl acetate to each 17extracted samples after rotary evaporator (Appendix.A-1)) and the yield of dye extracted from the sample at the experimental conditions (i.e. extraction temperature, extraction time, and orange peel to ethanol ratio) were calculated in (Table 4-2) according to eq(5).

**Figure 4-2:** Extracted dye of samples

## 4.4. Experimental design

Table 4-2 shows the result of the 17 experimental runs carried out according to the box Behnken design (BBD). Box Behnken design is the commonly used experimental design model for three-level three-factor experiments and always has three levels for each factor and is purpose-built to fit a quadratic model. The box Behnken design does not have runs at the extreme combinations of all the factors but compensates by having better prediction precision in the center of the factor space. In this study, Design-Expert Software 11.1.0.1 was used in the least squares regression ANOVA. The statistical software program was used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variables constant.

**Table 4-2:** Experimental results of BBD Matrix for extraction of dye

| | Factor 1 | Factor 2 | Factor 3 | Weight of dye extracted(gram) | Response 1 |
|---|---|---|---|---|---|
| Std | A:Temperature (°C) | B:Extraction time (h) | C:orange peel/Volume of ethanol ratio (g/mL) | | Yield of Dye (%) |
| 1 | 65 | 1.5 | 0.075 | 6.12 | 21.64 |
| 2 | 80 | 1.5 | 0.075 | 9.15 | 32.32 |
| 3 | 65 | 5 | 0.075 | 6.55 | 23.13 |
| 4 | 80 | 5 | 0.075 | 11.35 | 40.106 |
| 5 | 65 | 3.25 | 0.05 | 6.25 | 22.09 |
| 6 | 80 | 3.25 | 0.05 | 9.99 | 35.29 |
| 7 | 65 | 3.25 | 0.1 | 6.39 | 22.59 |
| 8 | 80 | 3.25 | 0.1 | 9.75 | 34.46 |
| 9 | 72.5 | 1.5 | 0.05 | 7.04 | 24.89 |
| 10 | 72.5 | 5 | 0.05 | 8.65 | 30.57 |
| 11 | 72.5 | 1.5 | 0.1 | 7.02 | 24.79 |
| 12 | 72.5 | 5 | 0.1 | 8.38 | 29.61 |
| 13 | 72.5 | 3.25 | 0.075 | 7.72 | 27.28 |
| 14 | 72.5 | 3.25 | 0.075 | 7.58 | 26.80 |
| 15 | 72.5 | 3.25 | 0.075 | 7.97 | 28.16 |
| 16 | 72.5 | 3.25 | 0.075 | 7.43 | 26.25 |
| 17 | 72.5 | 3.25 | 0.075 | 7.68 | 27.14 |

## 4.5. Statistical Analysis of the Experimental Results

### 4.5.1. Analysis of variance (ANOVA)

The analysis of variance of the quadratic regression model was a significant model, from evident of Fisher's "F" test with a very low probability value [(P-model > F) < 0.0001]. From Table 4-3 it was observed that the values of "Prob > F" less than 0.0500 indicate model terms were significant. In this case A, B, $A^2$, AB was significant model terms. Values greater than 0.1000 indicate the model terms were not significant. This indicates that orange peel to volume of ethanol ratio, temperature, extraction time, the interaction between orange peel to volume of ethanol ratio and temperature, interaction between orange peel to volume of ethanol ratio and extraction time affects the extraction of natural dye from orange peels.

**Table 4-3:** Analysis of variance (ANOVA) for Response Surface Quadratic Model

| Source | Sum of Squares | DF | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| Model | 420.39 | 9 | 46.71 | 106.88 | < 0.0001 | Significant |
| A-temperature | 347.58 | 1 | 347.58 | 795.34 | < 0.0001 | |
| B-extraction time | 48.95 | 1 | 48.95 | 112.00 | < 0.0001 | |
| C-orange peel/volume of ethanol | 0.2411 | 1 | 0.2411 | 0.5516 | 0.4818 | |
| AB | 9.91 | 1 | 9.91 | 22.68 | 0.0021 | |
| AC | 0.4390 | 1 | 0.4390 | 1.00 | 0.3496 | |
| BC | 0.1858 | 1 | 0.1858 | 0.4253 | 0.5351 | |
| $A^2$ | 11.54 | 1 | 11.54 | 26.41 | 0.0013 | |
| $B^2$ | 1.12 | 1 | 1.12 | 2.56 | 0.1538 | |
| $C^2$ | 0.1284 | 1 | 0.1284 | 0.2939 | 0.6046 | |
| Residual | 3.06 | 7 | 0.4370 | | | |
| Lack of Fit | 1.09 | 3 | 0.3640 | 0.7401 | 0.5811 | not significant |
| Pure Error | 1.97 | 4 | 0.4918 | | | |
| Cor Total | 423.45 | 16 | | | | |

The Model F-value of 106.88 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, AB, $A^2$ are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The Lack of Fit F-value of 0.74 implies the Lack of Fit is not significant relative to the pure error. There is a 58.11% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good. The following second order polynomial model was derived to explain the extraction of natural dye from orange peels.

Final equation in terms of coded factors:

$$\text{Yield of dye} = +27.13 + 6.59A + 2.47B - 0.174C + 1.57AB - 0.331AC - 0.216BC + 1.66A^2 + 0.515B^2 - 0.175C^2 \quad (6)$$

The equation (6) in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. From the regression model equation developed in terms of coded factors, the response yield of dye was affected by linear terms extraction temperature(A) , extraction time(B) and orange peel to volume of ethanol ratio(C) and pure quadratic terms ($A^2$, $B^2$, $C^2$) and interaction quadratic terms (AB, BC, AC). On the basis of the coefficient in the equation, it was evident that the response yield of dye increases with an increase in the extraction temperature (A), and extraction time(B) which have positive linear effect on yield of dye but extraction temperature has a more weighty linear effect on yield of dye compare to extraction time. Pure quadratic terms ($A^2$, $B^2$) have positive effects on the response yield but the pure quadratic term ($C^2$) has a negative effect than the other quadratic terms. Interaction of temperature and extraction time (AB) has a positive effect on response yield. Interaction of temperature and orange peel to volume of ethanol ratio (AC), and interaction of extraction time and orange peel to volume of ethanol ratio (BC) has a negative quadratic effect on yield of dye.

Final equation in terms of actual factors:

$$\text{Yield of dye} = +131.71 - 3.65 \times \text{temperature} - 8.01 \times \text{extraction time} + 179.08 \times \text{grinded orange to volume of ethanol ratio} + 0.12 \times \text{temperature} \times \text{extraction time} - 1.77 \times \text{temperature} \times \text{orange peel to volume of ethanol ratio} - 4.93 \times \text{extraction time} \times \text{orange peel to volume of ethanol ratio} + 0.029 \times \text{temperature}^2 + 0.168 \times \text{extraction time}^2 - 279.43 \times \text{orange peel to volume of ethanol ratio}^2 \quad (7)$$

The equation (7) in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

**Table 4-4:** Model adequacy measures

| | | | | |
|---|---|---|---|---|
| Std. Dev. | 0.66 | | $R^2$ | 0.993 |
| Mean | 28.07 | | Adjusted $R^2$ | 0.984 |
| C.V. % | 2.36 | | Predicted $R^2$ | 0.952 |
| Press | 20.54 | | Adeq Precision | 35.76 |

The Predicted $R^2$ of 0.952 is in reasonable agreement with the Adjusted $R^2$ of 0.984; i.e. the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 35.76 indicates an adequate signal. This model can be used to navigate the design space. The regression coefficient ($R^2$) quantitatively evaluates the correlation between the experimental data and the predicted responses. Results of $R^2$= 0.993 and Adj.$R^2$= 0.984 from (Table 4-5) obtained explicates that the predicted values were found to be in good agreement with experimental values. Since the $R^2$ value was closer to 1.0 it indicates that the regression line perfectly fits the data. The model's goodness of fit was checked by regression coefficient ($R^2$). In this case, the value of the coefficient ($R^2$ =0.993) from Table 4.4 indicated that only 0.70 % of the total variance was not explained by the developed regression model. The adjusted determination coefficient (Adj.$R^2$= 0.984) was also satisfactory for confirming the significance of the model. Pred. R-Squared indicating that the model will probably explain a high percentage (about 95.20%) of the variability in new data.

## 4.6. Model Adequacy Check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R -Squared, adjusted R-Squared and predicted R-Squared having a value of 0.993, 0.984 and 0.952 respectively. The quality of the model developed could be evaluated from their coefficients of correlation and the value of R-squared for the developed correlation is 0.993. It implies that 99.30% of the total variation in the percentage of conversion is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure 4-4. The results in Figure 4-4 demonstrate that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three variables to the extraction of dyes.

The adequacy of the model was further checked with ANOVA, based on a 95% confidence level, F-value is a test for comparing model variance with residual (error) variance. If the variances are close to be the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P-value less than 0.05. It was calculated by model mean square divided by residual mean square. The effectiveness of the model could also be measured so as to assure its approximation to the true value. Thus, regression coefficient, $R^2$, could be used for checking its adequacy. The regression value is between 0 and 1, and as it approaches to 1 it fits well to the experimental data otherwise it indicates failure of approximation. In this case, $R^2$, 0.993 was obtained, which was close to one and the value Adj.$R^2$ was 0.984.and it is in a reasonable agreement with $R^2$.

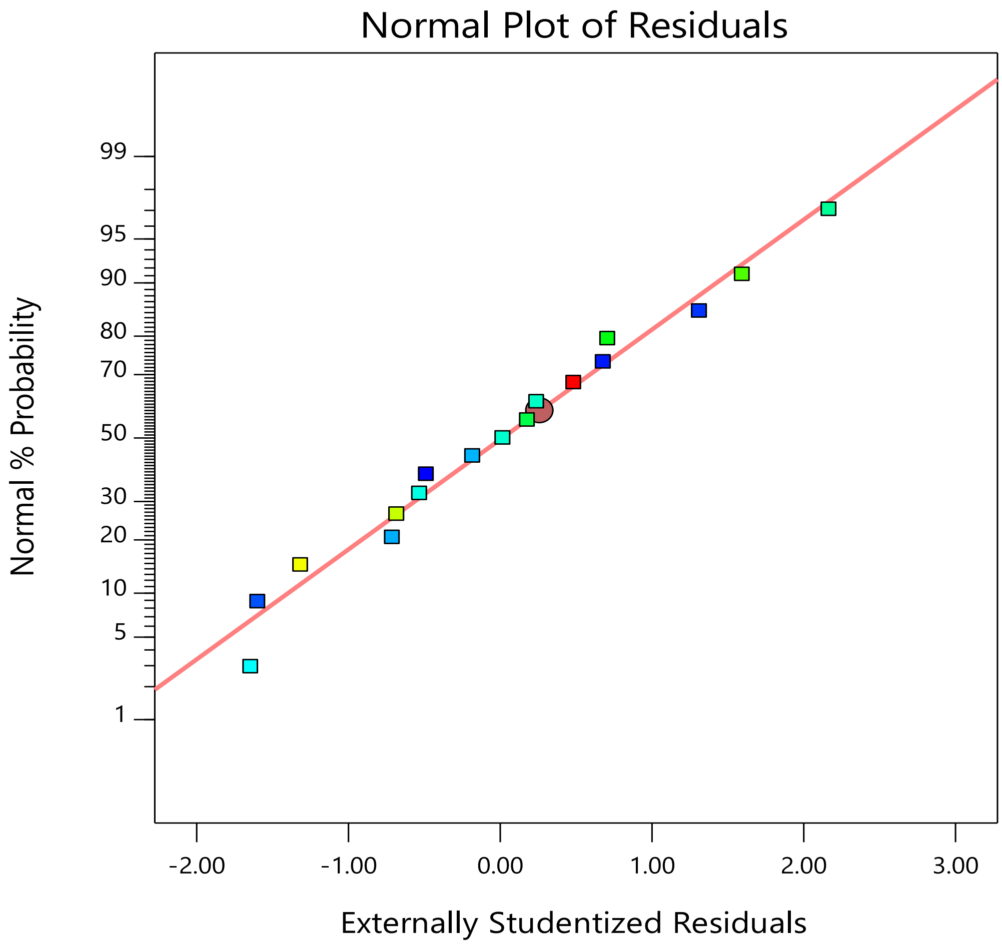


**Figure 4-3:** Normal plots of residuals

From the plot (Fig 4-3) the normal probability plot indicates that the residuals following by the normal % probability distribution, in the case of this experimental data the points in the plot shows fitted to the straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) and no deviation of variance i.e. the error distribution was approximately normal.

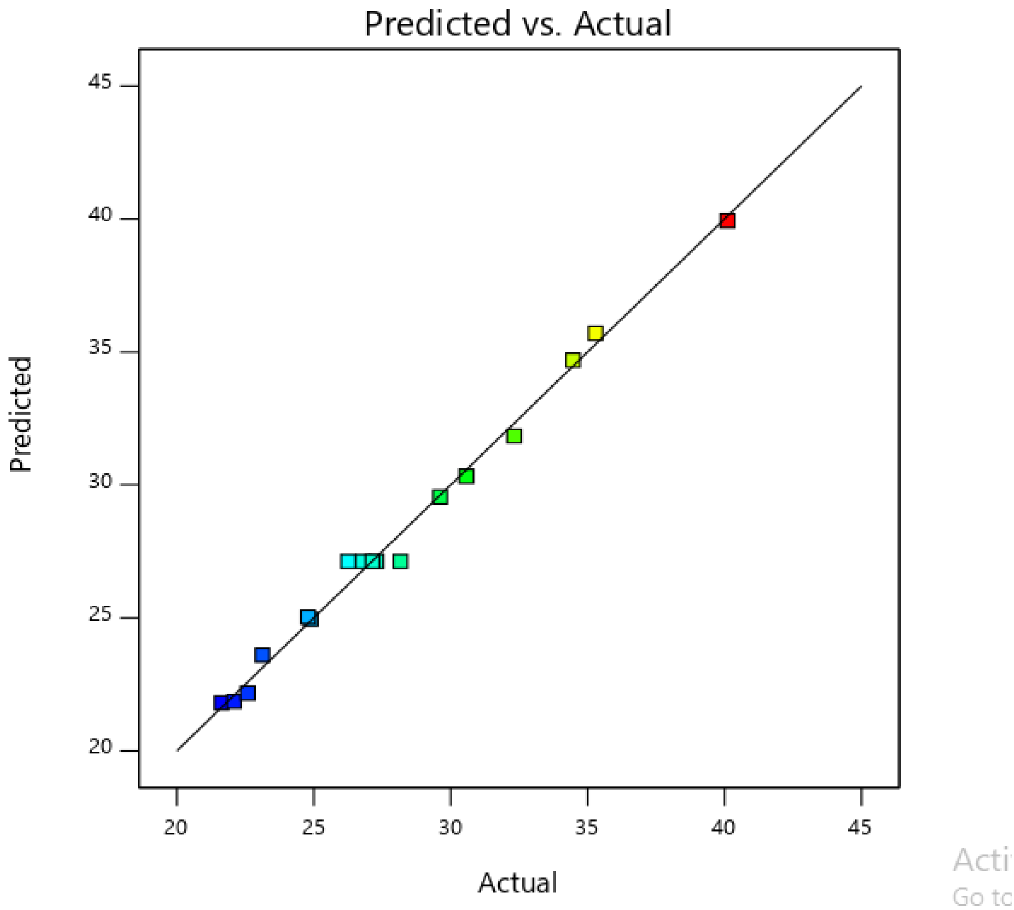


**Figure 4-4:** Predicted versus actual value

As shown from figure 4-4 the predicted versus actual value of yield of dye shows how precisely the model modeled. The points show how the predicted value and actual values of each run approach the straight line. The straight line shows how the predicted and actual values were closer to each other. When the point was above the straight line predicted value was greater than the actual value and the reverse was also true.

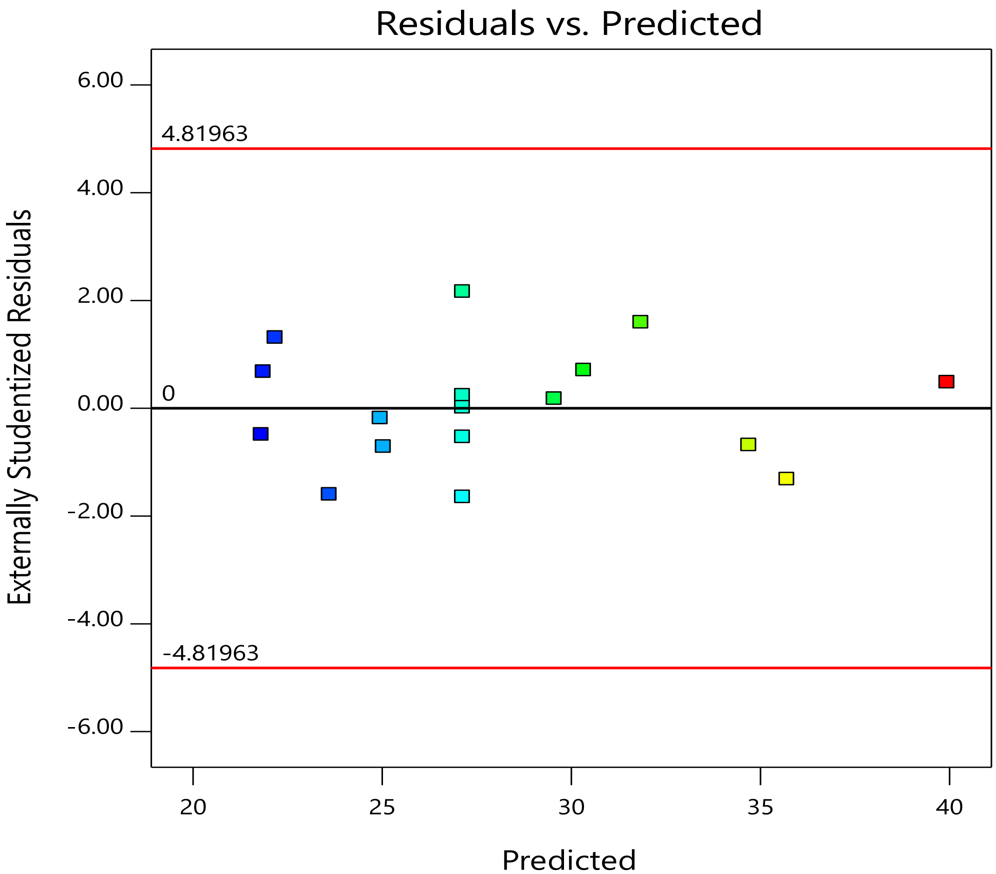


**Figure 4-5:** Residuals versus Predicted

A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. As shown from figure 4-5, if the model was correct and the assumptions were satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. The plot shows random scatter which justifying no need for an alteration to minimize personal error.

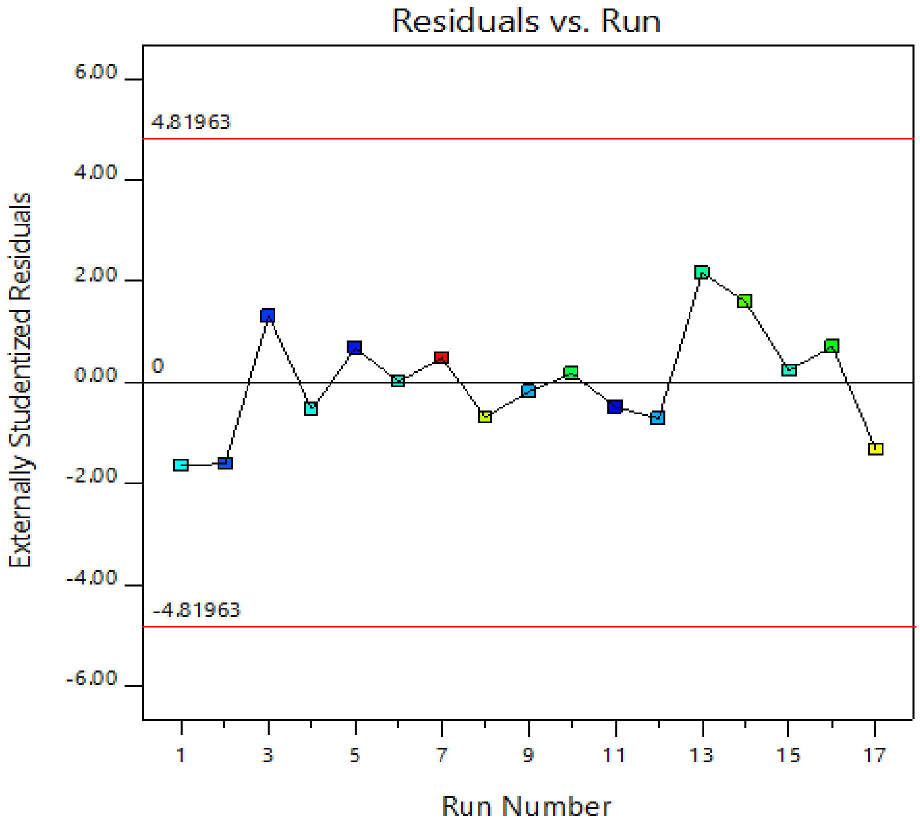


**Figure 4-6:** Residuals versus run

Figure 4-6 shows the plot of residuals versus the experimental run order. It shows that all the data points lie within the limits $(\pm 2)$. As one can easily notice, the plot showed a random scatter and no more blocking or any other solutions are needed.

## 4.7. Effect of the operating conditions on the yield of dye

### 4.7.1. Effect of temperature on the yield of dye

Figure 4-7 represents the effect of extraction temperature on the yield of dye at constant extraction time and orange peel to volume of ethanol at the center point. As shown from the plot yield of dye is very sensitive to the extraction temperature. Yield of dye was highly increased from 21.64% to 40.106% as temperature increase from 65°C to 80°C. Optimum yield of dye was obtained around 80°C extraction temperature. Beyond 80°C extraction temperature the yield of dye is slightly decrease from 40.106%. The reason that dye yield (21.64%) is low at low level of temperature 65°C might be due the temperature is not sufficient enough for solubility of the dye on the organic solvent. The other case is the amount of dye yield is low(below 40.106%) at high temperature above 80°C due to the reason that other compounds are extracted from the orange peel which is difficult for purification and solvent losses increased.

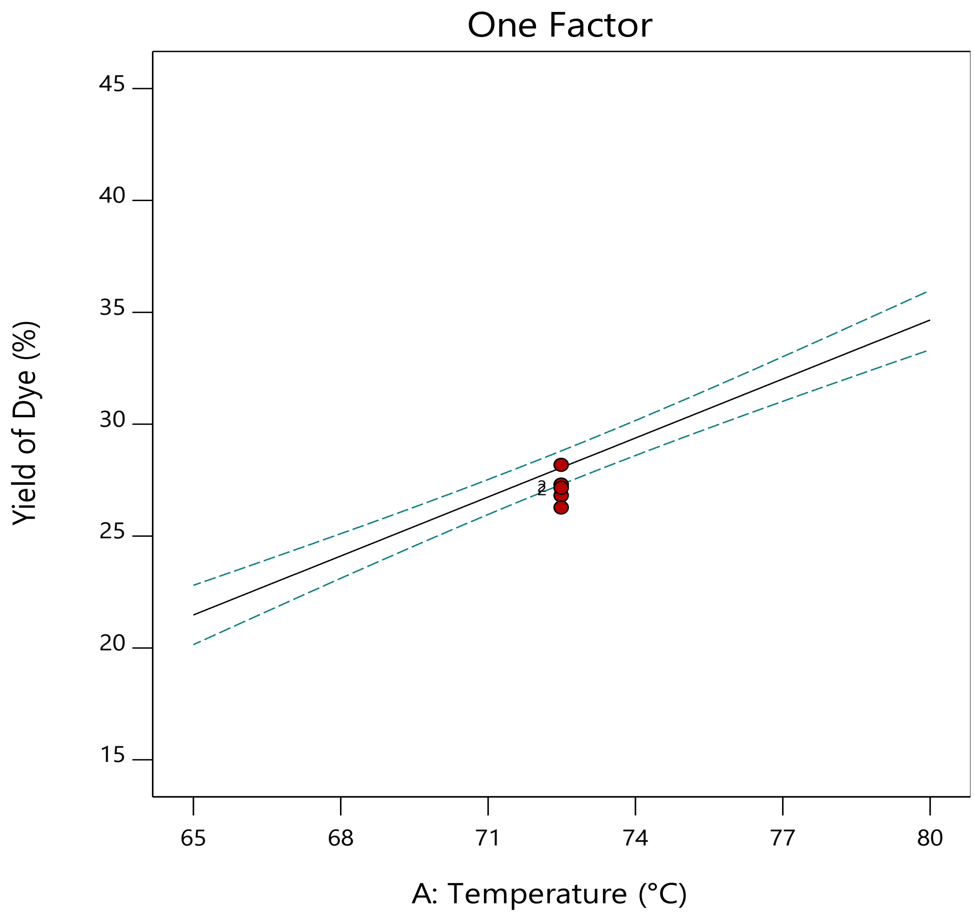


**Figure 4-7:** Yield of dye versus extraction temperature

### 4.7.2. Effect of extraction time on the yield of dye

As figure 4-8 shows how yield of the dye changes when extraction time changes from lower level (1.5h) to higher level (5h). This figure shows the yield of natural dye from orange peels using soxhlet extraction method increases from 21.64% to 40.106% as the extraction time increases from 1.5h to 5h. This resulted to increase the colour strength of the dye as the extraction of time rises from 1.5-5hrs. Experimental results showed that the extraction time (1.5h, 3.25h or 5h) was uniformly influence the extraction of dyes from orange peels. It was observed that the yield of dye in the extracts increased from 1.5-5hrs (Table 4-2).The increased extraction time potentially increases the loss of organic solvent (i.e. ethanol in this study) by evaporation. It is therefore suggested that an extraction time of no longer than 1-10h is employed. Comparing the different extraction times (1.5-5h), it was concluded that the extraction time affect the yield of natural dye.

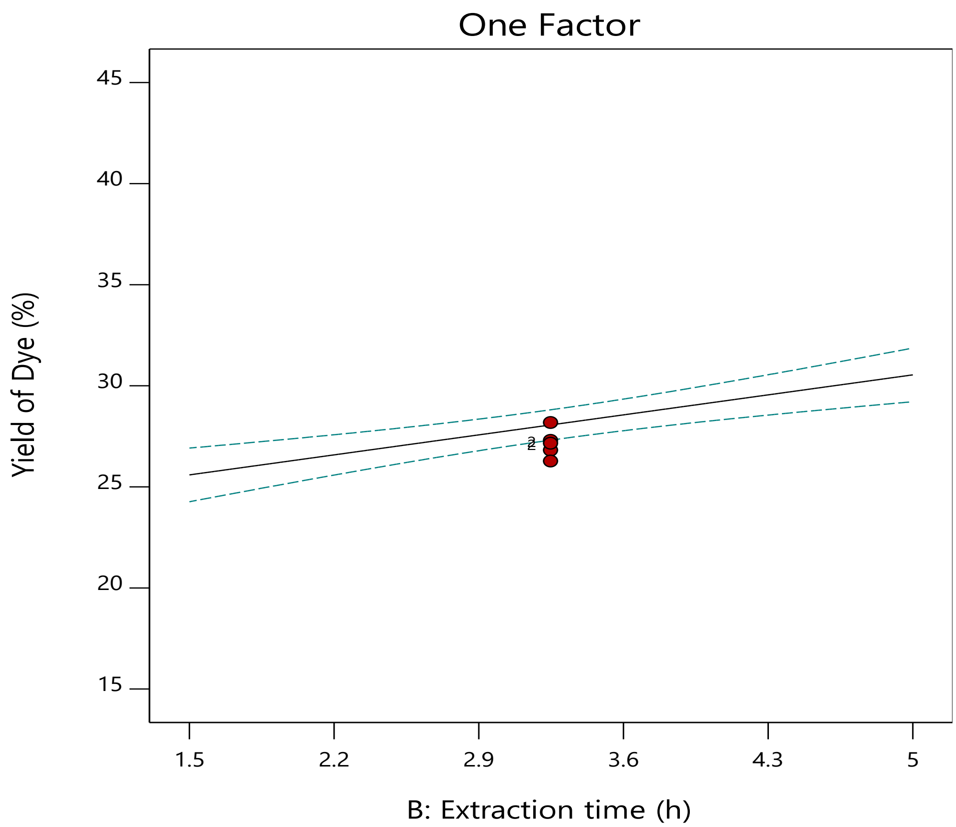


**Figure 4-8:** Yield of dye versus extraction time

### 4.7.3. Effect of orange peel to volume of ethanol ratio on yield of dye

Figure 4-9 shows how yield of dye changes when orange peel to volume of ethanol ratio changes from 0.05g/mL to 0.1g/mL. The graph shows the yield of dye fluctuates from 40.106% to 34.46% and from 21.64% to 34.46% (Table 4.3) when the ratio orange peel to volume of ethanol changes from lower level (0.05g/mL) to higher level (0.1g/mL). The plot shows that the effect of the orange peel to volume of ethanol on the yield of dye is small.

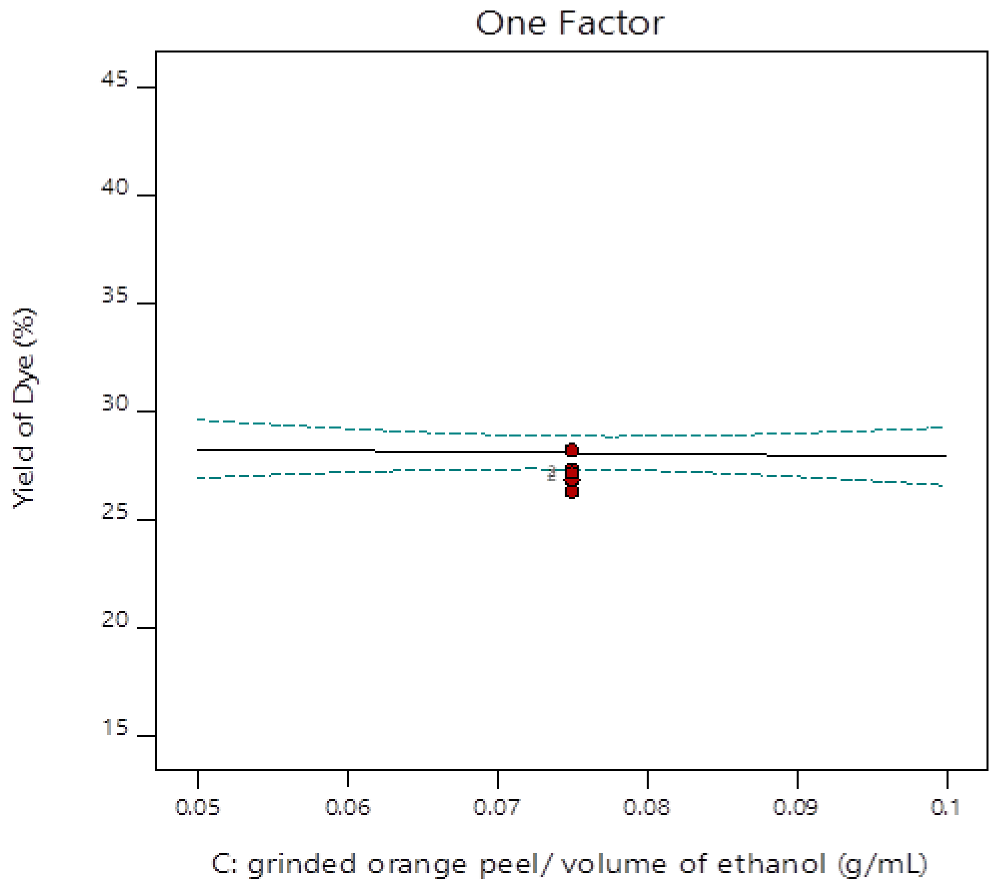


**Figure 4-9:** Yield of dye versus grinded of orange peel to volume of ethanol

## 4.8. Effect of Interactive Parameters between Process Variables

The interaction response was also significantly affected by two interactive variables at fixed third variable. Three dimensional (3D) response surface plots (plotted in order to understand the interaction between the variables and the optimum level of each variable) and contours plots (presented the effect of two variables) were generated to determine the optimum levels of the variables that were investigated in this study. The plots were generated by keeping one variable constant at the center point and varying the others within the experimental range. The resulting response surfaces showed the effect of extraction temperature, extraction time and orange peel to volume of ethanol ratio on natural dye extraction from orange peels. The significance of the interaction between the corresponding variables was indicated by saddle nature of the contour plots. An interaction occurs when the response was different depending on the setting of two factors. Plots make it easy to interpret two factors interact. They would appear with two nonparallel lines, indicating that the effect of one factor depends on the level of other. If the plotted points fall outside of the range, the differences are unlikely to be caused by error alone and can be attributed to the factor. Therefore, in this study three interaction factors were analyzed by the model equation.

AB- extraction temperature and extraction time

AC- extraction temperature and orange peel to volume of ethanol ratio

BC – extraction time and orange peel to volume of ethanol ratio

Among these three interaction factors interaction of extraction temperature and extraction time (AB) was the most significant factor for dye extraction as a response, because it has the highest coefficient (1.57) of the rest. Therefore, the interaction factors with positive sign have positive effect on yield of dye (as interaction factors increase yield of dyes also increase). Whereas, interaction factors with negative signs have a negative effect on extraction of dye (as the interaction factors increase yield of dyes decrease). The 3D response surface and contour plots of the effect of the interaction of extraction temperature, extraction time and orange peel to volume of ethanol ratio with the response of natural dye extraction are discussed below.

### 4.8.1. Effect of extraction temperature and extraction time on the yield of dye

Figure 4-10 shows the interaction effect of extraction temperature and extraction time on yield of dye at fixed value of orange peel to volume of ethanol ratio (0.075g/mL). From this figure it was shown that the extraction of natural dye however was not affected by the interaction of extraction temperature and extraction time since the lines in the plot were far apart. But it indicates that the yield of dye rises from 23.13% to 40.106% at constant extraction time as the extraction temperature increases from 65°C to 80°C than varying the extraction time from 1.5h to 5h with fixed value of orange peel to volume of ethanol ratio. Therefore, the extraction of dye was highly dominated by extraction temperature with insignificance interaction effect.

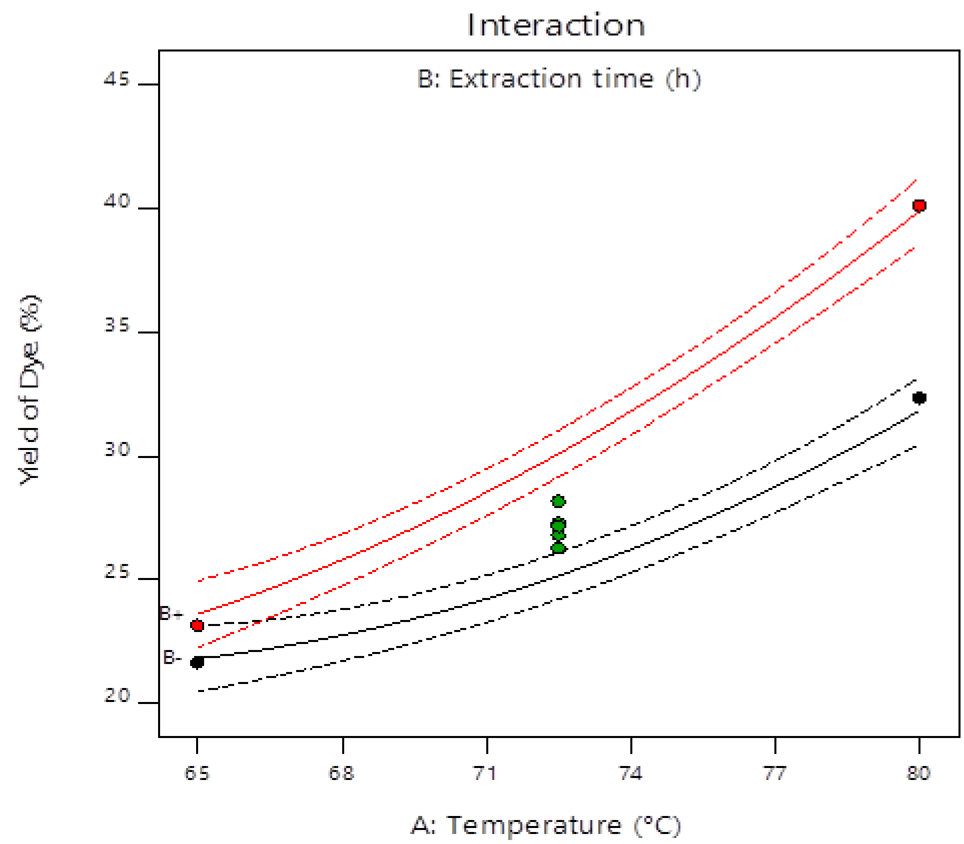


**Figure 4-10:** Interaction effect of extraction temperature and extraction time on yield of dye at the center point of orange peel to volume of ethanol

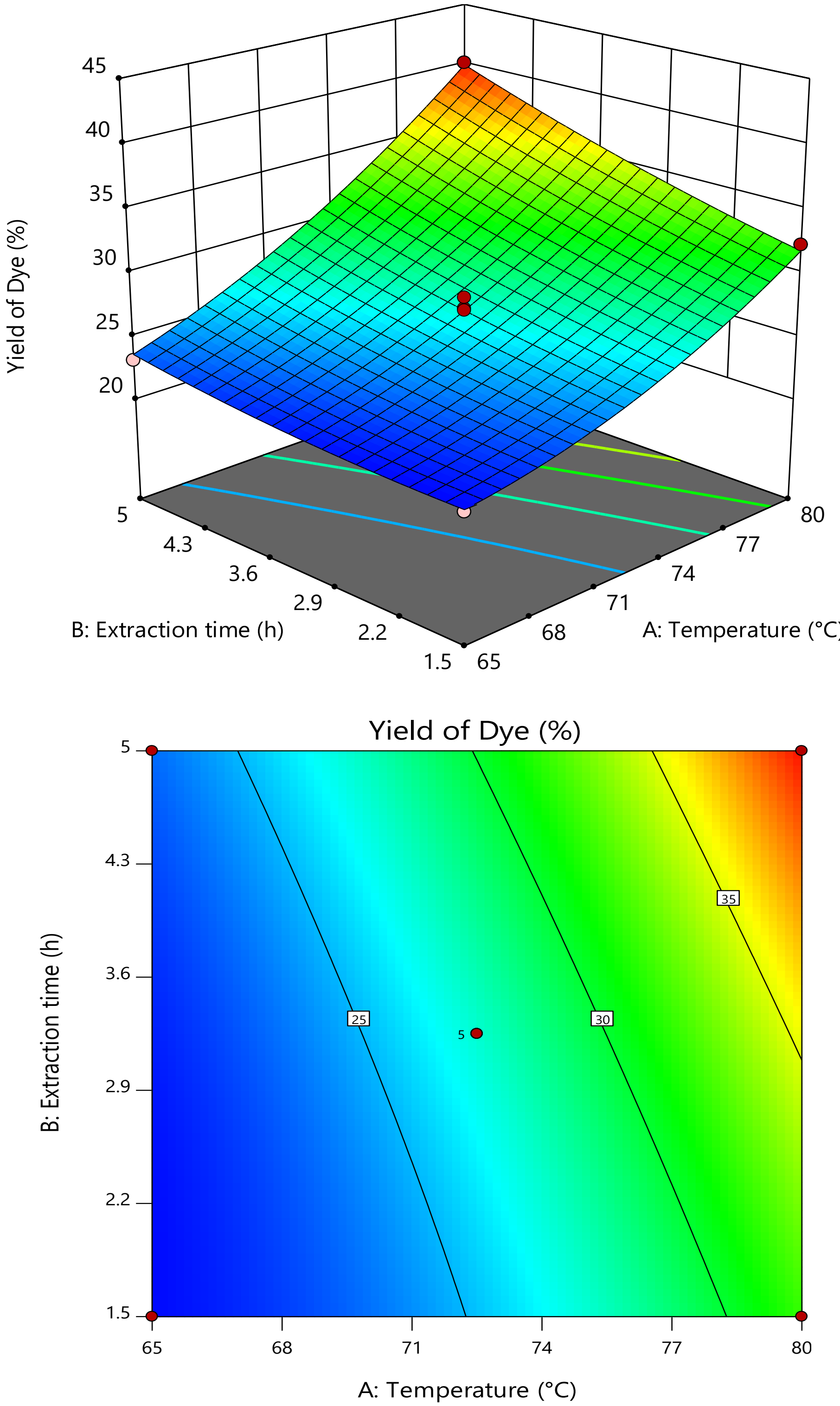


**Figure 4-11:** 3D and corresponding contour plot showing the effect of extraction temperature and extraction time on the yield of dye

Figure 4-11 represents the response surface of 3D and contour plots developed as a function of extraction temperature and extraction time respectively, while the orange peel to volume of ethanol ratio was kept constant at 0.075g/mL. The yield of dye increased from 21.64% to 40.106% with extraction temperature from 65 to 80°C and extraction time from 1.5h to 5h. However, upon increasing the extraction temperature beyond 80°C and extraction time beyond 5h there was decline of the yield of dye from 40.106% to 32.32%, because difficulty of purification occurred due to the extraction of unwanted compounds. There is color change on the graph and the response variable is increasing from blue color to red. The graph suggests that operating at the orange peel to volume of ethanol where the response variable shows maximum amount (27.28%) than in blue color (21.64%). Operating in the red region is good to have high amount of dye yield (40.106%).

### 4.8.2. Effect of extraction temperature and orange peel to ethanol ratio on yield of dye

Figure 4-12 shows the interaction effect of extraction temperature and orange peel to volume of ethanol ratio on yield of dye at fixed value of extraction time (3.25h). From this figure it was shown that the extraction of natural dye was affected by the interaction of extraction temperature and orange peel to volume of ethanol ratio since the lines in the plot were interacted. This figure indicates that the yield of dye rises from 22.09% to 35.29% at constant orange peel to volume of ethanol ratio as the extraction temperature increases from 65°C to 80°C than varying the orange peel to volume of ethanol ratio from 0.05g/mL to 0.1g/mL with fixed value of extraction time.

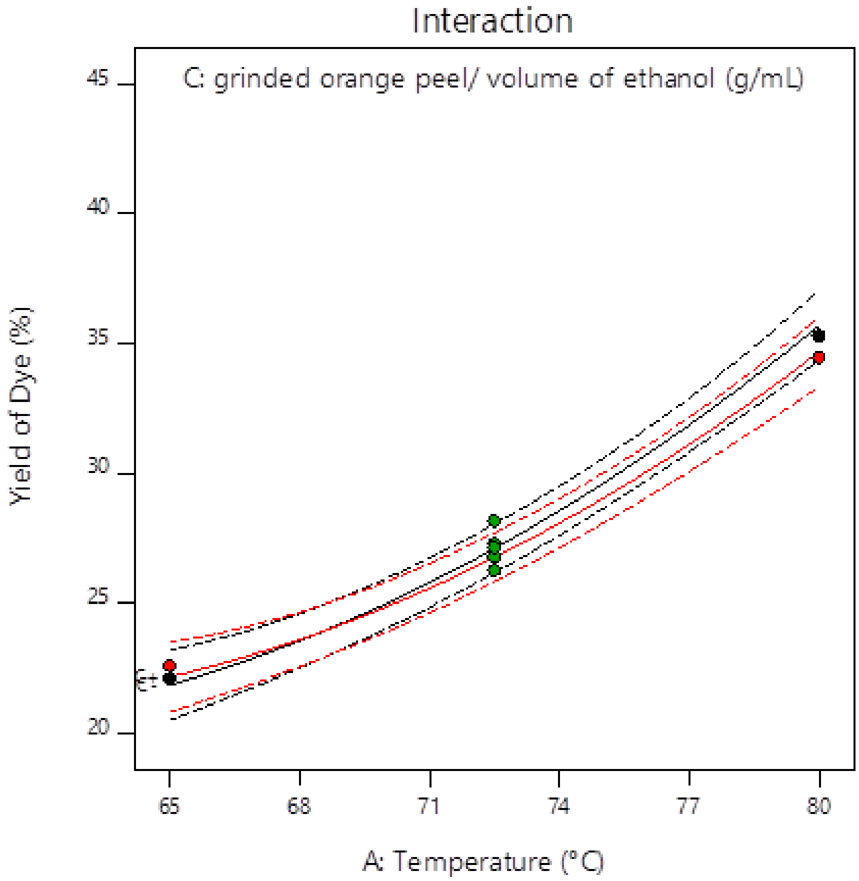


**Figure 4-12:** Interaction effect of extraction temperature and orange peel to volume of ethanol ratio at the center point of extraction time

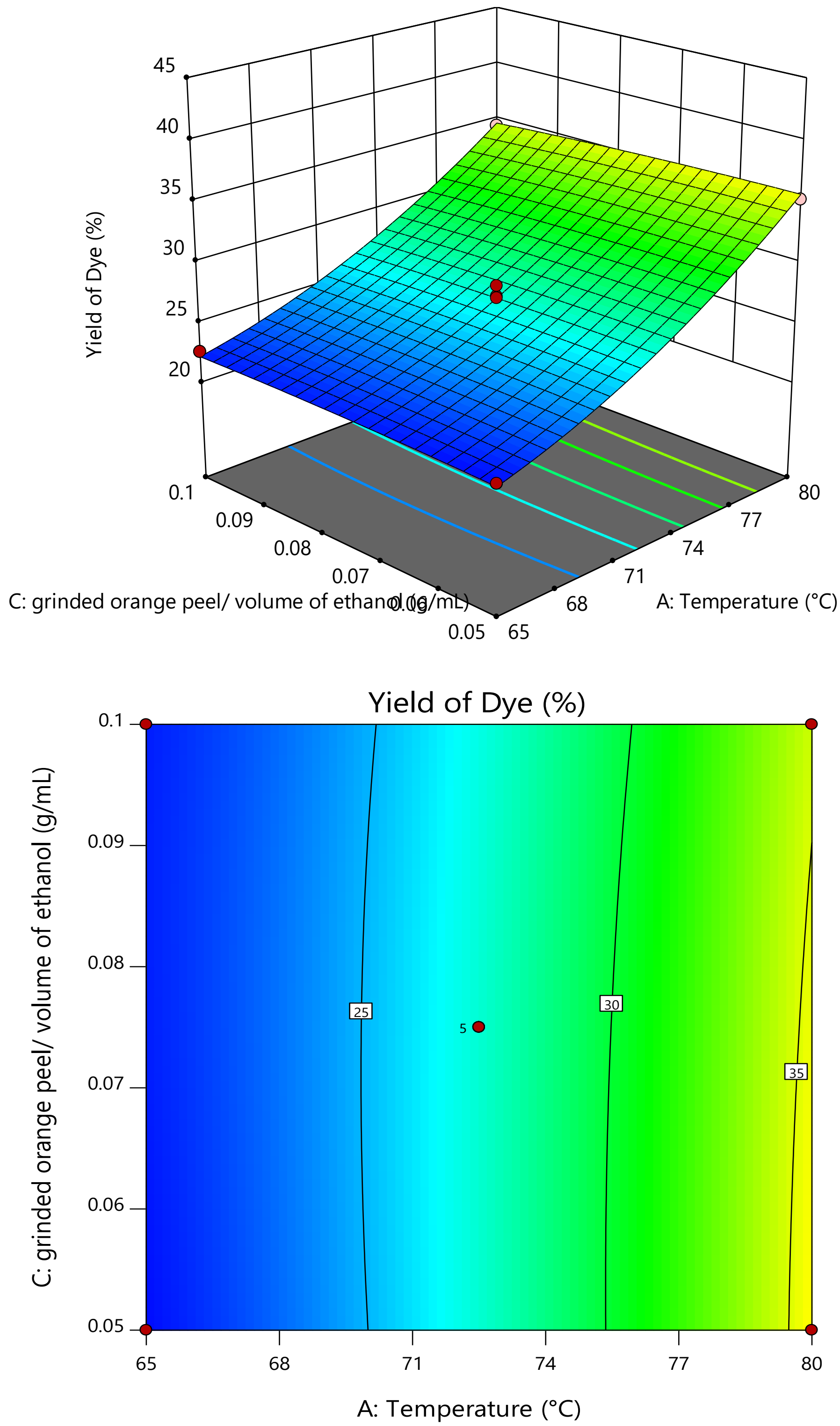


**Figure 4-13:** 3D and corresponding contour plot showing the effect of extraction temperature and orange peel to volume of ethanol ratio on the yield of dye

Figure 4-13 represents the response surface of 3D and contour plots developed as a function of extraction temperature and orange peel to volume of ethanol ratio respectively, while the extraction time was kept constant at 3.25h. The yield of dye increased from 22.09% to 35.29% with rising extraction temperature from 65 to 80°C but the effect of orange peel to volume of ethanol ratio from 0.05g/mL to 0.1g/mL fluctuates since the yield increased from 22.09% to 22.59% at constant 65°C and reduced from 35.29% to 34.46% at constant 80°C. There is color change on the graph and the response variable is increasing from 22.59% to 34.46% at constant orange peel to volume of ethanol ratio (0.1g/mL) and rise in temperature from 65°C to 80°C.

### 4.8.3. Effect of extraction time and orange peel to volume of ethanol ratio on yield of dye

Figure 4-14 shows the interaction effect of extraction time and orange peel to volume of ethanol ratio on the yield of dye at fixed value of extraction temperature (72.5°C) at the center point. From this figure it was shown that the extraction of natural dye was affected by the interaction of extraction time and orange peel to volume of ethanol ratio since the lines in the plot were interacted. Figure 4-14 indicates that the yield of dye rises from 24.89% to 30.57% at constant orange peel to volume of ethanol ratio as the extraction time increases from 1.5h to 5h than varying the orange peel to volume of ethanol from 0.05g/mL to 0.1g/mL with fixed value of extraction temperature. And figure 4-15 shows the yield of the dye increases from 24.89% to 29.61% with extraction time of 1.5-5h than the orange peel to volume of ethanol ratio at which 72.5°C extraction temperature is at the center point. There is color change on the graph and the response variable is increasing from 24.89% to 30.57% at constant orange peel to volume of ethanol ratio (0.05g/mL) and rise in extraction time from 1.5h to 5h.

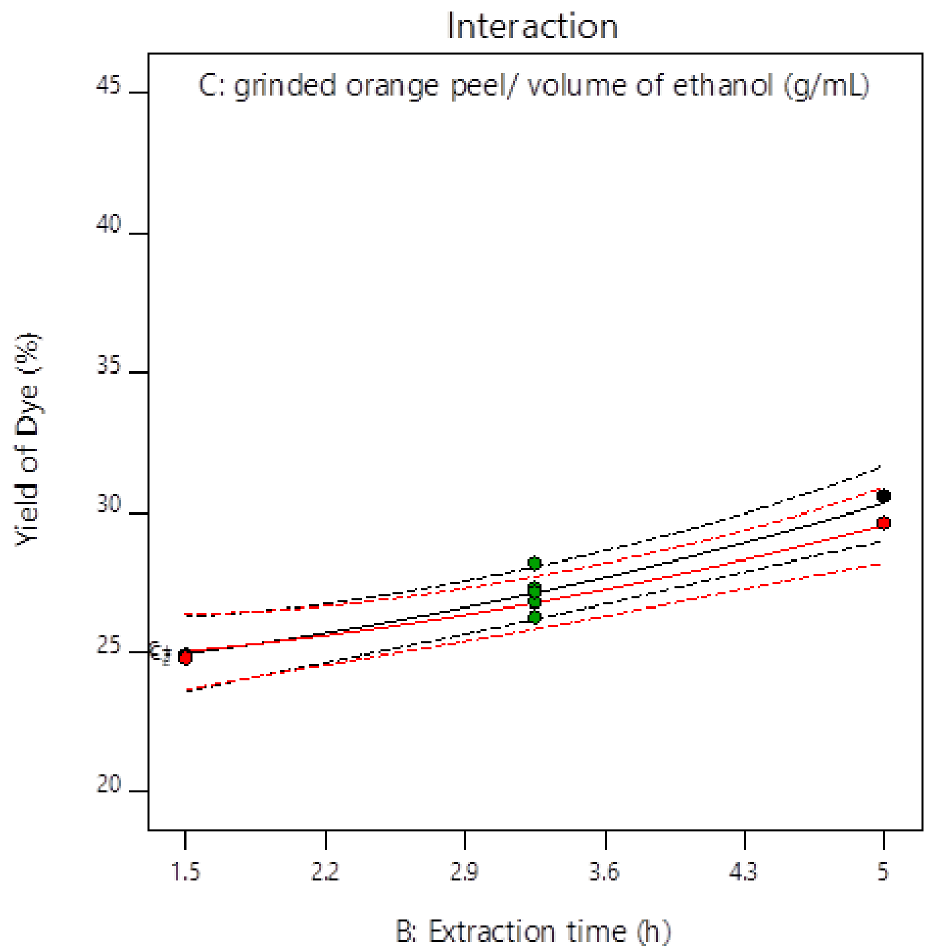


**Figure 4-14:** Interaction effect of extraction time and orange peel to volume of ethanol at the center point of extraction temperature

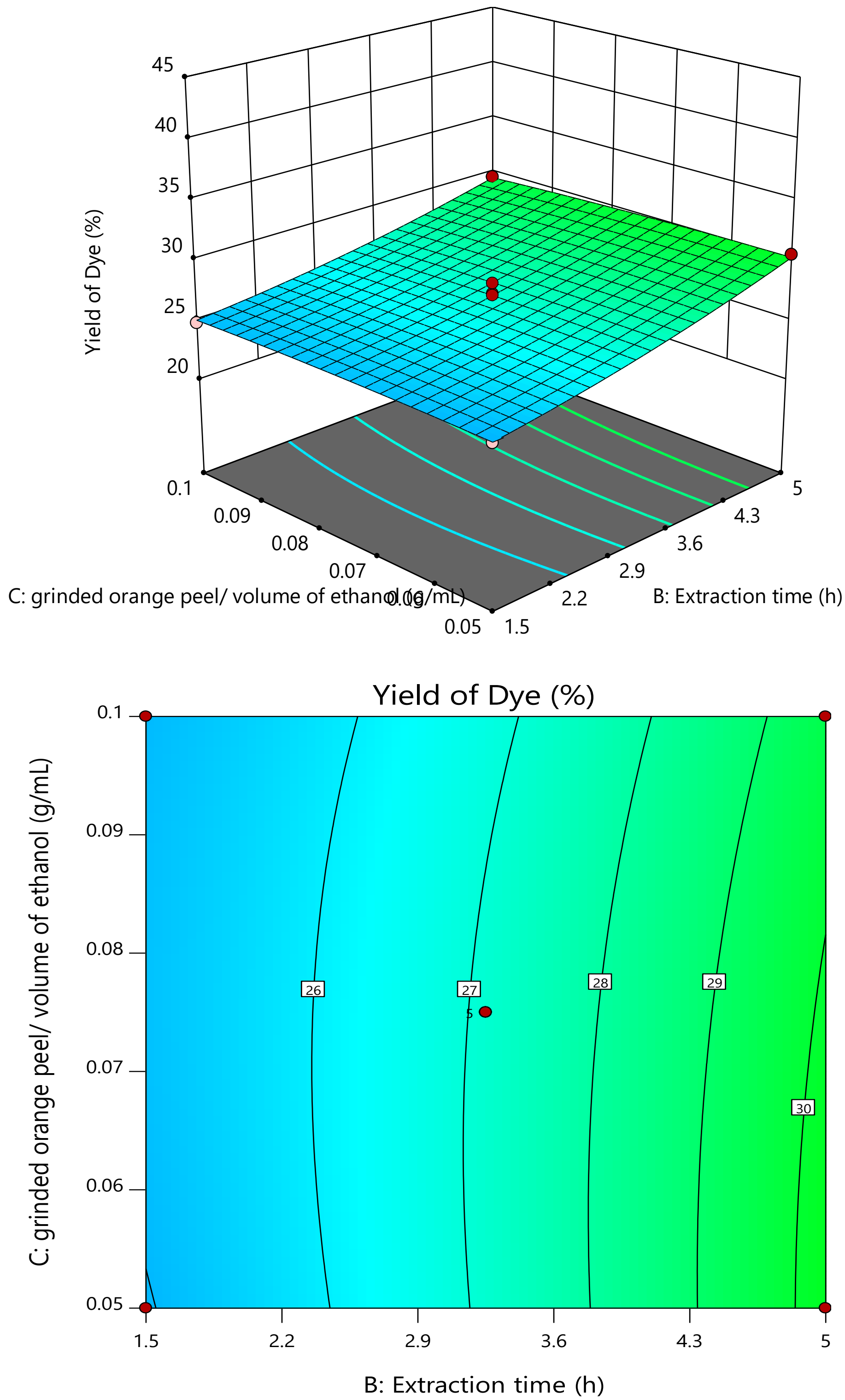


**Figure 4-15:** 3D and corresponding contour plot showing the effect of extraction time and orange peel to volume of ethanol ratio on the yield of dye

## 4.9. Experimental Optimization

One of the objectives of the present study was to find the optimal process variables for a better extraction yield of dye at minimum process economy. The process variables such as extraction temperature, extraction time and orange peel to volume of ethanol ratio were optimized. In optimizing the extraction process, extraction temperature, extraction time and orange peel to volume of ethanol ratio are a set of process variables held to be in range while the natural dye yield was the response that needs to be maximized. Table 4-5 showed the summary of factors, goals and the corresponding set of specific objectives that could optimize the process condition to have the highest responses. The expert design has three different optimization choices, namely, numerical optimization (set goal for each response), graphical optimization (set minimum and maximum limits for each response and then create an overlay highlighting an area of operability) and point predication optimization (enter desired operating conditions and discover predicted response values with confidence interval). In numerical optimization choice, depending on constraints selected different alternatives solution of optimization was given by expert design. For this study, numerical optimization was selected to obtain the better highest response of extract.

**Table 4-5:** Constraints Applied for Optimization

| Name | Goal | Lower Limit | Upper Limit |
|---|---|---|---|
| A:Temperature | is in range | 65 | 80 |
| B:Extraction time | is in range | 1.5 | 5 |
| C:orange peel/Volume of ethanol ratio | is in range | 0.05 | 0.1 |
| Yield of Dye | maximize | 21.64 | 40.106 |

The design expert under numerical optimization gave 20 different optimization solutions. Depending on the parameters by compromising yield, economy and energy carrying, the best solution was selected among the alternatives. Undertaking the consideration of these constraints, 0.066g/mL, 4.995h and 79.97°C were selected which gave 40.109% yield of dye among optimizing alternatives given by the design expert software. Desirability function was used to identify the optimum level of factors and get a maximum desirable response. The optimized batch was selected with maximum combined yield desirability value (i.e. 1.00). As shown in Table 4-6, the numerical optimization can be taken as an optimal value because the predicted value is close enough with the actual value.  The predicted highest screened yield was produced from a solution of optimization at orange peel to volume of ethanol ratio (0.066 g), extraction time (4.995h) and temperature (79.97ºC) where the screened yield was at 40.109% as summarized in Table 4-6. In order to verify this prediction, the experiment was conducted and the results were computable with prediction. This is good in terms of cost efficiency for commercial scale, as the only small amount of energy power and moderate chemicals are a need for the quality natural dye extraction.

**Table 4-6:** Different Alternative Optimization

| Number | Temperature (°C) | Extraction time (h) | orange peel/ volume of ethanol (g/mL) | Yield of Dye (%) | Desirability | Selected Trial |
|---|---|---|---|---|---|---|
| 1 | 79.780 | 4.996 | 0.050 | 40.123 | 1.000 | |
| 2 | 79.993 | 4.913 | 0.050 | 40.208 | 1.000 | |
| 3 | 79.945 | 4.997 | 0.051 | 40.376 | 1.000 | |
| 4 | 80.000 | 4.885 | 0.052 | 40.107 | 1.000 | |
| 5 | 79.977 | 4.966 | 0.063 | 40.109 | 1.000 | |
| 6 | 79.992 | 4.996 | 0.064 | 40.197 | 1.000 | |
| 7 | 79.937 | 4.946 | 0.053 | 40.176 | 1.000 | |
| 8 | 79.929 | 4.993 | 0.057 | 40.226 | 1.000 | |
| 9 | 79.831 | 4.977 | 0.052 | 40.114 | 1.000 | |
| 10 | 79.870 | 4.992 | 0.057 | 40.142 | 1.000 | |
| 11 | 79.967 | 4.935 | 0.053 | 40.184 | 1.000 | |
| 12 | 79.923 | 4.959 | 0.054 | 40.178 | 1.000 | |
| 13 | 79.993 | 4.974 | 0.064 | 40.140 | 1.000 | |
| 14 | 79.983 | 4.964 | 0.054 | 40.288 | 1.000 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 15 | 80.000 | 4.997 | 0.068 | 40.106 | 1.000 | |
| 16 | 79.898 | 4.995 | 0.059 | 40.148 | 1.000 | |
| 17 | 79.969 | 4.982 | 0.054 | 40.322 | 1.000 | |
| 18 | **79.973** | **4.995** | **0.066** | **40.109** | **1.000** | **Selected** |
| 19 | 79.855 | 4.994 | 0.055 | 40.155 | 1.000 | |
| 20 | 79.981 | 4.993 | 0.055 | 40.351 | 1.000 | |

The ramp plot of the optimization solution for the extraction conditions was shown in Figure 4-16. The ramp display combines the individual graphs for easier interpretation and the dot on each ramp reflects the factor setting or response prediction for that solution.

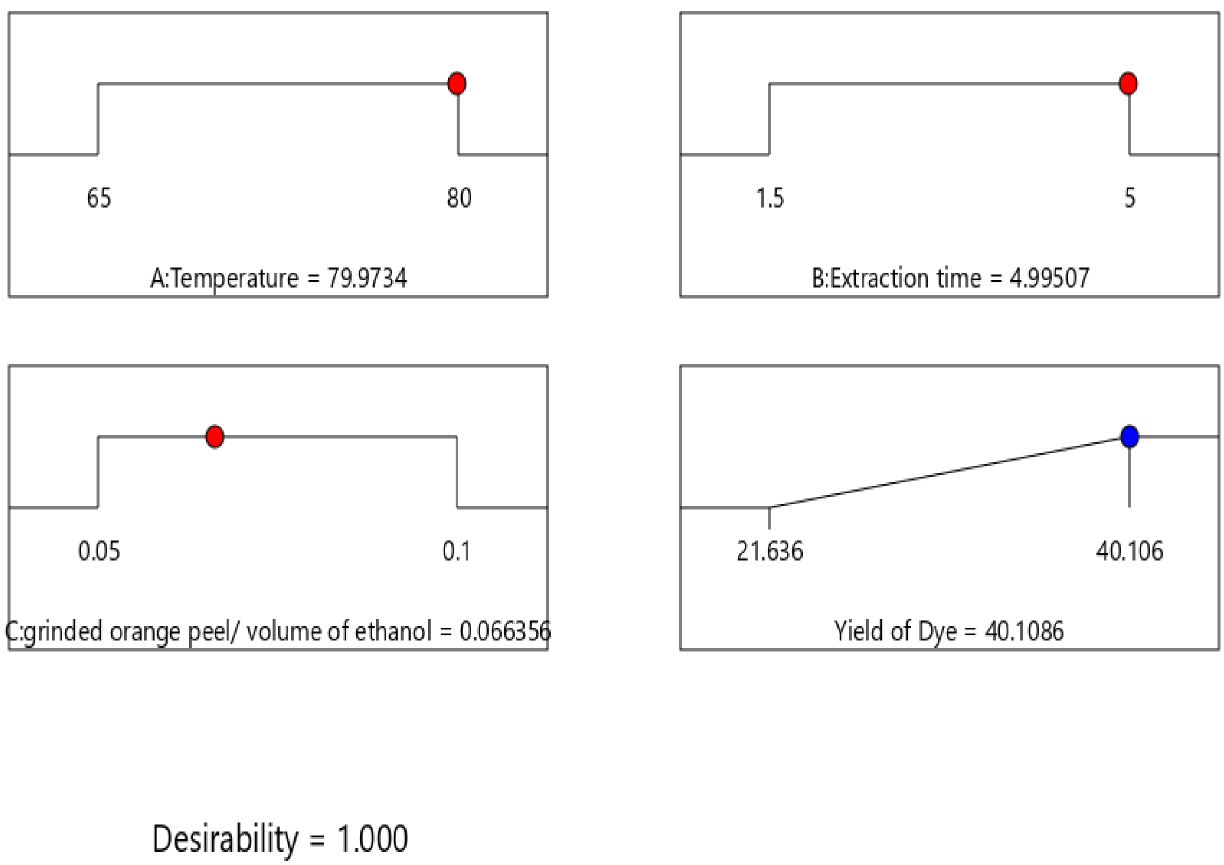


**Figure 4-16:** Ramp Plot of Optimization Solution for the Response

## 4.10. Characterization of the dye

### 4.10.1. Determination of maximum absorbance of orange peel dye

The absorbance of extracted optimum amount of dye from orange peels was measured at different wavelengths (i.e. 350nm, 375nm, 400nm, 425nm, 450nm, 475nm, 500nm, 525nm and 550nm) using uv-vis spectrophotometer (Appendix.B-4J) in order to generate the characteristic absorption spectra of the sample. The absorbance for three samples of optimum dye plant solution was prepared in cuvette and the average absorbance results for the samples of dye were reported in Table 4-7. The maximum wavelength that gave maximum absorption ($\lambda_{max}$) was recorded at wavelength of 475nm from spectrophotometer shown in figure 4-17 which is slightly less than the standard value to quantify the dye amount.

**Table 4-7:** Absorbance of extracted dye at different wavelengths

| Wavelength (nm) | Absorbance |
|---|---|
| 350 | 0.0253 |
| 375 | 0.0196 |
| 400 | 0.0215 |
| 425 | 0.0642 |
| 450 | 0.0598 |
| 475 | 0.9963 |
| 500 | 0.3571 |
| 525 | 0.3684 |
| 550 | 0.3876 |

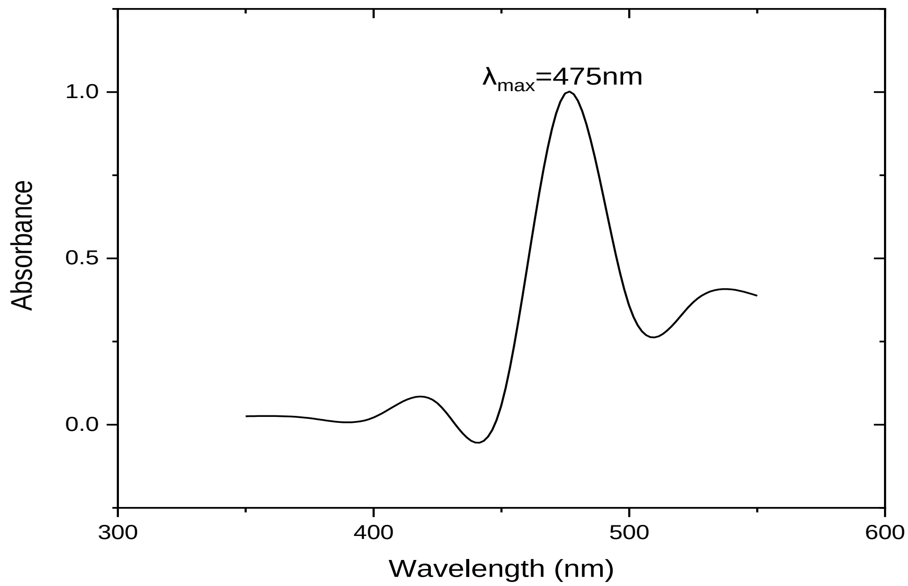


**Figure 4-17:** Absorbance of dye sample at different wavelengths

### 4.10.2. Fourier transformation infrared (FTIR) analysis of natural dye yield

FTIR spectrum of the produced natural dye after purification is demonstrated in Figure 4-18. The IR spectroscopy of dye extract shows the range of Phenol compound is at the peak of 3400.5cm$^{-1}$ (3200-3550cm$^{-1}$) and this strong signal corresponding to the characteristic O-H vibration, Alkanes are obtained at 2922.16cm$^{-1}$ (2850-2950cm$^{-1}$), 1723.43cm$^{-1}$ is carboxylic acid of C=O stretch, 2086.48cm$^{-1}$ peak is alkyne, 1454.33cm$^{-1}$ peak is H-C-H stretch and C=C aromatic group vibrational frequency, amines are at 1168cm$^{-1}$ and 721.38cm$^{-1}$ peak is in C-H bending. Moreover, FTIR spectrum of the extracted dye product is same to the spectra of the natural dyes in (Appendix.C), which is further validated for the quality of produced natural dye. Therefore, the functional groups of phenols, alkanes, amines and hydroxyl groups are responsible for the orange peel dye according to the standard in figure 4-19.

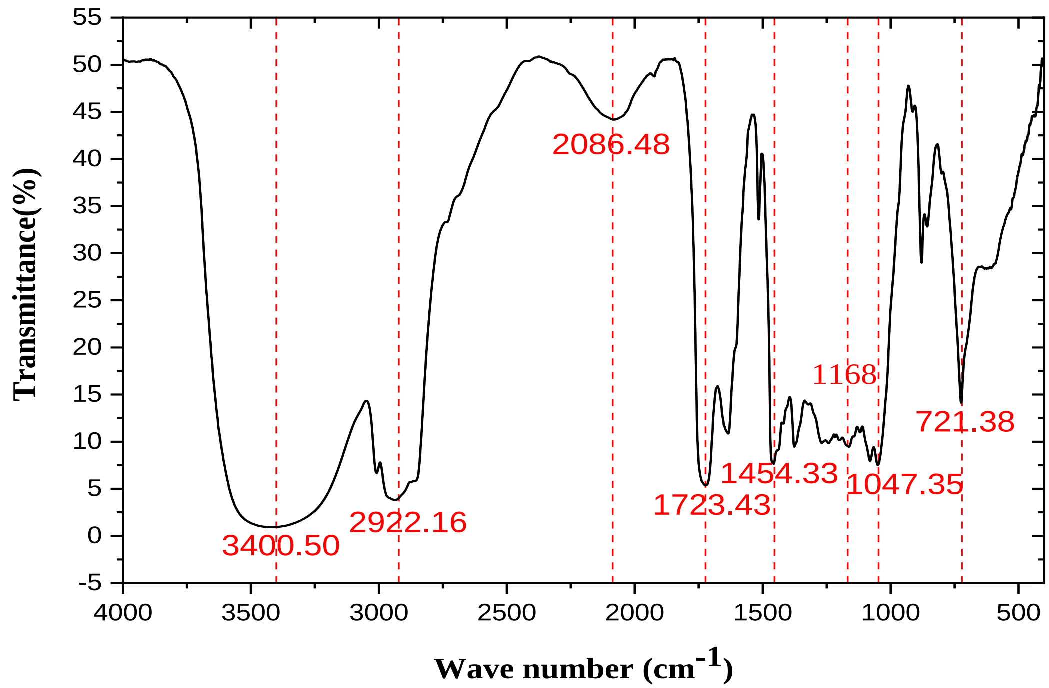


**Figure 4-18:** FTIR analysis of dye extract from orange peels

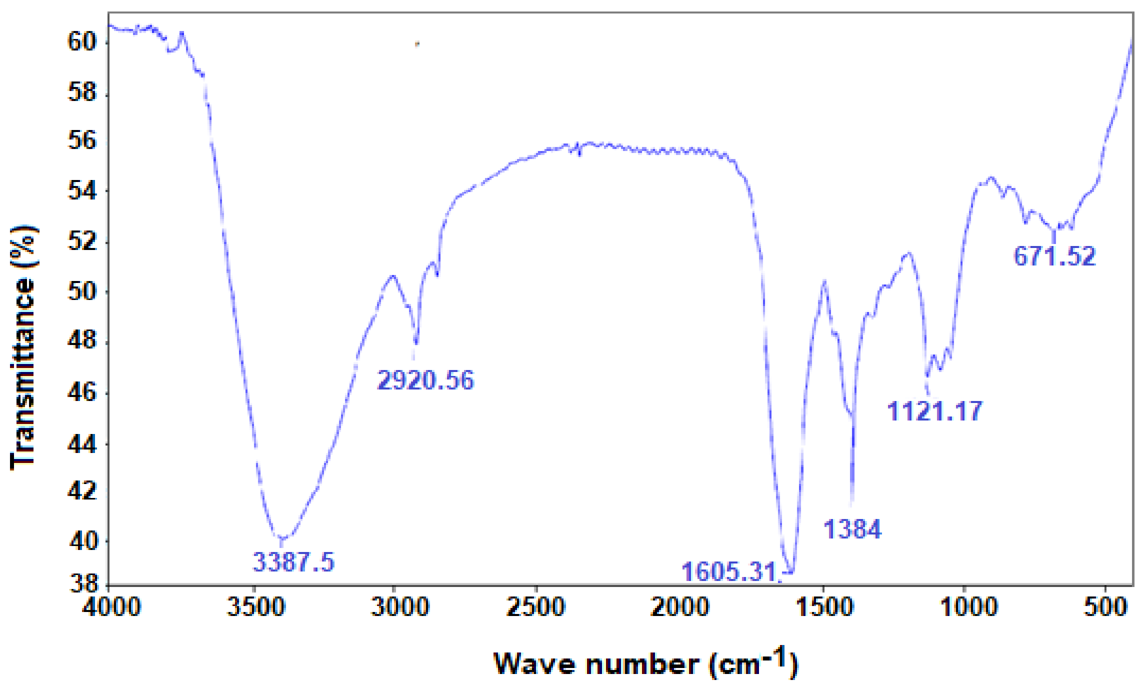


**Figure 4-19:** FTIR analysis of natural dye standard (Sumathy, 2013)

## 4.11. Application of Extracted Dye from orange peels for dyeing cotton fabric

### 4.11.1. Application of Extracted Dye

Cotton fabric has been dyed using dye extracted and analyzing the results which are given in figure below. Yellow orange shades were obtained from the dye extracted from orange peels. The shades obtained showed an acceptable evenness of dyes on both sides (grain and flesh) of cotton fabric. From the visual inspection, the dyed specimens exhibited a good variety of shades and all the specimens were found in good levelness of shade and showed deeper colour. The result of the shade indicated that the dispersion and distribution of dye has been uniform, and extracted dye can be used for dyeing of cotton fabrics.

### 4.11.2. Colour analysis for the dyed cotton fabric

The CIE colour difference values were studied for cotton textile dyed with yellow orange natural dye extracted from orange peels by 600 data colour tools. A total 60ml solution of extracted dye and water was prepared in $B_2K_2$ beaker adjusted with spring coded as 82 and putted into dispenser machine after mixing in mixer station (Appendix.B-4K). Save the orange colour in a computer with desired concentration of dyestuff (1%, 2% and 4%) and the computer gave a signal to the dispense machine (Appendix.B-4L) through auto lab dispenser to pour these desired concentrations of dyestuff from beaker-82. In addition 1.8g, 2.4g and 3g of salt (i.e. for better exhaustion) and 10g cotton were added to each dyestuff concentrations respectively.

Then dyeing of the prepared cotton samples were performed at 60$^{o}$C for 20min through dyeing machine according to (Appendix.B-3G) and sodium carbonate was added as a mordant for fixation after 20mins and put into the dyeing machine for 10 min. Then the cotton fabric was neutralized after 30min with 0.25g/L acetic acid and put into gyro-wash for 15min at 35$^{o}$C and dried using dryer machine. Lastly, the dyed cotton fabrics were tested its colour strength using spectrophotometer and fastness property (i.e. wash fastness and rubbing fastness). The results were listed in Table 4-8 and comparison of dyed cotton fabric from orange dye extract with itself and with reactive dyes were performed.

**Table 4-8:** Colour fastness properties result of dyed cotton fabric

| Colour fastness properties | | | |
|---|---|---|---|
| Natural dye Sample | Rubbing fastness | | Washing fastness |
| Concentration (%) | Dry fabric (GS value) | Wet fabric (GS value) | Dry fabric (GS value) |
| 4% | 4 | 3-4 | 4 |
| 2% | 3.5 | 3.21 | 3.5 |
| 1% | 2.85 | 2.5 | 2.82 |

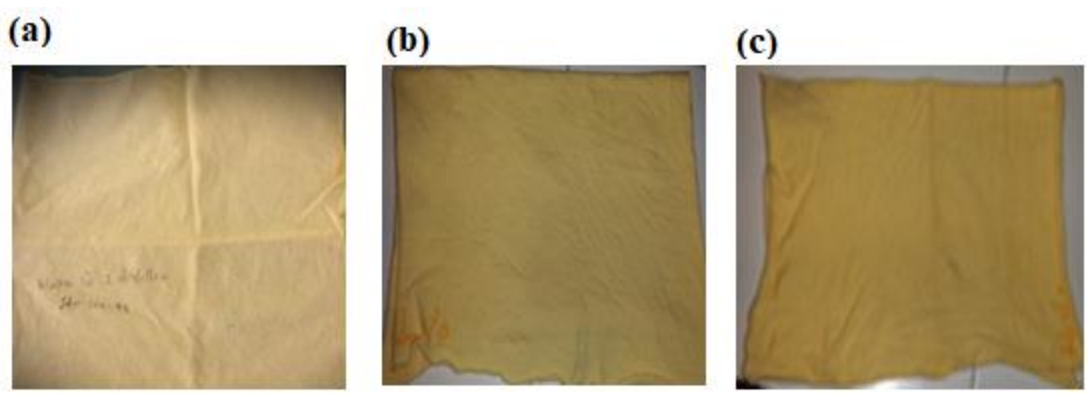


**Figure 4-20:** Cotton fabric dyed with (a) 1% Orange peel dye; (b) 2% Orange peel dye; (c) 4% Orange peel dye.

**Table 4-9:** Standards for colour fastness properties

| Colour fastness properties | | | |
|---|---|---|---|
| | Rubbing fastness | | Washing fastness |
| | Dry fabric (GS rating) | Wet fabric (GS rating) | Dry fabric (GS rating) |
| Natural dye (Repon et al., 2017) | 4 | 3-4 | 4 |
| Reactive dye | 1-5 | 4-5 | 4-5 |

The dyed cotton sample from 1% concentration of dyestuff is green which was reflected in $a^*$ (-) and yellow in $b^*$ (+) as shown in the CIE $L^*$ $a^*$ $b^*$ color space. The value of $a^*$ (greenness) obtained in directly dyed cotton samples was lower than the samples mordanted with the sodium carbonate according to (appendix.D-1). At 1% orange standard using 2% orange FN-2R Lab as a batch: darker, more yellow and more red with strength difference 91.1 was obtained.

The dyed cotton sample from 2% concentration of dyestuff is redness which was reflected in $a^*$(+) and yellow in $b^*$ (+) as shown in CIE color space. The value of $a^*$ (redness) obtained in dyed cotton fabric is higher than that of obtained from 1% concentration. At the standard of 4% orange standard, batch 2% Novocol yellow a strength difference of 109.88 and darker, more blue and more red batch was obtained from the data color tool. This indicates the dyed cotton from 4% concentration is better comparing with 1% and 2% and 4% is closer to replace reactive dyes.

The dyed cotton sample from 4% concentration of dyestuff is redness which was reflected in $a^*$(+) and blue in $b^*$ (-) as shown in CIE color space. The value of $a^*$ (redness) obtained in dyed cotton fabric is higher than that of obtained from 1% concentration and 2% concentration. From the result at standard name of 4% orange using 2% orange FN-2R Lab batch name: lighter, more yellow and more green colour of the cotton fabric with strength difference of 94.61 was obtained from 600 data color tool comparing both orange peel dyes. According to the AATcc_61 (ISO C01 to C06) the washing fastness for 4% dyestuff concentration is higher than that of 1% and 2% dyestuff conc. and also the rubbing fastness is higher according to crocking ISO 105×12.

# 5. Conclusions and Recommendation

## 5.1. Conclusions

In this study, Valorization of orange peels for dye synthesis and its application for natural fiber (i.e. cotton) was investigated. Orange peels are used for the extraction of dyes and sodium carbonate is used as a mordant for fixing the dye into the fabric. A three-variable, three-level box Behnken design was used to study the simultaneous effect of extraction temperature, extraction time and orange peel to volume of ethanol ratio. A statistically significant model ($p<0.0001$) was developed to describe the relationship between the yield of natural dye and the chosen independent variables. The extraction conditions were optimized using response surface methodology and the statistical model showed a good fit with the experimental data ($R^2=0.993$) with a low standard deviation.

From the results, it was observed that, the extraction conditions have significant effects on the extraction yield of dyes. ANOVA showed that the effects of all variables (Extraction temperature, extraction time and orange peel to volume of ethanol ratio) were significant and quadratic models were developed for predicting the responses. Optimal values of extraction conditions which gave maximum yield of dyes were selected using numerical optimization of design expert. Based on the experimental result obtained, it was found that the process variables revealed insignificant interaction effect on the yield of natural dye result except for the interaction between extraction temperature and time. The maximum yield of dye obtained after conducting the experiment at selected optimum condition was 40.109% at 0.066g/mL, 4.995h and 79.97°C with a high value of combined desirability. These values were selected from 20 alternative optimal solutions set by design expert, based on considerations and compromise of yield, energy, and economy during extraction. FTIR analyzed the functional groups of natural dyes and double beam uv-vis spectrophotometer investigated the maximum wavelength 475nm that gave highest absorbance (0.996) of light through the sample.

The extracted dye gave better color strength with good color coordinates ($L^*$, $a^*$, $b^*$, $c^*$) values which is obtained from 600data color tool. From the CIELAB color space, the dyed cotton from 4% concentration of dyestuff was higher than 1% and 2% dyestuff concentration. The dye extracts from orange peels showed very good to excellent color fastness properties. According to AATcc_61 (ISO C01 to C06) and crocking ISO 105×12, the washing fastness, rubbing fastness for dyed cotton fabric from 4% dyed concentration was higher. And the washing fastness of dyed cotton fabric from 2% dyed cotton fabric was also higher than that of 1% dyestuff concentration. Therefore, results indicated that extracted dye from orange peels have strong affinity to textile cotton fabrics at higher concentration of natural dyestuff, the washing and rubbing fastness increases from 1% to 4% dyestuff concentration which leads 4% dyestuff conc. was more comparable with the reactive dye.

Finally, it can be concluded that valorization of orange peels for extraction of natural save valuable foreign exchange by reducing the synthetic dye imported and also the hazardous impact of synthetic dyes. Due to the increasing awareness among people natural dye from orange peel should be promoted and their suitability for dyeing fabric.

## 5.2. Recommendations

The following recommendations was made for future work

- Storage techniques of orange peels could be studied for the extraction of natural dye.
- Further research needs to be carried out to increase the yield of natural dye from orange peels by exploring other advanced extraction methods (supercritical fluid extraction) which are capable of producing high yield of dye.
- Economic analysis need to be investigated to compare the cost of natural dye with that of synthetic dye.
- Additional studies are needed to determine the fastness properties of dyes using other mordants like alum (potassium aluminum sulphate), copper sulphate and natural source mordants.

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# Appendices

## Appendix A: Proximate Analysis of orange Peels

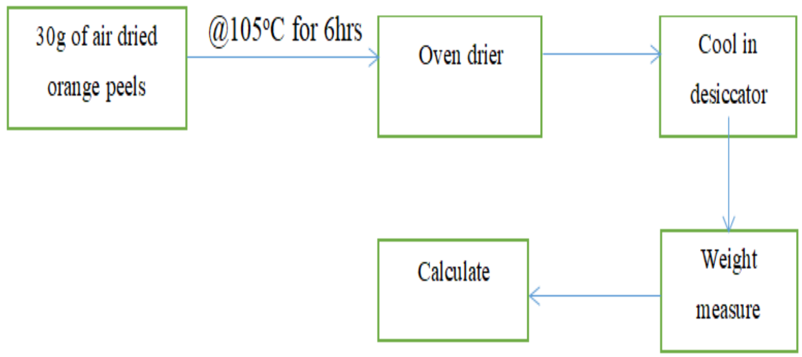


Figure A - 1: Determination of moisture Content of the sample (orange peels)

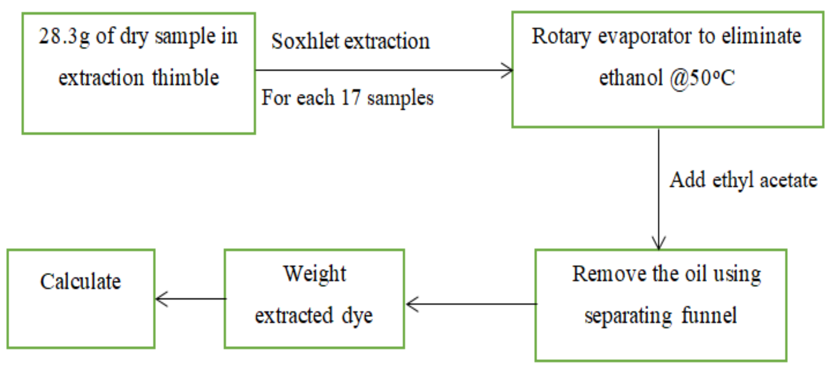


Figure A - 2: Determination of yield of natural dyes by Soxhlet extraction method

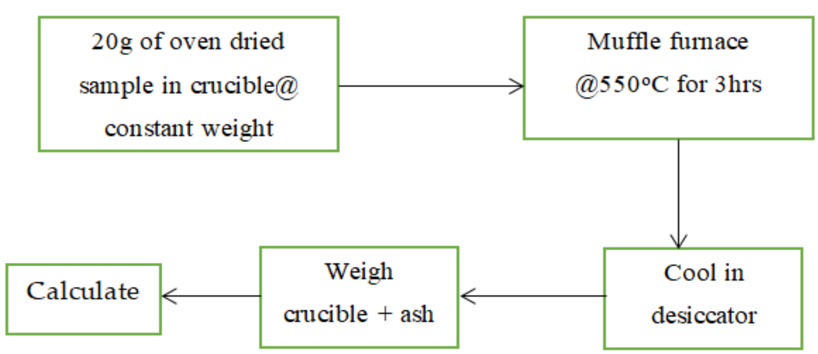


Figure A - 3: Determination of Ash Content of the sample

## Appendix B: Laboratory Equipment's and Results

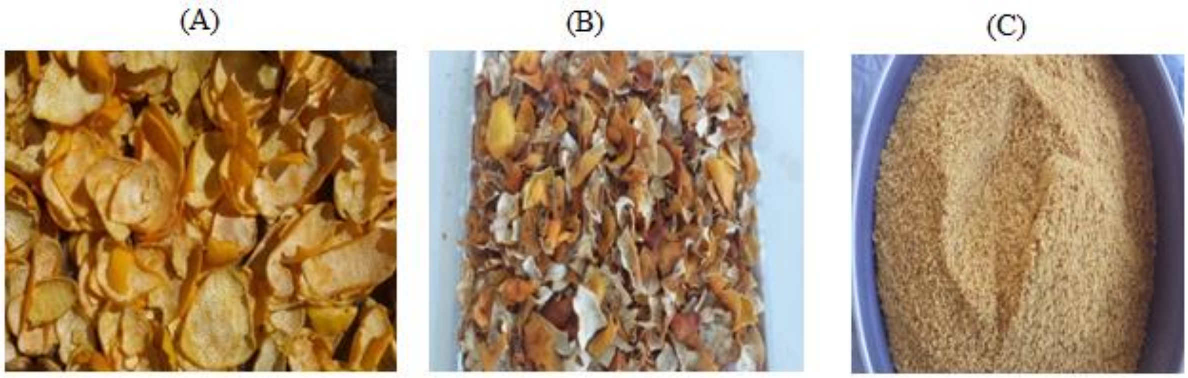


Figure B-1: Prepared (A) fresh peel, (B) oven dried peel, and (C) grinded peel

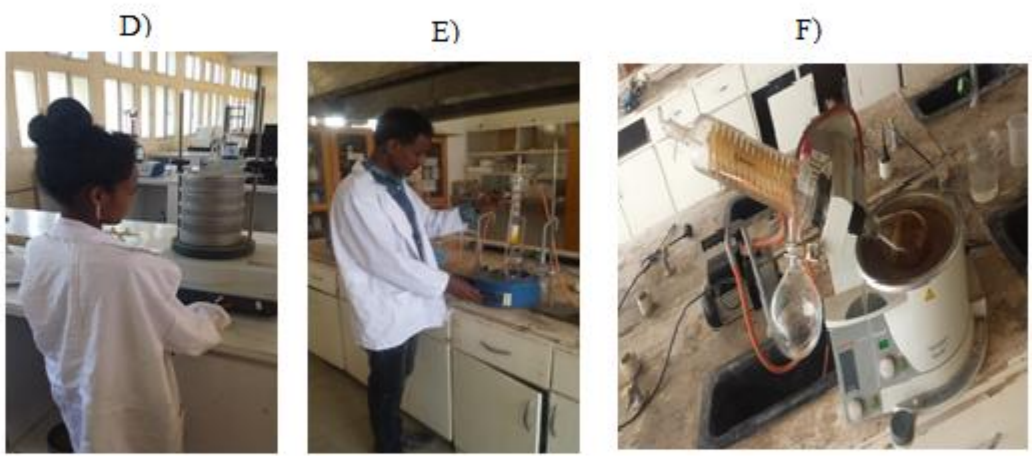


Figure B-2: (D) Sieving analysis, (E) soxhlet extraction method, and (F) rotary evaporator

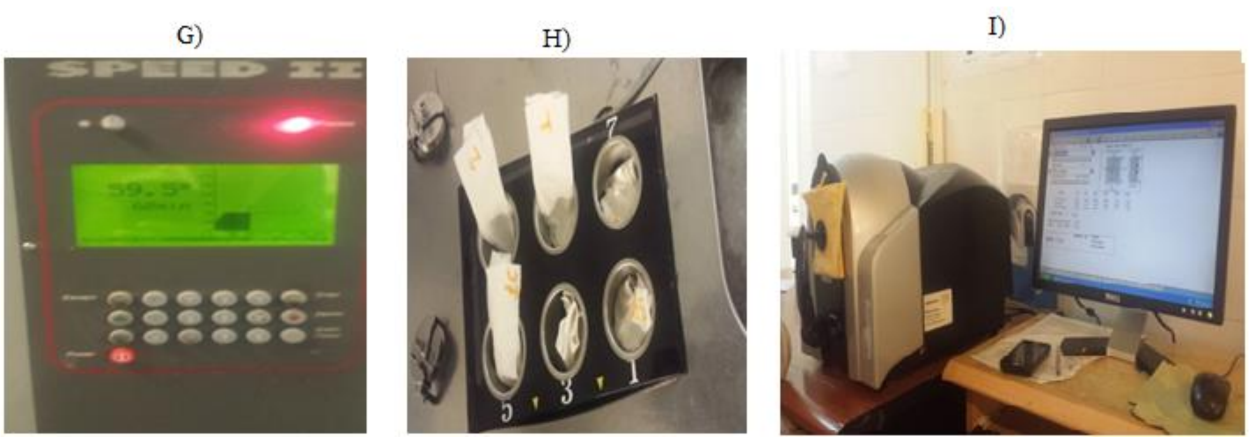


Figure B-3: (G) Dyeing machine (H) cotton dyeing process, and (I) 600 data color Spectrum

J) K) L)

Figure B-4: (J) Uv-vis spectrophotometer, (K) Mixer station and (L) Dispenser machine

M) N) O)


Figure B-5: (M) gyrowash, (N) rubbing fastness tester and (O) checked cotton fastness

P) Q)

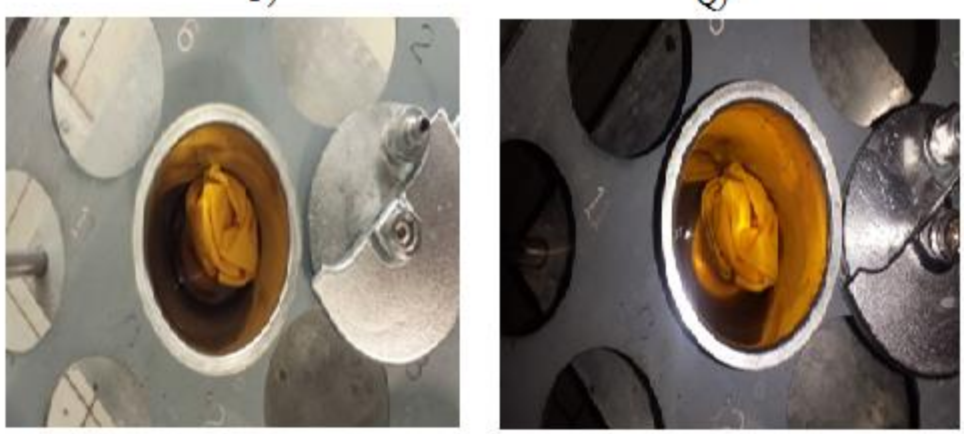

Figure B-6: Process of cotton dyeing after addition of mordant

## Appendix C: FTIR Correlation Table

| Functional group names | Characteristic Absorption($cm^{-1}$) | Type of vibration causing IR absorption |
|---|---|---|
| Phenols and alcohols | 3550-3200 | Hydrogen bonded- OH stretch |
| Carboxylic acids | 3000-2500 | Hydrogen bonded-OH stretch |
| | 1780 - 1710 | C=O stretch |
| Ketones | 1750-1680 | C=O stretch |
| Aldehyde | 1740-1690 | C=O stretch |
| Ester | 1750-1735 | C=O stretch |
| Amide | 1690-1630 | C=O stretch |
| | 3700-3500 | N-H stretch |
| Ethers, alcohols and sugars | 1300-1000 | C-O-C and C-OH |
| Alkenes and aromatic cpds | 1000-650 | =C-H |
| Amine | 3500-3300 | N-H stretch |
| Nitrile | 2260-2220 | C≡N stretch |
| Alkane | 2950-2850 | C-H stretch |
| | 1500-1440 | H-C-H stretch |
| Alkene | 3100-3010 | C - H stretch |
| | 1680-1620 | C=C stretch |
| Alkyne | ~3300 | C - H stretch |
| | 2260-2100 | C≡C stretch |
| Aromatic | ~3030 | C - H stretch |
| | 860-680 | C-H bending |
| | 1700-1500 | C=C bending |

## Appendix D: spectrophotometer analysis result of dyed cotton fabrics

Table D-1: Data colour tool analysis of 4% and 2% orange colour

| Standard name: 4% orange<br>Batch name: 2% orange FN-2R lab<br>P/F: warn batch is: lighter<br>More yellow<br>More green | | | |
|---|---|---|---|
| $DL^*$ | $Da^*$ | $Db^*$ | $Dc^*$ |
| 0.11 | -0.88 | 0.86 | 0.65 |
| 0.05 | -0.59 | 0.61 | 0.42 |
| 0.06 | -0.81 | 0.91 | 0.76 |

Table D-2: Data colour tool analysis of 1% and 2% orange colour

| Standard name: 1% orange<br>Batch name: 2% orange FN-2R lab<br>P/F: pass batch is: darker<br>More yellow<br>More red | | | |
|---|---|---|---|
| $DL^*$ | $Da^*$ | $Db^*$ | $Dc^*$ |
| -0.41 | 0.58 | 1.52 | 1.60 |
| -0.28 | 0.58 | 1.73 | 1.82 |
| -0.27 | 0.22 | 1.70 | 1.71 |

Table D-3: Data colour tool analysis of 4% and 2% orange colour

| Standard name: 4% orange<br>Batch name: 2% Nov. yellow FN-2R lab<br>P/F: pass batch is: darker<br>More yellow<br>More red | | | |
|---|---|---|---|
| DL* | Da* | Db* | Dc* |
| -0.34 | 0.82 | -0.97 | -0.77 |
| -0.30 | 0.54 | -0.76 | -0.57 |
| -0.31 | 0.78 | -1.03 | -0.89 |

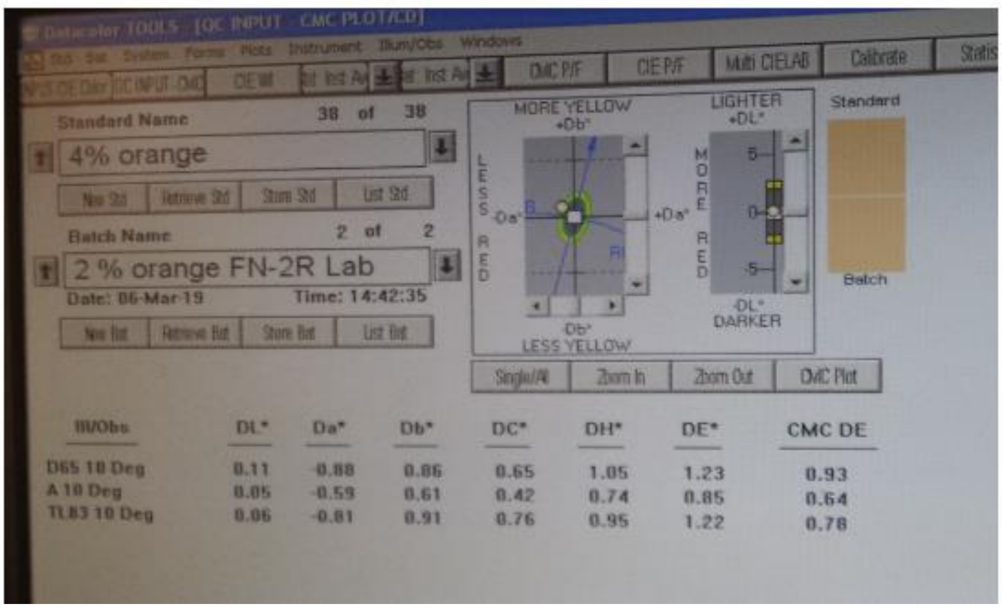


Figure D-1: Data colour tool analysis of 4% and 2% orange FN-2R Lab colour